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Search for the Global Minimum Structures of AlB_3H_{2n} ($n = 0 - 6$) Clusters

İskender Muz,[a] Osman Canko,*[b] Murat Atiş,[c] and Erdem Kamil Yıldırım[d]

The global minimum structures of AlB_3H_{2n} ($n = 0$–6) clusters are determined using the stochastic search method at the B3LYP/6–31G level of theory. These initially specified geometries are recalculated using B3LYP and CCSD(T) methods using the 6–311++G** basis set. The structural and electronic properties of the two lowest-lying isomers are presented. The structural parameters obtained for aluminum borohydride are compared with the experimental and theoretical results. The H_2 fragmentation energies of the most stable isomers are investigated. Chemical bonding analyses for the global minimum of AlB_3H_{2n} ($n = 0$–6) clusters are performed using the adaptive natural density partitioning method. © 2014 Wiley Periodicals, Inc.

Introduction

The Lewis theory of bonding reveals the importance of valence electrons in chemical bonding and explains the single, double and triple bonds obtained by sharing two, four, and six electrons between two atoms, respectively. However, it fails to account for certain elements such as boron and does not predict which isomer of the clusters is the lowest-lying structure. An investigation of the lowest-lying isomer of an atomic cluster is indispensable as this structure is a promising candidate as a building block which can be encountered in nature. Furthermore, atomic clusters may have significant meaning in the understanding of bulk materials once the primitive cell of the crystal is specified.

Elements of the same group generally have similar properties; however, boron has some unique and different properties from the rest of the group despite their isovalency.[1] Therefore, the replacement of a boron atom by an aluminum atom in a cluster provides a unique chemical environment that may induce a significant change in the electronic properties and the possibility of new types of material.[2–8] Group 13 hydrides are of importance in the chemistry of materials, organic synthesis, organometallic catalysis, hydrogen storage applications,[9,10] and jet fuel.[11] For instance, aluminoborane compounds may have very attractive properties for hydrogen storage, as boron has many different types of hydrides[12–15] and aluminium reduces the decomposition temperatures of hydrides. Hence, aluminoborane compounds may be good candidates for hydrogen storage due to their very high hydrogen capacity, moderate stability in terms of a decomposition temperature, fast hydrogen recharging kinetics, and attractive hydrogen fragmentation temperature, see Refs. [16,17]. For these reasons, the determination and understanding of the stability and hydrogenation/dehydrogenation properties of aluminoborane hydrides are also of great interest.[17]

There are various theoretical approaches to cluster searching. However, the best is to use only stoichiometric ratios without using the structural information from experimental observations or alleged geometry. Theoretically, a lot of randomly generated geometries can be searched and calculated by ab initio methods, and afterward the energetically lowest-lying structure can easily be determined from the results. The reliability and success of the method can be tested by comparison with known experimental outcomes. Once the unknown structure is determined, this will save both time and expense. The possibility of producing clusters of a given size provides hope for new classes of materials that could be synthesized.[18]

By virtue of the unusual structures of mixed compounds observed in Group 13 elements, in the literature, several attempts have been carried out to obtain hydrogenated boron–aluminum clusters.[9,11,19–23] For instance, aluminum borohydride, $Al(BH_4)_3$, was synthesized quite early on and investigated in detail by different groups, see Refs. [24,25]. However, to the best of our knowledge, theoretical investigation of the $Al(BH_4)_{n = 1 \to 4}$ structure has not been carried out until recently.

For these kinds of materials, the challenging issues are fragmentation temperatures, diborane formation during fragmentation and reversibility.[26] The aim of this work is to investigate systematically the hydrogenation of a four-membered system involving one aluminum and three boron atoms using the stochastic search method.[27] The structural variation and electronic properties of AlB_3H_{2n} ($n = 0$–6) clusters will be explored when the hydrogen atom is systematically

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augmented. Hence, this study gives an insight into structural variety and its interconversion.

