Theoretical studies on a series of nitroaliphatic energetic compounds*

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(Received 11 September 2013; revised manuscript received 3 December 2013; published online 20 April 2014)

Density functional theory calculations at the B3LYP/6-311G** level are performed to study the geometric and electronic structures of a series of nitroaliphatic compounds. The heats of formation (HOF) are predicted through the designed isodesmic reactions. Thermal stabilities are evaluated via the homolytic bond dissociation energies (BDEs). Further, the correlation is developed between impact sensitivity $h_{50\%}$ and the ratio (BDE/E) of the weakest BDE to the total energy E containing zero point energy correction. In addition, the relative stability of the title compounds is evaluated based on the analysis of calculated Mulliken population and the energy gaps between the frontier orbitals. The calculated BDEs, HOFs, and energy gaps consistently indicate that compound 1,1,1,6,6,6-hexanitro-3-hexyne is the most unstable and the compound 3,3,4,4,-tetranitro-hexane is the most stable. These results provide basic information for the molecular design of novel high energetic density materials.

Keywords: density functional theory, heats of formation, bond dissociation energy, isodesmic reaction

PACS: 31.15.E–, 82.60.Cx, 33.15.Fm, 82.20.–w **DOI:** 10.1088/1674-1056/23/6/063103

1. Introduction

Synthesis and structural characterization of new insensitive energetic materials with new properties has become a research focus of some investigators. Energetic materials are used extensively in civil and military areas. Recently, because of many catastrophic explosions resulting from unintentional initiation of munitions by aboard ships, aircraft carriers, munitions trains, impact or shock, continuous efforts have been made to develop new materials with good thermal stability, impact and shock insensitivity, better performance, and an economic and environmentally friendly syntheses in order to meet the requirements of future military and space use.[1,2]

It is well known that the evaluation of the explosive performance of energetic materials requires knowledge of the heats of formation (HOFs). Moreover, HOF is one of the most important thermochemical properties for energetic explosives because it is related directly to detonation parameters. The HOFs of stable compounds can be found experimentally. However, for unstable compounds, it is sometimes impractical or dangerous to measure the HOFs of energetic materials experimentally because they are difficult to synthesize. Hence, it would be useful to develop a reliable theoretical means to calculate the HOFs of energetic materials, and computational approaches have shown their great advantages and they have been employed to obtain the HOFs of those demanding materials.[3–8] These days, the density functional theory (DFT) has emerged as a very reliable theoretical method to calculate the geometries of molecules. In particular, the B3LYP hybrid DFT method, which not only produces reliable geometries and energies but also requires less time and computer resources, has been widely employed and it has become an important and economical tool to deal with complex electron correlation problems.[9–13]

The strength of a chemical bond, expressed in terms of bond dissociation energy (BDE), is of considerable importance in the area of energetic materials. BDE is not only efficient for the characterization of bond strength but may also be connected with impact sensitivity.[14] Numerous studies have been carried out with the aim of more specifically identifying molecular properties that relate to measures of impact sensitivity, many of which support the idea that the R–NO_2 (R = C, N or O) bond is the trigger spot and the weakest bond in nitro-contained explosives. Research results[15,16] have shown that the rupture of this bond is the first step in the decomposition process. The chemical stabilities and impact sensitivities of energetic materials have recently been related to the strengths of the weakest bond R–NO_2, which may be obtained by calculating the BDE.[17–23]

Organic compounds with energetic groups, such as nitroaromatic compounds, are hazardous materials that can decompose, ignite, and explode by heat and impact. Before synthesis it is necessary to predict their thermochemical properties to ensure their safe handling, storage, transport, and process design. Considerable efforts in the field of energetic materials, including nitroaliphatic compounds, have been focused on the reliable predictions of their properties. Utilizing some

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11304022 and11347010), the Research Foundation of Education Bureau of Hubei Province, China (Grant Nos. Q20131208, T201204, and XD2014069), the Foundation of Yangtze University for Outstanding Young Teachers, China (Grant Nos. cyq201321 and cyq201322), and the Project for Basic Subjects (Grant No. 2013cjp10).

