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Ab Initio Search for Global Minimum Structures of the Novel B_3H_y (y=4−7) Neutral and Anionic Clusters

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We sampled potential energy surfaces of neutral and anionic B_3H_y clusters using the Gradient Embedded Genetic Algorithm (GEGA) program at the B3LYP/3-21G level of theory. The lowest energy isomers were recalculated at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory. We found a diverse set of global minimum structures and low-lying isomers for the studied clusters. The Adaptive Natural Density Partitioning (AdNDP) method was then used for chemical bonding analysis for all global minimum structures and low-lying isomers. The chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very exotic isomers and global minima.

Introduction

Boron is one of the lightest chemical elements that can form strong covalent bonds with hydrogen and thus provides excellent opportunities to design new lightweight materials on the basis of novel boron hydride building blocks, in the form of $B_xH_y^{0/n+/n-}$ clusters with a potential for high hydrogen storage capacity. To realize this potential requires an understanding of the electronic structure, chemical bonding, and stability of the $B_xH_y^{0/n+/n-}$ clusters with variable stoichiometry. Boron hydride compounds such as $LiBH_4$, $Li_4BH_4(NH_2)_3$, NH_4BH_4, NH_3BH_3, NH_2BH_2, and $NH_3B_3H_7$ have been studied extensively with regard to their potential hydrogen storage properties.[1−11] Boron and hydrogen also form a wide variety of three-dimensional compounds such as the well-known deltahedral boranes and their numerous derivatives with a lesser degree of hydrogenation than the above-mentioned borohydrides.[12−16] While a large number of boron hydride compounds are known, there are still entire classes of yet unknown $B_xH_y^{0/n+/n-}$ clusters and molecules with various new x/y ratios which may be good candidates for hydrogen storage or as intermediates of borane dehydrogenation.

Very limited work on new B_xH_y structural units has been carried out previously. Fehlner and co-workers[17−19] have reported synthesis and crystal structures of two remarkable triple-deck $(Cp^*ReH_2)B_5Cl_5$ and $(Cp^*Re)_2B_6H_4Cl_2$ compounds containing planar B_5Cl_5 and $B_6H_4Cl_2$ structural fragments, respectively. It is believed that the planar B_5Cl_5 and $B_6H_4Cl_2$ structural fragments in Fehlner's compounds acquire six electrons from the Re atom formally and thus become six π-electron aromatic compounds similar to the predicted $B_5H_5^{6-}$ and $B_6H_6^{6-}$ building blocks in the $Li_6B_5H_5$ and $Li_6B_6H_6$ salt molecules.[20,21]

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Felhner and co-workers also reported the synthesis and characterization of a variety of new compounds containing novel structural groups such as B_3H_7,[17] B_4H_7 and B_4H_8,[18] and B_4H_{11},[19] with highly unusual B:H stoichiometries. Surprisingly, there have been few prior experimental works on $B_xH_y^{0/n+/n-}$ type clusters in the gas phase. To the best of our knowledge, the only relevant work is by Anderson et al., who studied the dynamics of B_x^+ cluster ($x = 1-16$) reactions with D_2.[22] Among the various reaction channels, they observed the formation of B_xD^+ and D_2 adducts, $B_x^+(D_2)$, and estimated the B_x^+-D bond energies. Interactions of the B_3 cluster with H atoms and H_2 molecules have been studied by Hernandez and Simons.[23] This work stimulated a theoretical study by Ricca and Bauschlicher, who calculated the structures of B_xH^+ ($x = 1-13$) and the B_x^+-H bond energies.[24] Interestingly, they found that the structures of the B_xH^+ clusters are similar to the bare B_x^+ clusters with the H atom bonded to the edge of planar or quasi-planar B_x^+ clusters. Alexandrova et al.[25] performed a global minimum structure search and rationalized chemical bonding in terms of aromaticity/antiaromaticity in the $B_7H_2^-$ cluster anion. Alexandrova et al.[26] also studied a series of boron−hydrogen anions analogous to planar aromatic hydrocarbons. A few groups have previously studied the B_3H_7 cluster.[27−30] Five different isomers were found in early theoretical studies with geometry optimization at the Hartree−Fock level with small basis sets.[27] In follow up studies,[28−30] high-level calculations were performed for one,[28] two,[29] or three[30] isomers of B_3H_7.

There are still many new undiscovered structural units with almost continuous B:H ratios. The nonstoichiometric and nonconventional boron hydride clusters with three boron atoms and variable number of hydrogen atoms $B_3H_y^{0/-1}$ will be the main focus of the research presented in this paper. Counter cations may affect the relative stability of the corresponding anionic $B_3H_y^-$ isomers. In this article, however, we will concentrate on the intrinsic properties of these anions free of such influence. We believe that understanding the structure, stability, and bonding of bare $B_3H_y^-$ anions is an important first step in predicting novel boron−hydrogen species. We plan to study the influence on $B_3H_y^-$ from counter cations in our future works.

