Theoretical study on structure and properties of $B_2H_m(NO_2)_n$(m=2-5;n=1-4)

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This paper conducts theoretical research of B_2H_m (NO_2) n (m = 2-5; n = 1-4) with density functional theory, determines the most stable structure through structural optimization and frequency analysis, and calculates enthalpy of formation by applying atomization reaction method and isodesmic reaction method for the most stable structure, calculates molar volume, theoretical density and explosion heat of B_2H_m (NO_2) n (m = 2-5; n = 1-4) at B3LYP / 6-31G * level, and studies detonation velocity, detonation pressure and other thermodynamic properties with K-J empirical formulas. Studies show that explosion heat of $B_2H_3(NO_2)_3$, $B_2H_2(NO_2)_4$ are1.34KJ / mol and 0.85KJ / mol respectively, less than 1.37KJ / mol of conventional explosive TNT; explosion heat of $B_2H_5NO_2$ and $B_2H_4(NO_2)_2$ are 1.83KJ / mol and 1.57KJ / mol, greater than that of TNT explosion heat; detonation velocity and pressure of adding compound $B_2H_m(NO_2)_n$(m=2-5;n=1-4) more and more approach TNT as substituting cardinal number increases; ΔEgap of titled compound are 5.94eV, 5.76eV, 5.10eV and 4.76eV respectively, showing that as nitro substituent increases, ΔEgap value decreases. In Wiberg bond order analysis, B-NO_2 bond is relatively weak in $B_2H_m(NO_2)_n$(m=2-5;n=1-4) molecule, probably pyrolysis or detonation trigger bond of titled compound.

Keywords: Enthalpy of formation, High energy compounds, Density functional theory, Explosion heat, Detonation pressure, Detonation velocity.

INTRODUCTION

Since high-energy compounds has been very widely applied in civil and military use, research on new high-energy compounds has always been a subject interested by scientists who try to find new high-energy, low-sensitivity energetic materials to meet the development needs of military and aerospace technology[1]. There are two sources of high-energy compounds, one is conventional explosives whose energy is mainly from rapid oxidation [2] of carbon chain or cage-type tension structure [3]; another is high-nitrogen compound whose energy is mainly from very high enthalpy of formation [4].

Enthalpy of formation is a fundamental thermodynamic property of compounds, moreover an important parameter to measure explosiveness and security for enthalpy of formation of explosives, as enthalpy of formation can directly affect explosion heat, indirectly impact detonation velocity, detonation pressure and capacity for work. For stable compound, their enthalpy of formation can be obtained directly by information search; while enthalpy of formation of high-energy compounds is difficult to be directly measured experimentally as there is a certain danger in actual

measurement. Therefore, to estimate enthalpy of formation of high-energy compounds with a variety of theoretical approaches has become scientists' research focus, and quantum chemistry method has opened up a new way for calculation of enthalpy of formation [5-7]. In theoretical calculation, estimation of enthalpy of formation with group adding subjects to many restrictions[8] due to consideration to bond and some group's contribution value for enthalpy of formation and correction value interactional with group, which renders theoretical calculation value not trusted. Atomization reaction method has been affirmed by scientists and widely used for calculation of enthalpy of formation. Based on density functional theory DFT-B3LYP[9-10] method, it takes into account electron correlation effect, can obtain more reliable energy in optimization of molecular structure, while reducing computing cost; however atomization reaction method is not applicable to all molecules. For those large molecular systems with cage-like or delocalized bond, calculation of enthalpy of formation with atomization reaction method will damage its system with relatively big error, also relatively complicated [11-13]. Hence, it is necessary to design a reasonable isodesmic reaction to calculate enthalpy of formation. Isodesmic reaction method based on the advantage that reactants and products have similar electronic environment offsets error caused by electron

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correlation energy, and accurately calculates enthalpy of formation of titled compound [5.10.14.15].

Enthalpy of formation of B_2H_6 calculated by atomizaion reaction method based on B3LYP / 6-31G * level is 34.83 KJ / mol which approaches experimental value (35.60 KJ / mol), indicating reliability of atomization reaction method. Effort has been made to replace hydrogen in the molecule with nitro and generate a class of new compounds. If such compounds have good thermodynamic properties, then they are probably a class of new high-energy compounds. Thus, its research significance lies in that it is more environmentally friendly compared to traditional explosives. After reaction, B element generates B_2O_3 and boron, and there will be no CO, SO_2 and other harmful gases causing environmental pollution.