Computational Methods

We have performed the global minimum search of AlB_3H_{2n} ($n = 0–6$) clusters using the stochastic search method.[27] The positions of atoms in a cluster are moved by random kicks and a new structure is produced from the previous one. Whether or not the modified structure is fragmented is also checked after each movement. These new atom coordinates are accepted as input data for further electronic calculation. The above steps are repeated 400 times to generate different geometries for each cluster size. These randomly kicked structures are optimized by means of the B3LYP [28] hybrid method with the 6–31G [29] basis set. After the isomers are sorted according to their energies, low-lying isomers up to 50 kcal/mol are reoptimized using the B3LYP/6–311++G** level of theory. Furthermore, single point calculations are performed at the CCSD(T)/6–311++G** level of theory. More detailed information can be found in our previous papers.[30,31] We should also mention that electronic structure calculations are performed by considering singlet and triplet states using the Gaussian 09 program[32]; structural and orbital visualization was done using the MOLDEN[33] and MOLEKEL programs,[34] respectively.

Enthalpy is a measure of the stability of a cluster and is determined by the strength of the chemical bonds in it. Hence, thermodynamic stability specifies whether H_2 loss from AlB_3H_{2n} will be energetically favorable or not. The enthalpies of a reaction can be calculated using thermochemical properties as follows:

$$\Delta H(298K) = \sum (\varepsilon_0 + H_{corr})_{products} - \sum (\varepsilon_0 + H_{corr})_{reactants} \quad (1)$$

where $\varepsilon_0 + H_{corr}$ for a reaction at 1 atm and 298 K in the gas phase, is the sum of the total electronic energy and correction to the enthalpy due to internal energy, respectively. H_{corr} is obtained from $k_B T$ and internal energies due to translational, rotational, vibrational and electronic motions. To probe fragmentation energy,

$$E_f = (E_{AlB_3H_{2n-2}} + E_{H_2})_{products} - (E_{AlB_3H_{2n}})_{reactants} \quad (2)$$

The $E_{AlB_3H_{2n-2}} + E_{H_2}$ and $E_{AlB_3H_{2n}}$ indicate the products and reactants, respectively. The ionization potentials can be calculated as follows:

$$AIP = E(optimized cation) - E(optimized neutral) \quad (3)$$

$$VIP = E(cation at optimized neutral geometry) - E(optimized neutral) \quad (4)$$

where adiabatic ionization potential (AIP) is the difference in zero-point vibrational energy between cationic and neutral clusters at their respective equilibrium geometries. The vertical ionization potential (VIP) is defined as the energy difference

between the ground state of neutral and cationic clusters, optimized by the geometry of the neutral clusters.
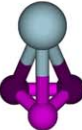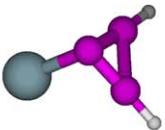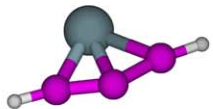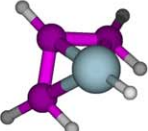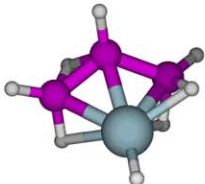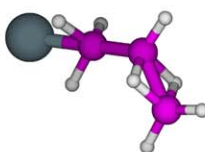
Results and Discussion

Structures and stabilities

The two lowest isomer geometries and their relative energies are presented in Table 1. The other isomers ($\Delta E < 50$ kcal/mol or the top 15 lowest-lying isomers) are also presented in Supporting Information (Figs. S1 and S2). The isomers are ordered according to the energies of the optimized structures at the CCSD(T)/6–311++G** level of theory. The energy differences between the second isomers and the lowest isomers are given for the CCSD(T)/6–311++G**, CCSD(T)/6–311++G**//B3LYP/6–311++G**, and B3LYP/6–311++G** levels of theory. To ensure whether or not all the calculated structures reside in the local minima on the potential energy surface, the vibrational frequencies of the optimized geometries are also calculated.