Computational Details

We initially performed searches for the global minimum of B_3H_y and $B_3H_y^-$ ($y = 4-7$) using our gradient embedded genetic algorithm (GEGA) program written by A. N. Alexandrova.[31,32] Briefly, within the GEGA procedure, the initial geometries of individuals in a population are randomly generated and optimized to the nearest local minima on the potential energy surface using the Gaussian 03 package. If a saddle point is encountered, the normal mode of the first imaginary frequency is followed until a local minimum is found. Further, the population, composed of the thus selected good individuals, undergoes breeding and mutations. Probabilities to be bred are assigned according to the best-fit (lowest-energy) criterion. Based on the probabilities, couples of parents are randomly selected. The geometries of parents are cut by a random cutting plane, and the newly obtained halves (genes) are then recombined either in a simple or head-to-tail manner forming a child. The number of atoms in the newly generated geometry is checked, and the child is optimized to the nearest local minimum. After the number of individuals in the population is doubled within the breeding process, the best-fit group is selected, and convergence of the algorithm is checked. GEGA is considered as converged if the current lowest energy species (global minimum or at least very stable local minimum) remains leading for 20 iterations. If the convergence is not yet met, the highest energy species in the population undergo mutations. The mutation rate is set to 33.33%. Mutations are shifts of random atoms of a species in random directions, with the purpose of changing the initial geometry so as to push the structure out of the current local minimum to another well on the potential energy surface. Mutants are then optimized to the nearest local minima. After this optimization, the algorithm proceeds with the new cycle of breeding. All low-lying isomers are detected and stored throughout the execution of the GEGA algorithm and are reported to the user at the end of the run. A more complete description of the GEGA algorithm is contained in ref 32.

For the global minimum search, we used a hybrid method known as B3LYP[33−35] with small split-valence basis sets (3-21G) for energy, gradient, and force calculations. Geometries were then reoptimized, and frequencies were calculated for the lowest energy structures using B3LYP with polarized split-valence basis sets (6-311++G**).[36−38] Following this reoptimization, for the few lowest structures found at the B3LYP/6-311++G** level of theory, we reoptimized geometries and calculated harmonic frequencies at the second-order Moller−Plesset perturbation theory (MP2)[39−41] and coupled-cluster with single, double, and noniterative triple excitations method [CCSD(T)][42−44] using the 6-311+G* basis set for both calculations. Relative energies reported in this work were corrected for zero-point energies (ZPE) at the corresponding level of theory.

To understand the relationship between chemical bonding and structure in $B_3H_y^{0/-1}$ clusters, we performed chemical bonding analysis for the lowest energy isomers using the recently

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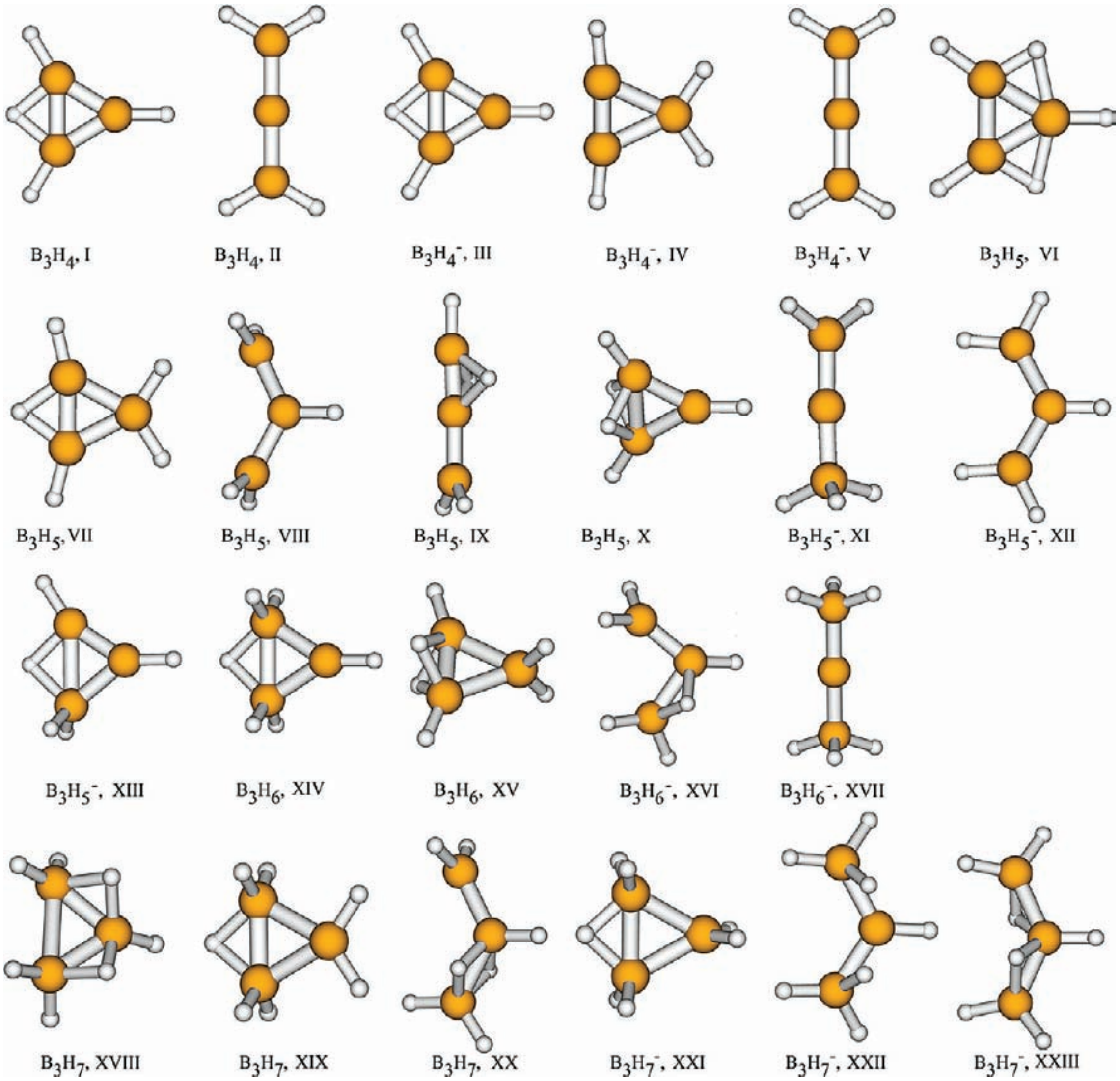

