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 $B_2H_2(NO_2)_3$, $B_2H_2(NO_2)_4$ are 1.34 KJ/mol and 0.85 KJ/mol respectively, less than 1.37 KJ/mol of conventional explosive TNT; explosion heat of $B_2H_2NO_2$ and $B_2H_2(NO_2)_2$ are 1.83 KJ/mol and 1.57 KJ/mol, greater than that of TNT explosion heat; detonation velocity and pressure of adding compound $B_2H_5(NO_2)_3(m=2-5;n=1-4)$ more and more approach TNT as substituting cardinal number increases; $\Delta E_{\text{gap}}$ of titled compound are 5.94 eV, 5.76 eV, 5.10 eV and 4.76 eV respectively, showing that as nitro substituent increases, $\Delta E_{\text{gap}}$ value decreases. In Wiberg bond order analysis, B NO bond is relatively weak in $B_2H_5(NO_2)_3(m=2-5;n=1-4)$ 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 interational 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...
correlation energy, and accurately calculates enthalpy of formation of titled compound [5,10,14,15].

Enthalpy of formation of B₃H₆ calculated by atomization 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 B₂O₃ and boron, and there will be no CO, SO₂ 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 B₃H₆, B₃H₆(NO₂)₄(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 B₃H₆, B₃H₆(NO₂)₄(m=2-5; n=1-4) is shown in Figure 2.1.

![Fig. 2.1. The most stable structure of B₃H₆, B₃H₆(NO₂)₄(m=2-5; n=1-4)](image)

The paper next takes compound AₓBᵧHₓ 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.

AₓBᵧHₓ → xA+yB+zH (1)

Standard reaction enthalpy of the reaction at 298K is ΔH₉₈ (equal to atomization energy ΣD₀ of molecule)

\[ ΔH₀ = Σd₀(AₓBᵧHₓ) = [xΔd₀(A) + yΔd₀(B) + zΔd₀(H)] - ε₂E(P) (AₓBᵧHₓ) - ε₂E(P) (AₓBᵧHₓ) \]

In the formula, ΣD₀(AₓBᵧHₓ) is atomization energy of AₓBᵧHₓ, Δd₀(A), Δd₀(B), Δd₀(H) and ε₂E(P) (AₓBᵧHₓ).
ΔHₜ

ΔHₜ= \[ \Delta H^p_{AxByHz}(298K) - \Delta H^p_{AxByHz}(0K) \] - x[\Delta H^p_A (298K)- \Delta H^p_A(0 K)] - y[\Delta H^p_B(298 K) - \Delta H^p_B (0 K)] - z[\Delta H^p_{(298 K)} - \Delta H^p_{(0 K)}]

In the formula, \( \Delta H^p(\text{A},\text{B},\text{H}_2,0\text{K}) \) and \( \Delta H^p(\text{A},\text{B},\text{H}_2,298\text{K}) \) are enthalpy of formation of compound at 0 K and 298 K respectively, \( \Delta H^p(\text{A}, 0 \text{ K}) \), \( \Delta H^p(\text{B}, 0 \text{ K}) \), \( \Delta H^p(\text{H}, 0 \text{ K}) \) are enthalpy of formation of atoms A, B and H respectively at 0 K which can be obtained by checking the manual, \( [\Delta H^p_A (298K)- \Delta H^p_A(0 K)], [\Delta H^p_B (298 K) - \Delta H^p_B (0 K)], [\Delta H^p_{(298 K)} - \Delta H^p_{(0 K)}] \) are heat correction values of atoms A, B and H respectively which can also be obtained by checking the manual. Similarly, \( [\Delta H^p_{AxByHz}(298K) - \Delta H^p_{AxByHz}(0K)] \) is heat correction value of compound \( \text{A},\text{B},\text{H}_2 \).