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new methods and computed values, Mohammad *et al*.,[24] Mohammad and Hamid,[25] and Mohammad[26–28] predicted the gross and net heats of combustion, density, enthalpy of fusion, and impact sensitivity of important classes of energetic compounds.

However, at present, to the best of our knowledge, for title nitroaliphatic energetic compounds, which contain several nitro groups, less experimental BDE values are available and the weakest bond has not been evaluated. In addition, due to the problems of safety and the difficulty in purifying and the lack of a systematic theoretical study, the HOF values for title compounds are also uncertain.

In this article we discuss the calculated BDEs of the weakest C–NO_2 bond, the impact sensitivities and the HOFs using B3LYP hybrid DFT method with 6-311G** basis set via homolytic reaction, and the isodesmic reaction for a series of nitroaliphatic compounds. Based on the calculated results, the relationship between structure and stability is also analyzed. These results may provide useful information for the molecular design of novel high energetic density materials.

2. Computational methods

All computational studies are performed with computational methods as they are implemented in the GAUSSIAN 03 package.[29] The optimizations are performed without any symmetry restrictions using the default convergence criteria in the programs.

For all of the studied compounds, geometry optimization is conducted. For those situations that are not convergent without any constraint each optimized structure is confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency. The equilibrium geometries and BDEs are obtained by the Becke-style three-parameter Density Functional Theory[30] with the Lee–Yang–Parr correlation function (B3LYP).[31] The 6-311G** basis set is employed for the three hybrid DFT methods mentioned above. For its explanation see Ref. [32]. The seven nitroaliphatic compounds are 1,1,1,3-tetranitrobutane ($C_4H_6N_4O_8$), 1,1,1,3,5,5,5-heptanitropentane ($C_5H_5N_7O_{14}$), 1,1,1,6,6,6-hexanitro-3-hexyne ($C_6H_4N_6O_{12}$), 1,1,1,6,6,6-hexanitro-3-hexene ($C_6H_6N_6O_{12}$), 3,3,4,4,-tetranitro-hexane ($C_6H_{10}N_4O_8$), 2,2,4,4,6,6-hexanitroheptane ($C_7H_{10}N_6O_{12}$), and 2,2,4,6,6-pentanitro-heptane ($C_7H_{11}N_5O_{10}$). The molecular frameworks of seven title explosives are listed in Fig. 1.