Figure 1. The lowest energy isomers for neutral B_3H_y and anionic $B_3H_y^-$ ($y = 4-7$) structures at B3LYP/6-311++G**.

developed by Dmitry Yu. Zubarev Adaptive Natural Density Partitioning (AdNDP) method.[45-47] AdNDP performs analysis of the first-order reduced density matrix with the purpose of obtaining its local block eigenfunctions with optimal convergence properties for describing the electron density. The local blocks of the first-order reduced density matrix correspond to the sets of n atoms (from one to all the atoms of the molecule) that are tested for the presence of a two-electron object (nc-2e bonds, including core electrons and lone pairs as a special case of $n = 1$) associated with this particular set of n atoms. The n-atomic sets are formed and checked in an exhaustive manner, so that the recovered nc-2e bonding elements always correspond to the point-group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given n-atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the established threshold value, usually close to 2.00 |e|. Thus Lewis's idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient since it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform the analysis. In order to avoid complications due to spin-polarization in open-shell systems, we added one extra electron to singly occupied MO (SOMO) and performed the AdNDP analysis for such systems.

The B3LYP, R(U)MP2, and R(U)CCSD(T) calculations were performed using the Gaussian 03 program.[48] Molecular visualization was performed using the MOLDEN3.4 program,[49]

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Table 1. Spectroscopic States, Electronic Configurations, and Relative Energies of Each Isomer for Each of the Neutral B_3H_y and Anionic $B_3H_y^-$ ($y = 4$-7) Species

			relative energy (kcal/mol)[a]		
cluster	isomer	state	B3LYP[b]	MP2[b]	CCSD(T)[b]
B_3H_4	I	C_{2v}, $^2B_2$, $1a_1^{2}2a_1^{2}1b_2^{2}3a_1^{2}4a_1^{2}1b_1^{2}2b_2^{1}$	0	0	0
	II	D_{2h}, $^2B_{3u}$,$1a_g^{2}1b_{1u}^{2}2a_g^{2}1b_{2u}^{2}1b_{3g}^{2}2b_{1u}^{2}1b_{3u}^{1}$	7.9	16.7	12.5
$B_3H_4^-$	III	C_{2v}, $^1A_1$, $1a_1^{2}2a_1^{2}1b_2^{2}3a_1^{2}4a_1^{2}1b_1^{2}2b_2^{2}$	0	0	0
	IV	C_{2v}, $^1A_1$, $1a_1^{2}1b_2^{2}2a_1^{2}3a_1^{2}2b_2^{2}4a_1^{2}1b_1^{2}$	2.0	2.3	2.4
	V	D_{2h}, ^1A_g, $1a_g^{2}1b_{1u}^{2}2a_g^{2}1b_{2u}^{2}1b_{3g}^{2}2b_{1u}^{2}1b_{3u}^{2}$	6.4	17.6	10.7
B_3H_5	VI	C_{2v}, $^1A_1$, $1a_1^{2}1b_2^{2}2a_1^{2}3a_1^{2}2b_2^{2}4a_1^{2}1b_1^{2}$	0	0	0
	VII	C_{2v}, $^1A_1$, $1a_1^{2}2a_1^{2}1b_2^{2}3a_1^{2}2b_2^{2}4a_1^{2}1b_1^{2}$	0.4	0.7	0.3
	VIII	C_{2v}, $^1A_1$, $1a_1^{2}1b_2^{2}2a_1^{2}1b_1^{2}1a_2^{2}3a_1^{2}2b_2^{2}$	14.1	23.3	17.6
	IX	C_s, $^1A'$, $1a'^{2}2a'^{2}3a'^{2}1a''^{2}4a'^{2}5a'^{2}2a''^{2}$	18.9	23.0	19.5
	X	C_{2v}, $^1A_1$, $1a_1^{2}2a_1^{2}1b_2^{2}3a_1^{2}1b_1^{2}4a_1^{2}2b_2^{2}$	27.3	29.9	26.8
$B_3H_5^-$	XI	C_s, $^2A''$, $1a'^{2}2a'^{2}3a'^{2}4a'^{2}1a''^{2}5a'^{2}6a'^{2}2a''^{1}$	0	0	0
	XII	C_s, $^2A''$, $1a'^{2}1a''^{2}2a'^{2}3a'^{2}2a''^{2}4a'^{2}3a''^{2}5a'^{1}$	6.5	7.0	4.6
	XIII	C_s, $^2A''$, $1a'^{2}2a'^{2}3a'^{2}4a'^{2}1a''^{2}5a'^{2}6a'^{2}2a''^{1}$	8.9	6.8	7.8
B_3H_6	XIV	C_{2v}, $^2B_2$, $1a_1^{2}2a_1^{2}1b_2^{2}1b_1^{2}3a_1^{2}4a_1^{2}1a_2^{2}2b_2^{1}$	0	0	0
	XV	C_{2v}, $^2B_2$, $1a_1^{2}2a_1^{2}1b_2^{2}1b_1^{2}3a_1^{2}4a_1^{2}2b_1^{2}2b_2^{1}$	3.7	1.2	2.6
$B_3H_6^-$	XVI	C_1, ^1A, $1a^{2}2a^{2}3a^{2}4a^{2}5a^{2}6a^{2}7a^{2}8a^{2}$	0	0	0
	XVII	D_{3d}, $^1A_{1g}$, $1a_{1g}^{2}1a_{2u}^{2}2a_{1g}^{2}1e_u^{4}1e_g^{4}2a_u^{2}$	−0.2	6.7	3.7
B_3H_7	XVIII	C_s, $^1A'$, $1a'^{2}1a''^{2}2a'^{2}3a'^{2}2a''^{2}4a'^{2}3a''^{2}5a'^{2}$	0	0	0
	XIX	C_{2v}, $^1A_1$, $1a_1^{2}2a_1^{2}1b_2^{2}1b_1^{2}2b_2^{2}3a_1^{2}4a_1^{2}1a_2^{2}$	1.8	3.7	3.2
	XX	C_s, $^1A'$, $1a'^{2}2a'^{2}3a'^{2}1a''^{2}4a'^{2}5a'^{2}2a''^{2}6a'^{2}$	6.8	9.1	7.7
$B_3H_7^-$	XXI	C_{2v}, $^2B_2$, $1a_1^{2}2a_1^{2}1b_2^{2}1b_1^{2}3a_1^{2}4a_1^{2}1a_2^{2}2b_1^{2}2b_2^{1}$	0	0	0
	XXII	C_s, $^2A''$, $1a'^{2}1a''^{2}2a'^{2}3a'^{2}2a''^{2}4a'^{2}3a''^{2}5a'^{2}6a'^{1}$	21.7	25.9	30.4
	XXIII	C_2, ^2A, $1a^{2}1b^{2}2a^{2}2b^{2}3a^{2}3b^{2}4a^{2}4b^{2}5a^{1}$	25.9	29.6	30.4

