Hydrogen storage capabilities of the most stable isomers of Na_nB_m $(m+n=6)$ clusters*

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The most stable isomers of Na_nB_m $(m+n=6)$ clusters and their hydrogen storage properties are investigated by means of density functional theory with a 6-311+G(d) basis set. To study the hydrogen storage properties, all of the stable structures of $Na_nB_mH_x$ $(m+n=6)$ clusters have been optimized. It shows that boron atoms of Na_nB_m are separated from the other boron atoms, and form satellite BH_x $(x=3, 4)$ clusters around the centre, which attach to the system by a bridging bond of a hydrogen atom or an Na atom. Compared with the hydrogen storage capabilities, the Na_3B_3 has the highest hydrogen storage capacity among Na_nB_m clusters. The binding energies, interaction energies of hydrogen atom with Na_nB_m clusters and second difference in energy of $Na_3B_3H_x$ clusters have been calculated. The results show that the stability of the $Na_nB_mH_x$ clusters present an odd–even oscillatory effect, as the number of H atoms increases.

Keywords: density functional theory, Na–B clusters, geometric property, hydrogen storage capabilities

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1. Introduction

Recently, nano-clusters have found potential utilization in the development of new materials since they present different physical and chemical properties compared to their bulk counterparts. As a large branch of physical chemistry, boron clusters[1–9] and metal boride clusters have attracted much attention. For example, Li *et al.* investigated the ground-state geometries, electronic structures and vibrational frequencies of MB_5 (M = Li , Na, K, Rb, and Cs) and MB_5^+ (M = Be, Mg, Ca, and Sr) clusters,[10] and the structures and stabilities of MB_7 (M = Li, Na, K, Rb, Cs) species by *ab initio* and density functional theory (DFT) methods.[11] Zhao *et al.*[12] investigated the various geometries and vibrational frequencies of MB_{10} (M = Li, Na, K) clusters at the B3LYP/6-311+G(d) level. Kolmogorov *et al.* studied the existence of stable high-T_c superconducting metal borides. They proposed various metal borides sandwich structures, including Li–B and Na–B systems.[13]

Due to the high gravimetric densities of hydrogen, alkali boride systems have potentially important applications for hydrogen storage.[14,15] Among these alkali borides, Li–B-based materials and Na–B-based materials are especially important. For example, Zhang *et al.*[16] found that $NaBH_4$ can contain a relatively higher hydrogen concentration for 10.7% by mass. Yasumitsu *et al.*[17] investigated the $NaBH_4$ system and found that Na^+ and BH_4^- are associated in the solvent forming contact ion pairs. Li *et al.*[18] found that the stability of $NaBH_4$ in water relies on the acidity and alkalinity and temperature, and the velocity of hydrogen output can be controlled by changing these parameters.

In order to study the Na–B system amply, we have presented the physical and chemical properties, such as the stable structures, binding energies, HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) energy gaps, point groups, electronic states, and vibrational frequencies of the most stable isomers of Na_nB_m clusters $(m+n=6)$ and the hydrogen capacity of Na_nB_m systems. The rest of this paper is arranged as follows. In the second section, the computational details are given. The results and discussions are presented in the third section. Finally, the conclusions are drawn in the last section.

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2. Computational methods

The initial structure of Na_nB_m is formed by replacing a B atom with an Na atom in the lowest energy structure of the B_6 cluster,[6] i.e., the initial structure of NaB_5 is formed in this way. For the next cluster, the lowest energy structure of the NaB_5 is considered and then another B atom is replaced by an Na atom to form the initial Na_2B_4. In the next steps, similar procedures are followed to form the remaining initial Na_nB_m clusters. We choose the lowest energy configurations of Na_nB_m $(m+n=6)$ clusters that have no imaginary frequencies as the most stable isomers, and then add the hydrogen atoms one at a time, in a stepwise manner, to form $Na_nB_mH_x$ clusters. All geometry optimizations and calculations are performed in the density functional theory (DFT) framework. Generalized gradient approximations are employed by using Becke's three-component hybrid exchange parameter functional and Lee–Yang–Parr (LYP) nonlocal correlation functional.[19−22] We have employed the 6-311+G(d) basis set for the final geometry optimizations and all calculations of the physical parameters. Because of the size of the basis set, the computational time increases very much and the choice of the starting geometry is very important. In order to choose the appropriate starting geometry and reduce the computational time, we have followed a three-step procedure. Firstly, in order to get reasonable initial geometries, we have used a relatively small 3-21G basis set with tight SCF convergence criteria. Secondly, the geometries obtained in the first step are used as the starting point to obtain a stable wave function by using the larger 6-311+G(d) basis set. Finally, the geometry optimizations, vibrational frequencies, total binding energies (BEs), point group symmetries, HOMO–LUMO energy gaps and other physical properties are calculated at the same level of theory as in the second step. All of these calculations are performed by using the Gaussian03W program package.[23] All figures are generated directly from the Gaussian log file by using the Gaussview program.[23] The total binding energies of the optimized clusters are calculated by using the following equation,

$$E_{\rm BE} = E_{\rm tot} - nE_{\rm Na} - mE_{\rm B}, \tag{1}$$

where, $E_{\rm Na}$ and $E_{\rm B}$ are the energies of single neutral sodium and boron atoms, respectively, and $E_{\rm tot}$ is the total energy of the Na_nB_m cluster.

