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The 2D-3D structural transition and chemical bonding in elemental boron nanoclusters

Kah Chun Lau and Ravindra Pandey[1]
Department of Physics
Michigan Technological University
Houghton, MI 49931, USA

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Abstract: The rich chemistry of boron compounds are often found dominated by its structural dimensionality and chemical bonding from which some of the qualitative features of boron clusters can easily be extracted. In this article, we review such features to discuss structural properties of B_n clusters. In both small-cluster regime of $n \leq 20$ and large-cluster regime of $n \geq 20$, the preferred topological structures are the result of the interplay between bonding factors related to the delocalized π bonds and the inter-icosahedral and intra-icosahedral bonds. The bulk fragments of boron are also expected to become a competitive isomeric configuration with the increase in the cluster-size, in contrast to 3D spherical cages observed in the large carbon clusters.

Keywords: boron clusters, boron nanostructures

1 Introduction

The rapid developments in science and technology at nanoscale starting in the last decade have encompassed multi-disciplinary areas extending through physics, biology, chemistry, and materials science with promising applications in everyday life. The primary task of both experimental and theoretical studies at nanoscale is to understand the physics and chemistry of objects of few nanometers in size (e.g. 1 - 100 nm), which can be consisted of few to thousands of atoms and may extend to the larger microscopic size before approaching the bulk matter. The physical and chemical properties of a given material at nanoscale are often peculiar, and can vary dramatically with the size. For example, carbon exhibits novel structural and electronic properties in the form of clusters [1, 2], fullerenes [3] and nanotubes [4].

In this reference, boron nanostructures have attracted the attention due to the remarkable properties of the elemental boron which is defined as 'electron-deficient' [5, 6] (i.e. the number of available valence electron is less than the available orbitals in the electronic configuration). In general, the 'electron deficient' nature does not suggest that it is inferior in bonding, but simply that novel structures based on the elemental boron are expected to be adopted. With insufficient electrons to support a structure by conventional '2-electron two-center' bonds, the boron-based compounds generally tend to adopt a novel mechanism to resolve its 'electron-deficiency' through '2-electron multi-center' bonds topologically connected in a complex networks [5, 6]. Thus, the most observed phases of boron crystalline structures have hundreds of atoms per primitive unit cell, and only the simplest elemental α-B_{12} and T_{50}, and thermodynamically stable β-B_{105} rhombohedral

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[1] Corresponding author: pandey@mtu.edu

phases are reported to have 'simpler' icosahedral-based networks [5, 7, 8, 9, 10, 11]. Similar to its complex bulk structure, a large diversities in the topological configurations of boron nanostructures [12, 13, 14, 15] was to be expected leading to a series of synthesis and characterization studies of clusters [16, 17, 18] nanowires, nanoribbons, nanowhiskers, and nanotubes [19, 20, 21]. Both experimental and theoretical studies find that the existence of nanotubes and clusters are closely related, and can be categorized as a new class of topological structure, in contrast to nanowires and nanoribbons which are more closely related to the boron solids. However, a relatively more subtle question of whether the clusters can be considered as a basic building block of nanotubes has not been fully elucidated. The correlation among the formation and size-dependent structural evolution of boron clusters together with the growth mechanism of boron nanotubes remains to be an active research area.

In this review article, we will focus on the issues related to the size-dependent structural evolution of the boron clusters (B_n, n $\leq$ 100). Specifically, we will discuss 2D-3D structural transition by giving the qualitative arguments relating the structural dimensionality to the bonding features in the boron clusters.

