3358 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***66****, 3358—3361(1993)* [Vol. 66, No. 11

Ab Initio Study of Neutral and Cationic B_{12} and B_{13} Clusters[#]

Hiroshi KATO, Koichi YAMASHITA,* and Keiji MOROKUMA†
Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki, Sakyo, Kyoto 606
† Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, U.S.A.

(Received May 24, 1993)

The geometries, electronic structures, and energies of the neutral and cationic B_{12} and B_{13} clusters were investigated by the *ab initio* molecular orbital method. Several planar and non-planar stationary structures were optimized for neutrals and cations of each cluster size. A characteristic C_{2v} cyclic form with one atom in the middle was found to be stable for each cluster. While the D_{5d} icosahedral B_{12}^{+} was found to be the most stable, the triplet D_{5d} icosahedral B_{12} was stable but energetically unfavorable than the C_{2v} cyclic B_{12}. All the three-dimensional structures considered for B_{13} and B_{13}^{+} clusters were unstable.

The structures and energetics of small atomic clusters have been the focus of many experimental and theoretical studies in the past several years.[1,2] Anderson and co-workers[3] have examined the bonding in boron-cluster cations B_{2-13}^{+} by measurement of the appearance potential and fragmentation pattern in collision-induced dissociation (CID). They found a characteristic size dependency of different fragmentation channels. In particular, 13 appears to be a magic number. Thirteen-atom clusters are often considered with special interest in cluster chemistry.[4] *Ab initio* studies have been preformed only for small boron clusters so far.[2,3,5—7] Anderson and co-workers[3] performed *ab initio* calculations for both neutral and cationic boron clusters B_{1-6} to obtain cluster geometries, ionization potentials, and dissociation energies to compare with their experimental findings. The *ab initio* optimized geometeries for B_{2-8} and B_{2-8}^{+} have been reportd by Bonacic–Koutecky et al.[2] Kato and Tanaka[5] have investigated the geometries and vibrational structures of B_{2-8} clusters by *ab initio* calculations. Several low-lying valence states have been studied for B_2 by Langoff and Bauschlicher[6] and for B_3 by Hernandez and Simons.[7]

For boron clusters consisting of more than eight atoms, little is known theoretically except for the B_{12} icosahedron. In a very early study by Longuet-Higgins and Roberts[8] and in a more recent SCF-$X\alpha$ calculation by Bambakidis and Wagner,[9] the bonding in the B_{12} icosahedron is investigated. Kawai and Weare have studied the stability of the B_{12} icosahedron using the Car–Parrinello method.[10] In this situation, we have recently performed *ab initio* molecular orbital calculations (HF, MP4(SDTQ)/3-21G, 6-31G*) to investigate the geometries, electronic structures and energies of the neutral and cationic boron clusters of 2—11 atoms and preliminary of 12-atom clusters.[11] The conclusion there was that the geometries of boron-cluster cations B_{3-11}^{+} were essentially the same as those of the neutral clusters, planar (or pseudo-planar) cyclic structures. The clusters of 8—11 atoms characteristically had the most stable structure of a C_{2v} cyclic form with one atom in the middle. It should be noted here that the density functional calculations by Jones predict for Al_n clusters ($n=5$—10) the tendency to form quasi-planar structures.[12] Quite recently, Kawai and Weare have investigated the three-dimensional structures of B_{13} clusters.[13]

In this paper, we continue and extend our theoretical study on the neutral and cationic B_{12} and B_{13}. The results are discussed in comparison with the experiment by Anderson and co-workers[3] as well as the theoretical study by Kawai and Weare.[10,13]

Ab Initio Calculations

The geometries of boron clusters were fully optimized by using the Hartree-Fock method (HF)[14] with the 3-21G basis set.[14] For open-shell systems, such as doublet and triplet clusters, the spin-unrestricted HF method[14] was used. Various stationary points of different symmetry were obtained for each size of cluster. For each stationary point, the harmonic force constants and associated vibrational frequencies were evaluated to determine whether this is an equilibrium structure or not. The energies of the HF optimized structures were calculated and compared with the results of the second (MP2), third (MP3), and fourth-order (MP4(SDTQ)) Møller–Plesset perturbation methods[14] with the 3-21G basis set. In our previous study,[11] the 3-21G results for the cluster size of 2—8 atoms were shown to be consistent with those with the 6-31G* basis set.[11] All the calculations were performed with the GAUSSIAN 90 program code.[15]

Results and Discussion

The optimized stationary structures of the neutral and cationic B_{12} and B_{13} clusters and their HF/3-21G energies and stability are summarized in Table 1. Stable structures with all real normal frequencies are denoted by S and unstable stationary structures with one or more imaginary frequencies by US. The numbers in parentheses correspond to those of imaginary frequencies. Some low frequencies for the stable structures and

---

[#] In memory of Professor Hiroshi Kato.