The approximate interaction energies of one H atom with the Na_nB_m and B_6 clusters are calculated by using the following equations,

$$E_{\rm int}[(Na_nB_m)\text{–}H] \approx [E_{\rm tot}(Na_nB_mH_x) - E_{\rm tot}(Na_nB_mH_{x-1}) - E_{\rm H}],\ x \geq 1, \tag{2}$$

$$E_{\rm int}[(B_6)\text{–}H] \approx [E_{\rm tot}(B_6H_x) - E_{\rm tot}(B_6H_{x-1}) - E_{\rm H}], \tag{3}$$

$$\Delta^2 E(Na_nB_mH_x) = E_{\rm tot}(Na_nB_mH_{x+1}) + E_{\rm tot}(Na_nB_mH_{x-1}) - 2E_{\rm tot}(Na_nB_mH_x), x \geq 1, \tag{4}$$

where $E_{\rm tot}$ is the optimized energy of the cluster, and $E_{\rm H}$ is the energy of a single H atom calculated by using the same level of theory as mentioned above. $\Delta^2 E$ is the second difference in energy of $Na_nB_mH_x$. The HOMO–LUMO energy gaps of Na_nB_m are calculated by taking the difference between the energy values corresponding to the HOMO and LUMO states. All of the data are presented in Tables 1 and 2.

Table 1. Properties of Na_nB_m clusters.

cluster	point group	electronic state	total energy/eV	binding energy/eV	frequency/cm^{-1}	HOMO–LUMO energy gap/eV
					lowest/highest	α electron/β electron
NaB_5	C_s	1-A′	−7792.1332	−20.6957	58.24/1312.26	2.7045/—
Na_2B_4	S_2	1-A	−11533.1279	−16.7951	38.47/1192.83	1.9442/—
Na_3B_3	C_s	3-A′	−15274.2134	−12.9854	74.88/1125.81	1.5537/2.4917
Na_4B_2	C_4	1-A	−19016.0155	−9.8923	43.42/1167.17	2.0944/—
Na_5B	C_2	1-A	−22756.2291	−5.2107	58.78/378.56	1.6310/—
Na_6	C_1	1-A	−26498.9820	−3.0684	34.24/141.45	1.8245/—

3. Results and discussion

We choose the lowest energy isomers of the Na_nB_m clusters that have no imaginary frequencies as the most stable structures, as shown in Fig. 1. The results are presented in Table 1. The properties for $Na_3B_3H_x$

clusters are given in Table 2. All of the values are obtained either directly from the optimizations or from the calculations by using Eqs. (1)–(4). The results are discussed in the following subsections.

Table 2. Properties of $Na_3B_3H_x$ clusters.

cluster	electronic state	total energy/eV	binding energy per atom/eV	interaction energies of one H atom/eV	second difference in energy/eV
Na_3B_3H	2-A	−15292.0176	−2.4464	−3.9715	0.1960
$Na_3B_3H_2$	1-A	−15309.6258	−2.6336	−3.9439	0.3695
$Na_3B_3H_3$	2-A	−15326.8645	−2.7381	−3.5744	0.7247
$Na_3B_3H_4$	1-A	−15343.3785	−2.7493	−2.8497	0.0991
$Na_3B_3H_5$	2-A	−15359.7934	−2.7494	−2.7506	−0.8923
$Na_3B_3H_6$	1-A	−15377.1006	−2.8238	−3.6429	2.1419
$Na_3B_3H_7$	2-A	−15392.2659	−2.7220	−1.5010	−2.9980
$Na_3B_3H_8$	1-A	−15410.4292	−2.8489	−4.4990	4.1825
$Na_3B_3H_9$	2-A	−15424.4100	−2.6801	−0.3165	−3.6272
$Na_3B_3H_{10}$	1-A	−15442.0180	−2.7591	−3.9437	1.6685
$Na_3B_3H_{11}$	2-A	−15457.9575	−2.7306	−2.2752	−1.4648
$Na_3B_3H_{12}$	1-A	−15475.3618	−2.7867	−3.7400	2.2187
$Na_3B_3H_{13}$	2-A	−15490.5474	−2.7200	−1.5213	−1.9559
$Na_3B_3H_{14}$	1-A	−15507.6889	−2.7579	−3.4772	2.8381
$Na_3B_3H_{15}$	2-A	−15521.9923	−2.6570	−0.6391	−3.6553
$Na_3B_3H_{16}$	1-A	−15539.9510	−2.7314	−4.2944	2.4494
$Na_3B_3H_{17}$	2-A	−15555.4603	−2.6929	−1.8450	−2.1520
$Na_3B_3H_{18}$	1-A	−15573.1216	−2.7472	−3.9970	3.6424
$Na_3B_3H_{19}$	2-A	−15587.1405	−2.6515	−0.3546	−3.9871
$Na_3B_3H_{20}$	1-A	−15605.1465	−2.7165	−4.3417	3.9987
$Na_3B_3H_{21}$	2-A	−15619.1538	−2.6286	−0.0245	−4.0212
$Na_3B_3H_{22}$	1-A	−15637.1823	−2.6905	−4.3642	——

3.1. Structures and energies of the Na_nB_m $(n + m = 6)$ clusters

The most stable structure of NaB_5, as seen in Fig. 1(a), shows that the boron atoms tend to form a boron cluster, which coordinates the Na atom to form a stable structure. The boron cluster has a very similar form to that of bare optimized B_5,[6] with the average bond length of 1.6372 Å (1 Å = 0.1 nm), which is slightly smaller than that of the bare B_5 (1.6440 Å),[6] and the Na–B distance is 2.4350 Å. This implies that the presence of one Na atom does not change the overall cluster size. This result is in good accordance with the ground-state geometry of NaB_5 in Ref. [10].

