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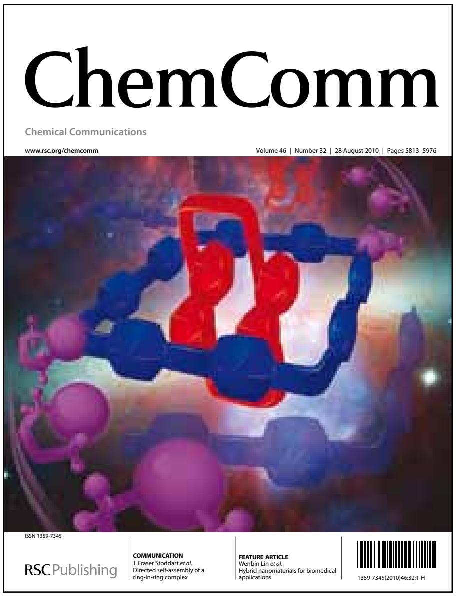

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COMMUNICATION

A Disk-Aromatic Bowl Cluster B_{30}: Toward Formation of Boron Buckyballs

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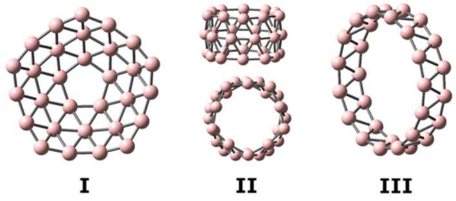
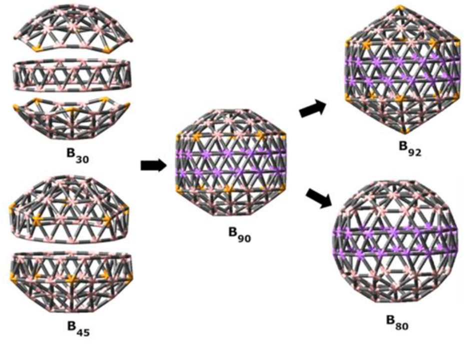
The B_{30} boron cluster has a bowl structure, rather than double-ring or triple-ring tubular structure. This bowl isomer exhibits disk-aromaticity similar to that found for B_{20}^{2-} and B_{19}^{-} clusters. We confirmed that the concept of disk-aromaticity can be applied for both planar and non-planar systems.

Over the past decade, boron clusters have been of great interest owing to their conundrum, intriguing geometrical characteristics and aromaticity.[1-12] Boron is a rare element whose atomic clusters B_n retain either planar or quasi-planar geometries as the size goes beyond 20 atoms. Combined theoretical and experimental studies showed that anionic boron clusters B_n^- with n up to 24 have either planar or quasi-planar structures.[3] The neutral and cationic boron clusters adopt three-dimensional structures at smaller sizes.[3,4,7,10,11] The B_{20} cluster was theoretically found to have double-ring form in which the two ten-membered rings are connected together in antiprism bonding motif,[4] whereas most smaller species are planar.[1-3,7-9] In addition, theory previously predicted that the clusters B_{22}, B_{24}, B_{32} and B_{36} also have double-ring geometries which contain two 11-, 12-, 16- and 18-membered rings, respectively.[1] These observations result in a popular thinking that intermediate-sized boron clusters B_n with $n \geq 20$ exhibit similar tubular geometries. Nevertheless, while experimental infrared (IR) spectroscopic studies recently confirmed the planar geometries of B_{11}, B_{16} and B_{17}, there is no good agreement between theoretical and experimental spectra for B_{20}.[5] Although a satisfactory explanation for such a discrepancy is still lacking, it casts a certain doubt about the double-ring characteristic of these intermediate-sized boron clusters and therefore motivates us to investigate further their structures.

In this context, we performed a careful search for low-lying isomers of B_{30} whose size is located just before the double-ring B_{32}. We found that the B_{30} cluster prefers a bowl-shaped structure **I** as a convex cluster rather than a double-ring tubular shape **III** like B_{32}. More interestingly, this bowl species contains a disk-aromatic character similar to those found for B_{19}^- and B_{20}^{2-}, and this is the main reason for high stability of **I**. Our findings not only give new insights into the bonding motif and aromaticity of boron clusters, but also suggest a new pattern for formation of fullerene-like boron buckyballs such as B_{80} and B_{92}.



a) Shapes of the lowest-lying isomers of B_{30}



b) Route for formation of B_{80} and B_{92}

Fig. 1 a) Shape of the lowest-lying isomers of B_{30} and b) Route for formation buckyballl B_{80} and B_{92} from B_{30}. Orange colored points are atoms located at the centres of five-membered rings

The unbiased search for possible B_{30} structures was performed using a stochastic search method that was recent developed by us.[13] The local minima with relative energies of 0.0 - 5.0 eV were further optimized using several density functionals, such as the TPSSh, PBE, PBE0 and PW91, with the 6-311+G(d) basis set. Recent studies showed that functionals such as TPSSh, PBE, PBE0 can reasonably provide the relative energies of the isomers of boron clusters and are comparable to those obtained by CCSD(T) calculations.[7e,14] Finally, the calculations of electronic single point energies for three lowest-lying isomers of the B_{30} cluster are performed at the CCSD(T)/6-311G(d) level of theory with the PBE/6-311+G(d) geometries. Our computed results at the CCSD(T)/6-311G(d) revealed that while double-ring tubular isomer **III** (C_i, ^1A_g) (Fig. 1a) is less stable with relative energy of 18.7 kcal/mol, a triple-ring tubular isomer **II** (D_{5d}, $^1A_{1g}$) in which three ten-membered rings are connected together in an antiprism bonding motif, is the second lowest-lying isomer. More interestingly, the global minimum of B_{30} is calculated to be a bowl-shaped structure **I** (C_{5v}, $^1A_1$), which is 13.3 kcal/mol more stable than **II**.

