

## Geometries and Electronic Structures of Boron Clusters: Planar Structures and All-boron Fullerenes

Lei Liu<sup>1,2\*</sup> and Binit Lukose<sup>3,4\*</sup>

<sup>1</sup>Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn

<sup>2</sup>Department of Physics & Earth Sciences, Jacobs University

<sup>3</sup>School of Chemical and Biomolecular Engineering, 113 Ho Plaza, Cornell University

<sup>4</sup>School of Electrical and Computer Engineering, 8 St. Mary's Street, Boston University, Boston, USA

**\*Corresponding author:** Lei Liu, Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn, Beringstr. 4, 53115 Bonn, Germany; E mail: liulei3039@gmail.com

Binit Lukose, School of Chemical and Biomolecular Engineering, 113 Ho Plaza, Cornell University, 14853 Ithaca, USA; E mail: binitl@gmail.com

**Article Type:** Mini Review, **Submission Date:** 1 October 2016, **Accepted Date:** 21 October 2016, **Published Date:** 23 December 2016.

**Citation:** Lei Liu and Binit Lukose (2016) Geometries and Electronic Structures of Boron Clusters: Planar Structures and All-boron Fullerenes. JApI Theol 1(2): 5-8.

**Copyright:** © 2016 Lei Liu and Binit Lukose. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Boron by itself and in combination with other elements can form a variety of atomic clusters. These clusters can be categorized into pure boron clusters, boron-hydrogen mixtures, called boranes (or borohydrides), boron-carbon-hydrogen mixtures, called carboranes, and boron-transition metal mixtures, called metallocarboranes. Because of their peculiar structures and unusual chemical bonding, boron clusters yield a variety of applications in different areas, such as coordination polymers [1], liquid crystals [2], ionic liquids [3], luminescent materials [4], and medicine [5]. Thus, they attract the interests of interdisciplinary researchers. A primary task in the research of boron clusters is to find the most stable structures of clusters containing given numbers and types of atoms. In this mini-review, we summarize the geometries and electronic structures of two commonly studied boron clusters, planar boron clusters and all-boron fullerenes.