The most stable isomer of Na_2B_4 clusters is given in Fig. 1(b). This is based on the first isomer of optimized B_4 clusters,[6,9] which has a rhombus form, and the Na atoms are positioned at equal distances from the opposite sites of the rhombus. They affect the average bond length of the B_4 cluster, increasing from 1.5300 Å[9] to 1.5817 Å. In other words, these two Na atoms stretch the boron cluster, and increase the overall cluster size. The averaged distance between Na and B atoms is about 2.4299 Å, which is slightly smaller than that of NaB_5.

The most stable isomer of Na_3B_3 clusters is presented in Fig. 1(c). It is planar with a triangular form of the B_3 cluster, which has the same structure as the first isomer of optimized B_3.[6] The average bond length of this B_3 cluster is 1.6044 Å, which is larger than that of the B_3 (1.5480 Å).[6] This implies that the surrounding Na atoms stretch the inner B_3 cluster. The averaged Na–B distance for this isomer is 2.4722 Å. Because of the triplet state, the HOMO–LUMO energy gap of the β-electron is 2.4917 eV (See Table 1).

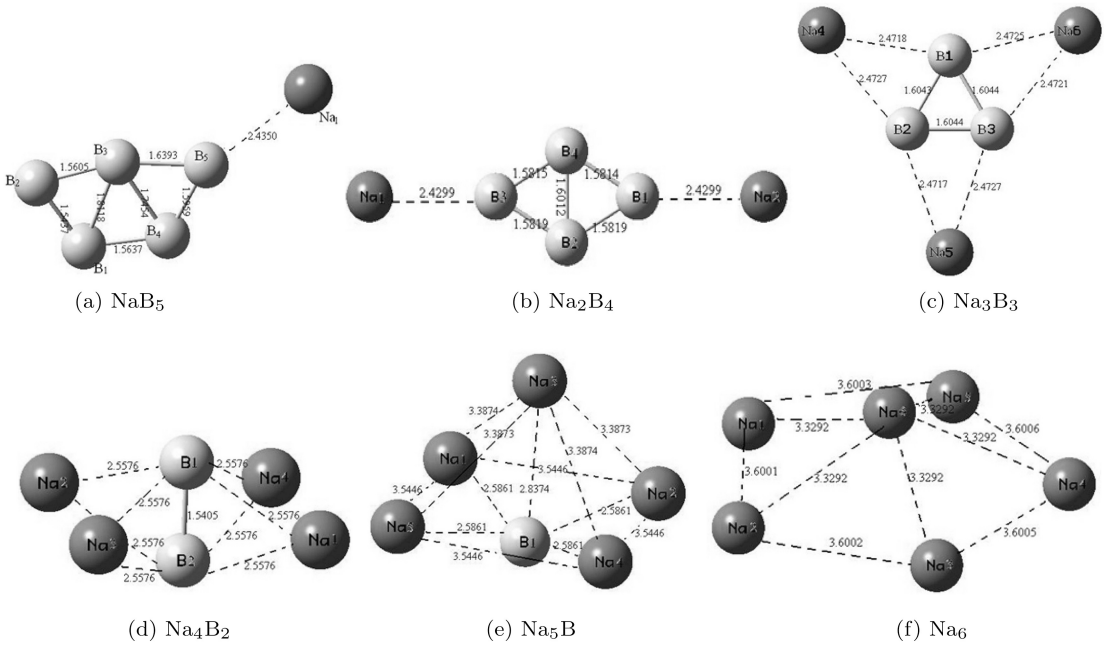


Fig. 1. The most stable isomers of Na_nB_m clusters.

The lowest energy structure of Na_4B_2 is shown in Fig. 1(d). It has a square arrangement of the Na atoms with a B_2 dimer at the centre of this square, and the orientation of the B_2 dimer is perpendicular to the plane of the square. The bond length of the B_2 in this cluster is smaller (1.5405 Å) than that of optimized B_2 (1.571 Å),[6] and the average Na–B distance is 2.5576 Å. The HOMO–LUMO energy gap of this isomer is 2.0944 eV.

The most stable structure of Na_5B clusters is shown in Fig. 1(e), which has a square bipyramid shape formed by one Na atom and one B atom. The boron atom is located right below the Na atom at the top. The average Na–B distance is 2.5861 Å. The most stable structure of Na_6 clusters (Fig. 1(f)) has a pentagonal pyramid structure, which is in agreement with Ref. [24]. The average bond length in the pentagonal ring is 3.6003 Å, and the bond between the apex and the other atoms is 3.3292 Å.

For the most stable Na_nB_m clusters, the binding energy per atom increases linearly with the number of Na atoms (Fig. 2). The rate of change is about −0.65 eV, i.e., the replacement of the B atoms with Na atoms causes a decrease in the stability of the cluster, which in turn may cause an increase in the probability of reactivity of the cluster.

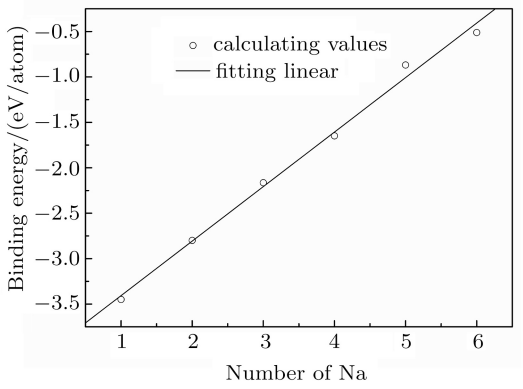


Fig. 2. Binding energy per atom as a function of the number of Na atoms for the Na_nB_m clusters.