[a] Relative energy was corrected by zero-point vibrational energies at the corresponding level of theory. [b] Calculations were performed with the 6-311++G** basis set.

and molecular orbital visualization was completed using the MOLEKEL 4.3 program.[50]

Computational Results

We initially performed GEGA searches for the global minimum of the neutral B_3H_y and anionic $B_3H_y^-$ ($y = 4-7$) isomers at the B3LYP/3-21G level of theory. The lowest energy isomers were then recalculated at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory. Figure 1 shows the lowest energy structures identified in our scanning of the potential energy surfaces for the neutral B_3H_y and anionic $B_3H_y^-$ ($y = 4-7$) species.

The corresponding spectroscopic states, electronic configurations, and relative energies of each isomer (at the B3LYP/6-311++G**, MP2/6-311++G**, and CCSD(T)/6-311++G** levels of theory) for each of the neutral B_3H_y and anionic $B_3H_y^-$ ($y = 4-7$) species are summarized in Table 1.

From our calculations we found that isomers with the lowest possible multiplicities were found to be the lowest energy states for all clusters studied here. Several of the neutral B_3H_y and anionic $B_3H_y^-$ ($y = 4-7$) species have two or more structures competing for the global minimum isomer. The low-lying isomers were found to be structures with the triangular and linear core B_3 units. There is no clear pattern why for some species, isomers with the triangular B_3 core are more stable, while for others isomers with the linear B_3 core are more stable. Previously reported results[27−30] on B_3H_7 clusters showing that isomer XVIII is the most stable structure with isomers XIX and XX being the second and third most stable structures are in excellent agreement with our results.

Table 2 summarizes the dissociation energies for B_3H_y and $B_3H_y^-$ ($y = 5-7$) species for H_2 release. All of the B_3H_y and $B_3H_y^-$ ($y = 5-7$) species, except for the $B_3H_5^-$, are thermochemically stable toward spontaneous hydrogen release.

Table 2. Stability of B_3H_y and $B_3H_y^-$ ($y = 5$-7) Species Towards H_2 Release