2 Small boron clusters(i.e., B_n, n $\leq$ 15)

The elemental boron clusters have received relatively little attention [22, 23, 24, 25, 26], as compared to its neighboring elemental clusters, such as C, Al and Si. One of the earliest experimental observation of a prominent B_{13}^{+} cluster[22] was catalyst for a number of theoretical [27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37] as well as experimental [23, 24, 25, 26] studies on small B_n (with n $\leq$ 15) clusters. It was predicted that the ground state structural configurations of small boron clusters do not resemble with the fragments of either crystalline or amorphous lattice of the boron. They were found to be planar, convex, or quasi-planar structures[32, 33, 34, 35, 36, 37]. Furthermore, instability of the B_{12} icosahedral cluster was predicted [27], though the bulk boron consists of the B_{12}-icosahedral networks. In order to have a more comprehensive understanding of the small boron clusters, recent theoretical [38, 39, 40, 41, 42, 43] and experimental studies [16, 44, 45, 46, 47, 48] have focussed on structure, bonding, electronic and vibrational properties of both neutral and ionized boron clusters. The stability of previously proposed planar, convex and quasi-planar structures of the neutral and ionized B_n clusters, with n = 3 - 15), has been verified and also confirmed experimentally by the photoelectron spectroscopy measurements. Analogous to hydrocarbons, it was also proposed that the concepts of aromaticity and anti-aromaticity (Figure1), can be applied to explain the cluster stability in conjunction with the planarity found in small boron clusters regime (B_n, where n $\leq$ 15) [46, 47, 48, 16, 49, 50]. Following the Hückel rule which defines aromaticity as $(4n+2)$ and anti-aromaticity as $(4n)$ where n is the integer which defines the number of sets of degenerate bonding orbitals in the molecular orbitals (MOs) diagram. The B_{10}, B_{11}^{-} and B_{12} clusters possessing six π-electrons are aromatic, while B_{13}^{-} and B_{14} possessing eight π-electrons are anti-aromatic. B_{15}^{-} which possess ten π-electrons, is again aromatic. [16]

The electronic structure calculations [16, 29, 30, 31, 32, 33, 34, 35, 36, 37, 42, 43, 44, 45, 46, 47, 48] in the small clusters regime have also shown that the cluster binding energy increases with the size approaching to the cohesive energy of bulk boron around 6.0 eV/atom [51]. On the other hand, the ionization-induced changes in the structural configurations of these small clusters are small. All the lowest-energy geometrical configurations of neutral, anionic and cationic clusters are usually similar, without much of the controversies. It was noticed that in spite of the preference for planarity, some of the common features in the small clusters can be extracted from their predicted stable configurations. For example, the 'electron-deficient' nature of boron is reflected in the preference of a triangular $B-B-B$ unit in these clusters beginning with the the smallest unit of B_3. The photoelectron spectroscopy measurements have also suggested the ground states of $B_6 \leq$