The bowl **I** is composed of an inner five-membered ring, surrounded by two larger ten- and fifteen-memebred rings (Fig. 1). The HOMO-LUMO gap of **I** is equal to 2.2 eV and much larger as compared to the values of 1.3 eV for **II** and 0.2 eV for **III**. The PBE cohesive energy (E_c) of **I** amounts to 5.499 eV/atom and is close to the value of 5.640 eV/atom of the buckyball B_{80}.[15] While the isomer **II** has relatively high E_c value of 5.485 eV/atom, that of isomer **III** is lower (E_c(**III**) = 5.461 eV/atom).

Since the neutral B_n with n = 20-24, 32 and 36 were reported to feature double-ring tubular structures, the present prediction marks a breakthrough in bonding motif and structural characteristics of boron clusters. Moreover, the existence of a bowl B_{30} cluster suggests a more consistent pattern for formation of the buckyball B_{80} which is still not well understood.

Although experimental results are yet to come, the buckyball B_{80} and its derivatives have attracted much attention.[15-17] With the high stability of the bowl B_{30}, formation of B_{80} becomes straightforward. As seen in Fig. 1b, B_{80} can effectively be formed from B_{30} units. Connection of two bowl B_{30} species to two up and down sides of double-ring B_{30} species, followed by removal of ten B-atoms from the centres of 10 five-membered rings (orange colored atoms, Figure 1b), will form a buckyball B_{80}. Additionally, a fullerene-like structure B_{92} will be formed as two excess B-atoms are added into the remaining holes of two five-membered rings. However, the latter species was theoretically reported to less stable, and its cohesive energy is smaller than that of B_{80}.[15]

In the same vein, another bowl structure is also located as a stable local minimum on potential energy surface of B_{45}. The bowl B_{45} cluster has a cohesive energy of 5.513 eV/atom, which is consistently higher than that of 5.499 eV/atom of the bowl B_{30} **I** mentioned above. It is worthy to note that a similar structure was found for B_{46} by Boustani.[2] Further study is necessary to confirm as to whether it is the B_{45} global minimum, but the presence of this stable bowl provides us with further evidence for high stability of B_{80}. It also suggests a route for formation of boron fullerenes: $B_{30} \rightarrow B_{45} \rightarrow B_{90} \rightarrow B_{80}$ and/or B_{92}.

Aromaticity is another consistent characteristic of boron clusters and was extensively discussed in the literature. While there is now a consensus in the evaluation of aromaticity of small boron clusters B_n, the aromaticity of larger clusters remains a challenging issue.[3,4,6-9] For instance, B_{19}^- and B_{20}^{2-} are indentified as aromatic species which have negative NICS values. However, each contains 12 valence π-electrons which does not obey the classical Hückel rule of $(4N + 2)$ electrons. To address this contradiction, we recently proposed the concept of *disk-aromaticity* on the basis of a simple model of a particle in a circular box.[6] Within its framework, a free particle is moved on a plane encircled by infinite walls. The radius of the disk is denoted by r = R. In polar coordinates, the Schrödinger equation for this problem is written as follows:

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right)\Psi(\varphi,r)=E\Psi(\varphi,r)\quad(1)$$

where $\hbar$ is Plank constant and μ is mass of particle. Because of the circular symmetry, the can be written as $R(r).\Phi(\varphi)$, with $\Phi(\varphi) = \exp(im\varphi)/(2\pi)^{1/2}$.

The cyclic boundary condition requires the angular part to be periodic. As a result, the cylindrical quantum number must be integer: $m = 0, \pm 1, \pm 2$... Substitution into the Schrödinger equation gives us the radial part:

$$\frac{\partial^2 R(r)}{\partial r^2}+\frac{1}{r}\frac{\partial R(r)}{\partial r}+\left(k^2-\frac{m^2}{r^2}\right)R(r)=0\quad(2)$$

with $\hbar^2k^2 = 2\mu E$. This equation is known as the Bessel's differential equation, and its solutions are the integer Bessel functions $J_m(kr)$.[18] The potential wall at $r = R$ requires the radial function to vanish at the boundary of the box: $J_m(kR) = 0$. The radii that correspond to the zeroes of the Bessel function are denoted as $a_{m,n}$. Here n is a radial quantum number that counts the zeroes. The $a_{m,n}$ quantities are dimensionless. They give rise to a quantisation of the energy as:

$$E=\frac{\hbar^2\left(a_{m,n}\right)^2}{2\mu R^2}\ with\!: n=1,2,3,\ldots m=0,\pm1,\pm2,\pm3\quad(3)$$