dissociation channel	dissociation energy[a]
B_3H_5 VI (C_{2v}, $^1A_1$) → B_3H_4 I (C_{2v}, $^2B_2$) + 1/2H_2	+ 31.2 kcal/mol
$B_3H_5^-$ XI (C_s, $^2A''$) → $B_3H_4^-$ III (C_{2v}, $^1A_1$) + 1/2H_2	- 6.5 kcal/mol
B_3H_6 XIV (C_{2v}, $^2B_2$) → B_3H_5 VI (C_{2v}, $^1A_1$) + 1/2H_2	- 15.6 kcal/mol
B_3H_6 XIV (C_{2v}, $^2B_2$) → B_3H_4 I (C_{2v}, $^2B_2$) + H_2	+ 15.6 kcal/mol
$B_3H_6^-$ XVI (C_1, ^1A) → $B_3H_5^-$ XI (C_s, $^2A''$) + 1/2H_2	+ 25.8 kcal/mol
$B_3H_6^-$ XVI (C_1, ^1A) → $B_3H_4^-$ III (C_{2v}, $^1A_1$) + H_2	+ 19.3 kcal/mol
B_3H_7 XVIII (C_s, $^1A'$) → B_3H_6 XIV (C_{2v}, $^2B_2$) + 1/2H_2	+ 34.3 kcal/mol
B_3H_7 XVIII (C_s, $^1A'$) → B_3H_5 VI (C_{2v}, $^1A_1$) + H_2	+ 18.7 kcal/mol
$B_3H_7^-$ XXI (C_{2v}, $^2B_2$) → $B_3H_6^-$ XVI (C_1, ^1A) + 1/2H_2	+ 11.2 kcal/mol
$B_3H_7^-$ XXI (C_{2v}, $^2B_2$) → $B_3H_5^-$ XI (C_s, $^2A''$) + H_2	+ 37.0 kcal/mol

[a] ΔE calculated at the CCSD(T)/6-311++G**+ZPE/CCSD(T)/6-311++G** level of theory.

Chemical Bonding in B_3H_x and $B_3H_x^-$ ($x = 4-7$) Species

In order to facilitate the understanding between bonding and structure for B_3H_y and $B_3H_y^-$ ($y = 4-7$) species we performed chemical bonding analysis for the lowest isomers of each species using our newly developed AdNDP analysis. We briefly discussed this method in the Computational Details. A more extensive discussion on this method and its application to boron clusters, aromatic organic molecules, and golden clusters can be found in refs 45−48. The bonding pattern recovered in a particular chemical species by the

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(50) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000−2002. Portmann, S.; Lüthi, H. P. MOLEKEL: An Interactive Molecular Graphics Tool. *CHIMIA* 2000, *54*, 766.

Table 3. Bonds Recovered by the AdNDP Analysis for the Selected Isomers of B_3H_y and $B_3H_y^-$ ($y = 4$-7)

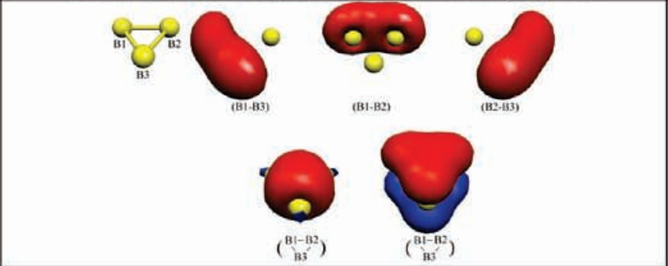
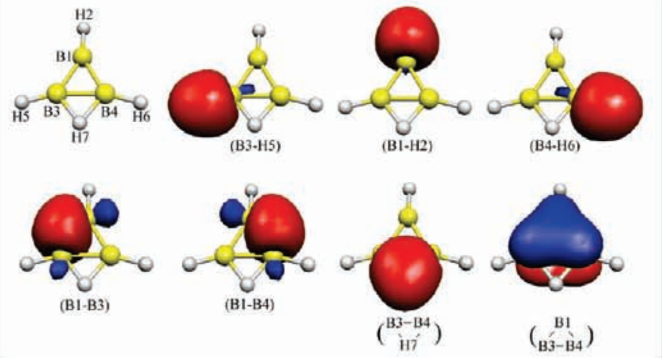
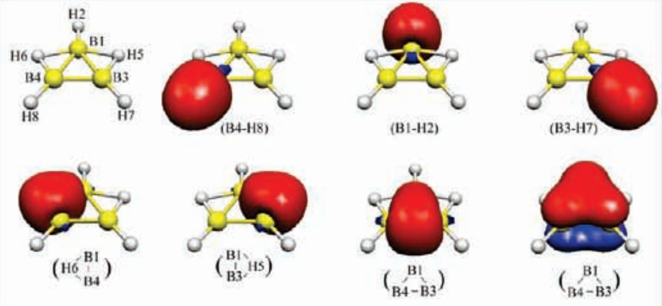
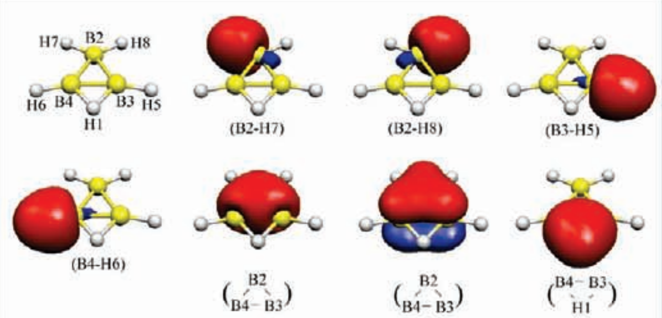
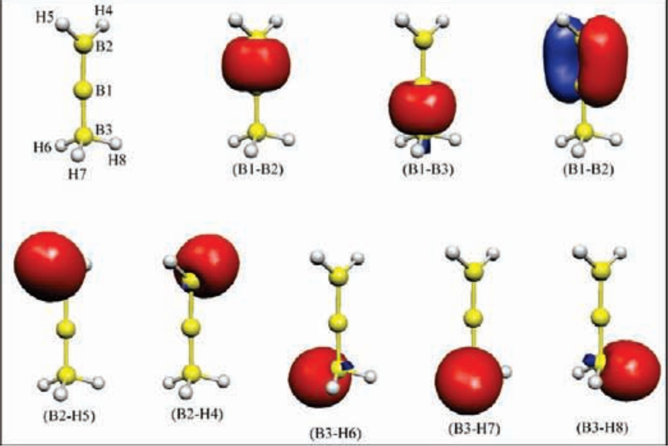
Cluster, Isomer	Structure and Bonding Elements Recovered by AdNDP	Occupation Number (|e|)
B_3^-		(B1 – B2) = 2.00 (B1 – B3) = 2.00 (B2 – B3) = 2.00 (B1 – B2 – B3) = 2.00 (B1 – B2 – B3) = 2.00
$B_3H_4^-$, III		(B3 – H5) = 1.98 (B1 – H2) = 1.99 (B4 – H6) = 1.99 (B1 – B3) = 1.89 (B1 – B4) = 1.89 (B3 – B4 – H7) = 2.00 (B1 – B3 – B4) = 1.96
B_3H_5, VI		(B4 – H8) = 1.97 (B1 – H2) = 1.97 (B3 – H7) = 1.97 (B1 – B4 – H6) = 1.99 (B1 – B3 – H5) = 1.99 (B1 – B3 – B4) = 1.88 (B1 – B3 – B4) = 2.00
B_3H_5, VII		(B2 – H7) = 2.00 (B2 – H8) = 2.00 (B3 – H5) = 2.00 (B4 – H6) = 2.00 (B2 – B3 – B4) = 1.92 (B2 – B3 – B4) = 1.99 (B3 – B4 – H1) = 2.00
$B_3H_5^{-,1)}$, XI		(B1 – B2) = 2.00 (B1 – B3) = 2.00 (B1 – B2) = 1.96 (B2 – H5) = 1.97 (B2 – H4) = 1.97 (B3 – H6) = 1.97 (B3 – H7) = 1.97 (B3 – H8) = 1.97