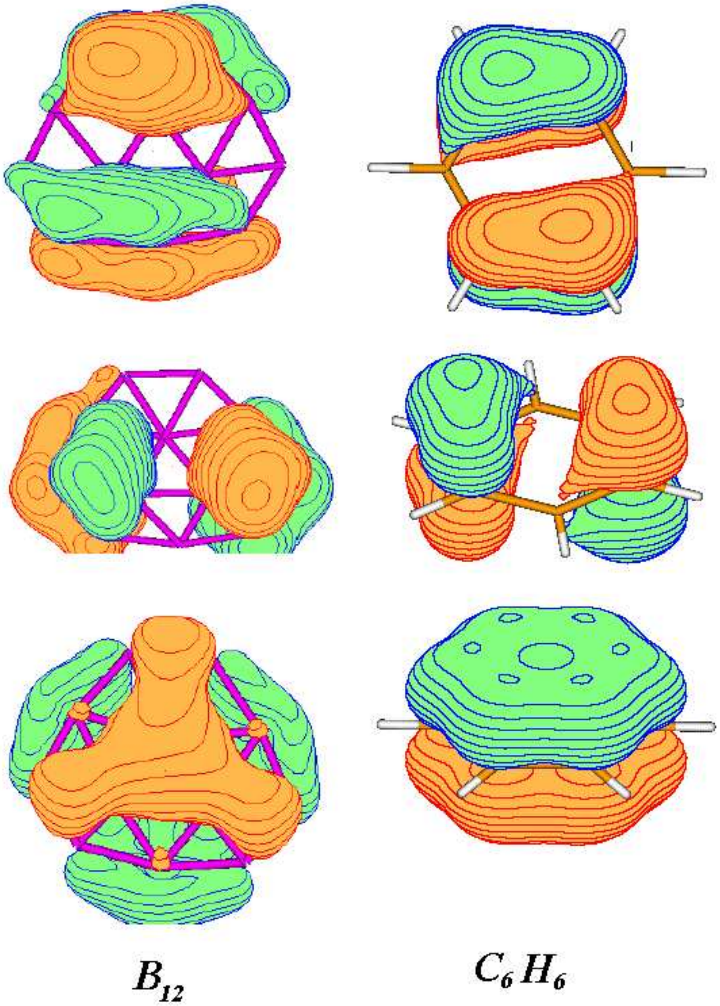

Figure 1: Selected occupied π-molecular orbitals of benzene together with those of the B_{12} cluster. [42]

$B_n \leq B_9$ to be cyclic or molecular 'wheel-like' structures [46, 47, 48]. While for $B_{10} \leq B_n \leq B_{15}$ clusters, the lowest-energy structures consist of a combination of B_6, B_7 and B_8 as the basic unit where the planarity prevails [16]. It is attributed to the effective delocalization of the π-electrons in 2D rendering aromaticity and anti-aromaticity in the clusters. The electron-deficiency of boron facilitates the multi-center bonds which effectively cause the delocalization of π and σ bonds [Figure 1] as well as saturate the dangling bonds in such 2D structures [16, 42, 43, 46, 47, 48]. Interestingly, similar arguments can also be used to explain the existence of the highly unusual coordination environments: hepta- andocta-coordinated boron atoms in the ground-state configurations of B_8 and B_9, respectively.[48] It was also suggested that these stable aromatic boron clusters can exhibit chemistry similar to the shown by benzene, such as forming sandwich-type metal compounds[48].

3 Large boron clusters(i.e., B_n, n $\geq$ 15)

In considering the large boron clusters, one can ask the obvious question whether the Hückel rules hold for the larger boron clusters leading to preferrence of the planarity in the ground state configurations. If planarity is not preferred, then one would like to determine the cluster size where the transition to 3D cages is likely to occur. However, there are relatively fewer experimental or theoretical studies have been performed in the cluster regime of (B_n, n $\geq$15). Recently, Zhai et al. have shown that the π-orbitals appear to be localized or 'fragmented' into different parts of B_{14} and B_{15} clusters. It appears that the Hückel rules which works quite well in explaining the high stability of planarity in the small clusters may not be applicable in the large clusters. The 2D-3D transition in the structural configuration is therefore expected for the cluster regime where the unsaturated dangling bonds in planarity become overwhelming.

For the large boron clusters (e.g. B_{20} [17, 52], B_{24} [18, 53], B_{32} [54], B_{60} [55] and B_{96} [56]), several distinctive shapes of configurations were considered for the electronic structure calculations, namely ring, chain, tubular, spherical cages, convex, quasiplanar, and bulk fragments as shown in Figure 2, instead of performing an exhaustive exploration of all possible isomers on the potential energy surface which is very onerous. The calculated results predict that the large clusters(i.e., B_{24} [18, 53], B_{32} [54] and B_{96} [56]) favor a tubular structure over the planar structure regardless of the charged states of the cluster [18]. Thus, the exact 2D-3D structural transition shown in Figure 3 should occur somewhere in the regime of $B_{15} < B_n < B_{24}$, and indeed the proposed range of the transition has also been suggested through the most recent experimental photoelectron spectra on B_{20} [17]. The calculated results based on density functional theory at the B3LYP/6-311+G* level found the double-ring (tubular) configuration to be the ground state for both B_{20} and B_{20}^-, but analysis of the photoelectron spectra appears to favor the planar structures. In fact, such incongruity can be explained by the difficulties associated with the experimental and computational techniques. Numerically, first principles calculations find the double-ring (tubular) and planar configurations to be degenerate (with ΔG = 0.02 eV). In the case of B_{20}^-, the four low-lying isomers are separated by less than 0.015eV/atom, which is the order of the precision of the quantum chemistry methods employed in the study [17]. On the other hand, experimentally it is known that the production of clusters is mainly controlled by kinematics, and is dependent on experimental techniques employed, as found in the case of C_{20} [57].

