

Origin of the Unusual Stability of B_{12} and B_{13}^+ Clusters

Boggavarapu Kiran,^{*,†} G. Gopa Kumar,[‡] Minh T. Nguyen,[‡] Anil K. Kandalam,[§] and Puru Jena[⊥]

[†]Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609, [‡]Department of Chemistry, Katholieke Universiteit Leuven, 200-F, B-3001 Leuven, Belgium, [§]Department of Physics, McNeese State University, Lake Charles, Louisiana 70609, and [⊥]Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284

Received July 18, 2009

A novel way to analyze the boron clusters is proposed in which the cluster is partitioned as inner and outer rings. Fragment molecular orbital analysis, based on this fragmentation, reveals that the delocalized valence electrons in B_{12} and B_{13}^+ clusters can be trifurcated as $6\pi-6\sigma_{\text{delo}}-6\sigma_{3\text{-ring}}$, leading to triple aromaticity, which is unique to these clusters.

Boron never ceases to surprise. From simple hydrides to complex solid-state structures, boron offers a rich variety of bonding features that defy conventional thinking. For example, a polyhedral or three-dimensional structure, especially B_{12} icosahedra, is a recurring structural pattern in most of the boron compounds.¹ In contrast, bare boron clusters adopt planar, quasi-planar, or tubular structures depending on the size of the cluster.^{2,3}

Among the small B clusters, B_{12} and B_{13}^+ are particularly unique. In one of the earliest experimental studies, Anderson and co-workers observed an unusually high intense peak for B_{13}^+ in the mass spectrum of cationic boron clusters.⁴ In subsequent studies, the group further noticed an unusual reactivity pattern for B_{13}^+ , namely, a high threshold for oxidation,⁵ and low reactivity⁶ with D_2O compared to the similarly sized clusters. In addition, dissociation of the B_{13}^+ cluster to B_{12} and B^+ is more facile compared to other B_n^+ clusters, suggesting that B_{12} is very stable. This is consistent with the earlier theoretical prediction⁷ that most stable

clusters, conventionally referred to as magic clusters, are always the preferred byproducts in the dissociation of a parent cluster. Anion photoelectron spectroscopic studies corroborate this finding: B_{12}^- exhibits the *least* intense peak in the B_n^- mass spectra, and the neutral B_{12} has the *largest* HOMO–LUMO (H–L) gap (~ 2.0 eV).⁸ In comparison, the H–L gap of C_{60} is ~ 1.68 eV.⁹

In order to account for these observations, earlier theoretical studies^{3,8,10–12} have focused on π -electron delocalization as an important component for the planarity and stability of B_{12} and B_{13}^+ , where 6π electrons occupy orbitals akin to the benzene π levels. However, this cannot be the complete story because B_{10} also has benzene-like 6π electrons but its H–L gap (~ 1.0 eV) is much smaller than that of B_{12} . In addition, B_{14} has 8π electrons⁸ but has a H–L gap similar to that of B_{10} . Thus, studies based on π electrons alone cannot account for all of these observations.

In this Communication, we show that the extraordinary kinetic stability of B_{12} and B_{13}^+ is related to the *triple* aromatic nature of these clusters. We further show that the H–L gaps are, in fact, governed by the size and nature of the interaction between the outer and inner rings of the planar clusters. The computational details are given in the Supporting Information.

First, we focus on the nature of the bonding in B_{12} . In agreement with earlier studies,^{2a,8} we found that neutral B_{12} adopts a C_{3v} ground-state geometry with an outer nine-membered (B_9) ring and an inner B_3 ring [$B_9(B_3)$] (Figure 1). The inner ring is slightly out of the plane, and the planar D_{3h} structure is only 0.12 eV higher in energy. Inspection of the bond-length variations in B_{12} provides preliminary hints about the nature of electron delocalization. The B–B bond lengths in the B_9 ring (1.55 and 1.61 Å) are shorter than the B–B distance in the B_3 ring (1.65 Å), which is further shorter than the B–B distances (1.68 and 1.81 Å) between the B_9 and B_3 rings. To put these distances into

*To whom correspondence should be addressed. E-mail: kiran@mcneese.edu.

(1) (a) Jemmis, E. D.; Prasad, D. L. V. K. *J. Solid State Chem.* **2006**, *179*, 796–802. (b) Jemmis, E. D.; Balakrishnarajan, M. M. *Bull. Mater. Sci.* **1999**, *22*, 863–867. (c) Perkins, C. L.; Trenary, M.; Tanaka, T. *Phys. Rev. Lett.* **1996**, *77*, 4772.

(2) (a) Boustani, I. *Chem. Phys. Lett.* **1995**, *240*, 135–140. (b) Ricca, A.; Bauschlicher, C. W. *Chem. Phys.* **1996**, *208*, 233–242. (c) Boustani, I. *Surf. Sci.* **1997**, *370*, 355. (d) Boustani, I. *Phys. Rev. B* **1997**, *55*, 16426.

(3) Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **2000**, *104*, 397–403. (4) Hanley, L.; Whitten, J. L.; Anderson, S. L. *J. Phys. Chem.* **1988**, *92*, 5803–5812.