Table 3. Continued

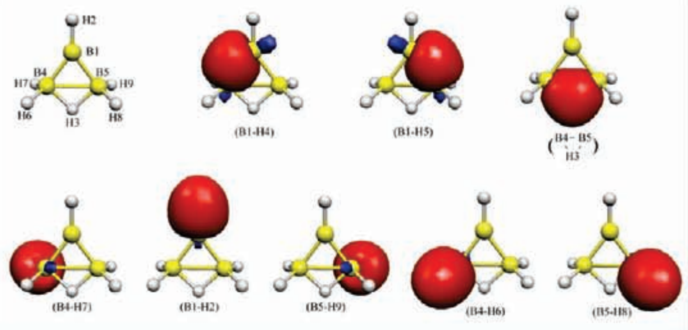
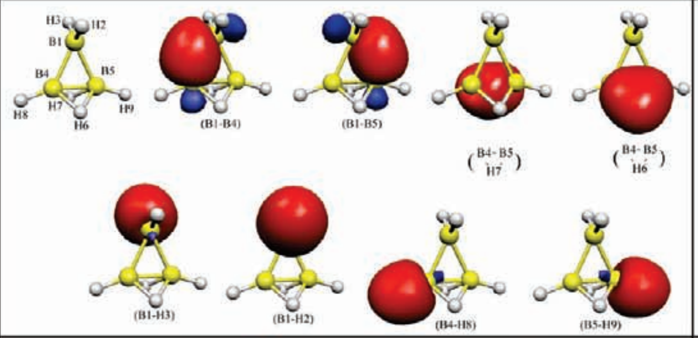
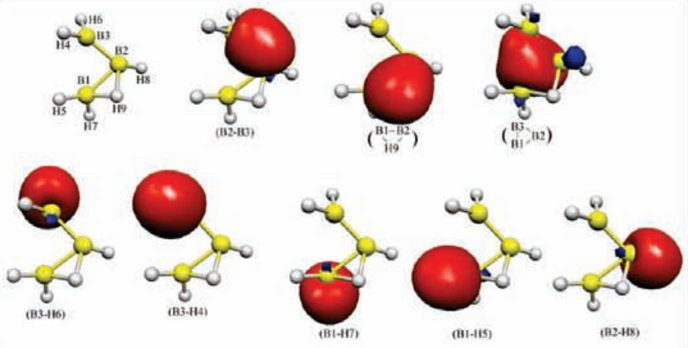
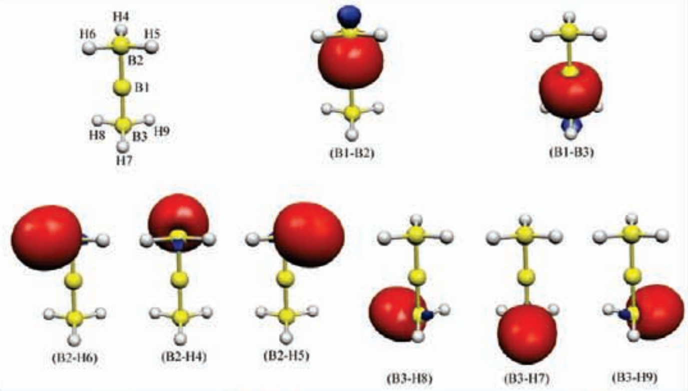
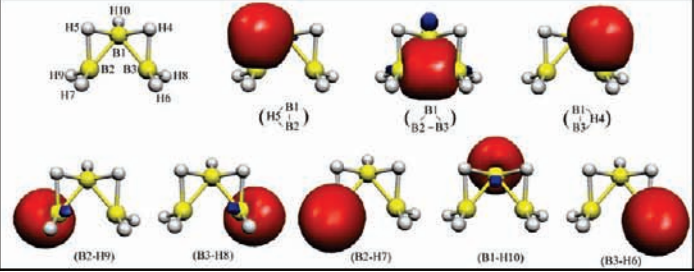
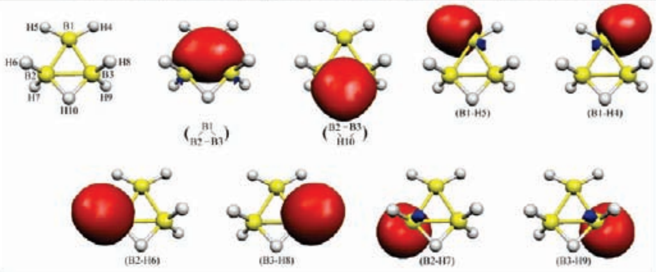
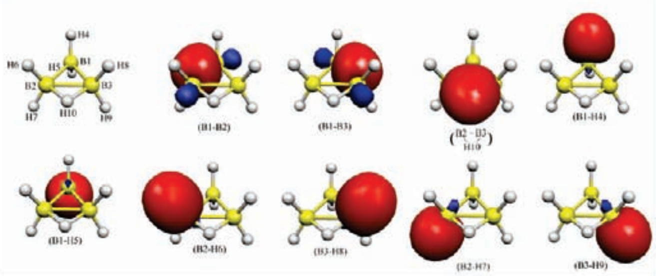
Cluster, Isomer	Structure and Bonding Elements Recovered by AdNDP	Occupation Number (lel)
$B_3H_6^{2)}$, XIV		(B1 – B4) = 1.93 (B1 – B5) = 1.93 (B4 – H7) = 1.97 (B1 – H2) = 1.97 (B5 – H9) = 1.97 (B4 – H6) = 1.97 (B5 – H8) = 1.97 (B4 – B5 – H3) = 1.97
$B_3H_6^{2)}$, XV		(B1 – B4) = 1.89 (B1 – B5) = 1.89 (B1 – H3) = 1.99 (B1 – H2) = 1.99 (B4 – H8) = 1.99 (B5 = H9) = 1.99 (B4 – B5 – H7) = 1.98 (B4 – B5 – H6) = 1.98
$B_3H_6^-$, XVI		(B2 – B3) = 1.99 (B3 – H6) = 1.98 (B3 – H4) = 1.98 (B1 – H7) = 1.98 (B1 – H5) = 1.98 (B2 – H8) = 1.98 (B1 – B2 – H9) = 1.99 (B3 – B2 – B1) = 1.94
$B_3H_6^-$, XVII		(B1 – B2) = 1.93 (B1 – B3) = 1.93 (B2 – H6) = 2.00 (B2 – H4) = 2.00 (B2 – H5) = 2.00 (B3 – H8) = 2.00 (B3 – H7) = 2.00 (B3 – H9) = 2.00
B_3H_7, XVIII		(B1 – B2 – H5) = 2.00 (B1 – B3 – H4) = 2.00 (B1 – B2 – B3) = 1.90 (B2 – H9) = 1.97 (B3 – H8) = 1.97 (B2 – H7) = 1.97 (B3 – H6) = 1.97 (B1 – H10) = 1.97

