



Bilayer B₅₄, B₆₀, and B₆₂ Clusters in a Universal Structural Pattern

Ling Pei,^[a,b] Yuan-Yuan Ma,^[a] Miao Yan,^[a] Min Zhang,^[a] Rui-Nan Yuan,^[a] Qiang Chen,^[a] Wen-Yan Zan,^[a] Yue-Wen Mu^{*[a]} and Si-Dian Li^{*[a]}

Abstract: Boron nanoclusters and few-layer borophenes have received considerable attention in recent years due to their unique structural and bonding patterns. Based on extensive global searches and density-functional theory calculations, we present herein the possibility of a new series of bilayer medium-sized boron clusters including $C_2 B_{54}$ (I), $C_{2h} B_{60}$ (II), and $C_1 B_{62}$ (III) in a universal structural pattern, with one, two, and three B_6 hexagonal windows on the waist around a B_{38} bilayer hexagonal prism at the center, respectively. Detailed orbital and bonding pattern, with three or four effective interlayer B-B σ -bonds formed to further stabilize the system. The IR, Raman, and UV-vis spectra of the bilayer species are theoretically simulated to facilitate their future spectral characterizations.

[a] Institute of Molecular Science, Shanxi University, Taiyuan 030006, China. E-mails: ywmu@sxu.edu.cn, lisidian@sxu.edu.cn
 [b] Department of Chemical Engineering and Safety, Binzhou University, Binzhou 256603, China.

Introduction

As a prototypical electron-deficient element in the periodic table, boron exhibits strong propensity to form multicenter-two-electron bonds (mc-2e bonds) in both polyhedral molecules and bulk allotropes.[1-7] Persistent joint photoelectron spectroscopy (PES) experimental and first-principles theory investigations in the past two decades on size-selected negatively-charged boron clusters Bn-(n = 3-42) have unveiled a rich landscape for boron nanoclusters from planar or quasi-planar structures (n = 3-38, 41-42) to cage-like borospherenes (n =39, 40).^[5-10] The first all-boron fullerenes D_{2d} B₄₀^{-/0}, dubbed borospherenes, were discovered in 2014,[8] while the first axially chiral borospherene C_3/C_2 B₃₉⁻ appears to be the only boron cluster monoanion observed to date with a cage-like global minimum (GM) structure.^[9] The borospherene family has been systematically expanded by our group at first-principles theory levels to the cage-like B_n^q series (n = 36-42, q = n-40) in different charge states which are all composed of twelve interwoven double chains with a universal σ + π double delocalization bonding pattern.^[8-14] Sea-shell-like C_2 $B_{28}^{-/0}$ and $C_s B_{29}^{-}$ were later observed as minor isomers in PES experiments.^[15,16] Following the same structural motif, our group predicted the possibility of sea-shell-like Cs B29⁺, C2 B31⁺, C2 B32, C2 B_{34} , C_2 , B_{35}^+ and cage-like C_8 , B_{39}^+ at first-principles theory levels recently^[17-20] which also follow the σ + π double delocalization bonding pattern. Ion mobility measurements in 2007 indicated that Bn+ monocations possess double-ring tubular structures in the size-range between n = 16-25, revealing another important structural domain for boron.[21] Another major breakthrough in boron nanostructures was the theoretical prediction [22,23] and experimental observation of two-dimensional (2D) boron monolayers (borophenes) deposited on Ag(111) substrate by molecular beam epitaxy (MBE).[24,25] Extensive theoretical investigations on a wide range of boron nanostructures have been reported in literature, with typical examples including the most stable boron α-sheet,^[26,27] 2D boron polymorphs,^[28] cage- and core-shell-like B₈₀,^[29-32] core-shell-like and quasi-planar B₈₄,^[33,34] and cage- and core-shell-like $B_{100 \sim 102}.^{[35,36]}$ Zhao and coworkers predicted the first bilayer neutral boron cluster D_{2h} B₄₈ at density functional theory (DFT) level in 2014, presenting another important structural motif for medium-sized boron clusters and 2D bilayer boron sheets.[37] However, if such a bilayer structural motif can be extended to bigger medium-sized boron clusters still remains unknown in both theory and experiments. The competition among quasi-planar, multi-ring tubular, core-shell, and bilayer structures makes the situation in medium-sized boron clusters extremely challenging.

