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 \( \text{B}_n \text{H}_6 \). Most of the boranes are shown to be cage-like, referred as deltahedra [11]. The representative example is \( \text{B}_3 \text{H}_6 \), which was first theoretically investigated by Longuet-Higgins and Roberts using molecular orbital theory [12]. They concluded that the \( \text{B}_3 \text{H}_6 \) structure could be stable only as a di-anion, \( \text{B}_3 \text{H}_6^{2-} \), having 13 skeletal bonding orbitals and 12 outward pointing external orbitals. This hypothesis was confirmed later by experimental data, and the structure of \( \text{B}_3 \text{H}_6^{2-} \) 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 \( \text{B}_n \) 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 \( \text{B}_2^+ \), 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, \( \text{B}_3^+ \), is shown to exist in cationic or anionic forms with a triangular structure of \( D_3^{h} \) 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 (\( \text{B}_n^+ \)), the largest planar or quasi-planar structure was established for \( n=15 \), and the transition from planar to cylindrical structure takes place for \( \text{B}_{19}^+ \) [16]. Combining experiment (photoelectron spectroscopy) with computational studies (global minimum search), Kiran et al [17] found that the neutral \( \text{B}_{19} \) 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 \( \text{B}_n \) 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...
The most stable planar structures of $B_{13}$ will be discussed in detail in the next section. It is important to note that a neutral $B_{13}$ is analogous to that in phenanthrene. More interestingly, $B_{36}^-$ 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 $B_{40}^-$. [25]. The global minimum search showed that the most stable configuration of $B_{36}$ is a bowl-shaped structure having a perfect $C_{1h}$ symmetry (Figure 1). It is analogous to that in phenanthrene, and the bonding in $B_{36}^-$ is analogous to that in phenanthrene. More interestingly, $B_{36}^-$ was shown to be a chiral boron cluster. (Figure 1) [23]. This was the first observation of chirality in boron clusters.

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 $B_{60}$ 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 $B_{13}$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 showed that a fullerene-like $B_{60}^-$ cage geometry is only 2 kcal mol$^{-1}$ less stable compared to the 2D planar global minimum structure [27]. Interestingly for the neutral $B_{36}$ cluster, the potential energy surface mostly reproduces cage-like structures. The most stable structure of $B_{60}^-$ shows $D_{3h}$ 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.
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, $B_{39}$ [30]. The cage-like structure of $B_{39}$ consists of 4 hexagons and 56 triangles with a high symmetry of $D_{5h}$. The overall shape of the $B_{39}$ 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 $B_{40}^+$ and $B_{39}$ 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 $B_6$ clusters connected by four additional boron atoms, that is, two boron atoms and one $B_3$ 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 $B_{60}$ cluster, provides convincing evidence for boron forming atom-thin nanosheets or borophenes. On the other hand, the discovery of an all-boron fullerene, $B_{28}$, 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**