Table 3. Continued

Cluster, Isomer	Structure and Bonding Elements Recovered by AdNDP	Occupation Number (|e|)
B_3H_7, XIX		(B1 – B2 – B3) = 1.96 (B2 – B3 – H10) = 2.00 (B1 – H5) = 1.94 (B1 – H4) = 1.94 (B2 – H6) = 1.94 (B3 – H8) = 1.94 (B2 – H7) = 1.94 (B3 – H9) = 1.94
$B_3H_7^{-1)}$, XXI		(B1 – B2) = 1.94 (B1 – B3) = 1.94 (B1 – H4) = 1.99 (B1 – H5) = 1.99 (B2 – H6) = 1.99 (B3 – H8) = 1.99 (B2 – H7) = 1.99 (B3 – H9) = 1.99 (B2 – B3 – H10) = 1.97

[a] The AdNDP analysis for this isomer was performed for the doubly charged anion by adding one extra electron to the SOMO. [b] The AdNDP analysis for this isomer was performed for the anionic state by adding one extra electron to the SOMO.

AdNDP analysis depends on how close the recovered bonds are to the ideal 2.00 |e| the occupation numbers (ON). Therefore we report ON for a particular bond for each isomer discussed in this section. We found that in all isomers ONs are indeed very close to the ideal values, thus providing us with confidence in our chemical bonding pattern. The results of the AdNDP analysis, including pictorial representations of the recovered "bond," are presented and summarized in Table 3.

