Structural phase diagram and bonding patterns of $B_xH_y (x + y = 20)$ binary systems: A theoretical investigation

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ABSTRACT

The borane clusters exhibit diverse geometries related with their special multi-center bonding patterns in different B/H ratios, due to the electronic deficiency character of boron atom. In this paper, global minimal structures of $B_xH_y (x + y = 20)$ are predicted using unbiased structural search programs and their structural phase diagram is plotted. Relative energies of these clusters go down firstly and then rise up with $B_{12}H_{10}$ as the turning point, and $B_{6}H_{3}$, $B_{12}H_{8}$, $B_{20}$ are magic numbers. The geometries of these clusters undergo the transition of 3D open cage – 3D closed cage – irregular 3D – 2D planar/quasi-planar along with the increasing B/H ratios, and their stability depends on flexibility of the multi-center bonding patterns. This study reveals the geometric evolution rule related with the electronic shells of $B – H$ binary systems, which makes sense in borane chemistry.

1. Introduction

Boron element, which is next to carbon in the periodic table, has the electronic deficiency character, which leads to the formation of special multi-center chemical bonding patterns in boron-based clusters. In 1950s, the theory of hydrogen-bridge bonding pattern was proposed by Lipscomb and coworkers [1,2], in which they pointed out that three-center two-electron (3c-2e) $B – H – B$ hydrogen bridge bond plays an important part in electronic stability of borane clusters. This theory revealed the nature of electronic shells in boranes, and after that plenty of borane clusters were reported experimentally and theoretically, the number of which is only next to hydrocarbon clusters.

The neutral all boron clusters $B_n$ [3-6] and the cationic $B_n^+$ clusters [7] undergo the 2D-3D structural transition at $n = 20$ and $n = 16$ respectively, except for the flat cage $B_4$ [8], whereas their anions keep the planar or quasi-planar structure until $n = 28$ [9-15]. However, the presence of hydrogen atoms would change geometries of these clusters. Recent studies revealed that $B_{27}H_{13}$ clusters were planar/quasi-planar when $m < n$ [16-19]. Li and coworkers [20,21] theoretically investigated a series of borane clusters, and the results indicated that the $B_{3}H_{2}$ ($n = 4, 6, 8, 10, 12$) and $B_{3}H_{2}$ ($n = 3, 5, 7, 9, 11$) were planar double rings [22], and $B_{27}H_{13}$ clusters, such as $B_{27}H_{13}$ and $B_{27}H_{13}^+$, also had planar configuration, which were confirmed by photoelectron spectroscopy (PES) researches [23]. Chemical bonding analysis revealed that these borane clusters had similar delocalized multi-center bonding patterns and aromaticity as hydrocarbon clusters [24-26]. Interestingly, Li et al. [27] also pointed out that some planar borane clusters with twin-hexagonal holes, such as $B_{29}H_{13}$, could be the building blocks of stable boron sheets. Further hydrogenation of planar borane cluster would break its peripheral B-B bonds, causing the structural transition [28]. Bōyikata and coworkers [29] revealed the effect of the hydrogens hosting on the $B_6H_{10}$ cages in $B_{2n}H_{m}$ ($m = 5\sim10$, $n \leq m$), of which the structures underwent the 2D-3D transition when $n = m$ [30]. Moreover, the structures of borane anions $B_{27}H_{13}^-$ were also proved to be 3D [31,32], such as icosahedral $B_{12}H_{12}^-$ [33,34]. They are classic borane series obtained in the early experiments, and their multi-center bonding patterns were discussed by Cheng et al. [35]. Toshihiko group [36] pointed out that dehydrogenation of $B_{12}H_{13}$ clusters would cause their 3D-2D structural transition, and their 3D structures keep the lower energy level when $n \geq 6$. Other investigations revealed that $B_{12}H_{13}^{0/-}$ underwent the 2D-3D structural transition when $n = 4\sim5$ [37], and this transition occurred for $B_{4}H_{2n}$ when $y = 4$ [38].