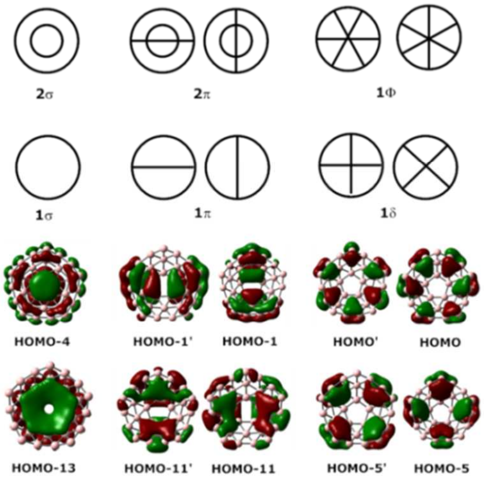


Fig. 2 Shapes of π-MOs of bowl B_{30} cluster and the lowest-lying wavefunctions for a particle in a circular box

The rotational quantum numbers are usually denoted by Greek letters as $m = \sigma, \pi, \delta, \square, \gamma\ldots$ States with non-zero values for m will be twofold degenerate. The lowest eigenstates in ascending order are 1σ, 1π, 1δ, 2σ etc… (Fig. 2). We consider that the systems containing the number of 2, 6, 10, 12, 16, 20… electrons which fully occupy degenerate eigenstates of model will exhibit a disk-aromaticity. Oppositely, the systems containing a number of 4, 8, 14, 18… electrons which only singly occupy one of two highest degenerate eigenstates will be disk-antiaromatic. This concept rationalizes the intriguing aromaticity of B_{19}^- and B_{20}^{2-}, in consistence with other indexes such as magnetic ring current, nuclear independent chemical shift (NICS) calculations and ipsocentric model. We expect that this concept can be applied to related systems such as the bowl B_{30} cluster, even though they are not strictly planar.

Shapes of selected molecular orbitals (MOs) in Fig. 2 reveal that **I** contains 20 valence π-electrons that fully occupy the orbitals HOMO, HOMO-1, HOMO-4, HOMO-5, HOMO-11 and HOMO-13. Based on the Hückel's rule, this species must be antiaromatic (4*N* electrons, *N* = 5). However, based on model of a particle in circular box, the isomer **I** is a disk-aromatic system whose valence π-electrons fully occupy the lowest eigenstates in ascending order of $(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2(2\pi)^4(1\square)^4$. These predictions agree with NICS calculations.[19] $NICS_{zz}$ values calculated at various positions (see ESI) show that **I** and **II** are highly aromatic species with large negative $NICS_{zz}$ values ($NICS_{zz}(1)$ (**I**) = -57.8 to - 71.1 and $NICS_{zz}(1)$ (**II**) = -4.1 to -29.8). On the contrary, the double-ring tubular structure **III** is antiaromatic with highly positive $NICS_{zz}$ values. The aromatic character of isomers **I** and **II** is presumably the main reason for their high stability, whereas the double-ring **III** becomes less stable due to its antiaromatic character.

Moreover, it is worthy to note that there is concurrence in the numbers of electrons (x) between the Hückel (4*N*+2) electrons and the model of a particle in a circular box as $x \leq 10$. The classical Hückel's rule is mostly effective for monocyclic compounds with a limited number (x) of valence π-electrons. A monocyclic compound with $x > 10$ is not observed yet. Thus, the proposed model of disk-aromaticity is promising in evaluation of aromaticity as it can be applied for both small monocyclic and larger polycyclic systems, irrespective of their planarity. Similar conclusions are also found when the ipsocentric model[20] is applied. As shown in the ESI, both isomers **I** and **II** are aromatic, whereas isomer **III** is antiaromatic in radial stack, but aromatic in tangential stack system.

Conclusions

In conclusion, we found that the B_{30} boron cluster has a bowl-shaped structure **I**, rather than double-ring or triple-ring tubular structures as previously suggested. This bowl isomer **I** exhibits disk-aromaticity similar to that found for B_{20}^{2-} and B_{19}^{-} clusters. These findings not only mark an important breakthrough in the understanding of bonding motif and structural characteristics of intermediate-sized boron clusters, but they also suggest a consistent route for formation of boron buckyballs such as B_{80} and B_{92}, that arise from multiple B_{30} units. Further investigations need to be performed to determine the energy barriers on the formation pathways of these buckyballs, and thereby to obtain more realistic molecular mechanisms. We also confirmed that the concept of disk-aromaticity can be applied to non-planar boron clusters. Following studies are highly desirable to apply this concept to other polycyclic compounds, and in particular to different classes of atomic clusters.

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Notes and references

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Electronic Supplementary Information (ESI) available: Computational methods; Shapes of selected MOs and shapes and relative energies of the low-lying isomers of B_{30} at the TPSSh/6-311+G(d) level**.** See DOI: 10.1039/c000000x/

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