The most stable isomer of the AlB_3 cluster has a planar geometry with the C_{2v} point group and the Al atom is bonded by one of the B atoms in the triangular B_3 cluster. The second lowest isomer has a three dimensional (3D) form with the C_{3v} point group and the Al atom sits on the hollow posi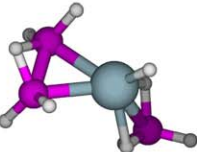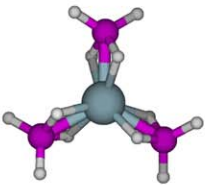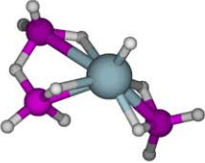tion of the triangular borons and causes a pyramidal structure. Boyukata and Guvenç[3] obtained these two isomers and calculated the energy difference between the isomers to be 0.145 eV (3.95 kcal/mol) at the B3LYP/6–311++G** level of theory. In this study, the energy difference is found to be 3.51 kcal/mol with the same level of theory, as seen in Table 1. Therefore, there is a remarkable agreement with some exceptions between our and literature results.[3] The most stable isomer of the AlB_3H_2 clusters has a quasi-planar geometry with the C_s point group. The second lowest isomer has a planar geometry with the C_s point group and ^3A electronic state. It should be noted that low-lying energy states prefer the lowest spin multiplicity rather than higher spin multiplicity, except for the second lowest isomer of the AlB_3H_2 cluster. The two additional hydrogen atoms cause the geometry of the most stable isomer of the AlB_3 cluster to change out of plane. When boron atoms in the AlB_3H_{2n} cluster maintain their B–B–B triangle form up to $n = 2$. For AlB_3H_4 clusters, the bonded hydrogen atom resides either connected to the two neighboring B atoms or attached to any B atom with a single bond. Up to this size, the most striking feature observed is that boron atoms maintain their B–B–B triangular form. In aluminum doped boron clusters, the Al atom prefers to stay on the peripheral position on the outer-side of clusters up to $n \leq 3$. However, the triangular form of boron atoms is exposed to a structural change in the lowest isomer of the AlB_3H_6 clusters. Here, the Al atom begins to settle toward the center of the B–B–B triangular boron cluster and this isomer has a quasi-planar geometry. Obviously, the second is reminiscent of the lowest isomer of the AlB_3H_4 cluster with two more hydrogen atoms bonded to the Al atom. The results so far show that the geometries and energies obtained by the B3LYP and CCSD(T)

Table 1. Geometries, point groups, electronic states and relative energies (kcal/mol) of lowest energy structures of AlB_3H_{2n} ($n = 0$–6) clusters calculated at the B3LYP/6–311++G** basis set extrapolation in cornered parentheses, those at the CCSD(T)/6–311++G**//B3LYP/6–311++G** in parentheses, and those otherwise at CCSD(T)/6–311++G**.

AlB_3

$C_s, {}^1A$

$\Delta E = 0.0$

$C_{3v}, {}^1A$
$\Delta E = 5.68$
$(\Delta E = 5.31)$
$[\Delta E = 3.51]$

AlB_3H_2

$C_s, {}^1A$

$\Delta E = 0.0$

$C_s, {}^3A$
$\Delta E = 0.37$
$(\Delta E = 0.56)$
$[\Delta E = 10.71]$

AlB_3H_4

$C_s, {}^1A$

$\Delta E = 0.0$

$C_s, {}^1A$
$\Delta E = 3.07$
$(\Delta E = 3.21)$
$[\Delta E = 4.52]$

AlB_3H_6

$C_s, {}^1A$

$\Delta E = 0.0$

$C_s, {}^1A$
$\Delta E = 0.28$
$(\Delta E = 0.17)$
$[\Delta E = -1.51]$

AlB_3H_8

$C_1, {}^1A$

$\Delta E = 0.0$

$C_1, {}^1A$
$\Delta E = 1.61$
$(\Delta E = 1.56)$
$[\Delta E = 3.57]$

AlB_3H_{10}

$C_s, {}^1A$

$\Delta E = 0.0$

$C_1, {}^1A$
$\Delta E = 2.99$
$(\Delta E = 3.12)$
$[\Delta E = 1.44]$

AlB_3H_{12}

$C_3, {}^1A$

$\Delta E = 0.0$

$C_s, {}^1A$
$\Delta E = 19.31$
$(\Delta E = 19.20)$
$[\Delta E = 17.95]$

methods agree well. However, it is worthwhile to note that the order of the isomers of the AlB_3H_6 cluster is switched for both calculations. For AlB_3H_8 clusters, the first isomer of the AlB_3H_8 cluster is similar to the first isomer of the AlB_3H_6 cluster with two additional hydrogen atoms. The coordination number of the Al atom continues to increase. The geometric growth of the second isomer is different from the previous