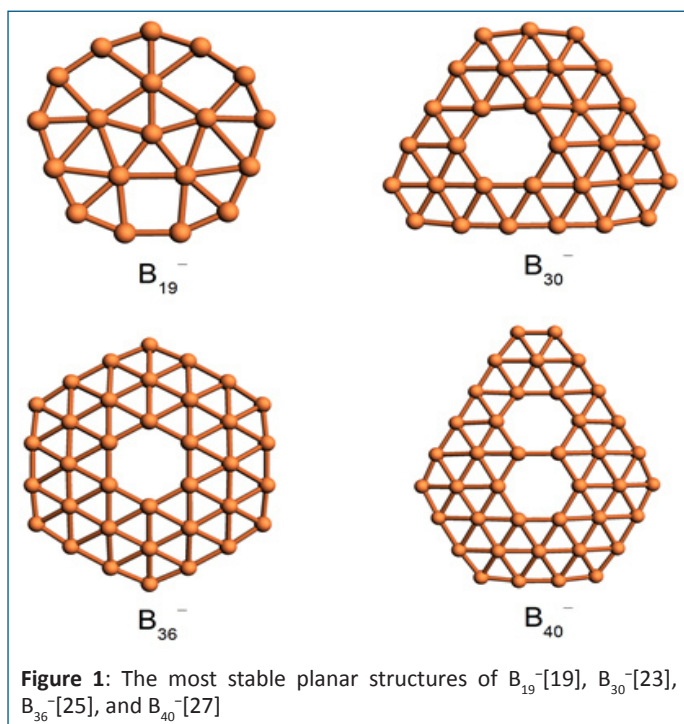
### Planar Boron Clusters

In the solid state, boron compounds often adopt three-dimensional (3D) structures [6-10]. One heavily studied type is boranes of general form  $B_nH_n$ . Most of the boranes are shown to be cage-like, referred as deltahedra [11]. The representative example is  $B_{12}H_{12}^{2-}$ , which was first theoretically investigated by Longuet-Higgins and Roberts using molecular orbital theory [12]. They concluded that the  $B_{12}H_{12}$  structure could be stable only as a di-anion,  $B_{12}H_{12}^{2-}$ , having 13 skeletal bonding orbitals and 12 outward pointing external orbitals. This hypothesis was confirmed later by experimental data, and the structure of  $B_{12}H_{12}^{2-}$  anion was shown to be icosahedral [13]. Unlike 3D cage structures, which are the dominant configurations of boron compounds in the solid state, the pure small boron clusters ( $n \leq 40$ ) are found to be two-dimensional (2D) planar or quasi-planar

in the gas phase, and the chemical bonding analysis suggests that this planarity is a consequence of  $\pi$  bonding in the cluster forms [9,10]. The simplest pure boron cluster is the diatomic  $B_2$ , which serves as the first example of unusual chemical bonding in the boron species. On the basis of Hartree-Fock and UMP4 (unrestricted fourth order Møller-Plesset perturbation theory) calculations [14], the next pure boron cluster,  $B_3$ , is shown to exist in cationic or anionic forms with a triangular structure of  $D_{3h}$  symmetry.

In 2004, Zubarev et al concluded that pure boron clusters containing up to 15 atoms retain planar or quasi-planar conformation [15]. However, there still remains a strong interest to determine the critical size at which structural transition from 2D to 3D occurs. This, however, is a challenging task due to the complexity of these systems and the existence of a large number of isomers. Such 2D-to-3D structural transition is also strongly affected by the charges of boron clusters. For cationic boron clusters ( $B_n^+$ ), the largest planar or quasi-planar structure was established for  $n=15$ , and the transition from planar to cylindrical structure takes place for  $B_{16}^+$  [16]. Combining experiment (photoelectron spectroscopy) with computational studies (global minimum search), Kiran et al [17] found that the neutral  $B_{20}$  cluster undergoes a 2D-to-3D structural transition, resulting in formation of a stable double-ring tubular structure with a diameter of 5.2 Å (Figure 1). The tubular structure was considered as the embryo of the thinnest single-walled boron nanotubes.

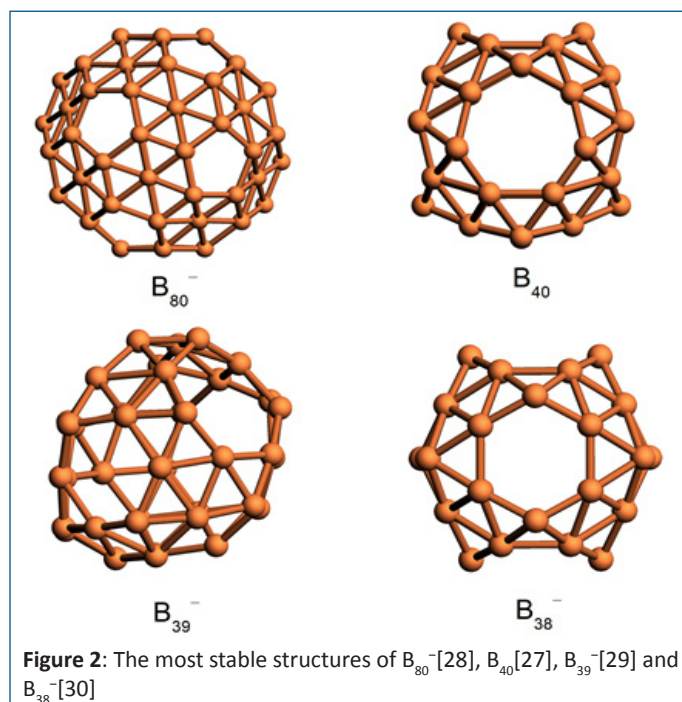
However, the upper limit for the  $B_n^-$  anionic clusters still remains an open question. Through a joint study of photoelectron spectroscopy and *ab initio* computation, Boldyrev and Wang confirmed that anionic boron clusters with up to nineteen atoms are planar or quasi-planar [18,19]. And a particularly attractive