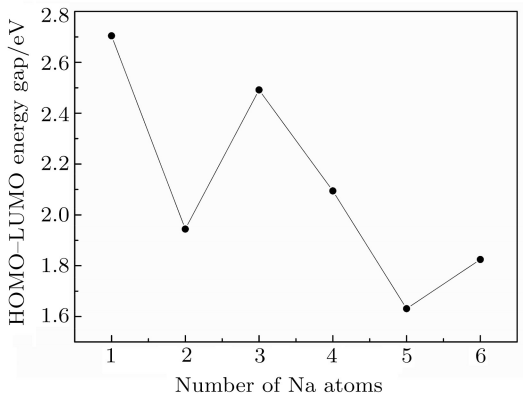


Fig. 3. Energy gaps as a function of the number of Na atoms for the Na_nB_m clusters.

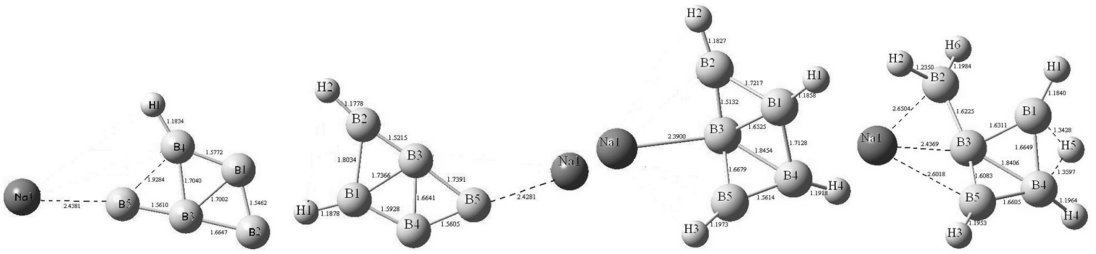
Figure 3 shows the HOMO–LUMO energy gaps as a function of the number of Na atoms. As is seen in the figure, the energy gap decreases in a stepwise manner as the number of Na atoms increases. It also indicates a decrease in the stability of the clusters, i.e., the reactivity of the clusters increases as the number of Na atoms increases.

3.2. Hydrogen hosting

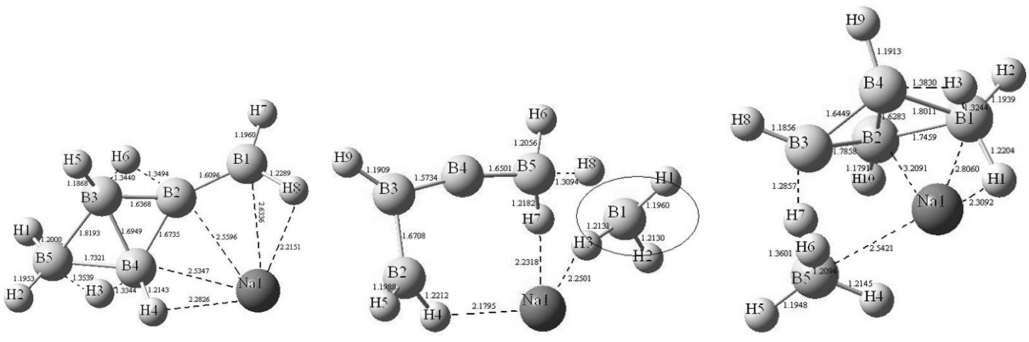
In order to understand the hydrogen storage capability of Na_nB_m clusters, we have chosen the most stable structures of the clusters as samples. The hydrogen atoms are added systematically to the maximum capacity limits, beyond which molecular hydrogen desorption takes place. And these hydrogenated structures are fully optimized at each step by the same method as mentioned above.