CALCULATION METHOD

This paper applies density functional theory and ab initio method in Gaussian 09 program package, combines 6-31G * basis set, conducts geometry optimization of B_2H_6, $B_2H_m(NO_2)_n(m=2$-$5;n=1$-$4)$ and other molecules, and obtains ground state total energy. Zero-point energy and enthalpy correction energy is acquired based on vibration analysis. Default program value is adopted for calculation of convergence precision, and the resultant structures are minimum points on potential energy surface, that is, no imaginary frequency. Calculation results of the most stable structure of B_2H_6 $B_2H_m(NO_2)_n(m=2$-$5;n=1$-$4)$ is shown in Figure 2.1.
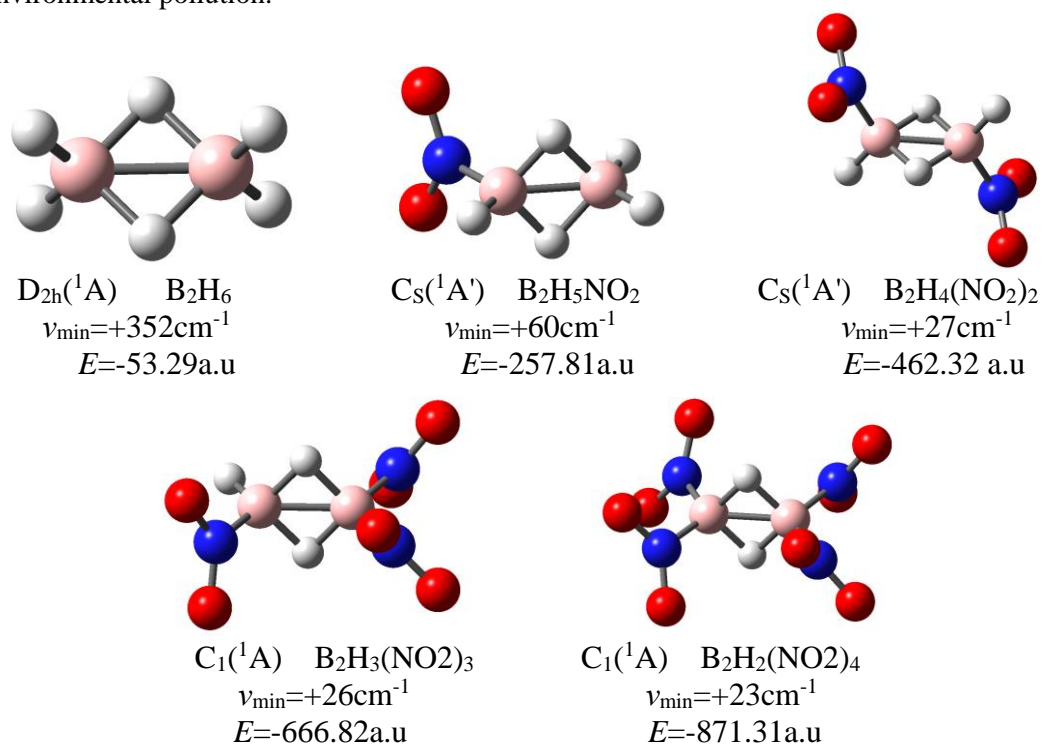

$D_{2h}(^1A)$ B_2H_6	$C_S(^1A')$ $B_2H_5NO_2$	$C_S(^1A')$ $B_2H_4(NO_2)_2$
$v_{min}=+352cm^{-1}$	$v_{min}=+60cm^{-1}$	$v_{min}=+27cm^{-1}$
$E=-53.29$a.u	$E=-257.81$a.u	$E=-462.32$ a.u

$C_1(^1A)$ $B_2H_3(NO2)_3$	$C_1(^1A)$ $B_2H_2(NO2)_4$
$v_{min}=+26cm^{-1}$	$v_{min}=+23cm^{-1}$
$E=-666.82$a.u	$E=-871.31$a.u