Based on extensive GM searches and DFT calculations, we predict in this work a new series of bilayer boron clusters including $C_2 B_{54}$ (I), $C_{2h} B_{60}$ (II), and $C_1 B_{62}$ (III) which possess one, two, and three B_6 hexagonal windows on the waist around a B_{38} bilayer hexagonal prism at the center, respectively. These bilayer structures as GMs of the systems appear to be much more stable than their previously reported planar, tubular, or cage-like counterparts.^[38-41] They follow the universal bonding pattern of $\sigma + \pi$ double delocalization previously observed in cage-like borospherenes, with three or four inter-layer B-B σ -bonds formed to further stabilize the systems. A 2D B_{34} bilayer borophene derived from B_{54} (II), B_{60} (III), and B_{62} (IIII) is predicted to be metallic in nature.

Results and Discussions

Structures and Stabilities

The optimized GM structures of $C_2 B_{54}$ (I), $C_{2h} B_{60}$ (II), and $C_1 B_{62}$ (III) are shown in Figure 1, with more alternative low-lying isomers and relevant previously predicted structures depicted in Figure S1. The configurational energy spectra of B_{54} , B_{60} , and B_{62} are shown in Figure 2. Bilayer B_{54} (I), B_{60} (II), and B_{62} (III) possess the calculated HOMO-LUMO energy gaps of ΔE_{gap} =1.98, 1.14, and 1.45 eV at PBE0 ^[42,43] level, respectively.

Interestingly, with the lowest vibration frequency of 142.4 cm⁻¹, the axially chiral bilayer C_2 B₅₄ (I) is the well defined GM of B₅₄ (Figure 2a and Figure S1a). It lies 0.85 eV lower than the second lowest-lying bilayer $C_1 B_{54}$ (2), 1.26 eV lower than the previously reported triple-ring tubular $C_i B_{54}$ (5),^[38] and 1.51 eV lower than quasi-planar C_1 B₅₄ (12) at PBE0. Similar relative energies are obtained at TPSSh level $[^{43,44}]$ (Figure S1a, ESI⁺). $C_2 B_{54}$ (I) is the second bilayer boron cluster reported to date after D_{2h} B₄₈.^[37] As shown in Figure 1, it can be constructed by adding a B₆ hexagonal window (highlighted in purple) to the previously reported D_{2h} B₄₈ ^[37] on the upper side, with a B₃₈ bilayer hexagonal prism (higtlighted in a black box) at the center. Three effective interlayer B-B σ bonds are formed between six inward-buckled atoms (highlighted in blue) in the top and bottom layers to further stabilize the system.

Adding one more B_6 hexagonal window to $C_2 B_{54}$ (I) on the opposite side results in bilayer $C_{2h}B_{60}$ (II), the GM of B_{60} at both PBE0 and TPSSh levels (Figure 2b and Figure S1b). B_{60} (II) with two B_6

hexagonal windows on the upper and lower sides and one B₃₈ bilayer hexagonal prism at the center follows the same structural pattern as B_{54} (I) (Figure 1). Four effective B-B σ bonds are formed between eight inward-buckled atoms in the top and bottom layers. The second to the fifth lowest-lying isomers of B_{60} ($C_{2h} B_{60}$ (2), $C_{2\nu} B_{60}$ (3), $C_1 B_{60}$ (4), and $C_{2\nu} B_{60}$ (5)) all possess bilayer geometries lying within 0.21 eV relative to the GM (Figure 2b). These bilayer isomers are practically iso-energetic species in thermodynamics which may coexist in gas-phase experiments. $C_{2^{h}} \; \mathsf{B}_{60}$ (II) appears to be obviously more stable than the previously reported triple-ring tubular D_{4h} B₆₀ (21),^[38]quisi-planar C_s B₆₀ (22),^[38] snub cage-like C_2 B₆₀ (23)^[39] and cage-like D_3 B₆₀ (24),^[40,41] and by 1.16, 1.78, 3.78, and 5.84 eV at PBE0 level, respectively. The lowest-lying core-shell-like $C_1 B_{60}$ (14) with a B core at the center appears to be 0.83 eV less stable than $B_{\rm 60}$ (II) (Fig.S1b).