3.2.1. NaB_5H_x

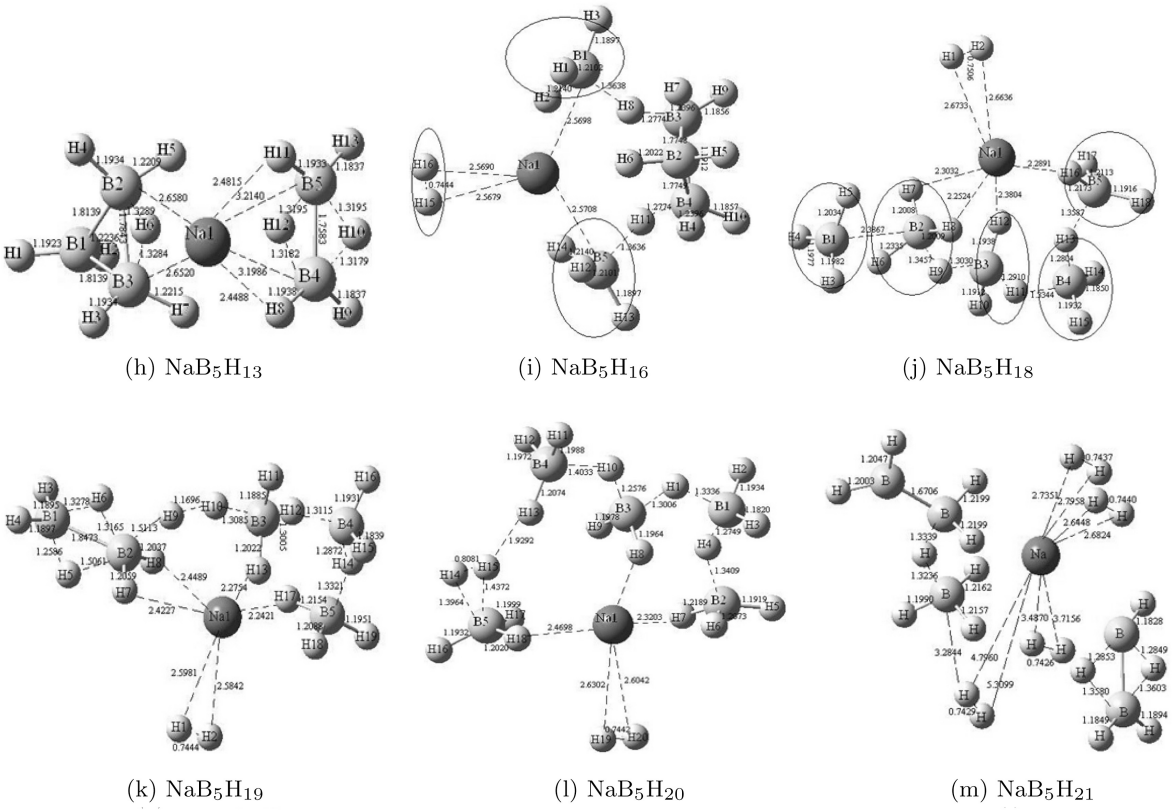
The structures of NaB_5H_x clusters are shown in Fig. 4. As is seen in the figures, the boron part of the clusters is gradually distorted, and finally disintegrates. And rather complicated new structures are formed with the addition of the hydrogen atoms. The disintegration of a boron cluster by the hydrogen atoms takes place in a stepwise manner and the first indication of this process can be seen at the NaB_5H_9 cluster (Fig. 4(f)), in which one boron atom is separated from the boron cluster. After that, this separation process stops until $x = 13$, where a B_2 dimer is formed. At $x = 16$ (Fig. 4(i)), there are two BH_3 satellites connected to the main part by bridging bonds. Two of the hydrogen atoms move away from the cluster and form a H_2 molecule, but still connected to the Na atom. At $x = 18$, separations are clearer (Fig. 4(j)), i.e., the B_5 cluster breaks up into five B atoms. One of the separated boron atoms is bonded to four hydrogen atoms and forms a BH_4 satellite cluster, while the other four boron atoms are bonded to three hydrogen atoms and form four BH_3 satellite clusters. These satellites are connected to the other groups of the cluster by bridging a hydrogen atom or an Na atom. We continue to increase hydrogen atoms, then at $x = 19$, one B_2 dimer is formed afresh. At $x = 20$, the B_5 cluster is separated into five B atoms again and most of are bounded to three hydrogen atoms (Fig. 4(l)). After a certain number of hydrogen atoms ($x = 21$ in this case) have been added, some of the hydrogen atoms break away from the cluster with the formation of a H_2 molecule, which is about 3.3 Å away from the nearest atom in the cluster (Fig. 4(m)).



(a) NaB_5H (b) NaB_5H_2 (c) NaB_5H_4 (d) NaB_5H_6



(e) NaB_5H_8 (f) NaB_5H_9 (g) NaB_5H_{10}



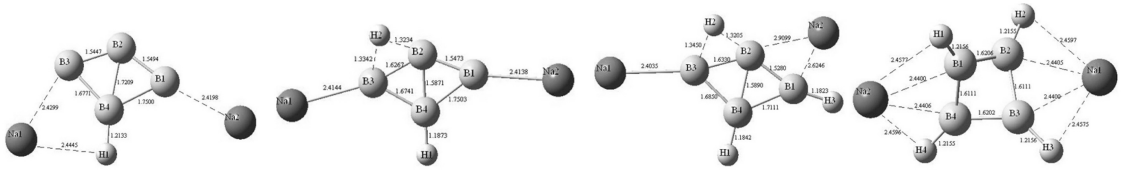
(h) NaB_5H_{13} (i) NaB_5H_{16} (j) NaB_5H_{18}

