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

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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 metallacarboranes. 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 π 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

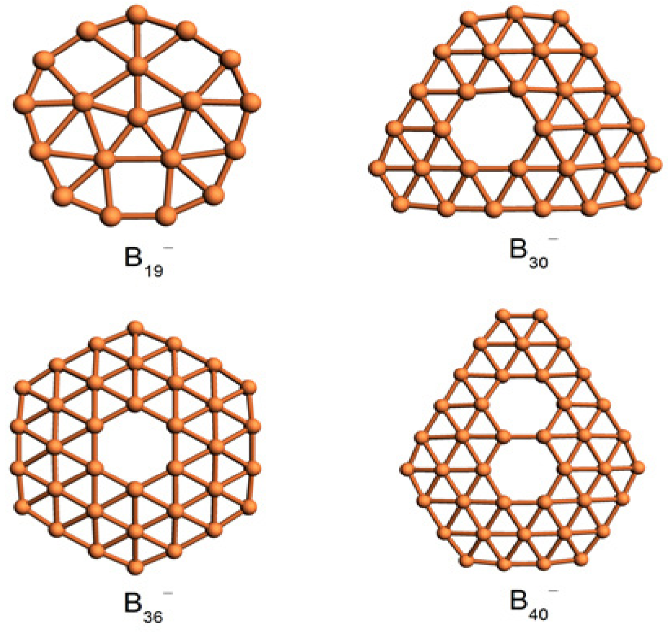

Figure 1: The most stable planar structures of B_{19}^-[19], B_{30}^-[23], B_{36}^-[25], and B_{40}^-[27]

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 π-aromaticity involving ten π-electrons delocalized between the inner pentagon and the outer B_{13} ring, similar to the case of cyclodecapentaene, and another two π-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) π-bonds were found from the chemical bonding analysis. A recent study reveals that delocalized 36c-2e π-bonds as well as three delocalized 12-center 2-electron (12c-2e) π-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.

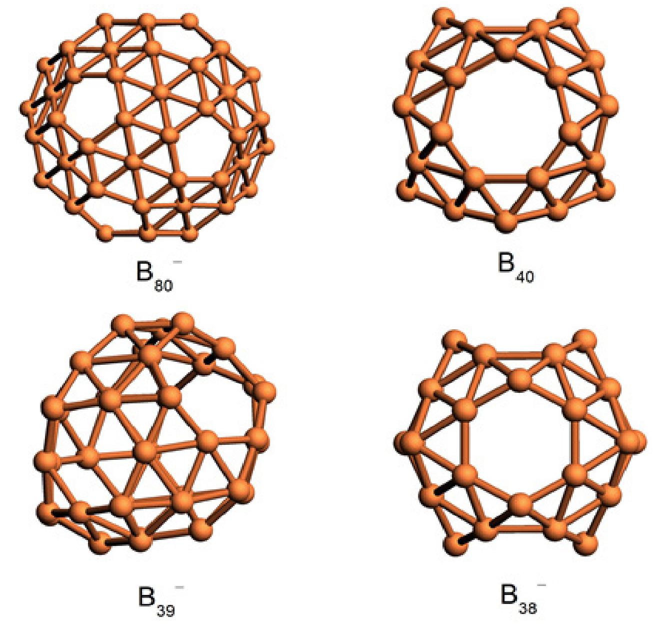

Figure 2: The most stable structures of B_{80}^-[28], B_{40}[27], B_{39}^-[29] and B_{38}^-[30]

In a combined experimental and computational study, Wang et al show that a fullerene-like B_{40}^- cage-geometry is only 2 kcal mol^{-1} 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^{-1} 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 fullerence (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.

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