Electronic shells of boranes were widely discussed to give the major consideration of the nature of their stability [39,40]. Localized molecule orbitals (LMOs) analysis was first proposed by Lipscomb and co-workers [41-44] to investigate the bonding patterns in small boranes. Recently,
Fig. 1. (a) Global minimal structures of $B_xH_y$ ($x + y = 20$) systems optimized at TPSSh/6-311+$G^{* *}$ level of theory, when $x \leq 5$, the separate hydrogen molecules in the systems are not shown (B in blue and H in white, the symmetries are labeled below each structure) (b) Structural phase diagram (SPD) of $B_xH_y$ ($x + y = 20$) systems, $E_{\text{rel}}$ is their energies relative to $B_{20}$ and $H_2$ at TPSSh/6-311+$G^{* *}$ level, and the structures for three magic numbers are labeled (The variation trend is represented by the red dash line, $B_{12}H_8$, $B_{16}H_4$ and $B_{20}$ are marked as the magic numbers).
the AdNDP program [45] was developed by Boldyreov group to give further insight into LMOs in nanostructures. They investigated the bonding patterns of $B_{10}H_{10}$ and pointed out that the boron atoms avoided sp$^2$ hybridization but formed the multi-center chemical bonds in these clusters [46]. The topological patterns of borane were also investigated by researchers to reveal their geometric characters, which indicated that these clusters could be classified into 4 types by Wade’s rule – c article, nido, arachno- and hypho-, due to the relationships between the numbers of their skeleton boron atoms and valence electrons [47–50]. As there are multi-center delocalized systems in polyhedral borane, their 3D aromaticity was discussed by researchers [51–57].

Although plenty of experimental and theoretical reports of boranes have been proposed in recent years, there are little studies focusing on their potential energy surface. Energies and geometric characters are critical for the properties of clusters, and their comprehensive evolution rules could be revealed by the structural phase diagram (SPD). In this paper, we intend to investigate borane clusters with different B/H ratios through SPD. As the double ring $B_{10}$ is the 2D-3D turning point of neutral boron clusters with special high stability [3,58,59], $B_{10}H_{x}$ ($x + y = 20$) systems are chosen as the objects of our study. Their potential energy surface is searched theoretically, and the SPD is plotted to give insight into their stabilities and geometric evolution rules. In order to reveal the mechanism of their structural transition, the multi-center bonding patterns in their electronic shells are discussed.

2. Computational details

The global minimal structures of $B_{10}H_{x}$ ($x + y = 20$) are searched by genetic algorithm (GA) coupled with density functional theory (DFT) method at TPSSh [60]/3-21G level, and further optimized using 6-311+G** basis set. The global search programs used in this study is developed by our group [61], in which the results of DFT calculation are called by main program of GA to carry out the global search (details could be found in Ref. [61]). The energies of these clusters are also calculated at the same level of theory. These methods have been proved to be reliable for main group elements [62–64]. Moreover, the bonding patterns of $B_{10}H_{x}$ ($x + y = 20$) are investigated using the adaptive natural density partitioning (AdNDP) programs [45,65,66]. All calculations are carried out using the Gaussian 09 package [67], and molecular orbitals (MO) visualization is performed by Molekel 5.4 [68].

3. Results and discussions

3.1. Structural optimization

The low-lying isomers of $B_{10}H_{x}$ ($x + y = 20$) are searched by GA/DFT method and further optimized (see Figs. S1–S4 of Supporting Information (SI)), and their global minimal structures are shown in Fig. 1(a) (Cartesian coordinates are given in Table S1 of SI)). The clusters in both singlet and triplet states are considered in our global search programs, and all the global minimums are proved to be singlet. As the number of hydrogen atoms is excessive in the optimized systems when $x \leq 5$, these systems are composed of separate hydrogen molecules and small classic borane clusters. $B_{10}H_{19}$ system contains eight hydrogen molecules and the $B_{10}H_{18}$ cluster which is the smallest borane molecule. $B_{2}H_{4}$ system is comprised of six hydrogen molecules and the $D_{2h}$ cluster. $B_{3}H_{7}$ system contains four hydrogen molecules and the $C_{2v}$ arachno-$B_{3}H_{10}$. $B_{4}H_{16}$ system contains three hydrogen molecules and the $C_{2v}$ arachno-$B_{4}H_{10}$. $B_{5}H_{15}$ system is composed of three hydrogen molecules and the $C_{2v}$, nido-$B_{5}H_{10}$. All these global minimums of $B_{x}H_{y}$ ($x + y = 20$, $x \leq 5$) are plotted in Fig. 1(a), in which the separate hydrogen molecules are not shown.