For \( \text{B}_2\text{H}_6(\text{NO}_2)_n(m=2-5;n=1-4) \), if isodesmic reaction is adopted to calculate its enthalpy of formation, then the designed isodesmic reaction is as follows:

\[
\begin{align*}
\text{B}_2\text{H}_6\text{NO}_2 + \text{CH}_4 & \rightarrow \text{B}_2\text{H}_6 + \text{CH}_3\text{NO}_2 & (2) \\
\text{B}_2\text{H}_6(\text{NO}_2)_2 + 2\text{CH}_4 & \rightarrow \text{B}_2\text{H}_6 + 2\text{CH}_3\text{NO}_2 & (3) \\
\text{B}_2\text{H}_6(\text{NO}_2)_3 + 3\text{CH}_4 & \rightarrow \text{B}_2\text{H}_6 + 3\text{CH}_3\text{NO}_2 & (4) \\
\text{B}_2\text{H}_6(\text{NO}_2)_4 + 4\text{CH}_4 & \rightarrow \text{B}_2\text{H}_6 + 4\text{CH}_3\text{NO}_2 & (5)
\end{align*}
\]

In the formula: \( \text{B}_2\text{H}_6 \) is the parent, \( \text{CH}_4, \text{CH}_3\text{NO}_2 \) are reference material methane and nitromethane respectively. Reaction heat \( \Delta H_{298} \) of

\[
Q \cong - \left[ \Delta_f \epsilon(\text{detonation products}) - \Delta_f \epsilon(\text{explosive}) \right] / \text{formula weight of explosive}
\]

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

\[
D=1.01[NM^{0.15}Q^{0.5}]^{0.5}(1+1.30\rho)
\]

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

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/cm³), \( N \) 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 H₂O 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 \( \text{B}_2\text{H}_6, \text{B}_2\text{H}_6(\text{NO}_2)_n(m=2-5;n=1-4) \) 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 \( \epsilon_0 \), zero-point energy \( \epsilon_{\text{ZEP}} \), enthalpy correction value \( H_T \) and enthalpy of formation \( \Delta H_f \) calculated by atomization reaction method of compounds \( \text{B}_2\text{H}_6, \text{B}_2\text{H}_6(\text{NO}_2)_n(m=2-5;n=1-4) \) 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 (\( \epsilon_0 \)) of B, H, N, O atoms. | 329 |
Table 3.2. Total Energy (ε₀), Zero-Point Energy (εZEP), Values of Thermal Correction (HT), and Heats of Formation (∆Hf) of the B₃H₆,B₃HNO₂,B₄(NO₂)₂,B₂H₃NO₂, B₂H₅(NO₂)₂, B₂H₄(NO₂)₃, B₂H₅(NO₂)₄, CH₄ and CH₃NO₂ Compounds at the B3LYP/6-31G* level

<table>
<thead>
<tr>
<th>Compound</th>
<th>ε₀ (a.u)</th>
<th>εZEP (a.u)</th>
<th>HT (KJ/mol)</th>
<th>∆Hf (KJ/mol) Atomic reaction</th>
<th>∆Hf (KJ/mol) Isodesmic reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₅(NO₂)₂</td>
<td>-257.81</td>
<td>0.068</td>
<td>17.69</td>
<td>-45.32</td>
<td>-35.09</td>
</tr>
<tr>
<td>B₂H₅(NO₂)₃</td>
<td>-462.32</td>
<td>0.072</td>
<td>24.78</td>
<td>-253.15</td>
<td>-85.16</td>
</tr>
<tr>
<td>B₂H₅(NO₂)₄</td>
<td>-666.82</td>
<td>0.075</td>
<td>31.918</td>
<td>-271.63</td>
<td>-109.22</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>-871.31</td>
<td>0.078</td>
<td>39.77</td>
<td>-319.75</td>
<td>-129.08</td>
</tr>
<tr>
<td>CH₄</td>
<td>-244.33</td>
<td>0.0513400</td>
<td>0.0053</td>
<td>-74.40[14]</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 shows that all enthalpy of formation of resulting compound B₃H₆(NO₂)₆ (m=2; n=0-4) after compound B₂H₆’s nitro-substitution of hydrogen atoms are negative, indicating that generation of this class of compound will release heat. Enthalpy of formation of CH₄, CH₃NO₂ is experimental value in the Table.