In this context, the carbon clusters have been reported to have a very interesting size-dependent structural evolution starting from chains to rings to fullerences [1]. However, such an evolution is not predicted for the boron clusters where a linear chain or a ring configuration is never found to be the preferred configuration. For example, the monocyclic ring configuration in B_{24} is at 1.00 eV/atom higher than the double-ring configuration [53]. In general, the double-ring configuration in B_{2n} clusters with n $\geq$ 6 is preferred in the staggered arrangements which facilitate the sp^2 hybridization, with the coordination number of four for each B atom. We note that the double-ring

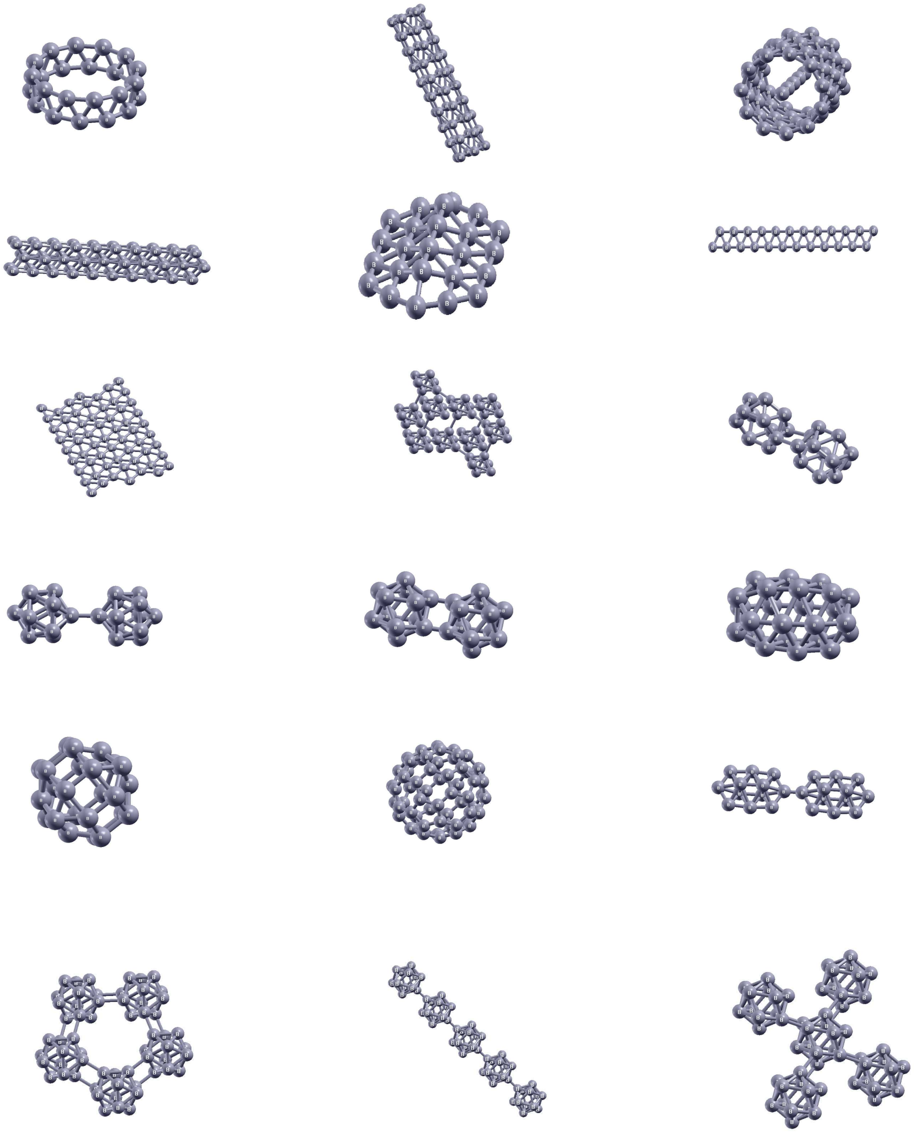

Figure 2: Several distinctive families of the possible configurations proposed in elemental boron clusters: ring, tubular, spherical cages, convex, quasiplanar, and hypothetical boron bulk fragments.