Some of these small classic borane clusters – $B_{2n}H_{2n}$, $B_{2n+1}H_{2n+1}$, $B_{2n+2}H_{2n+2}$, and $B_{2n+3}H_{2n+3}$ have already been obtained in the experimental studies [1,2,69–71], which confirmed the reliability of our theoretical method. As we know, $B_{10}H_{10}$ is a classic c article-borane cluster with $D_{4d}$ symmetry (as shown in Fig. 2(a)) which follows the Wade’s Law [47]. However, in our global search, the $C_{2v}$ structure in singlet state (the first structure in Fig. 2(b)) is the global minimum for neutral $B_{10}H_{10}$, and its electronic shell is totally different form the $D_{4d}$ $B_{10}H_{10}$. When an electron-pair is lost in $D_{4d}$ $B_{10}H_{10}$, the neutral $B_{10}H_{10}$ in singlet state is obtained (the second structure in Fig. 2(b)), it has the $C_{1v}$ symmetry with a little distortion from $D_{4d}$ structure, due to Jahn–Teller effect. Its energy is 0.18 eV higher than the global minimum. Moreover, when two single electrons are lost in the $B_{10}H_{10}$, the neutral $B_{10}H_{10}$ with open shell orbitals is obtained (the fourth structure in Fig. 2(b)), which is in triplet state. After optimization, its structure keeps $D_{4d}$ symmetry, and its energy is 0.73 eV higher than the global minimum, and also higher than all the first three local minimal structures in singlet states (the first three structures in Fig. 2(b)).

3.2. Structural phase diagram

In order to reveal the rule of geometric evolution related with energies for B–H binary systems, the structural phase diagram of $B_{10}H_{x}$ ($x + y = 20$) is plotted in Fig. 1(b), in which the $E_{rel}$ is defined as:

\[ E_{rel} = E_{B_{10}H_{x}} - \frac{x E_{B_{20}} + y E_{H_2}}{20} \]  

(1)

$E(B_{10}H_{x})$, $E(B_{20})$, and $E(H_2)$ are the energies of $B_{10}H_{x}$, $B_{20}$ and $H_2$, respectively. Thus, the $E_{rel}$ represents the energy of $B_{10}H_{x}$ relative to $B_{20}$ and $H_2$ and its value indicates the relative stability of these clusters, in which the more negative $E_{rel}$ value means the higher stability.

The shape of SPD indicates that, as the B/H ratio increases, the relative energies of these systems (Table S2) go down firstly and then rise up with $B_{10}H_{10}$ as the turning point, and the $E_{rel}$ values exhibit the
extra high stability. When core in the B

3.3. Chemical bonding analysis

3.3.1. \( \text{B}_9 \text{H}_y \) \((x + y = 20, x \leq 5)\)

When \( x \leq 5 \), the \( \text{B}_9 \text{H}_y \) \((x + y = 20)\) systems are composed of the classic borane clusters and separate hydrogen molecules. As mentioned above, \( \text{B}_3 \text{H}_3 \), \( \text{B}_2 \text{H}_6 \), \( \text{B}_3 \text{H}_8 \), \( \text{B}_4 \text{H}_{10} \) and \( \text{B}_3 \text{H}_9 \) are global minimums, their AdNDP chemical bonding are shown in Fig. 3(a)–(c) and Fig. 4(a) and (b). As the smallest borane molecule, \( \text{BH}_3 \) contains three B–H \( \sigma \) bonds (Fig. 3(a)). \( \text{B}_2 \text{H}_6 \) \((\text{D}_{2h})\) and \( \text{arachno-B}_3 \text{H}_9 \) \((\text{C}_{3v})\) are formed by B–H single bonds and B–H–B hydrogen-bridge bonds (Fig. 3(b) and (c)). As the ratio of B/H increases, multi-center \( \text{B}_9 \) bonds appear in the \( \text{arachno-B}_9 \text{H}_{10} \) \((\text{C}_{2v})\) and \( \text{nido-B}_9 \text{H}_{10} \) \((\text{C}_{3v})\). Beside B–H and B–H–B bonds, there are one 4c-2e \( \sigma \) B9 bond in \( \text{B}_9 \text{H}_{10} \) (Fig. 4(a), details of 4c-2e \( \text{B}_9 \) bond are shown in Fig. 5), and two 5c-2e \( \pi \) and one 5c-2e \( \sigma \) \( \text{B}_9 \) bonds in \( \text{B}_9 \text{H}_{10} \) (Fig. 4(b)). From the geometry structures, the clusters could be viewed...
Fig. 4. Optimized structures and AdNDP chemical bonding of (a) B$_4$H$_{10}$ and (b) B$_5$H$_9$ (B in blue and H in white, symmetries and occupy numbers are labeled below each structure).
as the 3D open cage when 3 ≤ x ≤ 5.