geometry was found for  $B_{19}^-$  (see Figure 1) [19]. In this circular planar structure, a central boron atom is surrounded by a pentagonal unit, which is directly bonded to the outer  $B_{13}$  ring. Interestingly, AdNDP (Adaptive Natural Density Partitioning) chemical bonding analysis showed that this cluster is characterized by a unique double  $\pi$ -aromaticity involving ten  $\pi$ -electrons delocalized between the inner pentagon and the outer  $B_{13}$  ring, similar to the case of cyclodecapentaene, and another two  $\pi$ -electrons delocalized over the central  $B_6$  unit. Later on, global minimum structures of the  $B_{21}^-$ ,  $B_{22}^-$ ,  $B_{23}^-$ ,  $B_{24}^-$ , and  $B_{30}^-$  anions are also confirmed to be planar [20-23]. The chemical bonding analysis reveals that the bonding in  $B_{22}^-$  is similar to that in anthracene, and the bonding in  $B_{23}^-$  is analogous to that in phenanthrene. More interestingly,  $B_{30}^-$  was shown to be a chiral boron cluster. (Figure 1) [23]. This was the first observation of chirality in boron clusters. The work by Li and Wang revealed that  $B_{36}$  has a quasi-planar structure with a central hexagonal hole [24]. A similar structure was confirmed for  $B_{36}^-$  [25]. The global minimum search showed that the most stable configuration of  $B_{36}$  is a bowl-shaped structure having a perfect  $C_{6v}$  symmetry and the depth of the bowl is about 1.2 Å (Figure 1). The chemical bonding analysis suggested that the  $B_{36}$  cluster could be visualized as six hexagonal units bound together. More interestingly, several totally delocalized 36-center 2-electron (36c-2e)  $\pi$ -bonds were found from the chemical bonding analysis. A recent study reveals that delocalized 36c-2e  $\pi$ -bonds as well as three delocalized 12-center 2-electron (12c-2e)  $\pi$ -bonds around the central hexagonal hole are the reasons for the high stability of this structure [26]. The largest boron cluster that has been confirmed to be planar so far is  $B_{40}^-$ . In 2014, Wang et al reported a joint experimental and computational investigation on the electronic structure of a  $B_{40}$  cluster [27]. Through the photoelectron spectroscopy and global minimum search, the researchers found out that the negatively charged  $B_{40}^-$  shows a 2D planar global minimum structure with two adjacent hexagonal holes having a  $C_s$  symmetry (Figure 1). It is important to note that a neutral  $B_{40}$  is, however, a 3D structure, which will be discussed in detail in the next section.

## All-boron Fullerenes

Since boron by itself can form planar or quasi-planar (2D) clusters similar to that of carbon, one may question whether it is possible to form all-boron fullerenes similar to the  $C_{60}$  fullerene. Several early attempts to design low dimensional boron nanostructures, including boron cage structures and boron nanotubes, have been carried out theoretically. Of them, the proposal of  $B_{80}$  borospherene using *ab initio* methods attracts a particular interest and opens a gate to the all-boron fullerenes [28]. The shape of this cluster is quite similar to that of  $C_{60}$ , but with additional boron atoms located at the center of all 20 hexagons (Figure 2). The calculated cohesive energy is 5.76 eV/atom, which is much larger than that of  $B_{12}$  icosahedrons (5.01 eV/atom) and indicates its high thermodynamical stability. Molecular dynamics simulations confirm its dynamical stability and shows that the cage structure remains unchanged for up to 1000 K. However, all predictions are based on density functional theory (DFT) calculations and in the lack of experimental verification. Hence, the possibility of existence of boron fullerenes is not beyond doubt.