Fig. 2.1. The most stable structure of B_2H_6 $B_2H_m(NO_2)_n(m=2$-$5;n=1$-$4)$

The paper next takes compound $A_xB_yH_z$ as an example to introduce the method to calculate standard enthalpy of formation of compound at 298 K with atomization reaction method. First, decompose molecules into atoms.

$$A_xB_yH_z \longrightarrow xA+yB+zH \qquad (1)$$

Standard reaction enthalpy of the reaction at 298K is ΔH_{298}^0 (equal to atomization energy ΣD_0 of molecule)

$$\Sigma D_0(A_xB_yH_z) = [x\varepsilon_0(A)+y\varepsilon_0(B)+z\varepsilon_0(H)] - \varepsilon_0(A_xB_yH_z) - \varepsilon_{ZEP} (A_xB_yH_z)$$

In the formula, $\Sigma D_0(A_xB_yH_z)$ is atomization energy of $A_xB_yH_z$, $\varepsilon_0(A)$, $\varepsilon_0(B)$, $\varepsilon_0(H)$ and $\varepsilon_0(A_xB_yH_z)$

are ground state total energy of A, B, H and compound $A_xB_yH_z$ at Gaussian 09 program computing, while ε_{ZEP} ($A_xB_yH_z$) is zero point energy of compound ε_{ZEP} ($A_xB_yH_z$);

$$\Delta H_{298}^0 = \Sigma D_0(M) = \Sigma x\varepsilon_0(X)-\varepsilon_0(M)- \varepsilon_{ZEP}(M)$$

$$\Delta_f H^0(A_xB_yH_z,0K)=\Sigma x\Delta_f H^0(X,0K) - \Sigma D_0(A_xB_yH_z)$$

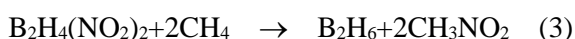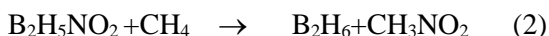$$= [x\Delta_f H^0(A, 0 K)+y\Delta_f H^0(B, 0 K)+z\Delta_f H^0(H, 0 K)] - \Sigma D_0(A_xB_yH_z)$$

$$\Delta_f H^0(A_xB_yH_z, 298 K) = \Delta_f H^0(A_xB_yH_z, 0 K)+$$

ΔH_T

$\Delta H_T= [H^0_{AxByHz}(298K) - H^0_{AxByHz}(0K)] - x[H^0_A (298 K)- H^0_A(0 K)] - y[H^0_B(298 K) - H^0_B (0 K)]-z[H^0_H (298 K)- H^0_H (0 K)]$

In the formula, $\Delta_f H^0(A_xB_yH_z,0K)$ and $\Delta_f H^0(A_xB_yH_z,298 K)$ are enthalpy of formation of compound at 0 K and 298 K respectively, $\Delta_f H^0(A, 0 K)$, $\Delta_f H^0(B, 0 K)$, $\Delta_f H^0(H, 0 K)$ are enthalpy of formation of atoms A, B and H respectively at 0 K which can be obtained by checking the manual, $[H^0_A (298K)- H^0_A(0 K)]$, $[H^0_B (298 K) - H^0_B (0 K)]$, $[H^0_H(298 K)- H^0_H(0 K)] \rightarrow$are heat correction values of atoms A, B and H respectively which can also be obtained by checking the manual. Similarly, $[H^0_{AxByHz} (298K) - H^0_{AxByHz} (0K)]$ is heat correction value of compound $A_xB_yH_z$.

For $B_2H_m(NO_2)_n(m=2-5;n=1-4)$, if isodesmic reaction is adopted to calculate its enthalpy of formation, then the designed isodesmic reaction is as follows:

$$B_2H_5NO_2 +CH_4 \rightarrow B_2H_6+CH_3NO_2 \quad (2)$$

$$B_2H_4(NO_2)_2+2CH_4 \rightarrow B_2H_6+2CH_3NO_2 \quad (3)$$

$$B_2H_3(NO_2)_3+3CH_4 \rightarrow B_2H_6+3CH_3NO_2 \quad (4)$$

$$B_2H_2(NO_2)_4+4CH_4 \rightarrow B_2H_6+4CH_3NO_2 \quad (5)$$

In the formula: B_2H_6 is the parent, CH4, CH3NO2 are reference material methane and nitromethane respectively. Reaction heat ΔH_{298} of reaction formulas (2) - (5) at 298 K can be expressed as:

$$\Delta H_{298} = \Sigma\Delta H_{f,P} - \Sigma\Delta H_{f,R}$$

In the formula: $\Sigma\Delta H_{f,P}$ and $\Sigma\Delta H_{f,R}$ are total heat formation of products and reactants respectively at 298 K. Gas phase formation heat of CH_4 andCH_3NO_2 can be obtained by checking the table. Hence, only by calculating ΔH_{298} can enthalpy of formation of titled compound be obtained.

$$\Delta H_{298}=\Delta\varepsilon_0+\Delta\varepsilon_{ZEP}+\Delta H_T+\Delta nRT$$

In the formula: $\Delta\varepsilon_0$ and $\Delta\varepsilon_{ZEP}$ are difference between the total energy and zero-point energy of reactant and product respectively, ΔH_T is enthalpy correction term of 0-298 K; under ideal gas conditions, $\Delta(PV)$ equals ΔnRT, Δn is the difference between mole number of product and reactant. For the above formula, $\Delta n=0$.

After enthalpy of formation of titled compound is obtained according to the above calculation method, seek explosion heat value according to explosion heat formula. Explosion heat is the maximum released energy (detonation chemical energy) per gram of explosive after explosion, i.e. negative of enthalpy change in detonation reaction, energy [15] that can be used to do mechanical work. Also, explosion heat can also be used to assess dynamite damage [14] to the environment. The formula [12-14] is as follows:

$$Q \cong \frac{- [\Delta_f H(\text{detonation products}) - \Delta_f H(\text{explosive})]}{\text{formula weight of explosive}}$$

Detonation velocity and detonation pressure can be estimated by K-J empirical formula, with its expression as follows:

$$D=1.01[NM^{0.5}Q^{0.5}]^{0.5}(1+1.30\rho)$$

$$P=1.558\rho^2NM^{0.5}Q^{0.5}$$

The formula is simple empirical formula to calculate detonation velocity and pressure based on experimental data analysis and summarization by Kamlet and Jacobs et al. [8]. In the formula, D is detonation velocity (km / s), P is detonation pressure (GPa) , $\rho$is density of explosives(g/cm^3), N is mole number of gaseous products generated by per gram of explosive detonation (mol / g), M is average molecular weight of gaseous products (g / mol). In the calculation process, suppose explosive reaction follows principle of maximum heat release, i.e. after explosion, hydrogen first generates H_2O with oxygen, boron and oxygen generate diboron trioxide solid, but due to lack of oxygen, the remaining boron exists as simple substance, and all nitrogen generates nitrogen oxides.

RESULTS AND DISCUSSION

In this paper, enthalpy of formation of compounds such as B_2H_6, $B_2H_m(NO_2)_n(m=2-5;n=1-4)$ is calculated with atomization reaction method based on level method DFT-B3LYP-6-31G*. Experimental standard gaseous enthalpy of formation, value of thermal correction and ground state energy obtained after calculation of B, H, N, O atoms are shown in Table 3.1. Total energy ε_0, zero-point energy ε_{ZEP}, enthalpy correction value H_T and enthalpy of formation ΔH_f calculated by atomization reaction method of compounds B_2H_6, $B_2H_m(NO_2)_n(m=2-5;n=1-4)$ at level of B3LYP / 6-31G * are shown in Table 3.2.

Table 3.1. The standard enthalpy of formation, Values of Thermal Correction , and Ground State Total Energy (ε_0) of B, H, N, O atoms.