With two more B atoms added in, the slightly twisted bilayer $C_1 \ B_{62}$ (III) with three B_6 hexagonal windows at three corners and one B_{38} bilayer hexagonal prism at the center is generated. It turns out to be the GM of B_{62} (Figure 2c and Figure S1c), with three B-B σ bonds formed between six inward-buckled atoms in the upper and lower layers.

 $C_1 B_{62}$ (III) lies 0.22 eV and 0.12 eV lower than the perfect bilayer $C_{2\nu} B_{62}$ (2) at PBE0 and TPSSh levels, respectively. These two isomers are practically isoenergetic species which may coexistin experiments. The nine most stable isomers of B₆₂ all possess bilayer structures, while other structural motifs lie much higher in energy than the bilayer GM (Figure S1c, ESI⁺), suggesting that bilayer structures dominate B₆₂ isomers in thermodynamics. For simplicity and clarity, we will take the high-symmetry $C_{2\nu}B_{62}$ (2) as an example to discuss the bonding and spectral properties of B62 in late sections.



Figure 1. Optimized structures of $C_2 B_{54}$ (I), $C_{2h} B_{60}$ (II), and $C_1 B_{62}$ (III) at PBE0/6-311+G(d) level, with the B_{38} bilayer hexagonal prisms at the center highlighted in black circles, inward-buckled B atoms colored in blue, and B_6 hexagonal windows at the corners highlighted in purple.



Figure 2. Configurational energy spectra of (a) B₅₄, (b) B₆₀, and (c) B₆₂ at PBE0/6-311+G(d) level, with energies relative to the GMs indicated in eV.

To check the dynamical stabilities of these bilayer species, we performed extensive Born-Oppenheimer molecular dynamics (BOMD) simulations on C_2 B₅₄ (I) and C_{2h} B₆₀ (II) for 30 ps at different temperatures. B₅₄ (I) appears to be dynamically stable at 1000 K with the small average root-mean-square-deviations of RMSD = 0.14 Å and maximum bond length deviations of MAXD = 0.66 Å, while B_{60} (II) appears to be stable at both 300 K and 500 K, with the small average deviations of RMSD = 0.11, 0.16 Å and MAXD = 0.60, 1.39 Å, respectively (Figure S2, ESI⁺).

Bonding Analyses

To interpret the bonding patterns of these stable bilayer species, we performed detailed AdNDP [45,46] bonding analyses on C_2 B₅₄ (I), C_{2h} B₆₀ (II), and C_{2v} B₆₂ (2). As shown in Figure 3a, B₅₄ (I) possesses 3 2c-2e B-B σ-bonds between six inward-buckled B atoms in the top and bottom layers with the occupation numbers ON=1.85-1.89 |e|, 20 2c-2e B-B σ -bonds on the waist with ON=1.71–1.83 |e|, 38 3c-2e σ bonds on the top and bottom layers with ON=1.80-1.93 |e|, 2 4c-2e σ bonds at two corners on the right and left with ON=1.77 |e|, and 2 7c-2e σ bonds on two B-centered B7 hexagonal units on the top and bottom layers with ON=1.81 |e|. The remaining 32 valence electrons are distributed in four types of delocalized π bonds over the σ -skeleton, including 2 6c-2e π bonds at two corners

on the left and right with ON=1.84 |e|, 8 6c-2e π bonds on the top and bottom layers with ON=1.84– 1.87 |e|, 4 6c-2e π bonds at the centers of the top and bottom layers with ON=1.73–1.79 |e|, and 2 6c-2e π bonds around the B₆ hexagonal window on the upper side with ON=1.65 |e|, in an overall symmetry of C_2 .