3.3.2. \( B_xH_y \) \((x + y = 20, 6 ≤ x ≤ 9)\)

With the increasing B/H ratio, more hydrogen atoms are included in the bonding systems. Therefore, there are no more separate hydrogen molecules in the \( B_xH_y \) \((x + y = 20)\) clusters when \( x ≥ 6 \). The clusters exhibit 3D open cage structure when \( 6 ≤ x ≤ 9 \) (Fig. 5), and there are B—H bonds, B—B hydrogen-bridge bonds and multi-center \( \sigma \) B\(_n\) bonds in their electronic shells.

As shown in Fig. 5(a), the structure of \( B_{6}H_{14} \) could be viewed as the combination of \( D_{3h} B_{4}H_{6} \) and \( C_{2v} B_{4}H_{10} \) through the B-B \( \sigma \) single bond of which the top hydrogen atom is dropped respectively, and there are eight 2c-2e \( \sigma \) B—H bonds, one 2c-2e \( \sigma \) B-B bond, six \( \sigma \) B—B hydrogen-bridge bonds and one 4c-2e \( \sigma \) B\(_{6}\) bond in the cluster. Similarly, \( B_{7}H_{13} \) is combined of \( B_{2}H_{6} \) and \( B_{5}H_{9} \) including seven 2c-2e \( \sigma \) B—H bonds, one 2c-2e \( \sigma \) B-B bond, six \( \sigma \) B—B hydrogen-bridge bonds and one \( \sigma \) B\(_{5}\) bond. \( B_{8}H_{12} \) cluster includes two kinds of B—H bonds as shown in Fig. 5(c) – one kind of eight B—H bonds has the higher occupied numbers (1.97–1.98 |e|), and the other kind of the rest two B—H bonds has the relative lower occupied numbers (1.52 |e|). Moreover, it also has two B—B hydrogen-bridge bonds and six 3c-2e \( \sigma \) B\(_{3}\) bonds.

From the details of the bonding patterns in these systems, it is found that the number of nc-2e B\(_n\) bonds increases while the number of the hydrogen-bridge bonds decreases along with the increasing B/H ratio, which indicates the boron atoms trend to interact with each other to form the B\(_n\) multi-center bonds instead of the hydrogen-bridge bonds.
Fig. 6. Optimized structures and AdNDP chemical bonding of (a) B$_{10}$H$_{10}$ (b) B$_{11}$H$_{9}$ (c) B$_{12}$H$_{8}$ (d) B$_{13}$H$_{7}$ and (e) B$_{14}$H$_{6}$ (B in blue and H in white, symmetries and occupy numbers are labeled below each structure).
3.3.3. \( B_2H_y (x + y = 20, 10 \leq x \leq 16) \)

When the B/H ratio reaches 1:1, the \( B_2H_y (x + y = 20) \) clusters are changed from the hydrogen-rich systems to the boron-rich systems. Meanwhile, their structures and bonding patterns undergo the obvious transition. On one hand, the hydrogen-bridge bonds disappear and all the hydrogen atoms are involved in the \( B=H \) single bonds. On the other hand, the boron atoms interact with each other to form the multi-center bonding systems, making their structures turn into the 3D closed cage.