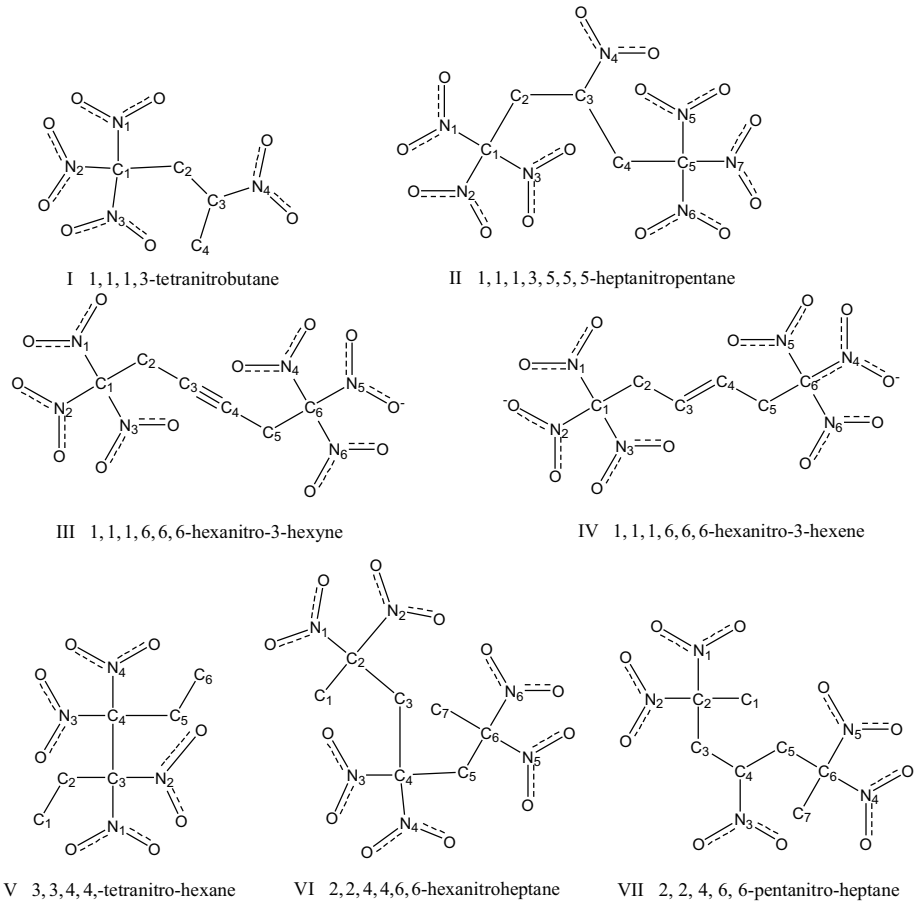


Fig. 1. Molecular frameworks and chemical names of seven title compounds.

Here, because we assume a homolytic cleavage of C–NO_2 in gas phase at 298 K and 1 atm (1 atm = 1.01325×10^5 Pa) while calculating BDEs, the fragments are radical species. The C–NO_2 bond strength is obtained by calculating the BDE, defined here as the enthalpy change of the dissociation reaction:

$$R-X \rightarrow R\cdot + X\cdot. \tag{1}$$

The BDE of the *R*–*X* bond is computed from the HOF in gas phase at 298.15 K of the species involved in the dissociation; that is,

$$E_{\mathrm{BDE}} = \Delta_{\mathrm{f}}H^0_{298.15,R} + \Delta_{\mathrm{f}}H^0_{298.15,X} - \Delta_{\mathrm{f}}H^0_{298.15,RX\cdot} \tag{2}$$

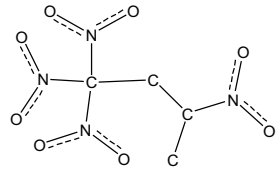
For many organic molecules, BDE and bond dissociation enthalpy (DH) are almost numerically equivalent, and as a result the terms BDE and DH often appear interchangeably. Therefore, for nitroaliphatic compounds studied in this work, the BDE can be given in terms of Eq. (3), as follows:

$$E_{\mathrm{BDE}} = E(R\cdot) + E(X\cdot) - E(R-X), \tag{3}$$

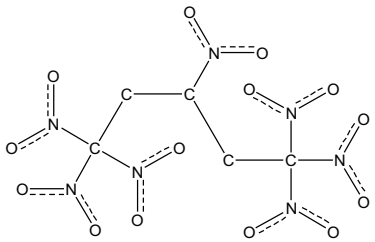
where the values of E_{BDEs} for all the molecules studied in this work are corrected by zero point energy (ZPV).

With respect to the computation of the standard HOF, isodesmic reactions are employed here. The isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are utilized with the application of the bond separation reaction rules. Isodesmic reaction often leads to the cancellation of systematic errors resulting from the bond environments, spin contamination, basis set superposition, and other non-random factors.[33] The accuracy of HOF obtained theoretically is conditioned by the reliability of HOF of the reference compounds.[34]

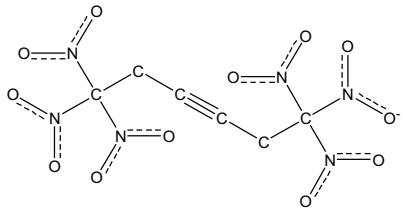
The HOFs of the title compounds at 298 K are calculated from the following isodesmic reactions:



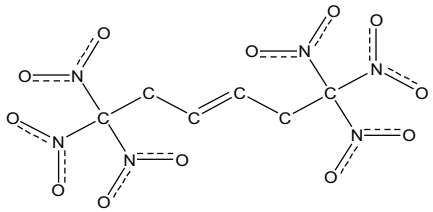
$$+ \quad 6CH_4 \longrightarrow 4CH_3NO_2 + 3C_2H_6, \tag{4}$$



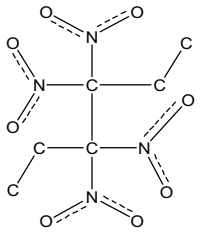
$$+ \quad 10CH_4 \longrightarrow 7CH_3NO_2 + 4C_2H_6, \tag{5}$$



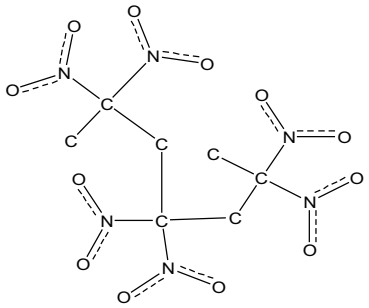
$$+ \quad 10CH_4 \longrightarrow 6CH_3NO_2 + 4C_2H_6 + C_2H_2, \tag{6}$$



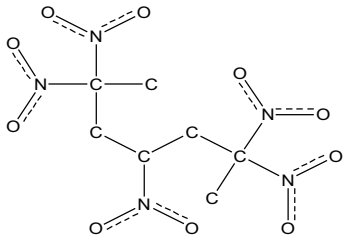
$$+ \quad 10CH_4 \longrightarrow 6CH_3NO_2 + 4C_2H_6 + C_2H_4, \tag{7}$$



$$+ \quad 8CH_4 \longrightarrow 4CH_3NO_2 + 5C_2H_6, \tag{8}$$



$$+ \quad 11CH_4 \longrightarrow 6CH_3NO_2 + 6C_2H_6, \tag{9}$$



$$+ \quad 10CH_4 \longrightarrow 5CH_3NO_2 + 6C_2H_6, \tag{10}$$

For isodesmic reactions (4)–(10), heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,p} - \sum \Delta H_{f,R}, \tag{11}$$

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

$$\begin{aligned} \Delta H_{298} &= \Delta E_{298} + \Delta(PV) \\ &= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \\ &= \sum_{\text{product}} \Delta H_f^0 - \sum_{\text{reactant}} \Delta H_f^0, \end{aligned} \tag{12}$$

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; $\sum_{\text{product}} \Delta H_f^0$ and $\sum_{\text{reactant}} \Delta H_f^0$ are sums of the HOF for products and reactants in gas phase at 298 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, and the values of thermal correction at the B3LYP/6-311G** level for five reference compounds enumerated in the isodesmic reactions (4)–(10). The experimental HOF of reference compounds CH_4, C_2H_2, C_2H_4, C_2H_6, and CH_3NO_2 are taken from Ref. [35]. Table 2 shows the total energies, zero-point energies, and the HOFs obtained via Eq. (2). Previous studies[36–40] have shown that the use of isodesmic work reactions by choosing appropriate reference compounds with accurate HOF values can result in considerable improvement in determining HOF values, based on which, our calculated results presented in Tables 1 and 2 are proved to be credible, although the experimental HOF values for title compounds are unavailable for comparison.

Table 1. Calculated values of total energy (E_0), zero-point energy (ZPE), thermal correction (H_T), and heats of formation (HOF) of the reference compounds at the B3LYP/6-311G** level.[a]

Compound	B3LYP/6-311G**			HOF[b]
	E_0	ZPE	H_T	
CH_4	–40.533759	27.5	30.4	–17.8
C_2H_2	–77.354697	16.9	19.3	54.2
C_2H_4	–78.613979	31.9	34.4	12.5
C_2H_6	–79.856260	46.7	49.4	–20.1
CH_3NO_2	–245.081685	31.2	34.5	–19.3

[a] E_0 is in a.u., ZPE, H_T, and HOF are in kcal/mol.