ones. Here, the Al atom is bonded to one of the B atoms and the triangular shape has not been maintained yet. Furthermore, the coordination number of Al decreases with respect to the first isomer. For AlB_3H_{10} clusters, both isomers have similar geometries. However, the first isomer has 2.99 kcal/mol lower energy than the second isomer at the CCSD(T)/6–311++G** level of theory, as seen in Table 1. The boron

Table 2. The Al-B, B-B, B-H_t, B-H_b, Al-H_t, and Al-H_b average bond lengths calculated for AlB$_3$H$_{2n}$ ($n = 0$–6) clusters at B3LYP/6–311++G** level of theory.

Size	d_{Al-B} (Å)	d_{B-B} (Å)	d_{B-H_t} (Å)	d_{B-H_b} (Å)	d_{Al-H_t} (Å)	d_{Al-H_b} (Å)
AlB$_3$H$_0$	2.19	1.54	–	–	–	–
AlB$_3$H$_2$	2.15	1.50	1.18	–	–	–
AlB$_3$H$_4$	2.27	1.54	1.19	1.31	–	–
AlB$_3$H$_6$	2.10	1.64	1.19	1.26	1.57	1.85
AlB$_3$H$_8$	2.09	1.72	1.19	1.30	1.60	1.90
AlB$_3$H$_{10}$	2.18	1.65	1.19	1.28	1.56	1.92
AlB$_3$H$_{12}$	2.16	–	1.19	1.27	–	1.76
	2.14[a]	–	1.19[a]	1.28[a]	–	–
	2.16[b]	–	1.19[b]	1.27[b]	–	–

[a] Ref. [25]. [b] Ref. [24].

atoms are separated from each other and the cluster is split into two parts with a central Al atom rather than a triangular form. The most stable isomer of the AlB$_3$H$_{12}$ cluster is known as aluminum borohydride or aluminum tetrahydroborate which is the chemical compound with the formula Al(BH$_4$)$_3$. The Al atom is bonded symmetrically to all boron atoms and all B-Al-B angles are close to 120°. Each boron atom, located at the corners of structure with the D$_{3h}$ point group, is bonded to four hydrogen atoms. Aluminum borohydride was synthesized first by Schlesinger et al. in 1940[35] and until now it has been extensively studied.[24,25,36,37] The experimental results show that the AlB$_3$H$_{12}$ compound could be either of the D$_{3h}$ (prismatic model) symmetry or of the D$_3$ (aprismatic model) symmetry.[25]

To make the comparison between theoretical and experimental results, the calculated Al—B, B—B, B—H_t, B—H_b, Al—H_t, and Al—H_b average bond lengths are listed in Table 2, where H_t and H_b, indicate the terminal or bridge bonding of the hydrogen atom with boron or aluminum, respectively. There is no considerable change in any of the bond lengths with respect to the increasing number of H$_2$ molecules for all cases. The B—H_t, B—H_b, and Al—H_t average bond lengths, in particular, have the same trend at around 1.2, 1.3, and 1.6 Å, respectively. A similar trend is also observed in the Al—H_b average bond length (with 1.9 Å), but a slight drop is seen in the AlB$_3$H$_{12}$ cluster. Although there is no considerable change in the B—B average bond lengths, they become relatively larger in the bigger size (AlB$_3$H$_{2n}$, $n = 3$–5). For Al—B average bond length, there are fluctuations around 2.1 and 2.3 Å without any typical trend. The average bridge bonding length is longer compared to those for the terminal bond for Al(or B)-H_b, as listed in Table 2. Therefore, the interaction of bridging H with Al(or B) is weaker than for terminal H. This may be due to the increase in the coordination of the bridging H atoms. In this study, we can only make comparison with the experimental results of terminal or bridge bonding of hydrogen for aluminum borohydride. The Al—B, B—H_b, and B—H_t (2.16, 1.27, and 1.19 Å) are in good agreement with the experimental values of 2.14, 1.28, and 1.19 Å[25] obtained using electron diffraction, and also in excellent agreement with the theoretical values of 2.14, 1.28, and 1.19 Å calculated at the MP2/6–311G** level of theory.[24] We should also mention that none of the structures,

except the most stable isomer of the AlB$_3$ and AlB$_3$H$_{12}$ clusters, have been previously reported in the literature.