(k) NaB_5H_{19} (l) NaB_5H_{20} (m) NaB_5H_{21}

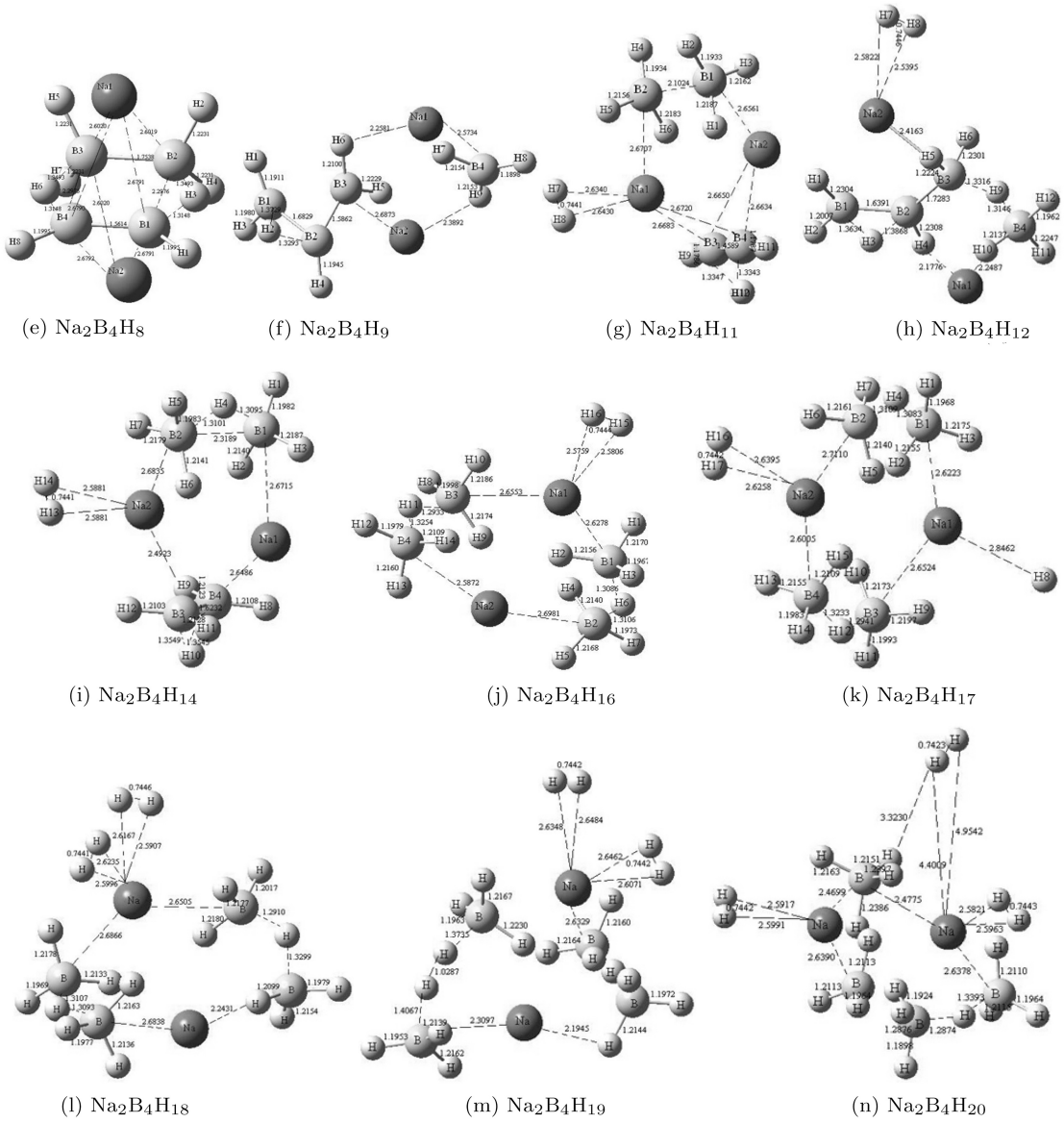
Fig. 4. Optimized geometries of NaB_5H_x clusters.

3.2.2. $Na_2B_4H_x$

The optimized structures of $Na_2B_4H_x$ clusters are presented in Fig. 5. As is seen in the figures, up to three hydrogen atoms are added and the cluster remains in its planar form (Fig. 5(c)). After that, the hydrogen atoms twist the Na_2B_4 cluster planar form. When the number of hydrogen atoms is 8, the boron core starts separating. With the number of hydrogen atoms increasing further, isolations of the boron atoms by the hydrogen atoms become more pronounced. The first BH_3 satellite is distinctly observed at $x = 9$ (Fig. 5(f)). For $x > 9$, the number of BH_3 satellites varies depending on the boron positions. Starting at $x = 11$ (Fig. 5(g)), some of the hydrogen atoms move away from the cluster and form aH_2 molecule. In accordance with that of the NaB_5H_x cluster, the H_2 molecule is still connected to the rest of the cluster through one of the Na atoms. The Na atom also plays a mediator role to connect some of the BH_3 satellites. For $x = 18$ (Fig. 6(l)), there are two hydrogen molecules attached to the same Na atom. This interesting feature is not observed for the NaB_5H_x. Addition of more hydrogen atoms to the cluster ($x = 20$) causes desorption of the hydrogen atoms in the form of a H_2 molecule, which is about 3.3 Å away from the nearest atom.