Table 1. Calculated Stationary Structures of Neutral and Cationic B_{12} and B_{13}

Cluster	Symmety	State	E(HF) hartree	Low frequency cm^{-1}	Stability
B_{12}	C_{2v} (I)	$^1A_1$	−294.0414	84, 97, 104	S
	C_{2v} (II)	$^1A_1$	−293.9656	405i, 45i, 40i[a)]	US(3)[b)]
	D_{5d} (I)	$^3A_{2u}$	−293.8876	361(e),[c)] 365	S
	D_{12h}	$^1A_{1g}$	−293.8854	36i(e)	US(2)
	D_{5d} (II)	$^1A_{1g}$	−293.7836	1152i(e)	US(2)
	D_{5d} (III)	$^1A_{1g}$	−293.7695	305i	US(1)
B_{12}^+	C_{2v}	$^2A_2$	−293.7744	43, 99	S
	D_{5d}	$^2A_{2u}$	−293.6124	428, 440	S
B_{13}	C_{2v} (I)	$^2B_2$	−318.5379	56, 79	S
	C_{3v}	$^2A_1'$	−318.5198	1340i, 1336i, 132i(e)	US(4)
	C_{2v} (II)	$^2A_1$	−318.4821	72i	US(1)
B_{13}^+	C_{2v}	$^1A_1$	−318.2395	68, 78	S
	D_{12h} (I)	$^1A_{1g}$	−318.0883	184i(e), 97i	US(3)
	D_{12h}(II)	$^3A_{1g}$	−318.0578		US(8)
	D_{3h}	$^1A_1'$	−317.9303	484i(e), 359i, 238i	US(4)
	D_{2h}	$^1A_{1g}$	−317.8042		US(9)
	D_{5d}	$^1A_{1g}$	−317.7976		US(12)

a) Imaginary frequency. b) The number of imaginary frequencies. c) A degenerate vibrational mode.

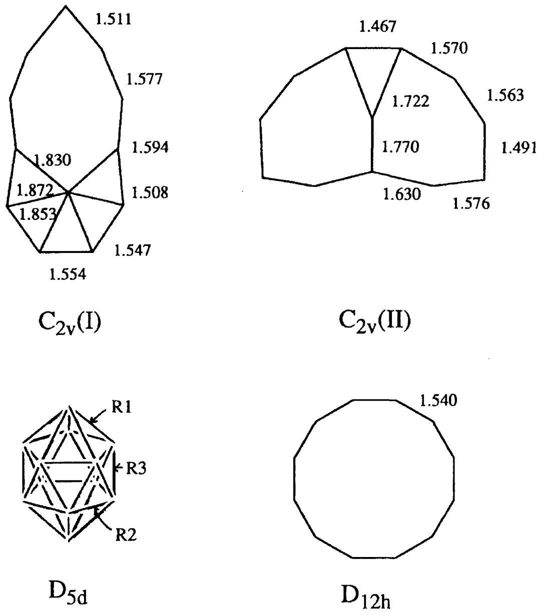


Fig. 1. Optimized structures of B_{12} clusters. The geometrical parameters of the D_{5d} icosahedron are given in Table 2. Bond lengths are in Å.

imaginary frequencies for the unstable structures are also listed in the table. The geometries of optimized structures are given in Figs. 1, 2, and 3 respectively for B_{12}, B_{12}^+, and B_{13} and B_{13}^+. The bond lengths of the D_{5d} icosahedra are given in Table 2. In Table 3, MP/3-21G energies at the HF/3-21G stable clusters and the MP4(SDTQ)/3-21G relative energies reference to the corresponding most stable neutral cluster are given.