Electronic properties

To examine the energy needed for hydrogen storage and release, we have calculated the H$_2$ fragmentation properties of Al doped B$_3$ clusters. In particular, we calculated the enthalpy changes for AlB$_3$H$_{2n}$ → AlB$_3$H$_{2n-2}$ + H$_2$ with $1 \leq n \leq 6$ in the gas-phase reaction at 298 K and 1 atm. The results are plotted in Figure 1a.

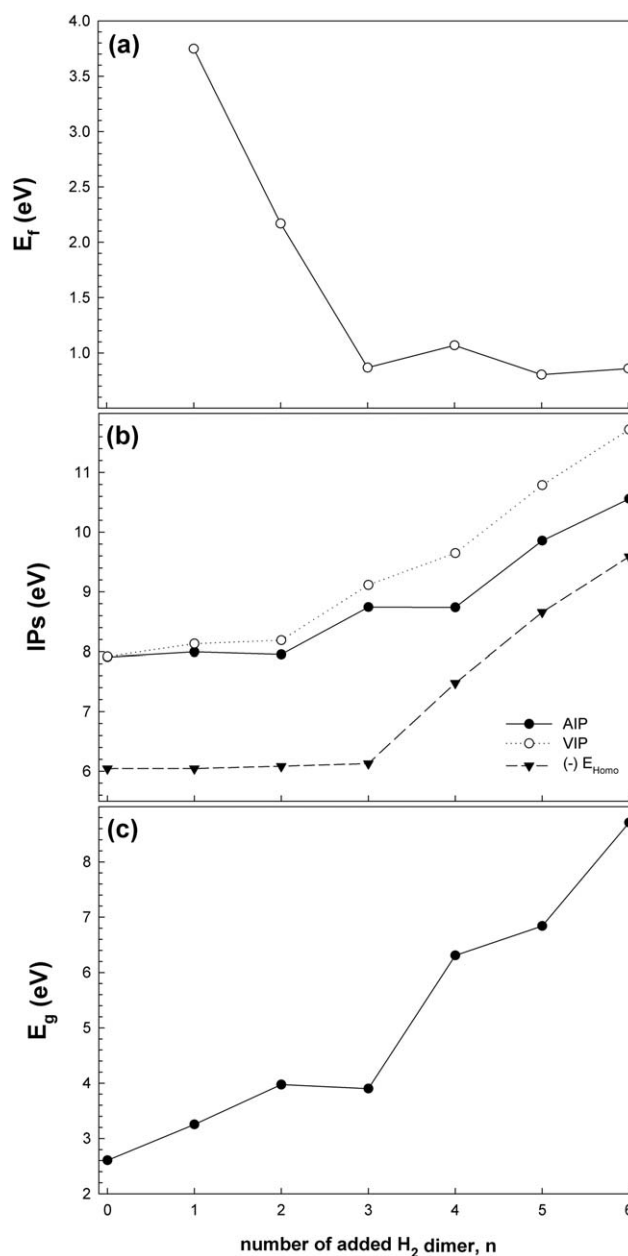The energy needed for H$_2$ fragmentation decreases with increasing amount of hydrogen. This trend shows that the

Figure 1. The B3LYP/6–311++G** level of theory calculations: a) the fragmentation energies of H$_2$. b) The ionization potentials and HOMO energies. c) The HOMO-LUMO energy gaps.

hydrogen storage capability of the Al doped B_3 cluster decreases when the number of hydrogen atoms increases. The decrease in fragmentation continues up to AlB_3H_6 and then it generally remains stable, as seen in Figure 1a. It is worthwhile noting that the fragmentation energy of the clusters with high hydrogen content ($n = 3–6$) falls up to 0.8 eV. This value is close to the energy needed for the release of hydrogen, which should preferably be in the range 0.2–0.6 eV/H_2.[38–40] Boyukata and Guvenç[23] calculated the energy needed for evaporation of H_2 from the Al doped $B_{12}H_n$ ($n = 2–13$) clusters in the range 1.5–3.5 eV. Accordingly, the H_2 fragmentation from the Al doped hydrogenated B_3 clusters, particularly in large sizes, is lower than that in Al doped hydrogenated B_{12} clusters. This can be explained by the large number of boron atoms in the cluster. The boron atom makes a strong bond with hydrogen atoms and this results in difficult H_2 fragmentation.