(a) Na_2B_4H (b) $Na_2B_4H_2$ (c) $Na_2B_4H_3$ (d) $Na_2B_4H_4$



(e) $Na_2B_4H_8$ (f) $Na_2B_4H_9$ (g) $Na_2B_4H_{11}$ (h) $Na_2B_4H_{12}$

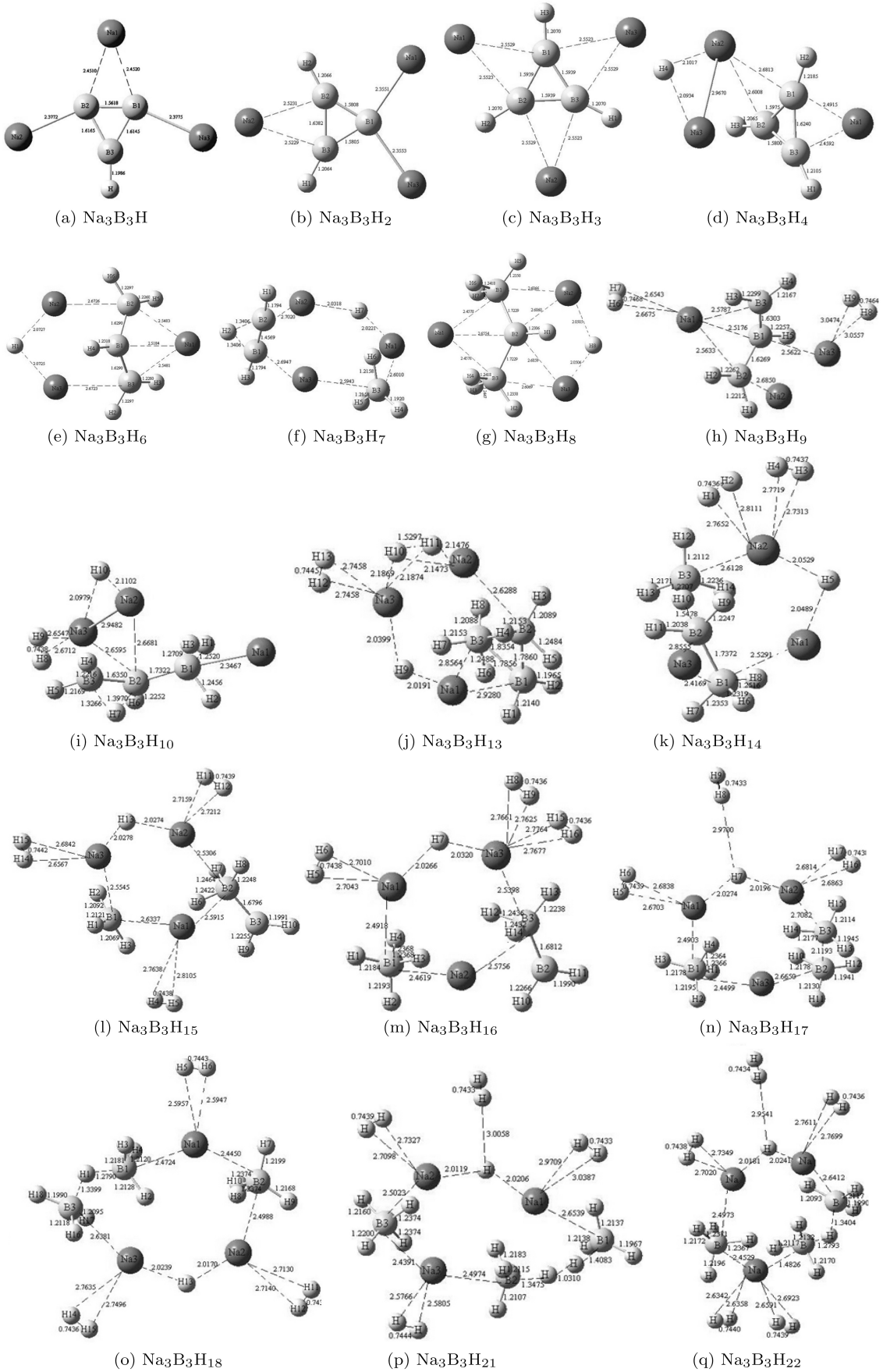
(i) $Na_2B_4H_{14}$ (j) $Na_2B_4H_{16}$ (k) $Na_2B_4H_{17}$

(l) $Na_2B_4H_{18}$ (m) $Na_2B_4H_{19}$ (n) $Na_2B_4H_{20}$

Fig. 5. Optimized geometries of $Na_2B_4H_x$ clusters.

3.2.3. $Na_3B_3H_x$

The optimized structures of hydrogenated $Na_3B_3H_x$ clusters are shown in Fig. 6. These clusters have not changed the symmetric and planar form until four hydrogen atoms are added. The initial sign for the separation of the boron cluster comes at $x = 7$ (Fig. 6(f)), in which the first BH_3 satellite is formed. However, a B_3 cluster is reformed by adding another hydrogen, and it is not affected until $x = 14$. As is seen in the fiugres, the separation of the total boron cluster comes at $x = 17$. After that, the boron atoms continue to hold more hydrogen atoms (Fig. 6(n)). With the number of hydrogen atoms increasing, new BH_3 and BH_4 structures are formed (Fig. 6(o)). We have continued to increase the number of hydrogen atoms up to 22. As is seen in Figs. 6(p) and 6(q), most of the H_2 molecules are still connected to the cluster via Na atoms. At $x = 21$ and $x = 22$, desorption of a H_2 molecule that is not connected to the cluster via Na atom takes place. The vibrational frequency calculations show that these clusters have one imaginary frequency, which indicates a transition state. We have not optimized this system with more than 22 hydrogen atoms because of the huge increase in computational time. Therefore, we think that the hydrogen intake capacity of these clusters could be more than 22.



(a) Na_3B_3H (b) $Na_3B_3H_2$ (c) $Na_3B_3H_3$ (d) $Na_3B_3H_4$

(e) $Na_3B_3H_6$ (f) $Na_3B_3H_7$ (g) $Na_3B_3H_8$ (h) $Na_3B_3H_9$

(i) $Na_3B_3H_{10}$ (j) $Na_3B_3H_{13}$ (k) $Na_3B_3H_{14}$

(l) $Na_3B_3H_{15}$ (m) $Na_3B_3H_{16}$ (n) $Na_3B_3H_{17}$

(o) $Na_3B_3H_{18}$ (p) $Na_3B_3H_{21}$ (q) $Na_3B_3H_{22}$

Fig. 6. Optimized geometries of $Na_3B_3H_x$ clusters.

3.2.4. $Na_4B_2H_x$ and B_6H_x

The hydrogen intake capacity of the Na_4B_2 clusters has also been investigated by the same method as mentioned above (structures are not shown). As the number of hydrogen atoms increases, a similar course as that in the above clusters is observed. The B_2 dimer is separated at $x = 9$. Because this cluster has only two boron atoms, the Na atoms play mediator roles for the connections between the hydrogen atoms and the rest of the cluster. However, this system is not very successful at holding more hydrogen atoms since desorption of a H_2 molecule occurs at $x = 14$. For comparison, we have optimized the geometries of the B_6H_x clusters (structures are not shown). The maximum value of tge hydrogen atoms is $x = 16$, which is in good agreement with Ref. [16].