In a combined experimental and computational study, Wang et al show that a fullerene-like  $B_{40}^-$  cage-geometry is only 2 kcal mol<sup>-1</sup> less stable compared to the 2D planar global minimum structure [27]. Interestingly for the neutral  $B_{40}$  cluster, the potential energy surface mostly reproduces cage-like structures. The most stable structure of  $B_{40}$  shows  $D_{2d}$  symmetry, which consists of 16 tetra-coordinated and 24 penta-coordinated boron atoms (Figure 2). The next three isomers are also cage-like but with lower symmetries. The 2D quasi-planar structure is, however, 23 kcal mol<sup>-1</sup> less stable than the most stable cage-like structure. This observation strongly indicates that boron indeed can form fullerene-like structures similar to carbon.

Based on the same methodology (photoelectron spectroscopy and global minimum searches), Wang et al expanded the all-boron fullerene family to include a  $B_{39}^-$  cluster [29]. They showed that  $B_{39}^-$  cluster has a  $C_3$  cage global minimum. This

cage structure contains three hexagons on the top, and three heptagons at the bottom connected by 47 triangles (Figure 2). In fact, such  $C_3$ -symmetric  $B_{39}^-$  cluster can be obtained from  $B_{40}$  cage by replacing a heptagon ( $B_7$  unit) with a hexagon ( $B_6$  unit). It is important to note that  $B_{39}^-$  is the first chiral borospherene. On the ground of global minimum search, Ma et al. added a new member to the all-boron fullerenes family,  $B_{38}^-$  [30]. The cage-like structure of  $B_{38}^-$  consists of 4 hexagons and 56 triangles with a high symmetry of  $D_{2h}$ . The overall shape of the  $B_{38}^-$  cage structure is nearly spherical with a diameter of 5.85 Å (Figure 2). Later on, the all-boron fullerene (or borospherene) family was expanded to include  $B_{41}^+$  and  $B_{44}$  clusters [31,32]. Based on the global minimum search, Zhao et al. found that the smallest all-boron fullerene is  $B_{28}$  [33]. The most stable structure of  $B_{28}$  is a cage-like structure which consists of thirty-six triangles, one hexagon and two octagons. Such a  $B_{28}$  cage can be built from two quasi-planar  $B_{12}$  clusters connected by four additional boron atoms, that is, two boron atoms and one  $B_2$  dimer.

In short, boron is a promising element for several applications and can form diverse structures similar to that of carbon. The observation of planar or quasi-planar boron clusters, in particular the discovery of a quasi-planar  $B_{36}$  cluster, provides convincing evidence for boron forming atom-thin nanosheets or borophenes. On the other hand, the discovery of an all-boron fullerene,  $B_{40}^+$ , reveals that a family of borospherenes might exist, similar to the C-fullerene family. Interestingly, some boron clusters of certain number of boron atoms exist in either 2D or 3D form depending on its charge. It is believed that the studies of boron clusters will help to discover certain unusual chemical bonds as well as some interesting structures with fantastic applications.