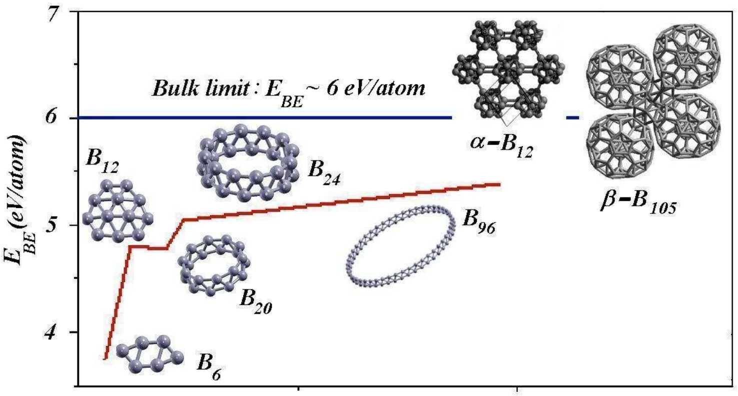

Figure 3: Size-dependent 2D planar to 3D tubular structure transition in elemental boron clusters

without the staggered configuration, and with the coordination number of three for each B atom found to be less stable [18, 42, 55]. Though both carbon and boron clusters are found to exhibit the 2D-3D structural transition around a 20-atom cluster [17, 57], dissimilar bonding character determine the composition of the 3D configuration. The boron clusters prefer the 3D configuration to be a double-ring (tubular), while the carbon clusters prefer it to be a cage-like configuration. We therefore believe that the stable cage structures, similar to those of C_{20}, C_{32} and C_{36} [1, 2, 58], are not likely to be found for the large boron clusters. Figure 4 shows the size-dependent stability of the 3D configuration relative to the 2D configuration in terms of ΔE_{BE} defined as E_{BE}*(3D)* - E_{BE}*(2D)*. In the small cluster regime (e.g. B_{12}) where the 2D planarity is preferred, ΔE_{BE} is -0.19eV/atom [42]. When we double the cluster-size to B_{24}, the 3D double-ring configuration gains about 0.26 eV/atom in energy yielding ΔE_{BE} to be 0.07 eV/atom [18]. A similar trend can also be seen in the large clusters regime for B_{32}, B_{60} and B_{96} clusters [54, 55, 56]. As also mentioned in the previous section, the emergence of preference over 2D planarity boron clusters can be comprehended as a consequence of effective charge delocalization from Hückel Rules. Thus, the trend in the stability of the 2D Vs. 3D configurations defined in ΔE_{BE} as shown in Figure 4, can be explained in terms of a competition between the curvature strain (favoring 2D planarity) and elimination of dangling bonds(favoring 3D staggard double-ring) [18, 54].

Figure 5 shows the molecular orbitals (MOs) of the ground state of B_{24} where the notation HOMO-n is used to represent the selected occupied molecular orbitals in these clusters. Analysis of MOs reveals the interesting features of delocalized π, σ, and multi-centered σ bonds between the boron atoms. The highest occupied molecular orbital (HOMO) shows the π bond between the atoms of each ring, while the lowest unoccupied molecular orbital (LUMO) shows a lateral $p-p$ overlap between the atoms of both rings. The HOMO and (HOMO-1) are doubly-degenerate giving rise to an effective delocalization. While the (HOMO-2) and (HOMO-3) orbitals show localized π-bonding in B_1 state, the (HOMO-6) and(HOMO-7) degenerate orbitals show a delocalized π-bonding at both sides of the rings in E state. Besides finding the similar bonding features as benzene in small 2D clusters (Figure 1), a similar feature of fully delocalized benzene-like π bonds between the two staggered rings is achieved in A_1 state of (HOMO-8) orbital.