In \( B_{10}H_{10} \) cluster, ten hydrogen atoms are just bonded with ten boron atoms to form the \( B=H \) bonds, and the \( B_{10} \) core with unpaired electrons form the closed spherical cage structure with multi-center bonds. As shown in Fig. 6(a), the \( B_{10}H_{10} \) cluster contains ten 2c-2e \( B=H \) single bonds, and the rest twenty valence electrons are involved in seven 3c-2e \( B=H \) bonds and three 4c-2e \( \sigma \) bonds. \( B_1H_9, B_2H_9 \) and \( B_3H_9 \) have the similar cage structure and bonding pattern, as shown in Fig. 6(b)-(d). \( B_3H_9 \) cluster contains nine \( B=H \) bonds and twelve 3c-2e \( B=H \) bonds. The \( B_3 \) core of \( B_3H_9 \) has the stableicosahedral geometry with a slightly distortion, of which fourteen faces are occupied by 3c-2e \( B=H \) bonds, the rest six are empty. Besides, there are also eight \( B=H \) bonds in the \( B_3H_9 \). \( \sigma \) bond, which is the magic number of neutral boron cluster, and there are four \( B=H \) bonds, eight B-B bonds, twelve 3c-2e \( \sigma \) bonds and five 5c-2e \( \pi \) bonds (two different kinds with the occupy numbers of 1.81 |e|/1.96 |e|). As the number of unpaired electrons further increases in the \( B_3H_9 (x + y = 20) \) clusters, the B-B single bonds appear in the electronic shell of \( B_1H_9 \). This cluster contains six \( B=H \) bonds, two 2c-2e \( B=H \) bonds and sixteen 3c-2e \( B=H \) bonds.

When the ratio of B/H reaches 3:1 (\( x \geq 15 \)), \( B_{13}H_9 \) and \( B_{19}H_4 \) exhibit the 3D boat-shape closed cage structure. \( B_{13}H_5 \) cluster is comprised of five \( B=H \) bonds, five B-B bonds, fourteen 3c-2e \( \sigma \) B-B bonds and one 6c-2e \( \sigma \) B-B bond (Fig. 7(a)). \( B_{19}H_4 \) cluster has the similar \( D_{2d} \) configuration as \( B_{14} \) which is the magic number of neutral boron cluster, and there are four \( B=H \) bonds, eight B-B bonds, twelve 3c-2e \( \sigma \) B-B bonds (two different kinds with the occupy numbers of 1.81 |e|/1.96 |e|) and two 6c-2e \( \sigma \) B-B bonds (Fig. 7(b)). As the B/H ratio in \( B_{13}H_5 (x + y = 20) \) further increases, the number of B-B bonds increases, while the amount of \( B_6 \) multi-center bonds decreases.

3.3.4. \( B_2H_y (x + y = 17, x \leq 20) \)

As shown in Fig. 8, the geometries of the \( B_2H_y (x + y = 20) \) clusters are changed into the irregular 3D when \( x = 17, 18 \). \( B_1H_5 \) cluster contains three 2c-2e \( \sigma \) B-B bonds, seven 2c-2e \( \sigma \) B-B bonds, fifteen 3c-2e \( \sigma \) B-B bonds, one 5c-2e \( \sigma \) B-B bond and one 10c-2e \( \pi \) bond. \( B_5H_4 \) cluster is composed of two \( \sigma \) B-B bonds, eleven B-B bonds, eleven 3c-2e \( \sigma \) B-B bonds, two 5c-2e \( \sigma \) B-B bonds (two different kinds with the occupy number of 1.89 |e|), one 6c-2e \( \sigma \) B-B bond and one 7c-2e \( \sigma \) B-B bond.

When \( x = 19 \), \( B_{10}H \) cluster has the 2D quasi-planar structure, which could be viewed as the quasi-planar \( B_{10}H \) bonded with the BH group through two 3c-2e \( B=H \) bonds. AdNDP result in Fig. 9 reveals that there is one \( B=H \) bond, ten B-B bonds, twelve 3c-2e \( \sigma \) B-B bonds, three 5c-2e \( \sigma \) B-B bonds, one 6c-2e \( \sigma \) B-B bond, one 18c-2e \( \pi \) bond and one 19c-2e \( \pi \) bond.

When \( x = 20 \), the double ring \( B_{12}H \) cluster is the 2D-3D structural turning point and magic number of the neutral boron clusters. It could be viewed as the 2D folded ribbon with the special planar structure. As shown in Fig. 10, there are twenty 2c-2e \( \sigma \) B-B bonds, five 20c-2e delocalized \( \sigma \) bonds and five \( \pi \) bonds which include both radial and axial delocalized systems.

3.4. Transition of the geometries related with bonding patterns

As we know, neutral boron clusters \( B_{n} \) keep planar or quasi-planar structures until \( B_{20} \), except for \( B_{14} \) cage as the magic number. Presence of hydrogen atoms makes planar structures less stable in \( B_{20}H_y (x + y = 20, x \leq 18) \). As some valence electrons in boron atoms are involved in the \( B=H \) 3D geometries are preferred, which benefit of hydrogen atoms makes planar structures less stable in \( B_{14}H_5 \) and \( B_{19}H_4 \) is the 3D-2D turning point in this series of clusters.
Fig. 8. Optimized structures and AdNDP chemical bonding of (a) $B_{17}H_{33}C_{1}$ and (b) $B_{18}H_{22}C_{1}$ (B in blue and H in white, symmetries and occupy numbers are labeled below each structure).