[b]The experimental data are cited from Ref. [35].

From Table 2, it can be noted the HOF of 2,2,4,6,6-pentanitro-heptane (VII) is the smallest (−66.7 kcal/mol) and the HOF of 1,1,1,6,6,6-hexanitro-3-hexyne (III) is the largest (30.8 kcal/mol). In addition, Table 2 shows that the value of HOF relates to the number of nitro groups among 2,2,4,6,6-pentanitro-heptane (VII), 2,2,4,4,6,6-texanitroheptane (VI), and 1,1,1,3,5,5,5-heptanitropentane (II). The general trend is that the computed HOF increases as the number of nitro (NO_2) group increases for these three nitroaliphatic compounds, with the HOF values being −66.7 kcal/mol, −52.0 kcal/mol, and −29.6 kcal/mol for $CH_3C(NO_2)_2CH_2CH(NO_2)CH_2C(NO_2)_2CH_3$ (VII), $CH_3C(NO_2)_2CH_2C(NO_2)_2CH_2C(NO_2)_2CH_3$ (VI), and $C(NO_2)_3CH_2CH(NO_2)CH_2C(NO_2)_3$ (II), respectively.

Table 2. Calculated values of total energy (E_0), zero-point energy (ZPE), thermal correction (H_T), and heat of formation (HOF) of the title compounds at B3LYP/6-311G** level.[a]

No.	Compound	B3LYP/6-311G**			
		E_0	ZPE	H_T	HOF
I	1,1,1,3-tetranitrobutane	–976.673981	88.9	99.2	–34.7
II	1,1,1,3,5,5,5-heptanitropentane	–1629.601190	110.7	126.6	–29.6
III	1,1,1,6,6,6-hexanitro-3-hexyne	–1461.897229	97.1	112.1	30.8
IV	1,1,1,6,6,6-hexanitro-3-hexene	–1463.156519	112.0	126.9	–11.3
V	3,3,4,4,-tetranitro-hexane	–1055.311211	124.0	135.9	–39.1
VI	2,2,4,4,6,6-texanitroheptane	–1503.728859	145.2	160.7	–52.0
VII	2,2,4,6,6-pentanitro-heptane	–1299.213624	144.0	158.3	–66.7

[a]E_0 is in a.u., ZPE, H_T, and HOF are in kcal/mol.

It is noteworthy that when an H atom in $CH_3C(NO_2)_2CH_2CH(NO_2)CH_2C(NO_2)_2CH_3$ (VII) is substituted by a nitro (NO_2) group, the HOF increases from −66.7 kcal/mol to −52.0 kcal/mol for $CH_3C(NO_2)_2CH_2C(NO_2)_2CH_2C(NO_2)_2CH_3$ (VI). This scenario also occurs in the 1,1,1,3,5,5,5-heptanitropentane (I) (−34.7 kcal/mol) and 1,1,1,3,5,5,5-heptanitropentane (II) (−29.6 kcal/mol), with an H atom in compound I being replaced by a $C(NO_2)_3$ group in compound II.

From Table 2, we can also find that when the C=C bond in the alkene nitroaliphatic compound 1,1,1,6,6,6-hexanitro-3-hexene (IV) is replaced by the C≡C bond in the alkyne nitroaliphatic compound 1,1,1,6,6,6-hexanitro-3-hexyne (III), the HOF value increases dramatically from −11.3 kcal/mol to 30.8 kcal/mol. In search of the reason for this, we can see from the molecular structure in Fig. 1 that 1,1,1,6,6,6-hexanitro-3-hexyne (III) consists of a C≡C alkyne bond and shows a stronger repulsion interaction than the alkene nitroaliphatic compound.

3.2. Bond dissociation energy

The BDE could evaluate the strength of bonding that is fundamental to understanding chemical processes,[41] and provide useful information to understand the stability of nitroaliphatic compounds. To elucidate this, we calculate the dissociation energies for the possible initial steps in the pyrolysis route. It should be pointed out that we select the C–NO_2 bond as a possible breaking bond at the B3LYP/6-31G** level because the initial breakdown bond for many different families of energetic molecules including nitroaliphatic compounds is the bond R–NO_2. Table 3 provides the computed homolytic BDEs and the experimental sensitivity $h_{50\%}$ for each of the molecules.