## Reference

1. Hardie MJ. The Use of Carborane Anions in Coordination Polymers and Extended Solids. *J Chem Crystallogr.* 2007; 37(1):69–80. doi: 10.1007/s10870-006-9153-x
2. Binnemans K. Ionic Liquid Crystals. *Chem Rev.* 2005; 105(11):4148–4204. doi: 10.1021/cr0400919
3. Krossing I, Raabe I. Noncoordinating Anions--Fact or Fiction? A Survey of Likely Candidates. *Angew Chem Int Ed.* 2004; 43(16):2066–2090. doi: 10.1002/anie.200300620
4. Williams RE. The Polyborane, Carborane, Carbocation Continuum: Architectural Patterns. *Chem Rev.* 1992; 92(2):177–207. doi: 10.1021/cr00010a001
5. Kreuter J, Alyautdin RN, Kharkevich DA, Ivanov AA. Passage of Peptides through the Blood-Brain Barrier with Colloidal Polymer Particles (Nanoparticles). *Brain Res.* 1995; 674(1):171–174. doi:10.1016/0006-8993(95)00023-J
6. Farràs P, Vankova N, Zeonjuk, LL, Warneke J, Dülcks T, Heine T, et al. From an Icosahedron to a Plane: Flattening Dodecaiodo-Dodecaborate by Successive Stripping of Iodine. *Chem Eur J.* 2012; 18(41):13208–13212. doi: 10.1002/chem.201200828.
7. Zeonjuk, LL, Vankova N, Knapp C, Gabel D, Heine T. On the Gas-Phase Dimerization of Negatively Charged Closo-Dodecaborates: A Theoretical Study. *Phys Chem Chem Phys.* 2013; 15(25):10358–10366. doi: 10.1039/c3cp50722j.
8. Fagiani MR, Zeonjuk LL, Esser TK, Gabel D, Heine T, Asmis KR, et al. Opening of an Icosahedral Boron Framework: A Combined Infrared Spectroscopic and Computational Study. *Chem Phys Lett.* 2015; 625:48–52. doi: 10.1016/j.cplett.2015.02.030.
9. Sergeeva AP, Popov IA, Piazza ZA, Li WL, Romanescu C, Wang LS, et al. Understanding Boron through Size-Selected Clusters: Structure, Chemical Bonding, and Fluxionality. *Acc Chem Res.* 2014; 47(4):1349–1358. doi: 10.1021/ar400310g.
10. Wang L. Photoelectron Spectroscopy of Size-Selected Boron Clusters: From Planar Structures to Borophenes and Borospherenes. *Int Rev Phys Chem.* 2016; 35(1): 69–142. doi: 10.1080/0144235X.2016.1147816
11. Fox MA, Wade K. Evolving Patterns in Boron Cluster Chemistry. *Pure Appl Chem.* 2003; 75(9):1315–1323. doi: http://dx.doi.org/10.1351/pac200375091315
12. Longuet-Higgins HC, Roberts M deV. The Electronic Structure of an Icosahedron of Boron Atoms. *Proc R Soc Lond. A* 1955; 230(1180):110–119. doi: 10.1098/rspa.1955.0115
13. Pitochelli AR, Hawthorne FM. The Isolation of the Icosahedral  $B_{12}H_{12}^{2-}$  Ion. *J Am Chem Soc.* 1960; 82(12):3228–3229. doi: 10.1021/ja01497a069
14. Whiteside RA. PhD Thesis. Pittsburgh: Carnegie Mellon University; 1981.
15. Zubarev DYU, Boldyrev AI. Comprehensive Analysis of Chemical Bonding in Boron Clusters. *J Comput Chem.* 2007; 28(1):251–268. doi: 10.1002/jcc.20518
16. Oger E, Crawford NRM, Kelting R, Weis P, Kappes MM, Ahlrichs R. Boron Cluster Cations: Transition from Planar to Cylindrical Structures. *Angew Chem Int Ed.* 2007; 46(44):8503–8506. DOI: 10.1002/anie.200701915
17. Kiran B, Bulusu S, Zhai HJ, Yoo S, Zeng XC, Wang LS. Planar-to-Tubular Structural Transition in Boron Clusters:  $B_{20}$  as the Embryo of Single-Walled Boron Nanotubes. *Proc Natl Acad Sci USA.* 2005; 102(4):961–964. doi: 10.1073/pnas.0408132102
18. Sergeeva AP, Averkiev BB, Zhai HJ, Boldyrev AI, Wang LS. All-Boron Analogues of Aromatic Hydrocarbons:  $B_{17}^-$  and  $B_{18}^-$ . *J Chem Phys.* 2011; 134(22):224304. doi: http://dx.doi.org/10.1063/1.3599452
19. Huang W, Sergeeva AP, Zhai HJ, Averkiev BB, Wang LS, Boldyrev AI. A Concentric Planar Doubly  $\pi$ -Aromatic  $B_{19}^-$  Cluster. *Nat Chem.* 2010; 2(3):202–206. doi:10.1038/nchem.534
20. Piazza ZA, Li WL, Romanescu C, Sergeeva AP, Wang LS, Boldyrev AI. A Photoelectron Spectroscopy and Ab Initio Study of  $B_{21}^-$ : Negatively Charged Boron Clusters Continue to Be Planar at 21. *J Chem Phys.* 2012; 136(10):1043101–1043109. doi: 10.1063/1.3692967. doi: http://dx.doi.org/10.1063/1.3692967
21. Sergeeva AP, Piazza ZA, Romanescu C, Li WL, Boldyrev AI, Wang LS.  $B_{22}^-$  and  $B_{23}^-$ : All-Boron Analogues of Anthracene and Phenanthrene. *J Am Chem Soc.* 2012; 134(43):18065–18073. doi: 10.1021/ja307605t.
22. Popov IA, Piazza ZA, Li WL, Wang LS, Boldyrev AI. A Combined Photoelectron Spectroscopy and Ab Initio Study of the Quasi-Planar  $B_{24}^-$  Cluster. *J Chem Phys.* 2013; 139(14):1443071. doi: 10.1063/1.4824156.
23. Li WL, Zhao YF, Hu HS, Li J, Wang LS.  $B_{30}^-$ : A Quasiplanar Chiral Boron Cluster. *Angew Chem Int Ed.* 2014; 53(22):5540–5545. doi: 10.1002/anie.201402488.