Bonding in the bare B_3^- cluster was studied previously,[45,51−53] and it was shown that this cluster has three 2c-2e σ−B-B bonds, one 3c-2e σ-bond, and one 3c-2e π-bond (Table 3). Thus, this cluster is a doubly (σ- and π-) aromatic system. This double aromaticity explains its high symmetry cyclic structure and high atomization energy. The addition of four hydrogen atoms to B_3^- results in the global minimum structure III of the $B_3H_4^-$ anion. According to the AdNDP analysis the global minimum structure of $B_3H_4^-$ has three 2c-2e σ−B-H bonds, one 3c-2e BHB σ-bond, two 2c-2e σ−B-B bonds, and one 3c-2e π-bond (Table 3). Thus, this anion is only a π-aromatic system. Compared to the B_3^- anion, in the $B_3H_4^-$ anion, the addition of four hydrogen atoms led to the formation of three new B−H σ-bonds, the substitution of a 3c-2e BHB bridged σ-bond for a 2c-2e B−B σ-bond, and the removal of the delocalized 3c-2e BBB σ-bond responsible for σ-aromaticity of B_3^-. Addition of a H^+ to $B_3H_4^-$ with the formation of B_3H_5 led to the substitution of one 2c-2e B−B σ-bond by the 3c-2e BHB bridged σ-bond and one 3c-2e BHB σ-bond by the 3c-2e BBB σ-bond. The second lowest energy B_3H_5 isomer VI has three 2c-2e B−H σ-bonds, two 3c-2e BHB σ-bonds, one delocalized 3c-2e σ-bond, and one delocalized 3c-2e π-bond (Table 3). Thus, isomers VI and VII regain double (σ- and π-) aromaticity. When an extra electron is added to the B_3H_5 cluster, chemical bonding (performed for the $B_3H_5^{2-}$ dianion at the optimal geometry of the $B_3H_5^-$ anion) in the global minimum structure XI of the $B_3H_5^-$ species can be rationalized in terms of the classical structure with five 2c-2e B−H bonds, a single σ-bond between H_3B and the central boron atom, and a double (σ- and π-) bond between the central atom and the BH_2 fragment (Table 3). The B_3H_6 cluster has two low-lying isomers XIV and XV. Chemical bonding analysis was performed for the closed shell anionic isomer XIV and XV at the optimal geometries of the neutral clusters. In the global minimum structure XIV, we found five 2c-2e B−H σ-bonds, two 2c-2e B−B σ-bonds, and one bridged 3c-2e BHB bond (Table 3). In the second isomer XV we found four 2c-2e B−H σ-bonds, two 2c-2e B−B σ-bonds, and two 3c-2e BHB bonds (Table 3). The transition of one of the terminal hydrogen atoms to a bridged position does not cost much energy, apparently. The two lowest isomers XVI and XVII of the $B_3H_6^-$ species are truly remarkable structures. In isomer XVI we found three types on bonding: the 2c-2e B−B σ-bond between B2 and B3, 3c-2e BHB σ-bond between B1 and B2, and the 3c-2e σ-bond responsible for bonding between B1 and B3 (Table 3). That chemical bonding pattern can easily explain the unusual geometric structure of the isomer XVI. The classical type structure of the isomer XVII can also be easily understood from the AdNDP analysis. Two BH_3 groups are attached to the central boron atom through two dative 2c-2e B−B σ-bonds (Table 3). The two lowest isomers XVIII and XIX of the B_3H_7 species have similar bonding patterns (Table 3)with the exception that one hydrogen atom migrates from the bridged position in isomer XVII to the terminal position in isomer XVIII. We noticed that such migrations do not cost much energy in the hydrogen−boron clusters discussed here. Finally, in isomer XXI we found that it has two classical 2c-2e B−B bonds, one 3c-2e BHB bond which keep the boron kernel together, with all other electron pairs used for the 2c-2e B−H σ-bonds (Table 3).

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(52) Zhai, H.-J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I.; Zakrzewski, V. G. *J. Phys. Chem. A* **2003**, *107*, 9319–9328.

(53) Nguyen, M. T.; Matus, M. H.; Ngan, V. T.; Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2009**, *113*, 4895.

The overall chemical bonding patterns revealed by the AdNDP analysis can easily explain the geometric structure of even very exotic isomers and global minima.

Conclusions

We found global minimum structures and low-lying isomers for a series of B_3H_y and $B_3H_y^-$ species using the GEGA method. We refined the relative energies at the CCSD(T)/6-311++G** level of theory and found a very diverse set of structures for global minimum and low-lying isomers of the studied species.

All of the B_3H_y and $B_3H_y^-$ ($y = 5-7$) species, except for the $B_3H_5^-$, are thermochemically stable toward hydrogen release. Chemical bonding in the global minimum and low-lying isomers was analyzed using the AdNDP method; from this analysis we found the chemical bonding patterns in all cases were consistent with the geometric structures of the studied clusters.

We hope that predictions made in our work will be tested in follow-up photoelectron studies of the anionic species studied in this work. We also hope that the bonding patterns presented here recovered by the AdNDP analysis will be useful for the future rational design of novel boron−hydrogen compounds. This is our first step in the probing of nonstoichiometric $B_xH_y^{n+/0/n-}$ species.

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