From Table 3, it can be noted that, except for 2,2,4,4,6,6-texanitroheptane with the weakest BDE being 15.7 kcal/mol, all of the computed weakest C–NO_2 BDEs are larger than 20 kcal/mol, which indicates that most of the molecules investigated in this paper are viable candidates for new high energy density materials.[42]

As seen from Table 3, for title molecules with all nitro groups attached to C atoms, the position of nitro has an important effect on the BDE. We can notice that the BDE of C_1–$N_1/N_2/N_3$ bond for 1,1,1,3-tetranitrobutane is 29.4 kcal/mol for B3LYP method, while the BDE of C_3–N_4 bond is 45.7 kcal/mol, which demonstrates that the rupture of C_1–$N_1/N_2/N_3$ bond is at the initial site in the decomposition process. It also shows that if the number of nitro groups attached to one C atom is bigger than that to other C atoms, the BDE value for this exact C–N bond is weakest. This phenomenon also lies in the molecules 1,1,1,3,5,5,5-heptanitropentane and 2,2,4,6,6-pentanitro-heptane.

For 2,2,4,6,6-pentanitro-heptane and 2,2,4,4,6,6-texanitroheptane, when an H atom attached to C_4 in 2,2,4,6,6-pentanitro-heptane is substituted by a nitro group in 2,2,4,4,6,6-texanitroheptane, the BDE of C_4–N_3 bond is reduced from 39.3 kcal/mol to 15.7 kcal/mol, which shows that the increase of nitro group number reduces the stability of the molecule. This observation can be characterized by the decrease of the weakest C–NO_2 bond energy.

As for 1,1,1,6,6,6-hexanitro-3-hexyne and 1,1,1,6,6,6-hexanitro-3-hexene, the weakest C–NO_2 bond energies are close to each other, with the BDE being 33.0 kcal/mol for the former and 32.2 kcal/mol for the latter. This may demonstrate that the C=C bond or the C≡C bond in these two compounds has a similar effect on the stability of the molecules.

According to the calculated results, we can find that the BDE/E value is smallest for compound III, which is consistent with the conclusion of HOF, with the largest HOF value being 30.8 kcal/mol for 1,1,1,6,6,6-hexanitro-3-hexyne (III). This phenomenon can be explained by the definition of HOF that the decreasing HOF is attributed to the stronger C–NO_2 bond strength and the increasing HOF is due to the weaker C–NO_2 bond strength.

Based on the experimental impact sensitivity $h_{50\%}$ available[43] and the calculated BDE/E values for the weakest bond for our title energetic explosives, a plot of $h_{50\%}$ versus BDE/E has been illustrated in Fig. 2. It is clear that the ratio of the BDE to the molecular total energy with zero point energy correction E and impact sensitivity indeed have a good linear relationship. The correlation function is given as follows:

$$h_{50\%} = 12.12527 + 4.48352\left(\frac{BDE}{E}\right) \times 10^5, \qquad (13)$$

The linear correlation coefficient is 0.998.

Since Song *et al.*[44] proved that basis set superposition error (BSSE) corrections have little influence on the linear relationship for the compounds studied, the BSSE corrections have not been considered in the calculations of BDE and BDE/*E* for nitroaliphatic explosives.

From the computational values and fitting curves, it is obvious that there is a nearly linear correlation between the ratio of the weakest BDE to the molecular total energy (BDE/*E*) and the impact sensitivity of nitroaliphatic energetic explosives, which is consistent with the conclusions in the literature.[45–47] BDE/*E* is undoubtedly a good index to predict the impact sensitivities for other nitroaliphatic compounds whose impact sensitivities are not available. Our research conclusion further substantiates the correlation between the BDE/*E* and the sensitivity $h_{50\%}$ in those energetic materials having similar molecular structures.