On the other hand, analysis of MOs of the 2D elongated quasi-planar reveals that the delocalized π bonds between boron atoms appear to be 'fragmented' into different parts of the cluster configuration. Instead of dominant features of delocalized π MOs found in small boron clusters

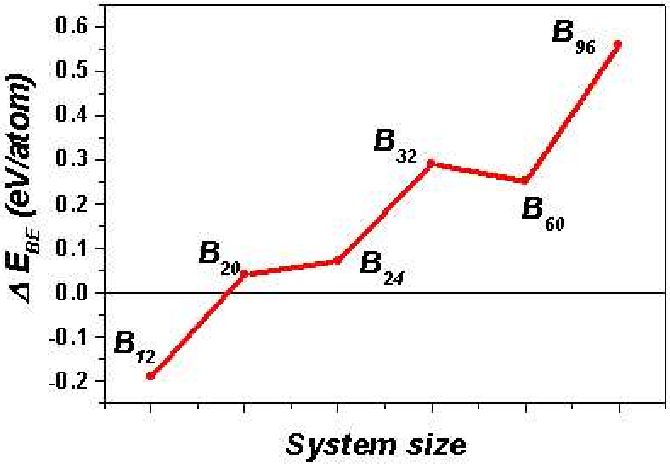

Figure 4: The size dependence of the relative stability of boron clusters (e.g. 2D planarity Vs. 3D double-ring (tubular)). The ΔE_{BE} is defined as E_{BE}*(3D)* - E_{BE}*(2D)*. The respective values of the energy are taken from the references [17, 18, 42, 54, 55, 56]

[16, 42, 46, 47, 48], the 2D planar isomer is mainly associated with the more 'localized' orbitals in this larger cluster regime. Therefore, we may conclude that the absence of delocalized π MOs in the 2D planar configuration in B_{24}, makes the corresponding structure energetically less favorable, due to an increase in the unsaturated dangling bonds with the increase of the size of the cluster. In this conjunction, the presence of delocalized π and multi-centered σ bonds in the double-ring (tubular) structure (e.g. B_{24}), plays a key role in stabilizing this structure, by overcoming the strain energy (or curvature energy) acted on the system.

For the B_n (i.e. $n \geq 30$) clusters, the experimental studies are not available and first principles calculations are rather limited. The reported Hartree-Fock calculations which used the standard STO-3G basis set together with the symmetry-constrained optimization predicted the low-lying stable structures to be quasi-planar and tubular configurations. [54, 56, 59] In the case of B_{32}, the double-ring (tubular) isomer in D_4 symmetry with a diameter of 8.1 $\AA$ is predicted to be more stable than C_{2h} quasi-planar and D_{4h} spherical cage by 0.29 and 0.36 eV/atom, respectively. The preferred topological structure of the B_{32} cluster suggested that the interplay between curvature-strain and elimination of dangling bonds determine the stability among these 2D and 3D configurations. A similarly argument can be applied to tubular and quasi-planar configurations of B_{96}. The Hartree-Fock calculations [56] reported that the segments of tubular and quasi-planar sheet turn out to be more stable than the unit cells of α-boron. In B_{60}, density functional theory calculations using the standard STO-3G basis set predict the C_{60}-like spherical cage to be about 1.0 eV/atom less stable in energy relative to the tubular structure of diameter of about 1.53 nm. Similarly, the C_{5v} boron bulk fragment (Figure 2) and the 2D convex (in C_2 symmetry) configurations are at 0.67 and 0.23 eV/atom relative to the tubular isomer.