The addition of H_2 to AlB_3H_{2n} ($n = 0–6$) clusters generally increases the IPs, and the IP values at $n = 0–2$ are lower than those at $n = 3–6$, as seen in Figure 1b. The VIPs are higher than the AIPs due to energy compensation as a result of orbital relaxation on ionization. The HOMO-LUMO energy gap (E_g) is very important to analyze the stability of clusters. As seen in Figure1c, it generally increases with the addition of hydrogen to the AlB_3 cluster and a significant increase (from 2.61 to 8.71 eV) is observed when the number of H atom equals the number of total valance electrons in the AlB_3 cluster. Therefore, the largest E_g occurs for the AlB_3H_{12} cluster. This means that the chemical stability of this cluster is stronger than those of other clusters and its chemical activities are also comparatively weaker than those of the others.

AdNDP analysis

Chemical bonding analysis was performed for the most stable isomers of the AlB_3H_{2n} ($n = 0–6$) clusters using the adaptive natural density partitioning (AdNDP) method which was recently developed by Zubarev and Boldyrev.[41] It is a very efficient and visual approach to the interpretation of the molecular orbital because it is an extension of the natural bond orbital analysis. AdNDP discovers both the localized Lewis bonding structure and the delocalized bonding structure which are associated with the concepts of aromaticity/antiaromaticity. Aromaticity explains enhanced thermodynamic stability, low reactivity, bond-length equalization, high symmetry, and so forth. We performed the AdNDP analysis of the lowest-lying structures at the B3LYP/STO-3G//B3LYP/6–311++G^{**} level of theory. As AdNDP analysis is not sensitive to the level of theory or basis set, the choice of the quality of the method used here is sufficiently adequate.[42] The occupation numbers (ONs) obtained by AdNDP analysis are expected to be close to the maximum values (2.00 |e|). The AdNDP analysis results and ONs for the most stable isomers are presented in Figure 2.

A total of 14 pairs of electrons for the AlB_3 structure and six valance electron pairs are bonded as follows: one 1c-2e Al lone pair (LP) (ON =1.95|e|), three 2c-2e B—B (ON = 1.64–1.99|e|), one 3c-2e B—B—B (ON =1.80|e|) σ bonds and one 3c-

2e B—B—B (ON = 1.98|e|) π bonds. As for the remaining eight electron pairs, they are simply core electrons so that five pairs are in the Al atom and three pairs are in the B atoms. For the AlB_3H_2 structure, 6 of the total 7 valence electron pairs are distributed as follows: one 1c-2e LP Al (ON = 1.96|e|), two 2c-2e B—B (ON = 1.91|e|), two 2c-2e B—H (ON = 1.99|e|) and one 3c-2e B—B—B (ON = 1.95|e|) σ bonds. The other is a 3c-2e B—B—B (ON = 1.81|e|) π bond. For the AlB_3H_4 structure, 7 valence electron pairs of the total 8 participants are partitioned into one 1c-2e LP Al (ON = 1.99|e|), three 2c-2e B—H (ON = 1.96–1.99|e|), two 2c-2e B—B (ON = 1.78–1.80|e|) and one 3c-2e B—B—H (ON = 1.99|e|) σ bonds. The other is a 3c-2e B—B—B (ON = 1.96|e|) π bond. For the AlB_3H_6 structure, 8 valence electron pairs of the total 9 participants are partitioned into one 2c-2e Al—H (ON = 1.99|e|), five 2c-2e B—H (ON = 1.81–1.98|e|) and two 3c-2e Al—B—B σ bonds (ON = 1.97|e|). The other is a 3c-2e B—B—B (ON = 1.71|e|) π bond. The 10 valence electron pairs of the AlB_3H_8 structure are partitioned into one 2c-2e Al—H (ON = 1.99|e|), three 2c-2e B—H (ON = 1.95–1.98|e|), one 3c-2e B—B—H (ON = 1.99|e|), three 3c-2e Al—B—H (ON = 1.96–1.98|e|) and two 3c-2e Al—B—B (ON = 1.83–1.98|e|) σ bonds. The 11 valence electron pairs of AlB_3H_{10} structure are partitioned into one 2c-2e Al—H (ON = 1.99|e|), six 2c-2e B—H (ON = 1.98|e|), one 3c-2e B-B-H (ON = 1.99|e|), two 3c-2e Al-B-H (ON = 1.98|e|) and one 3c-2e Al—B—B (ON = 1.88|e|) σ bonds. The 12 valence electron pairs of the AlB_3H_{12} structure are partitioned into six 2c-2e B—H (ON = 1.98|e|) and six 3c-2e Al—B—H (ON = 1.99|e|) σ bonds.