Fig. 9. Optimized structure and AdNDP chemical bonding of $B_{19}H$ (B in blue and H in white, symmetry and occupy numbers are labeled below each structure).
bonds decreases. The clusters exhibit the boat-shape structure when bonding patterns in the B\textsubscript{4}. Conclusions

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Therefore, 3D structure is more favorable before B\textsubscript{4}xH\textsubscript{y} core with diverse multi-center bonding systems forms the 3D closed cage structure. The B-B single bonds appear in the B\textsubscript{4} cluster, whereas the amount of the multi-center B hydrogen-bridge bonds, and the boron atoms form the multi-center B\textsubscript{4} bonds. When the B/H ratio reaches 1:1, the hydrogen-bridge bonds disappear and the hydrogen atoms are all involved in B–H single bonds. The B\textsubscript{4} core with diverse multi-center bonding systems forms the 3D closed cage structure. The B-B single bonds appear in the B\textsubscript{4}H\textsubscript{20} and their number further increases along with the increasing B/H ratio, whereas the amount of the multi-center B\textsubscript{4}H\textsubscript{20} bonds decreases. The clusters exhibit the boat-shape structure when x = 15 and 16, then turn into the irregular 3D structure when x = 17 and 18. B\textsubscript{4}H\textsubscript{20} is the 3D-2D turning point in these clusters with the quasi-planar structure. B\textsubscript{20} with the classic double ring structure could be viewed as the folded planar ribbon. Flexible multi-center bonding patterns play an important role in the stability of these clusters, which induce the diversity of their geometries. Compared with bare boron clusters, presence of hydrogen atoms bonds some valence electrons in boron atoms, and further enhances the electronic deficiency character of the clusters. Therefore, 3D structure is more favorable before B\textsubscript{4}H\textsubscript{20}, which benefits the formation multi-center bonds. The evolution rules of geometries, energies and electronic shells in B–H binary systems gives reference for design and prediction of borane clusters, which makes sense in borane chemistry.

4. Conclusions

In this study, structural phase diagram and localized chemical bonding analysis reveal the evolution rules of geometries, energies, and bonding patterns in the B\textsubscript{x}H\textsubscript{y} (x + y = 20) systems. When x ≤ 5, optimized systems are composed of small borane and separate hydrogen molecules. When the ratio of B/H < 1 (x ≤ 9), the clusters have the 3D open cage structure. The hydrogen atoms are bonded with boron to form B–H single bonds and B−H−B hydrogen-bridge bonds, and the boron atoms form the multi-center B\textsubscript{4} bonds. When the B/H ratio reaches 1:1, the hydrogen-bridge bonds disappear and the hydrogen atoms are all involved in B–H single bonds. The B\textsubscript{4} core with diverse multi-center bonding systems forms the 3D closed cage structure. The B-B single bonds appear in the B\textsubscript{4}H\textsubscript{20} and their number further increases along with the increasing B/H ratio, whereas the amount of the multi-center B\textsubscript{4}H\textsubscript{20} bonds decreases. The clusters exhibit the boat-shape structure when x = 15 and 16, then turn into the irregular 3D structure when x = 17 and 18. B\textsubscript{4}H\textsubscript{20} is the 3D-2D turning point in these clusters with the quasi-planar structure. B\textsubscript{20} with the classic double ring structure could be viewed as the folded planar ribbon. Flexible multi-center bonding patterns play an important role in the stability of these clusters, which induce the diversity of their geometries. Compared with bare boron clusters, presence of hydrogen atoms bonds some valence electrons in boron atoms, and further enhances the electronic deficiency character of the clusters. Therefore, 3D structure is more favorable before B\textsubscript{4}H\textsubscript{20}, which benefits the formation multi-center bonds. The evolution rules of geometries, energies and electronic shells in B–H binary systems gives reference for design and prediction of borane clusters, which makes sense in borane chemistry.

CRediT authorship contribution statement

Chang Xu: Investigation, Writing - original draft. Longjiu Cheng: Conceptualization, Software, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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