(5) Hanley, L.; Anderson, S. L. *J. Chem. Phys.* **1988**, *89*(5), 2848–2860. (6) Hintz, P. A.; Ruatta, S. A.; Anderson, S. L. *J. Chem. Phys.* **1990**, *92*(1), 292–303.

(7) Rao, B. K.; Jena, P.; Manninen, M.; Nieminen, R. *Phys. Rev. Lett.* **1987**, *58*, 1188.

(8) Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. *Nat. Mater.* **2003**, *2*, 827–833. (9) Wang, X. B.; Ding, C. F.; Wang, L. S. *J. Chem. Phys.* **1999**, *110*, 8217–8220.

(10) Aihara, J. *J. Phys. Chem. A* **2001**, *105*, 5486–5489. (11) Lau, K. C.; Deshpande, M. D.; Pandey, R. *Int. J. Quantum Chem.* **2005**, *102*, 656.

(12) Zubarev, D. Y.; Boldyrev, A. I. *J. Comput. Chem.* **2007**, *28*, 251–268.

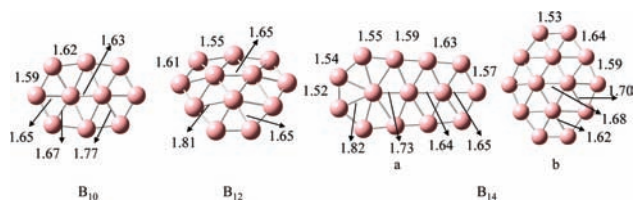


Figure 1. Geometries of B₁₀, B₁₂, and the two isomers (a and b) of B₁₄ along with important bond lengths (Å).

perspective, it should be noted that the B–B single bond distance in B₃H₃ (*D*_{3h}) is 1.73 Å and experimentally characterized B=B double-bond lengths vary between 1.57 and 1.59 Å. The above distribution of bond lengths indicates that there is strong delocalization of electrons between and within the rings.

Note that B₁₂ has 36 valence electrons (12 × 3), with each boron atom contributing three valence electrons. The manner in which these electrons are arranged can be rationalized as follows. First, 18 electrons are localized along the nine B–B single bonds of the outer B₉ ring. The remaining 18 electrons are divided into 6π electrons, which are delocalized over the entire cluster, and 6σ electrons, which are taken up to make the B₃ ring. The remaining 6 electrons are delocalized between the B₉ and B₃ rings. Thus, the 6π–6σ_{delo}–6σ_{3-ring} trifurcation can be viewed as giving rise to the triple aromaticity of the B₁₂ cluster and is responsible for its unusual stability.

To validate this simple picture, we performed fragment molecular orbital (FMO) calculations.¹³ An idealized orbital interaction diagram for the planar B₁₂ is presented in Figure 2. Important frontier orbitals of the B₃ and B₉ rings are shown on both sides of the diagram. The B₉ ring has partially filled levels and is unstable on its own. Therefore, interaction with B₃ is necessary for its stabilization. Besides the orbital interactions that constitute three B–B bonds in the B₃ ring (6σ_{3-ring}), three radial p-orbital combinations of the B₉ ring (5e' + 3a₁') interact with the corresponding B₃ orbitals (2a' + 2e') to form the σ-bonding combination of 5e' and 4a₁'. This "6-electron" three-orbital interaction between B₉ and B₃ rings is what constitutes a set of aromatic subunits (6σ_{delo}) of B₁₂. There are three π orbitals (1e'' + 1a₂''), which had also been identified earlier, that form another set of the aromatic sextets. Note that the 1e'' interaction stabilizes the π orbitals below the HOMO level. The additional 6 electrons arising from the three B–B bonds of the B₃ ring complete the triply aromatic nature of B₁₂. It is interesting to note that the LUMO of B₁₂ (2e'') is a π* orbital mostly localized on the B₉ ring. The important result from the FMO analysis of B₁₂ is that, in addition to the π bonding, there are three molecular orbitals between the B₉ and B₃ rings that contribute to the stabilization of the cluster.

In order to provide further justification to the above distribution of electrons, we performed topological analysis of the electron density using the "Atoms in Molecules" approach.¹⁴ A molecular graph of B₁₂ depicting the bond critical points (BCPs) and ring critical points (RCP) is shown in Figure 3. There are a total of 15 BCPs, nine of which are in

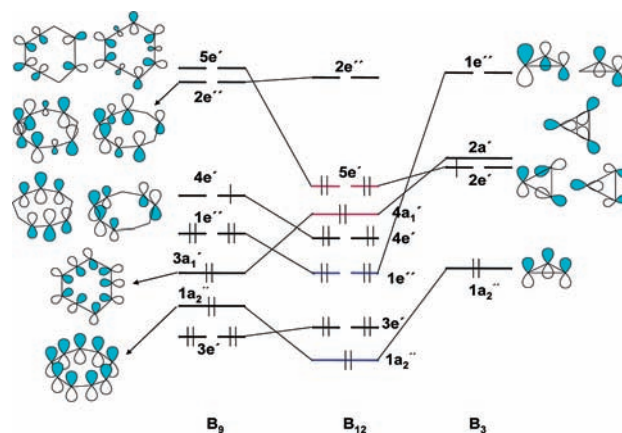


Figure 2. Idealized orbital interaction diagram for B₁₂ (*D*_{3h}).

