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Aromatic Cages $B_{42}^{0/+}$: Unprecedented Existence of Octagonal Holes in Boron Clusters

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The cage-like structures containing octagonal holes are located as the lowest-lying isomers for the $B_{42}^{0/+}$. The presence of octagonal holes which are found for the first time, not only gives us new insight into the bonding motif, but also marks a breakthrough in structural characteristics of boron clusters since they are never expected to be stable units for elemental clusters. These cages are composed of both declocalized σ and π electron systems, that consequently make them aromatic and thermodynamically stable.

Boron clusters have emerged as hot topic in the science of atomic clusters over the past decades in part due to their unique properties. Possessing deficient electron configuration of ($1s^2 2s^2 2p^1$), boron atoms can aggregate to form atomic clusters B_n with a wide range of geometrical structures, including quasi-planar and planar structures, bowled shapes, and tubular forms containing two or three *N*-membered rings which are connected together in antiprism bonding motif.[1,2,3.4,5] These species have attracted much attention of scientists by their interesting structural, aromatic characters and bonding characteristics.[6,7]

More recently, the discovery of cage-like structures B_n is remarkably intriguing, and stimulates further investigations on these systems.[8,9] Theoretical investigations showed that the neutral B_{40} is an all-boron fullerene containing two six-membered rings and four seven-membered rings.[10] Based on dynamical behaviours obtained from BO-MD simulations, Merino et al.[11] showed that there is a continuous transformation between the seven-membered and six-membered rings for the caged structure B_{40} at 200K and 1500K. Although being somewhat less stable than quasi-planar form, the cage-like structure B_{40}^- was observed in the photoelectron spectroscopic (PES) experiment by Wang and workers.[10b] Subsequently, the clusters B_{38}, B_{39}^-, B_{41}^+ and B_{42}^{2+} were also found to be all-boron cages with similar geometrical characteristics that are composed of the hexagonal and heptagonal rings.[12]

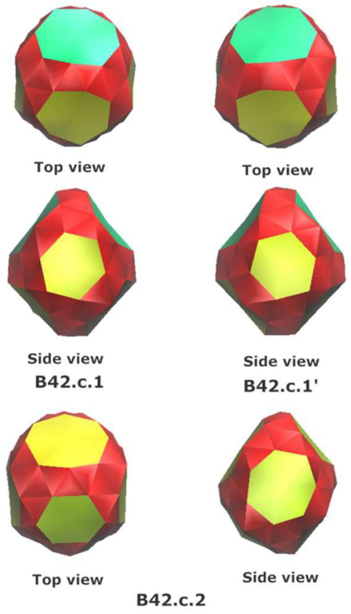

Fig. 1 Shapes of the lowest-lying isomers **B42.c.1** (enantiomer **B42.c.1'**) and **B42.c.2**

In recent report based on DFT results, Pham *et al.*[10a] showed that the neutral B_{42} is a tubular triple ring in which three fourteen-membered rings are connected together. The existence of such a tubular form as the most stable isomer for B_{42} is questionable but intriguing, since its dicationic species and a series of smaller clusters possess cage-like structures. Motivated by these reasons, we re-examined the structural characteristics of the neutral B_{42} and its cationic species by using both density functional theory (DFT) and coupled-cluster theory CCSD(T) methods.

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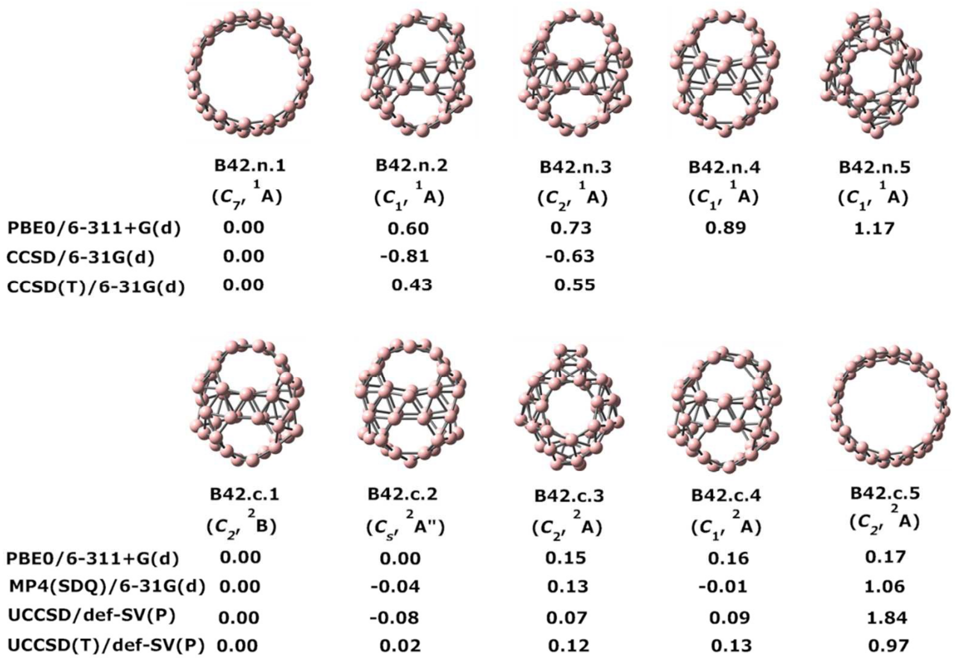