	ΔH_{atom}^0 [12] Cal/mol	H_T [$H^0(298)$-$H^0(0K)$][12] Cal/mol	ε_0/(a.u) at B3LYP/6-31G* level
B	136.2	0.29	-24.654354
H	51.63	1.01	-0.5002728
N	112.53	1.04	-54.5844894
O	58.99	1.04	-75.0606214

Table 3.2. Total Energy (ε_0), Zero-Point Energy (ε_{ZEP}), Values of Thermal Correction (H_T), and Heats of Formation (ΔH_f) of the B_4H_2,B_4HNO_2,$B_4(NO_2)_2$,$B_2H_5NO_2$, $B_2H_4(NO_2)_2$, $B_2H_3(NO_2)_3$, $B_2H_2(NO_2)_4$, CH_4 and CH_3NO_2 Compounds at the B3LYP/6-31G* level

	ε_0 a.u	ε_{ZEP} a.u	H_T a.u	ΔH_f KJ/mol Atomic reaction	ΔH_f KJ/mol Isodesmic reaction method
$B_2H_5NO_2$	-257.81	0.068	17.69	-45.32	-35.09
$B_2H_4(NO_2)_2$	-462.32	0.072	24.78	-253.15	-85.16
$B_2H_3(NO_2)_3$	-666.82	0.075	31.918	-271.63	-109.22
$B_2H_2(NO_2)_4$	-871.31	0.078	39.77	-319.75	-129.08
CH_3NO_2	-244.33	0.051340	0.0053	-74.40[14]	
CH_4	-40.33	0.046354	0.0038	-74.80 [13]	

Table 3.2 shows that all enthalpy of formation of resulting compound $B_2H_m(NO_2)_n$ (m=2-5;n=1-4) after compound B_2H_6's nitro-substitution of hydrogen atoms are negative, indicating that generation of this class of compound will release heat. Enthalpy of formation of CH_4, CH_3NO_2 is experimental value in the Table.

Calculation results of theoretical density, molar volume, explosion heat, detonation velocity, detonation pressure of compound $B_2H_m(NO_2)_n$ (m=2-5;n=1-4) and TNT at B3LYP / 6-31G * level are shown in Table 3.3.

Table 3.3. The density, size, detonation, detonation velocity and detonation pressure of $B_2H_m(NO_2)_n$(m=2-5;n=1-4)and TNT compounds at the B3LYP/6-31G* level.

	ρ g/cm³	V cm³/mol	N mol/g	M g/mol	Q KJ/g	P GPa	D km/s
$B_2H_5NO_2$	1.05	69.75	0.041	17	1.83(1.86)	12.38 (12.53)	6.42 (6.45)
$B_2H_4(NO_2)_2$	1.55	75.96	0.025	21.3	1.57(1.91)	17.89 (18.89)	6.58 (6.84)
$B_2H_3(NO_2)_3$	1.61	101.60	0.028	20.4	1.34(1.73)	18.29 (21.27)	6.65 (7.10)
$B_2H_2(NO_2)_4$	1.85	112.68	0.024	27.6	0.85(1.22)	19.55 (23.48)	6.59 (7.21)
TNT[11]	1.72	132.42	-	-	1.37	23.46	7.22

Note: Figures in parentheses are calculated values of isodesmic reaction method.

Table 3.3 shows that as density of adding compounds that substitute cardinal number increases, tetra-substituted compound density is greater than TNT density; molar volume is less than TNT, while explosion heat tri-substituted compound and tetra-substituted compound are significantly less than TNT; as number of substituent group grows, detonation velocity and pressure become closer to TNT. The reason is that when nitro number increases, oxygen elements in molecule increase, B2O3 mole number generated in reaction increases, gas phase enthalpy of formation of B2O3 after calculation is-819.92KJ / mol, so there is more

energy released during B2O3 generation, much larger than equimolar CO2 and H2O, and explosion heat will be huge. From calculation formula of detonation velocity and pressure, it can be known that explosion heat and density are the main factors affecting its size, as explosion heat and density become closer to TNT, detonation velocity and pressure are closer to TNT.

Frontier orbital energy E_{HOMO} 和 E_{LUMO} of five titled compound stable structure at B3LYP/6-31G* level and its energy gap ΔE_{gap} value is shown in Table 3.4.

Table 3.4. Energies (a.u.) of frontier molecular orbitals and their gaps at the B3LYP/6-31G* level.