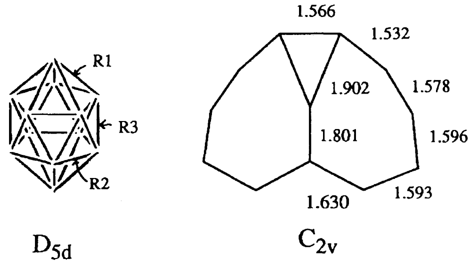


Fig. 2. Optimized structures of B_{12}^+ clusters. The geometrical parameters of the D_{5d} icosahedron are given in Table 2. Bond lengths are in Å.

Table 2. Optimized Geometrical Parameters of the B_{12} and B_{12}^+ Icosahedra

Cluster		State	Occupation	Bond distances[a)] R1	R2	R3
B_{12}	D_{5d} (I)	$^3A_{2u}$	$(a_{1g})^1(a_{2u})^1$	1.777	1.666	1.703
	D_{5d} (II)	$^1A_{1g}$	$(a_{2u})^2$	1.765	1.682	1.728
	D_{5d} (III)	$^1A_{1g}$	$(a_{1g})^2$	2.123	1.656	1.695
B_{12}^+	D_{5d}	$^2A_{2u}$	$(a_{2u})^1$	1.711	1.686	1.703

a) R1, R2, and R3 are the bond length of cap pentagon, intrapentagon, and pentagon–pentagon, respectively. See also Figs. 1 and 2.

Structures of B_{12} and B_{12}^+ Clusters. For the neutral B_{12} clusters we have obtained 6 different stationary structures, i.e., two C_{2v}, three D_{5d}, and one D_{12h} (see Table 1). In our previous study[11)] we tentatively concluded that the most stable B_{12} cluster was the D_{5d} icosahedron. A newly obtained C_{2v} (I) structure, an oval-shaped cyclic form with one atom in the middle (see Fig. 1) which resembles the msot stable B_{10}

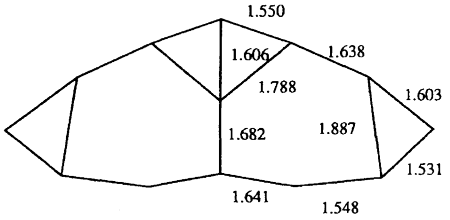
Table 3. MP/3-21G Energies (in hartree) at the HF/3-21G Stable B_{12} and B_{13} Clusters, MP4(SDTQ)/3-21G Ionization Energies IP and Energy Differences ΔE (in eV) Reference to the Corresponding Most Stable Neutral Cluster

Cluster			MP2	MP3	MP4(SDTQ)	IP,ΔE
B_{12}	C_{2v} (I)	($^1A_1$)	−294.7408	−294.7502	−294.8389	—
	D_{5d} (I)	($^3A_{2u}$)	−294.7330	−294.6596	−294.8049	0.93
B_{12}^+	C_{2v}	($^2A_2$)	−294.3277	−294.3775	−294.4403	10.84
	D_{5d}	($^2A_{2u}$)	−294.5032	−294.3959	−294.5757	7.16
B_{13}	C_{2v} (I)	($^2B_2$)	−319.2135	−319.2484	−319.3292	—
B_{13}^+	C_{2v}	($^1A_1$)	−318.9682	−318.9810	−319.0845	6.66

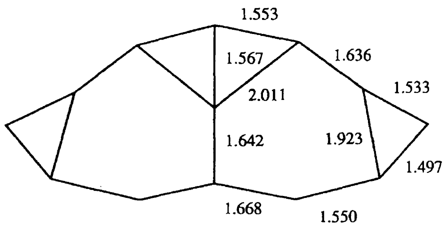
cluster,[11] however, is the most stable at both the HF/3-21G and MP4(SDTQ)/3-21G levels (see Table 3). The cyclic C_{2v} (II) B_{12}, similar to the most stable B_{11},[11] was found to be unstable with three imaginary frequencies. The D_{5d} (II) and (III) icosahedra were found to be unstable. While the geometries of the D_{5d} (I) and (II) icosahedra are similar to each other, the bond length of D_{5d} (III) cap pentagon is significantly longer (see Table 2). Owing to the result that the triplet D_{5d} (I) is stable, we cannot rule out a possibility of an open-shell singlet D_{5d} icosahedron with the $(a_{1g})^1(a_{2u})^1$ occupation. The D_{5d} (II) and D_{5d} (III) may correspond to the singly and doubly excited states of the open-shell singlet icosahedron. Kawai and Weare[10] have investigated the geometry of the B_{12} cluster using a Car–Parrinello *ab initio* molecular dynamics simulation. They have found that an icosahedral structure C_i is a local minimum, but it rearranges to a more stable open geometry. We have therefore performed the geometry optimization starting with their open structure and obtained the D_{5d} (III) icosahedron with one imaginary frequency and with an energy significantly higher than the most stable C_{2v} (I).