According to the AdNDP results, the hydrogen atoms generally prefer to make either 2c-2e B—H σ or 3c-2e B—B—H σ bonds. They also prefer 3c-2e Al-B-H σ bonds. The 3c-2e B—B—B bonds are observed up to AlB_3H_6 clusters. Moreover, the 1c-2e LP Al bonds are observed up to AlB_3H_4 clusters. These results indicate that the triangular form of boron atoms is exposed to structural distortion when the number of hydrogen increases. We should also mention that the ONs of the most stable isomers are very close to the ideal values. This provides confidence about the chemical bonding pattern presented in this study.

Conclusions

Using the stochastic search method, we have studied the geometric structures and stabilities of the AlB_3H_{2n} ($n = 0–6$) clusters with the B3LYP/6–311++G^{**} and CCSD(T)/6–311++G^{**} levels of theory. The increasing number of H_2 leads to the structural distortion of the B–B–B triangular form in the Al doped B_3 clusters. Furthermore, the Al atom both increases the coordination number and moves toward the center of the B–B–B triangle in the boron cluster. The AlB_3H_{12} cluster is arranged in the space so as to form a structure (D_{3h}) with six Al—B—H bridging and six B—H terminal hydrogen atoms. The structural parameters obtained for this cluster are in good agreement with experimental results. The analysis of the energetic and structural stability shows that it is more stable than its stoichiometric counterpart. We have also investigated the changes of enthalpy at 298 K and 1 atm in the gas phase.
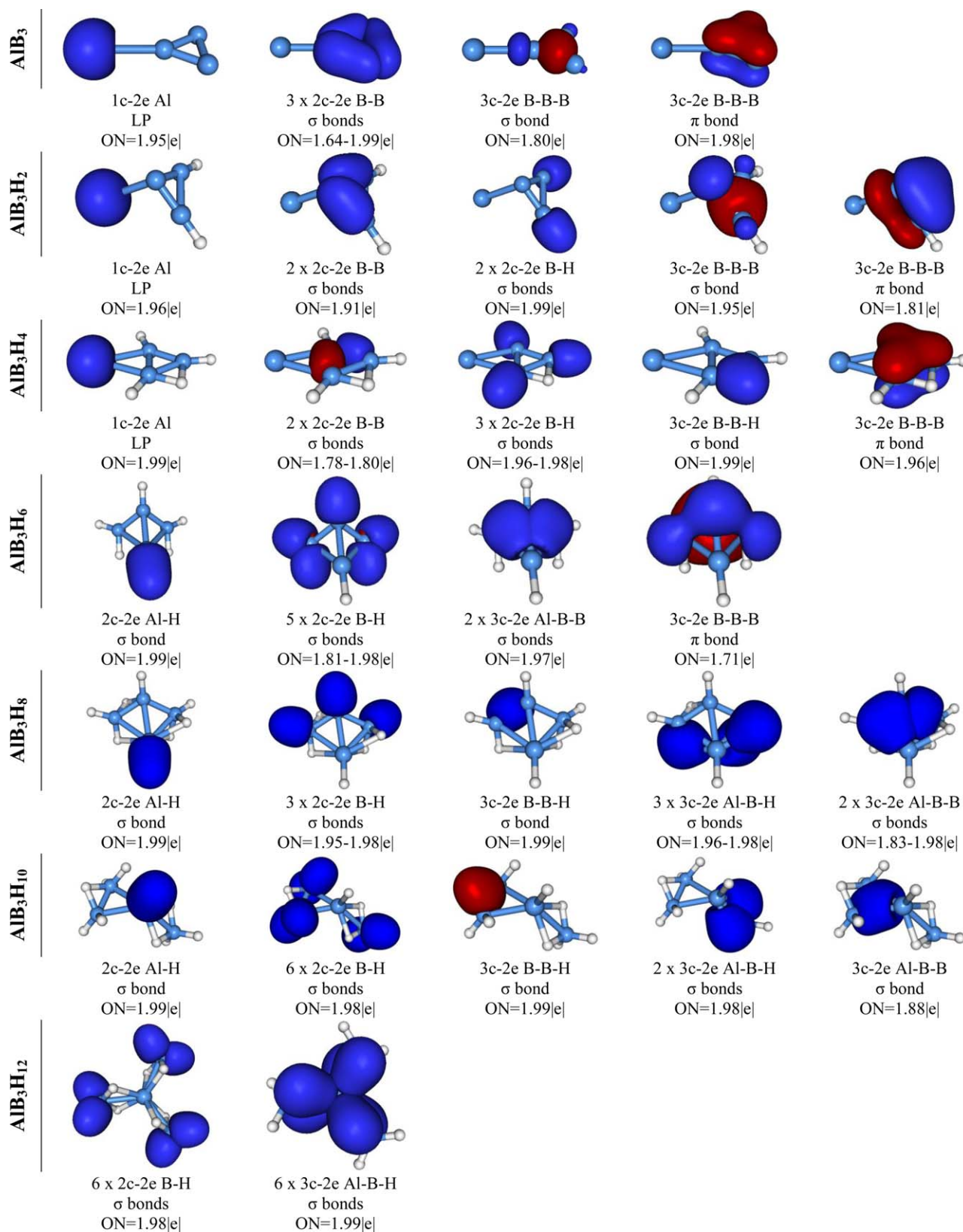
Figure 2. Chemical bonding patterns of the most stable isomers recovered by AdNDP analysis.