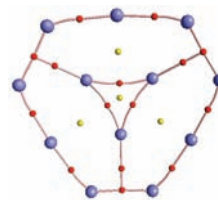


Figure 3. Molecular graph of B₁₂. The red dots indicate (3, –1) BCPs, and the yellow dots indicate (3, +1) RCPs.

the outer B₉ ring and three of which are in the B₃ ring. We were able to locate three BCPs, connecting the boron atoms of the inner B₃ ring with the three B–B BCPs of the outer B₉. This corresponds to a conflict structure, in which the boron atoms of the inner B₃ ring are in a competition to link with one of the boron atoms of the outer B₉ ring. Note that, in addition to the RCP located at the center of the B₃ ring, we were also able to find three RCPs between the B₉ and B₃ rings.

It is now easy to explain the stability of B₁₃⁺. It has 38 valence electrons and forms a planar (*C*_{2v}) structure, with 10 boron atoms forming the outer ring (B₁₀) and 3 forming the inner ring (B₃). Partition of the electrons, as was done for B₁₂, can explain the triply aromatic nature of the cluster: Out of 38 valence electrons, 20 are taken up to form the 10 B–B bonds of the B₁₀ ring while the remaining 18 electrons are distributed in exactly the same way as that for B₁₂, namely, as 6π + 6σ_{delo} + 6σ_{3-ring} electrons. Not surprisingly, the HOMO and LUMO of B₁₃⁺ are the same as those of B₁₂. In other words, both B₁₂ and B₁₃⁺ have very similar electronic structures (triply aromatic), except that the larger B₁₀ ring makes the B₁₃⁺ cluster planar. Therefore, the stability of the B₁₂ and B₁₃⁺ clusters is not just related to the number of π electrons alone but, in fact, to the presence of three distinct aromatic sextets (4*n* + 2), which are unique to these clusters. The H–L gaps in the planar boron clusters depend on the strength of the interaction between the outer and inner rings (such as B₉ and B₃ for B₁₂) and on the overall nature of the π distribution.

What about B₁₀ and B₁₄, which have six and eight π electrons, respectively, but have similar H–L gaps (~1.0 eV)? The orbital pictures of HOMO and LUMO of B₁₀, B₁₂, and B₁₄ in Figure 4 provide the answer. As noted above, the H–L gap in B₁₂ corresponds to the gap between the σ and π* levels. This is because the π electrons in B₁₂ are more stabilized. On the other hand, the H–L gap in B₁₀

(13) The extended Hückel theory based FMO calculations are done using the CACAO program: Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399–402.

(14) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.

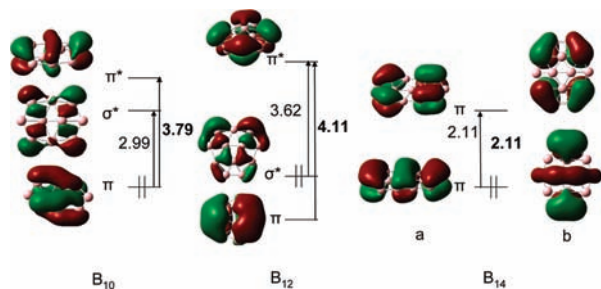


Figure 4. Orbital pictures for B_{10} , B_{12} , and B_{14} (a and b). Gaps of various energy levels are given in electronvolts; values in the bond correspond to $\pi-\pi^*$.

corresponds to the π and σ^* levels. With 8π ($4n$) electrons, B_{14} offers a complementary picture. The $\pi-\pi$ (H-L) gap in B_{14} is the energy difference of otherwise degenerate π orbitals (π orbitals with the same nodes). Not surprisingly, the $\pi-\pi^*$ energy difference is maximum in B_{12} (4.11 eV), followed by

(15) Aihara, J.; Kanno, H.; Ishida, T. *J. Am. Chem. Soc.* **2005**, *127*, 13324–13330.

B_{10} (3.79 eV) and B_{14} (2.11 eV). This is consistent with the recent study by Aihara et al., who, using graph theoretical methods, showed that in planar boron clusters the π delocalization reaches a maximum at B_{12} .¹⁵

In conclusion, we have shown that the unusual but similar electronic structures of B_{12} and B_{13}^+ are due to the existence of multiple $4n + 2$ sextets. The H-L gaps in these planar and quasi-planar boron clusters depend on the nature of the interacting units and not just the π -electron count alone.

Acknowledgment. B.K. and A.K.K. acknowledge support from Dr. Kiritsis and the Louisiana Board of Regents for providing faculty start-up funds through the Research Commercialization/Educational Enhancement Program. P.J. acknowledges partial support from the U.S. Department of Energy.

Supporting Information Available: Computational details, complete references, and a molecular graph of B_{13}^+ . This material is available free of charge via the Internet at <http://pubs.acs.org>.