For B_{12}^+, the cyclic C_{2v} structure and the D_{5d} icosahedron were found to be stable (see Fig. 2). While the cyclic C_{2v} B_{12}^+ is the most stable at the HF/3-21G level, the D_{5d} icosahedron is the most stable at the MP4(SDTQ)/3-21G level (see Table 3). This result is consistent with the speculation of the B_{12}^+ icosahedron by Anderson and co-workers[3] based on an icosahedral borane $(B_{12}H_{12})^{2-}$. All the bond lengths of the D_{5d} icosahedron (see Table 2) are slightly longer than that of B_2 (1.598 Å) and also the structure is deformed from the ideal icosahedron. The cap pentagon atoms are more weakly bound to the pentagons than the atoms of intrapentagon.

Structures of B_{13} and B_{13}^+ Clusters. The stable structure of B_{13} was calculated to be C_{2v} (I), which is again a characteristic cyclic form with one atom in the middle (see Fig. 3). This specificity of boron clusters may due to a strong preference of sp^2 over sp^3 hybridization in the bonding. Since the C_{2v} (I) was found to be stable, we did not search another possible oval-shaped cyclic C_{2v} structure. The C_{2v} (II) structure, very similar to the C_{2v} (I), was unstable. Kawai and Weare[13] have studied the stability of the filled icosahedron and found that it is not even a local minimum. Starting the icosahedron, they obtained the converged C_{3v} structure of staggered twin hexagonal pyramids with an atom missing. Our *ab initio* calculations also predicted that this C_{3v} structure is unstable with four imaginary frequencies. Kawai and Weare[13] finally obtained the lowest energy three hexagonal pyramids.



B_{13} C_{2v}(I)



B_{13}^+ C_{2v}

Fig. 3. Optimized structures of B_{13} and B_{13}^+ clusters. Bond lengths are in Å.

The stable structure of B_{13}^+ has been obtained to be the C_{2v} structure which is very similar to the B_{13} neutral cluster (see Fig. 3). Anderson and co-workers[3] speculated that B_{13}^+ is an icosahedron with the additional atom filling the empty cage. Our calculations, however, predict that the icosahedral structure is unstable and the optimized D_{5d} structure has 12 imaginary frequencies. We also studied several other three-dimentional filling structures, D_{3h} (3-7-3) and D_{2h} (2-2-5-2-2), which were all unstable. Kawai and Weare[13] assume that the lowest energy structure of B_{13}^{+} corresponds to that of B_{13} based on the following speculation. The large energy gap between the HOMO and the next HOMO calculated for B_{13} and removal of one electron from the HOMO leads a large HOMO–LUMO gap in B_{13}^{+} and its significant stability. The singlet and triplet D_{12h} cyclic structures were unstable both with several imaginary frequencies.

Cluster Ionization Potentials. The adiabatic ionization potentials (IP) are calculated to be 7.16 and 6.66 eV for B_{12} and B_{13}, respectively at the MP4(SDTQ)/3-21G level (see Table 2). According to the experimental estimates of IPs by Anderson and co-workers,[3)] B_{2-4} appear to have IPs substantially larger than that of the boron atom (7.62 eV at MP4 (SDTQ)/3-21G), while clusters of more than 5—6 atoms have IPs lower than the atom. This trend is well reproduced in our calculations for B_{12} and B_{13}. The IP of B_{13} is calculated to be smaller than that of B_{12} and this also nicely agrees with the observed trend that the IPs of clusters with odd numbers of atoms are significantly lower than that of each next-neighbor cluster.

Cluster Dissociation. The appearance potentials measured by Anderson and co-workers[3)] have shown that the lowest energy fragmentation channel is the loss of a single atom for cluster ions of all size (B_{2-13}^{+}) such as

$B_n^+ \rightarrow B^+ + B_{n-1}$ (process 1),
$B_n^+ \rightarrow B + B_{n-1}^+$ (process 2).