Accordingly, the fragmentation energies of Al doped hydrogenated B_3 clusters have a decreasing trend with the increasing number of hydrogen atoms. In particular, H_2 fragmentation in the range $n = 3$–6 for the Al doped B_3 clusters is lower than for the others, but a little higher (0.8 eV) than the energy level needed for the release of H_2 for which the desired energy is

assumed to be in the range of 0.2–0.6 eV. We should also mention that the H_2 fragmentation from the Al doped hydrogenated B_3 clusters is lower than that of the Al doped hydrogenated B_{12} clusters.[23] We have also calculated the ionization potentials of clusters using the B3LYP and CCSD(T) methods. Unfortunately, there are no experimental or theoretical IP data for these studied ranges. Thus, we hope that our results will be confirmed by further experimental or theoretical studies. According to the results of AdNDP analysis, nearly all the bonding elements for hydrogenated AlB_3 clusters make 2c-2e and 3c-2e σ bonds with an ON close to the ideal value of 2.00|e| and the chemical bonding patterns of the most stable isomers were found to be consistent with their geometric structures. In addition to typical 2c-2e and 3c-2e σ bonds for the AlB_3H_{2n} clusters, 3c-2e π bonds were found for $n = 0$–3. Apparently, low hydrogen numbered clusters need the presence of the π density in the planar or quasi-planar forms.

We hope that the examination of hydrogen storage properties in boron clusters doped with other types of metal atoms will shed light on the higher capacity system. We should also mention that geometries whose stability is supported by electronic and chemical analysis could be useful for the future design of novel aluminum boron clusters. Moreover, this is our first step in the investigation of hydrogenated aluminum boron clusters.

Acknowledgments

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