	B42.n.1 (C_7, ^{1}A)	B42.n.2 (C_1, ^{1}A)	B42.n.3 (C_2, ^{1}A)	B42.n.4 (C_1, ^{1}A)	B42.n.5 (C_1, ^{1}A)
PBE0/6-311+G(d)	0.00	0.60	0.73	0.89	1.17
CCSD/6-31G(d)	0.00	-0.81	-0.63		
CCSD(T)/6-31G(d)	0.00	0.43	0.55		

	B42.c.1 (C_2, ^{2}B)	B42.c.2 (C_s, ^{2}A")	B42.c.3 (C_2, ^{2}A)	B42.c.4 (C_1, ^{2}A)	B42.c.5 (C_2, ^{2}A)
PBE0/6-311+G(d)	0.00	0.00	0.15	0.16	0.17
MP4(SDQ)/6-31G(d)	0.00	-0.04	0.13	-0.01	1.06
UCCSD/def-SV(P)	0.00	-0.08	0.07	0.09	1.84
UCCSD(T)/def-SV(P)	0.00	0.02	0.12	0.13	0.97

Fig. 2 Shapes, point groups and relative energies (eV) of the low-lying isomers for neutral B_{42} (up) and cation B_{42}^+ (down)

Interestingly, we found that asymmetrical (or chiral) cage-like structures which contain octagonal (eight-membered) holes are located among the energetically lowest-lying isomers for both neutral and cationic species $B_{42}^{0/+}$ (Fig. 1). While the neutral B_{42} prefers the tubular form as previously reported,[10a] the cation B_{42}^+ favours cage-like structures. Two lowest-lying isomers **B42.c.1** and **B42.c.2** are degenerate in energy at the CCSD(T)/def-SV(P) level of theory (Fig. 1). These findings not only give us more insight into the bonding motif of boron clusters, but also mark a breakthrough in their structural characteristics, since the octagonal hole has not been expected yet to be a stable unit in the construction pattern of boron clusters.

Extensive structural searches were carried out by using stochastic random search procedures,[13] and manual structural construction based on the known structures of smaller sized boron clusters. Low-lying isomers of the $B_{42}^{0/+}$ with relative energies of 0.0 - 5.0 eV obtained from initial geometry optimizations at the PBE0/3-21G level were fully optimized at higher level of theory PBE0/6-311+G(d).[14] To identify a true global minimum, single-point electronic energies of a few lowest-lying $B_{42}^{0/+}$ isomers were calculated using the CCSD(T)/6-31G(d)[15] for the neutral B_{42} and UCCSD(T)/def-SV(P) for the cations B_{42}^+ at their PBE0/6-311+G(d) optimized geometries. These computational methods were effectively used to establish the energy landscape of boron clusters in the literature. All calculations were performed using the Gaussian 09,[16] Molpro 2012[17] and Turbomole 7.0 packages.[18]

At the PBE0/6-311+G(d) level, our calculations agreed with the previous report[10a] that the tubular form **B42.n.1** is the most stable isomer for the neutral B_{42}. The isomers **B42.n.2** and **B42.n.3** are the next isomers with relative energies of 0.60 and 0.73 eV, respectively (as compared to **B42.n.1**). Although the cage-like structures **B42.n.2** and **B42.n.3** become more stable at the CCSD/6-31G(d), the tubular form **B42.n.1** is indicated as the global minimum of the B_{42} with smaller energy gap at the higher level CCSD(T)/6-31G(d). The T1 diagnostics from CCSD calculations showed that the species have negligible multireference characteristics. The T1 diagnostics of species vary in range of 0.015 ÷ 0.028 which are comparable to the value of 0.02, as suggested by Lee and Taylor.[19] In agreement with earlier reports,[11b-d,20] while the PBE0 functional tends to favour planar and tubular forms, the CCSD method gives preference to caged structures as compared to CCSD(T) computed results.