24. Piazza ZA, Hu HS, Li WL, Zhao YF, Li J, Wang LS. Planar Hexagonal  $B_{36}$  as a Potential Basis for Extended Single-Atom Layer Boron Sheets. *Nat Commun.* 2014; 5:1–6. doi:10.1038/ncomms4113
25. Chen Q, Wei G, Tian WJ, Bai H, Liu Z, Zhai HJ, et al. Quasi-Planar Aromatic  $B_{36}$  and  $B_{36}^-$  Clusters: All-Boron Analogues of Coronene. *PhysChemChem Phys.* 2014; 16(34):18282-7. doi: 10.1039/c4cp02032d.
26. Liu L, Osorio E, Heine T. Understanding the Central Location of a Hexagonal Hole in a  $B_{36}$  Cluster. *Chem Asian J.* 2016; 11(22):3220-3224. doi: 10.1002/asia.201601106.
27. Zhai HJ, Zhao YF, Li WL, Chen Q, Bai H, Hu HS, et al. Observation of an All-Boron Fullerene. *Nat Chem.* 2014; 6(8):727–731. doi: 10.1038/nchem.1999.
28. Szwacki NG, Sadrzadeh A, Yakobson BI.  $B_{80}$  Fullerene : An Ab Initio Prediction of Geometry, Stability and Electronic Structure. *Phys Rev Lett.* 2007; 98(16):166804. doi: 10.1103/PhysRevLett.98.166804
29. Chen Q, Li W, Zhao Y, Zhang S, Hu H, Bai H, et al. Experimental and Theoretical Evidence of an Axially Chiral Borospherene. *ACS Nano.* 2015; 9(1):754–760. doi: 10.1021/nn506262c.
30. Lv J, Wang Y, Zhu L, Ma Y.  $B_{38}$  : An All-Boron Fullerene Analogue. *Nanoscale.* 2014; 6(20):11692–11696. doi: 10.1039/c4nr01846j.
31. Chen Q, Zhang S, Bai H, Tian W, Gao T, Li H, et al. Cage-Like  $B_{41}^+$  and  $B_{42}^{2+}$  : New Chiral Members of the Borospherene Family. *AngewChemInt Ed.* 2015; 54(28):8160–8164. doi: 10.1002/anie.201501588
32. Tai TB, Nguyen MT. A New Chiral Boron Cluster  $B_{44}$  Containing Nonagonal Holes. *ChemCommun.* 2016; 52(8):1653–1656. doi: 10.1039/c5cc09111j.
33. Zhao J, Huang X, Shi R, Liu H, Sua Y, King RB.  $B_{28}$  : The Smallest All-Boron Cage from an Ab Initio Global Search. *Nanoscale.* 2015; 7(37):15086–15090. doi: 10.1039/c5nr04034e.