	E_{HOMO}(a.u)	E_{LUMO}(a.u)	ΔE_{gap}(eV)
B_2H_6	-0.33	-0.030	8.14
$B_2H_5NO_2$	-0.30	-0.077	5.93
$B_2H_4(NO_2)_2$	-0.31	-0.10	5.76
$B_2H_3(NO_2)_3$	-0.33	-0.14	5.10
$B_2H_2(NO_2)_4$	-0.34	-0.17	4.76

Molecular orbital theory regards that, the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO exert greatest impact on chemical properties of compound. HOMO orbital has priority in provision of electrons, while LUMO orbital can receive electrons [11]. Size of HOMO-LUMO energy gap value ΔE_{gap} reflects electrons' ability to transit to unoccupied molecular orbital from occupied molecular orbital, which represents molecule strength in participation into chemical reaction to a certain extent. A bigger ΔE_{gap} value means that it is more difficult to have electron transition, and that molecule is more stable. Seen from the table, ΔE_{gap} of $B_2H_2(NO_2)_2$ is higher than that of $B_2H_2(NO_2)_2$, $B_2H_2(NO_2)_3$, $B_2H_2(NO_2)_4$, indicating that as nitro substituent increases in number, ΔE_{gap} value decreases, and that as nitro substituent increases in number, compound stability decreases. B-H-B bridged bond is electron deficient bond, while nitro is electron withdrawing group, so the more nitro, the more instability of compounds, which is consistent with calculation results of this paper.

Calculation results of wiberg electronic population of compound at B3LYP/6-31G* level are shown in Table 3.5.

Table 3.5. Wiberg bond（WBI_{A-B}）indexes of compounds at B3LYP/6-31G* level.

	WBI_{B-H}	$WBI_{B-H}(2)$	WBI_{B-B}	WBI_{B-NO2}
B_2H_6	0.99	0.48	0.68	
$B_2H_5NO_2$	0.96 0.98 0.98	0.49 0.45	0.68	0.76
$B_2H_4(NO_2)_2$	0.96	0.46	0.67	0.77
$B_2H_3(NO_2)_3$		0.44 0.47 0.43	0.65	0.78 0.77 0.77
$B_2H_2(NO_2)_4$		0.48 0.45	0.64	0.77

Interatomic bond level reflects relative strength of bond. The greater interaction between the bond, the greater bond order, the smaller interaction, the smaller bond order which represents the degree of electron cloud overlap. From wiberg bond order calculation results of compound at B3LYP / 6-31G * level in Table 2.5, it can be seen that hydrogen bridge bond WBIB-H (2) and WBIB-B are less than WBIB-NO2, but closed three-center two-electron stable structure forms between two B atoms and H atoms. Thus, B-H-B bond is relatively strong. In comparison, B-NO2 bond is relatively weak, probably pyrolysis or detonation trigger bond of titled compound, which is consistent with TNT as nitro nitrogen bond is pyrolysis or detonation trigger bond of titled compound.

CONCLUSIONS

Based on density functional theory B3LYP/ 6-31G* method, this paper adopts atomization reaction method for theoretical calculations of stability, enthalpy of formation, explosion heat, detonation velocity and detonation pressure and other parameters of compound $B_2H_m(NO_2)_n$ (m=2-5; n=1-4); and conducts simple theoretical calculation of thermal decomposition mechanism of compound, obtaining the following conclusions:

(1) Enthalpy of formation of compounds $B_2H_4(NO_2)_2$, $B_2H_3(NO_2)_3$ and $B_2H_2(NO_2)_4$ are -253.15, -271.63 and -319.75 KJ/mol respectively, indicating that a lot of energy will be released during chemical reaction of these compounds;

(2) With isodesmic reaction calculation method, detonation pressure of $B_2H_4(NO_2)_2$, $B_2H_3(NO_2)_3$ and $B_2H_2(NO_2)_4$ is obtained: 18.89,21.27 and 23.48 GPa, very close to 23.46 GPa of TNT explosive. Calculated value of $B_2H_2(NO_2)_4$ detonation pressure even exceeds detonation pressure value of TNT; detonation velocity of $B_2H_4(NO_2)_2$, $B_2H_3(NO_2)_3$ and $B_2H_2(NO_2)_4$ are 6.84,7.10 and 7.21 km/s

respectively, very close to TNT detonation velocity of 7.22 km/s.

(3) Through wiberg bond order analysis, it can be known that B-NO$_2$ bond in compound $B_2H_m(NO_2)_n$ (m = 2-5; n = 1-4) is relatively weak, indicating that chemical reaction of compound most likely begins from B-NO$_2$ bond rupture.

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