At the cationic state, our computed results at several different computational methods point out that both cage-like structures **B42.c.1** and **B42.c.2** are degenerate in energy, and turn out to be the most stable isomers for the cation B_{42}^+. The

B42.c.1 (and its enantiomer) which is the cationic species of the **B42.n.3** can be constructed by replacing two neighboured heptagonal rings of the B_{40} by two octagonal rings. Similarly, **B42.c.2** which is the cationic form of the neutral **B42.n.4** can be constructed by replacing two neighboured heptagonal rings of the B_{40} by one hexagonal ring and one octagonal ring. A common geometrical feature of these caged structures is that they contain remarkable octagonal holes that have never been observed before for elemental clusters.

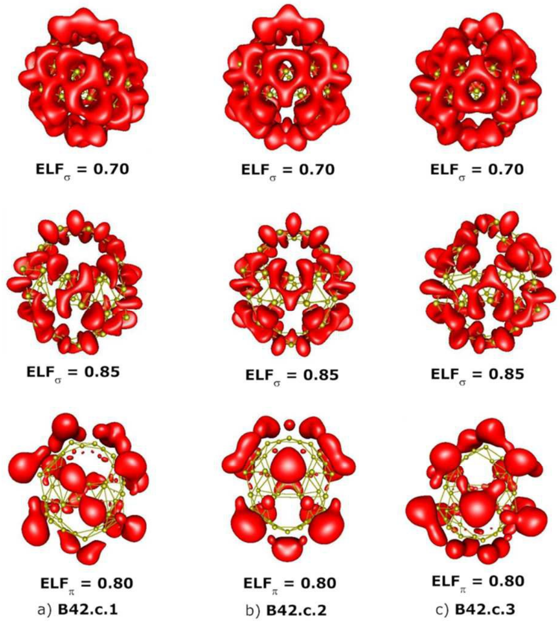

Fig.3 Plots of ELF$_\sigma$ (up and middle) and ELF$_\pi$ (down) of a) **B42.c.1**, b) **B42.c.2** and c) **B42.c.3**

The next isomers of the B_{42}^+ cation continue to have cage-like structures **B42.c.3** and **B42.c.4**, while the tubular form **B42.c.5** is 0.97 eV less stable than the **B42.c.1** at the UCCSD(T)/def-SV(P) level. We would like to note that the dication B_{42}^{2+} was reported to have a geometrical structure similar to that of **B42.c.3** which is composed of six heptagonal rings.[12d] The **B42.c.4** is only a distorted form of the **B42.c.1**.

The characteristics of chemical bonding and aromaticity of boron clusters have attracted much attention from the viewpoint of theory. Based on the topological analysis of electron localization function (ELF), canonical molecular orbital (CMO) and nucleus independent chemical shift (NICS) calculations, it was reported that most small boron clusters with planar and quasi-planar geometrical structures were singly and doubly aromatic systems.2′3′7 Some larger clusters B_n which have tubular and bowled structures were found to exhibit more particular feature of disk-aromaticity.[10a,21] The cage-like structures B_n with n = 38 - 42 at different charge states showed features of high aromaticity with two delocalized σ and π electron systems.[10b,12c-d] Recently, on the basis of the analysis of electron localizability indicator (ELI-D) and magnetic ring current, Nguyen and coworkers[10a] showed that the triple ring B_{42} is a tubular aromatic system. To probe more insight into the high stability of the cages **B42.c.1** – **B42.c.3**, their bonding patterns are examined by using the topological analysis of the electron localization function (ELF).[22] The total ELF maps can then be partitioned in terms of separate ELF$_\sigma$ and ELF$_\pi$ components that arise from the contributions of σ and π electrons, respectively. The latter can be used as useful indices describing the aromaticity of cyclic molecules[23] and boron clusters.3′7′[24] Accordingly, a π aromatic species possesses a high bifurcation value of ELF$_\pi$, whereas the corresponding bifurcation value in an anti-aromatic system is low.[23] The ELF analysis was carried out by using the Dgrid-4.6 package.[25]

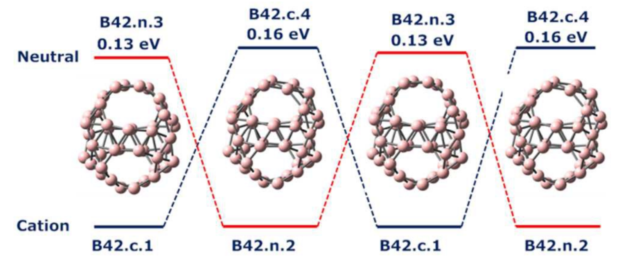

Fig. 4 Transformation in connectivity patterns between **B42.n.2** and **B42.n.3** (red line) and between **B42.c.1** and **B42.c.4** (black line)