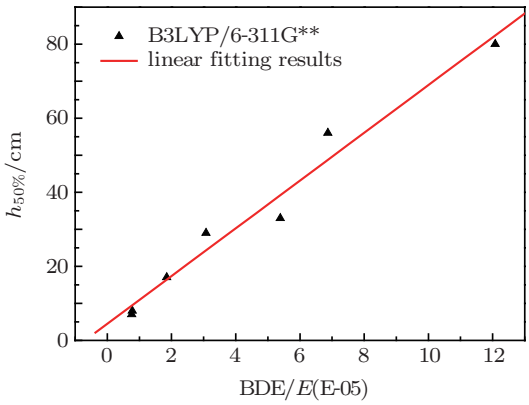


Fig. 2. (color online) Relationship between $h_{50\%}$ and BED/*E* title compound.

Table 3. Calculated C–NO_2 bond dissociation energies[a] (kcal/mol) of the title compounds at B3LYP/6-311G** level.

Bond / No.	B3LYP/6-311G**						
	I (33)[b]	II (8)	III (7)	IV (17)	V (80)	VI (29)	VII (56)
C_1–N_1/N_2/N_3	29.4	27.5	33.0	32.2	–	–	–
C_2–N_1/N_2	–	–	–	–	–	25.0	28.3
C_3–N_1/N_2/ N_4	45.7	38.1	–	–	22.4	–	–
C_4–N_3/N_4	–	–	–	–	22.4	15.7	39.3
C_5–N_5/N_6/N_7	–	27.5	–	–	–	–	–
C_6–N_4/N_5/N_6	–	–	33.0	32.2	–	25.0	28.3

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

[b]The value in each parenthesis corresponds to the experimental impact sensitivity of each title compound in cm, cited from Ref. [43].

3.3. Molecular stability

The values of the Mulliken population on the C–NO_2 bonds and the weakest C–NO_2 bond BDEs are listed in Table 4. As a whole, smaller populations have weaker bonding. Therefore, bonds with small populations are relatively weak and likely to rupture. In this work, the principle above is again proved by the calculated lowest Mulliken populations and the weakest C–NO_2 BDEs. From Table 4, it is found that for 1,1,1,3-tetranitrobutane for instance, the lowest Mulliken population is of 0.1643 on C_1–N_1/N_2/N_3 bond, and the calculated C_1–N_1/N_2/N_3BDE of 29.4 kcal /mol for B3LYP method is indeed the weakest bond with respect to other C–NO_2 bonds in this compound. In addition, taking the average Mulliken populations into account, we can find that the C–NO_2 bond in 2,2,4,4,6,6-hexanitroheptane has the smallest average Mulliken population of 0.1437, its sensitivity is reactive, and it is unstable for thermolysis according to the principle of the smallest bond order (PSBO).[8]

Table 4. The weakest C–NO_2 bond dissociation energies (in kcal/mol) and average Mulliken populations as well as the lowest Mulliken populations (a.u.) on the C–NO_2 bonds at B3LYP/6-311G** level.

No.	Compound	B3LYP/6-311G**		
		C–NO_2^a	C–NO_2^b	BDE
I	1,1,1,3-tetranitrobutane	0.1657	0.1643(C_1–N_1/N_2/N_3)	29.4
II	1,1,1,3,5,5,5-heptanitropentane	0.1659	0.1620(C_1–N_1/N_2/N_3)	27.5
III	1,1,1,6,6,6-hexanitro-3-hexyne	0.1687	0.1687(C_1–N_1/N_2/N_3)	33.0
IV	1,1,1,6,6,6-hexanitro-3-hexene	0.1675	0.1675(C_1–N_1/N_2/N_3)	32.2
V	3,3,4,4,-tetranitro-hexane	0.1510	0.1510(C_3–N_1/N_2/ N_4)	22.4
VI	2,2,4,4,6,6-hexanitroheptane	0.1437	0.1145(C_4–N_3/N_4)	15.7
VII	2,2,4,6,6-pentanitro-heptane	0.1658	0.1214(C_2–N_1/N_2)	28.3

[a]The average Mulliken population on the C–NO_2 bond in title compound.