Clusters smaller than six atoms preferentially lose B^+ (process1), while for the larger clusters the charge remains on the B_{n-1}^+ fragment (process 2). The appearance potential is the energy required to cause the dissociation if we assume that there is no transition state of reaction. The dissociation energies of the processes (1) and (2) are calculated to be 7.6 and 6.6 eV for B_{12} and 2.7 and 2.2 eV for B_{13}, respectively. These values should be compared with the experimental appearance potentials,[3)] 7.0±1.5 and 5.5±0.5 eV for B_{12} and 7.8±0.9 and 8.0±1.5 eV for B_{13}. The dissociation processes (1) and (2) are endothermic for both sizes of clusters as seen for the cluster sizes of 2—11.[11)] The calculated dissociation energies for B_{12} agree nicely with the experimental appearance potentials within the experimental error. On ther other hand, for B_{13} the discrepancy between the calculation and experiment is significant. This apparent discrepancy in the dissociation energy needs a search of a more stable structure of B_{13}^{+}. An oval-shaped cyclic C_{2v} structure similar to C_{2v} (I) B_{12} or the three-hexagonal pyramids of Kawai and Weare[13)] are possible candidates.

Concluding Remarks. The stable structures of neutral and cationic B_{12} and B_{13} clusters have been investigated based on the *ab initio* molecular orbital calcuation. A characteristic C_{2v} cyclic structure with one atom in the middle has been found to be stable for all the clusters. While this cyclic C_{2v} B_{12} has been found to be the most stable, the D_{5d} icosahedron is the most stable for B_{12}^{+}. An open-singlet D_{5d} icosahedral B_{12}, however, cannot be ruled out at the present stage. All the three-dimensional structures considered for B_{13} and B_{13}^{+} clusters are found to be unstable. Owing to a significant discrepancy between theory and experiment in the dissociation energies for B_{13}^{+}, the most stable structure of B_{13}^{+} and therefore the reason for a magic number 13 are still open questions.

The authors would like to thank Professor K. Fukui for his encouragement and Mr. H. Tanaka for his assistance at the early stage of calculations. The work has been supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture. A part of *ab initio* calculations were performed at the IMS Computer Center.

References

1) P. Jena, B. K. Rao, and S. N. Khanna, "Physics and Chemistry of Small Clusters," NATO ASI Series, Vol. 158, (1990); W. Weltner, Jr. and R. J. Van Zee, *Chem. Rev.*, **89**, 1713 (1989).

2) V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, *Chem. Rev.*, **91**, 1035 (1991).

3) L. Hanley, J. L. Whitten, and S. L. Anderson, *J. Phys. Chem.*, **92**, 5803 (1988); S. A. Ruatta, L. Hanley, and S. L. Anderson, *J. Chem. Phys.*, **91**, 226 (1989); P. A. Hintz, S. A. Ruatta, and S. L. Anderson, *J. Chem. Phys.*, **92**, 292 (1990).

4) U. Rothlisberger, W. Andreoni, and P. Giannozzi, *J. Chem. Phys.*, **96**, 1248 (1992); R. Kawai and J. Weare, *Phys. Rev. Lett.*, **65**, 80 (1990).

5) H. Kato and E. Tanaka, *J. Comput. Chem.*, **12**, 1097 (1991).

6) S. R. Langhoff and C. W. Bauschlicher, Jr., *J. Chem. Phys.*, **95**, 5882 (1991).

7) R. Hernandez and J. Simons, *J. Chem. Phys.*, **94**, 2961 (1991).

8) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. R. Soc. London, Ser. A*, **230**, 110 (1955).

9) G. Bambakidis and R. P. Wagner, *J. Phys. Chem. Solids*, **42**, 1023 (1981).

10) R. Kawai and J. H. Weare, *J. Chem. Phys.*, **95**, 1151 (1991).

11) H. Kato, K. Yamashita, and K. Morokuma, *Chem. Phys. Lett.*, **190**, 361 (1992).

12) R. O. Jones, *Phys. Rev. Lett.*, **67**, 224 (1991).

13) R. Kawai and J. H. Weare, *Chem. Phys., Lett.*, **191**, 311 (1992).

14) W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Pople, "*ab initio* Molecular Orbital Theory," Wiley, New York (1986).

15) M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, "GAUSSIAN 90," Gaussian Inc., Pittsburgh (1990).