The pictures of canonical molecular orbitals (CMOs) of three isomers **B42.c.1** – **B42.c.3** are similar in which each species contains 63 valence molecular orbitals (MOs) that are separated into 13 π-MOs and 50 σ-MOs. The ELF plots depicted in Fig. 3 show that there are excellent electron delocalization for both σ and π electron systems of each species. At the value of ELF$_\sigma$ = 0.85, the isosurface of the ELF$_\sigma$ are separated into 50 basins that contribute to chemical bonding of 50 triangular units of each system. Similar observations are found for the π-electron systems. At the ELFL$_\pi$ = 0.80, the isosurface of ELF$_\pi$ are separated and delocalized over each system. Overall, these electron distributions form two highly delocalized σ and π bonding systems, and consequently make the cages **B42.c.1** – **B42.c.3** aromatic and have thereby high thermodynamic stability. In addition, the high bifurcation values for ELF$_\pi$ and ELF$_\sigma$ indicate that these isomers exhibit highly aromatic features. Our NICS calculations at the central positions of the cages **B42.c.1** – **B42.c.3** consistently show that they in fact exhibit aromatic features with highly negative NICS values (NICS-**B42.c.1** = -33 ppm, NICS-**B42.c.2** = -29 ppm, NICS-**B42.c.3** = -28 ppm).

To gain more understanding about the thermodynamic stability of the isomers $B_{42}^{0/+}$, we perform molecular dynamic (MD) simulations for the lowest-lying isomers by using the CP2K programs.[26] The simulations are carried out at temperatures of 500K during a time of 30 ps. The PBE functional is used in conjunction with the 6-31G(d) basis set. The RMSD values are calculated using VMD code[27] and their plots are depicted in Figure S3 of the Supplementary information file (SI), together with the movies of simulation trajectories at 500 K (SI). During the BO-MD simulations at 500K, the global minimum **B42.n.1** retains its connectivity pattern with three fourteen-membered rings. Similar observation is found for the isomer **B42.c.2** whose bonding pattern including one hexagonal, four heptagonal and one octagonal rings is maintained.

Interestingly, there is a continuous transformation in connectivity pattern between **B42.c.1** and **B42.c.4** in which one octagonal ring of the **B42.c.1** is distorted to form the **B42.c.4** with an energy gap of 0.13 eV (Fig. 4). Similar observation is found for the neutral species **B42.n.2** and **B42.n.3** but with an inverted energy ordering. The isomer **B42.n.3** containing two octagonal rings is 0.12 eV less stable than the **B42.n.2** at the CCSD(T)/6-31G(d) level of theory. Although the **B42.c.3** is a local energy minimum, it is not thermodynamically stable. At the temperature of 500K, the bonding pattern of the **B42.c.3** is completely broken after hundred femtoseconds.

Conclusions

In this theoretical study, we found that the cage-like structures containing octagonal holes are located as the lowest-lying isomers for $B_{42}^{0/+}$. The presence of eight-membered rings which are discovered for the first time, not only gives more insight into the bonding motif, but also marks a breakthrough in structural characteristics of boron clusters since they have never been expected before to be stable building units.

In addition, the caged structures **B42.c.1** – **B42.c.3** are composed of two delocalized σ and π electron systems that consequently confer them a doubly aromatic character.

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Table of contents entry

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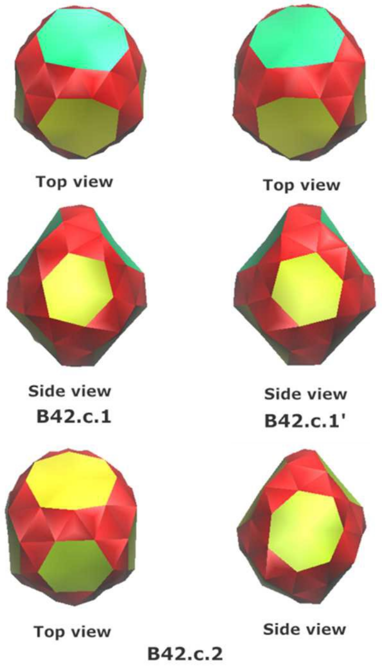

The cluster B_{42}^{+} exhibits an aromatic cage-like structure containing remarkable octagonal holes