[b]The lowest Mulliken population on the C–NO_2 bond in title compound.

Table 5 collects energies (a.u.) of frontier molecular orbitals and their gaps (ΔE) at the B3LYP/6-311G** level. As is well known, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is of great importance in several chemical processes and it is, therefore, an important stability index. The energy of the HOMO ($E_{\rm HOMO}$) measures the electron-donating characteristic of a compound, and the energy of the LUMO ($E_{\rm LUMO}$) measures its electron-accepting characteristic. The molecule 2,2,4,4,6,6-texanitroheptane has the biggest value of the energy gap, i.e., 0.20916 a.u., which shows that 2,2,4,4,6,6-texanitroheptane molecule is the most stable compound among the title compounds. The compound that has the smallest value of the energy gap from B3LYP method is 1,1,1,6,6,6-hexanitro-3-hexene molecule: the energy gap value is about 0.18010 a.u., which indicates that 1,1,1,6,6,6-hexanitro-3-hexene compound is the least stable molecule. The stability here refers to the chemical or photochemical stability with electron transfer or electron leap. It is noteworthy that the analysis of the energy gap $\Delta E_{\rm LUMO-HOMO}$ is in agreement with that of BDE in the above segment.

Table 5. Energies (a.u.) of frontier molecular orbitals and their gaps at the B3LYP/6-311G** level.

No.	Compound	B3LYP/6-311G**		
		$E_{\rm HOMO}$	$E_{\rm LUMO}$	$\Delta E_{\rm LUMO-HOMO}$
I	1,1,1,3-tetranitrobutane	–0.32316	–0.14043	0.18273
II	1,1,1,3,5,5,5-heptanitropentane	–0.34428	–0.15286	0.19142
III	1,1,1,6,6,6-hexanitro-3-hexyne	–0.32386	–0.13869	0.18517
IV	1,1,1,6,6,6-hexanitro-3-hexene	–0.31872	–0.13862	0.18010
V	3,3,4,4,-tetranitro-hexane	–0.32958	–0.12371	0.20587
VI	2,2,4,4,6,6-texanitroheptane	–0.33336	–0.12420	0.20916
VII	2,2,4,6,6-pentanitro-heptane	–0.31640	–0.11729	0.19911

4. Conclusions

We utilize density functional theory B3LYP in conjunction with 6-311G** basis set to investigate the structure and thermochemistry properties, including BDEs, HOFs, and impact sensitivity ($h_{50\%}$), Mulliken population analysis, and energies of frontier molecular orbitals and their gaps. The some conclusions can be drawn below.

(i) Among the 2,2,4,6,6-pentanitro-heptane (VII), the 2,2,4,4,6,6-texanitroheptane (VI), and the 1,1,1,3,5,5,5-heptanitropentane (II), the computed HOF increases as the number of nitro group increases. For compounds I and II, compounds VII and VI, when an H atom is substituted by an NO_2 group or a $C(NO_2)_3$ group of the former molecule, the HOF value of the latter molecule increases.

(ii) BDEs of all the C–NO_2 bonds are computed and the weakest bonds are estimated. The calculated results show that if the number of nitro groups attached to one C atom is bigger than to other C atoms, the BDE value for this exact C–N bond is weakest. Moreover, the observation shows that the increase of nitro group number reduces the stability of the molecule.

(iii) For title compounds, the ratio BDE/E and the impact sensitivity $h_{50\%}$ indeed have a good linear relationship, with the linear correlation coefficient R being 0.998.

(iv) The average and the lowest Mulliken population on the C–NO_2 bonds and the weakest C–NO_2 BEDs are also studied in this paper. Frontier molecular orbitals and their values of gap ΔE are investigated and 2,2,4,4,6,6-hexanitroheptane has the smallest average Mulliken population, which indicates that its sensitivity is reactive.

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