On the other hand, the bulk fragment (i.e.α-boron unit-cell cluster) of B_{96} is almost degenerate with the 2D quasi-planar sheet, though the tubular isomer with a diameter of 2.35 nm is predicted to be the ground state. Thus, it is noteworthy to point that the bulk fragments of boron can become a competitive isomeric configuration with the increase in the cluster-size, instead of 3D spherical cages observed in carbon clusters. We believe that as the delocalized π MOs which are

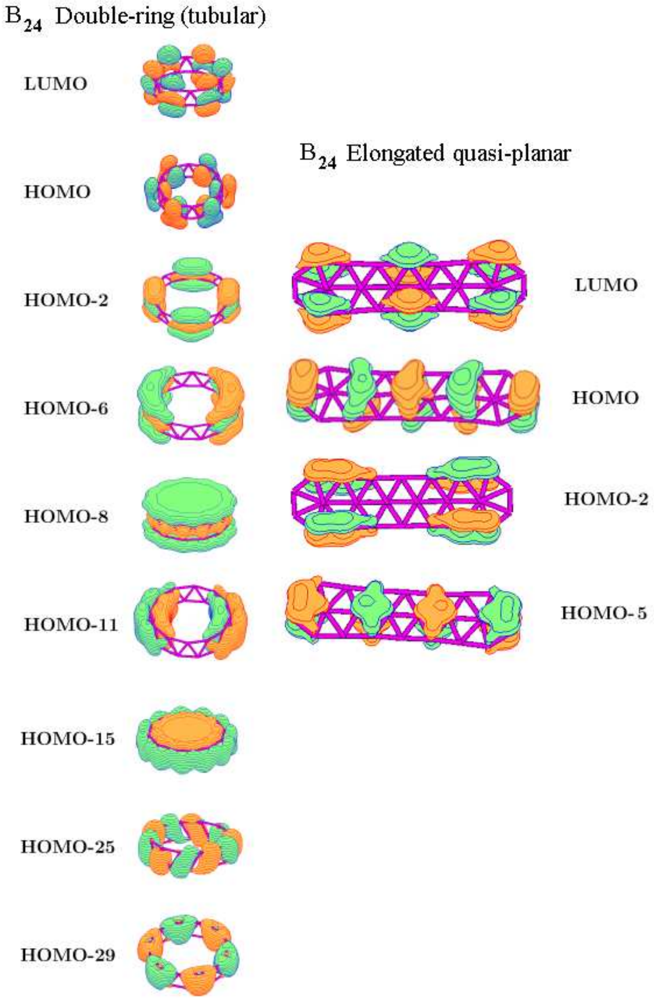

Figure 5: Selected molecular orbitals of the double-ring configuration and 2D elongated quasi-planar configuration of B_{24}. [18]

responsible in eliminating the dangling bonds of the 2D planar boron clusters, expected to be more 'fragment' and 'localized' in different parts of the clusters in the so-called boron supercluster regime, making the 2D planarity less favorable in this regime. The emergence of all possible boron bulk fragments based on the B_{12} icosahedral networks, thus cannot be ignored as a probable competitive isomer for large boron clusters. We may therefore conclude that the key role in determining the structural configuration is played by the delocalized π bonds in the small cluster regime, while the inter-icosahedral and intra-icosahedral bonds which coincide with the possible interlink of B_{12} icosahedrons begin to participate in determining the configurations in the large cluster regime of the elemental boron.

4 Summary

The research activities related to elemental boron clusters are comparatively younger than that related to carbon clusters. In this review article, we have presented an overview of the physical and chemical properties of elemental boron clusters, showing the interplay of structural dimensionality and chemical bonding as important factors in building up the structures that were synthesized in experiments or predicted in theoretical studies. The high stability of 2D planarity and aromaticity is anticipated in small clusters regime (e.g. $B_n \leq B_{15}$) suggesting their promising potential applications as a new 'sandwich-type' functional boron nanostructures which are doped with metallic atoms. Besides their potential applications in nanoelectronics, the proposed size-dependent 2D planar to 3D tubular transition beyond B_{20} regime can be regarded as a very promising evidence for the existence of a new 'homo-nuclear' boron nanotubes, which can be used as ultra-light radioactive detectors and neutron capture therapy nanodevices by enriching them with B^{10} isotope, which has a large cross section area for thermal neutron capture.

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