3.3. The stability of $Na_nB_mH_x$ clusters

In order to study the stability of $Na_nB_mH_x$ clusters, we have investigated the hydrogen–cluster interaction energy for the $Na_nB_mH_x$ clusters as the hydrogen atoms increase. It presents a large fluctuation due to the total number of electrons being an odd or an even number (Fig. 7). It indicates that the stability of the $Na_nB_mH_x$ clusters has odd–even oscillatory behaviour.

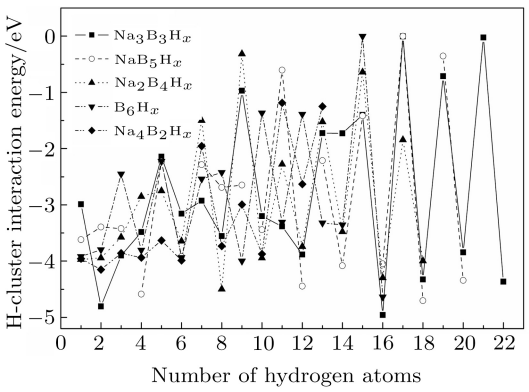


Fig. 7. Hydrogen–cluster interaction energies of the NaB_5H_x, $Na_2B_4H_x$, $Na_3B_3H_x$, $Na_4B_2H_x$ and B_6H_x as a function of the number of hydrogen atoms.

The binding energy of each atom in the cluster system reflects the energy changes of the whole cluster. Figure 8 shows the binding energy of $Na_3B_3H_x$. From Fig. 8, we can see that it also presents fluctuation due to the fact that the total number of electrons is an odd or even number. And because the surface effect of small clusters is obvious, the converging of its binding energy to the block material is very slow.

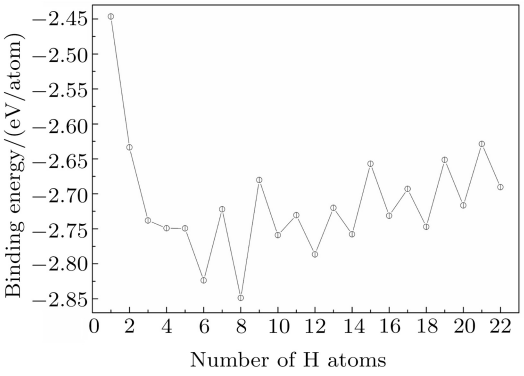


Fig. 8. Binding energy per atom of $Na_3B_3H_x$.

The second difference in energy is a very sensitive physical quantity to the stability of clusters: a bigger second difference in energy indicates a higher stability of clusters. Figure 9 shows that the second difference in energy changes as the cluster size increases, and it varies between positive and negative values with odd–even oscillatory behaviours. From Fig. 7 to Fig. 9, we can find that the even-sized $Na_3B_3H_x$ clusters are relatively more stable than the neighbouring odd-sized ones. In particular, the $Na_3B_3H_8$ is remarkably more stable than its neighbouring clusters.

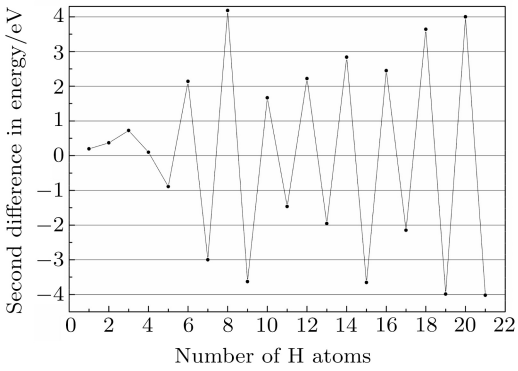


Fig. 9. Second difference in energy of $Na_3B_3H_x$.

4. Conclusion

For the Na_nB_m clusters, boron and Na atoms tend to form small clusters among themselves. The Na atoms are placed symmetrically around the boron clusters, which generally take a form similar to their corresponding bare boron clusters. Depending on the number of Na atoms and their positions, an increase or decrease in the averaged bond lengths of these small boron clusters is observed, indicating that the Na atoms stretch or compress the small boron clusters. Furthermore, the number of Na atoms can affect the stability of the cluster, i.e., as the number of Na

atoms increases, the total binding energy of the cluster increases, while the energy gap decreases. The binding energy per atom also increases linearly with an increasing number of Na atoms. These results suggest that the stability of a Na_nB_m cluster decreases and the probability of the reactivity of the cluster increases with the number of Na atoms increasing.

The observed hydrogen storage capacities are x=16, $x = 20$, $x = 19$, $x > 22$, and $x = 13$ for BH_x, NaB_5H_x, $Na_2B_4H_x$, $Na_3B_3H_x$, and $Na_4B_2H_x$, respectively. In fact, for the $Na_3B_3H_x$ cluster, we could not increase the number of hydrogen atoms beyond 22 due to a very long optimization time. If computational time can be reduced somehow, one may obtain optimized structures of these clusters with more than 22 hydrogen atoms. This shows that the $Na_3B_3H_x$ system has more promising reversible hydrogen storage potential than the others.

The odd–even oscillation features of the $Na_3B_3H_x$ cluster are shown in the hydrogen–cluster interaction energy, the binding energy of each atom and the second-order energy differences, which indicate that the stability of the $Na_nB_mH_x$ clusters presents fluctuation as the hydrogen atoms increase. For $Na_3B_3H_x$ clusters, the even-sized $Na_3B_3H_x$ clusters are relatively more stable than the neighbouring odd ones.

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