Calculation results of theoretical density, molar volume, explosion heat, detonation velocity, detonation pressure of compound B₂H₆(NO₂)₆ (m=2; n=0-4) 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 B₃H₆(NO₂)₆(m=2; n=0-4) and TNT compounds at the B3LYP/6-31G* level.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ρ (g/cm³)</th>
<th>V (cm³/mol)</th>
<th>N (mol/g)</th>
<th>M (g/mol)</th>
<th>Q (KJ/g)</th>
<th>P (GPa)</th>
<th>D (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆(NO₂)₂</td>
<td>1.05</td>
<td>69.75</td>
<td>0.041</td>
<td>17</td>
<td>1.83(1.86)</td>
<td>12.38</td>
<td>6.42(6.45)</td>
</tr>
<tr>
<td>B₂H₆(NO₂)₃</td>
<td>1.55</td>
<td>75.96</td>
<td>0.025</td>
<td>21.3</td>
<td>1.57(1.91)</td>
<td>17.89</td>
<td>6.58(6.84)</td>
</tr>
<tr>
<td>B₂H₆(NO₂)₄</td>
<td>1.61</td>
<td>101.60</td>
<td>0.028</td>
<td>20.4</td>
<td>1.34(1.73)</td>
<td>18.29</td>
<td>6.65(7.10)</td>
</tr>
<tr>
<td>B₂H₆(NO₂)₅</td>
<td>1.85</td>
<td>112.68</td>
<td>0.024</td>
<td>27.6</td>
<td>0.85(1.22)</td>
<td>19.55</td>
<td>6.59(7.21)</td>
</tr>
</tbody>
</table>
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 \( \Delta E_{\text{gap}} \) 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 \( \Delta E_{\text{gap}} \) value means that it is more difficult to have electron transition, and that molecule is more stable. Seen from the table, \( \Delta E_{\text{gap}} \) of \( \text{B}_2\text{H}_2(\text{NO}_2)_2 \) is higher than that of \( \text{B}_2\text{H}_4(\text{NO}_2)_2, \text{B}_2\text{H}_4(\text{NO}_2)_3, \) indicating that as nitro substituent increases in number, \( \Delta E_{\text{gap}} \) 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 (WBIB) indexes of compounds at B3LYP/6-31G* level.

<table>
<thead>
<tr>
<th></th>
<th>WBIB-H</th>
<th>WBIB-H(2)</th>
<th>WBIB-B</th>
<th>WBIB-NO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}_2\text{H}_6 )</td>
<td>0.99</td>
<td>0.48</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.96</td>
<td>0.49</td>
<td>0.68</td>
<td>0.76</td>
</tr>
<tr>
<td>( \text{B}_2\text{H}_3\text{NO}_2 )</td>
<td>0.98</td>
<td>0.49</td>
<td>0.45</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>0.98</td>
<td>0.45</td>
<td>0.68</td>
<td>0.76</td>
</tr>
<tr>
<td>( \text{B}_2\text{H}_4(\text{NO}_2)_2 )</td>
<td>0.96</td>
<td>0.46</td>
<td>0.44</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>0.96</td>
<td>0.47</td>
<td>0.65</td>
<td>0.77</td>
</tr>
<tr>
<td>( \text{B}_2\text{H}_3(\text{NO}_2)_3 )</td>
<td>0.96</td>
<td>0.43</td>
<td>0.48</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>0.96</td>
<td>0.45</td>
<td>0.64</td>
<td>0.77</td>
</tr>
</tbody>
</table>

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 \( \text{B}_2\text{H}_n(\text{NO}_2)_m \) (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 \( \text{B}_2\text{H}_2(\text{NO}_2)_2, \text{B}_2\text{H}_4(\text{NO}_2)_3 \) and \( \text{B}_2\text{H}_4(\text{NO}_2)_3 \) 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 \( \text{B}_2\text{H}_2(\text{NO}_2)_2, \text{B}_2\text{H}_4(\text{NO}_2)_3 \) and \( \text{B}_2\text{H}_4(\text{NO}_2)_3 \) is obtained: 18.89, 21.27 and 23.48 GPa, very close to 23.46 GPa of TNT explosive. Calculated value of \( \text{B}_2\text{H}_2(\text{NO}_2)_2 \) detonation pressure even exceeds detonation pressure value of TNT; detonation velocity of \( \text{B}_2\text{H}_2(\text{NO}_2)_2, \text{B}_2\text{H}_4(\text{NO}_2)_3 \) and \( \text{B}_2\text{H}_4(\text{NO}_2)_3 \) 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-NO₂ bond in compound B₂Hₘ(NO₂)ₙ (m = 2-5; n = 1-4) is relatively weak, indicating that chemical reaction of compound most likely begins from B-NO₂ bond rupture.

REFERENCES