Figure 3b clearly indicates that C_{2h} B₆₀ (II) exhibits similar bonding patterns with C_2 B₅₄ (I). It has 72 σ -bonds in total, including 4 2c-2e σ bonds between eight inward-buckled B atoms in the top and bottom layers, 20 2c-2e σ bonds on the waist, 44 3c-2e σ bonds on the top and bottom layers, 2 3c-2e σ bonds at two corners on the left and right, and 2 7c-2e σ bonds on the B-centered hexagonal units on the top and bottom layers. The corresponding π system includes 2 6c-2e π bonds at two corners on the left and right, 8 6c-2e π bonds at the centers of the

top and bottom layers, and 4 6c-2e π bonds surrounding the two B₆ hexagonal windows on the upper and down sides. We notice that both B_{54} (I) and B_{60} (II) follow the σ + π double delocalization bonding pattern previously reported in cage-like borospherenes.^[8-14] It should also be addressed that B_{54} (I) and B_{60} (II) possess three and four effective 2c-2e B-B σ bonds between the buckled top and bottom layers to further stabilize the systems, respectively. As shown in Figure S3, $C_{2\nu}$ B₆₂ (2) exhibits a similar σ + π double delocalization bonding pattern, with 3 2c-2e σ bonds formed between six inward-buckled B atoms in the top and bottom layers. Such bonding patterns render three-dimensional aromaticity to B54 (I), B60 (II), and B₆₀ (III), as evidenced by the calculated negative nuclear independent chemical shift values of NICS=-33.2, -41.5, and -31.8 ppm at their geometrical centers, respectively.



Figure 3. AdNDP bonding patterns of (a) $C_2 B_{54}$ (I) and (b) $C_{2h} B_{60}$ (II)

Spectral Simulations

The infrared (IR), Raman and UV-vis spectra of C_2 B₅₄ (I) and C_{2h} B₆₀ (II) are theoretically simulated in

Figure 4 to facilitate their future spectral characterizations. As shown in Figure 4, C_2 B₅₄ (I) exhibits five strong IR peaks at 470 cm⁻¹ (b), 585 cm⁻¹ (b), 962 cm⁻¹ (a), 1091 cm⁻¹ (b), and 1251 cm⁻¹ (b), while C_{2h} B₆₀ (II) possesses six intensive IR

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active modes at 160 cm⁻¹ (b_u), 551 cm⁻¹ (a_u), 886 cm⁻¹ (a_u), 1072 cm⁻¹ (a_u), 1144 cm⁻¹ (a_u), and 1177 cm⁻¹ (a_u), respectively. Figure 4 also shows that C_2 B₅₄ (I) has five symmetrical Raman active vibrational modes (a modes) at 295 cm⁻¹ (a), 410 cm⁻¹ (a), 479 cm⁻¹ (a), 719 cm⁻¹ (a), and 1218 cm⁻¹ (a), while C_{2h} B₆₀ (II) exhibits seven symmetrical Raman features at 263 cm⁻¹ (a_g), 292 cm⁻¹ (a_g), 437 cm⁻¹ (a_g), 571 cm⁻¹ (a_g), 688 cm⁻¹ (a_g), 1015 cm⁻¹ (b_g), and 1098

cm⁻¹ (a_g), respectively. The low wavenumber vibrational modes at 295 cm⁻¹ (a) and 410 cm⁻¹ (a) in B₅₄ (I) and at 292 cm⁻¹ (a_g) and 437 cm⁻¹ (a_g) in B₆₀ (II) represent typical "radial breathing modes" (RBMs) of the two bilayer structures which can be used to characterize hollow boron nanostructures.^[47] Similar IR and Raman spectra are simulated for $C_{2\nu}$ B₆₂(2) in Figure S4.



Figure 4. Simulated IR, Raman, and UV-vis of C₂ B₅₄ (I) and C_{2h} B₆₀ (II) at PBE0/6-311+G(d) level.

The simulated UV-vis absorption spectra of C_2 B₅₄ (I) and C_{2h} B₆₀ (II) are also shown in Figure 4 at TD-DFT-PBE0 level. The strongest UV absorption peak of C_{2h} B₆₀ (II) occurs at 298 nm (¹A_u) which mainly originates from the S0 \rightarrow S381 electronic excitation from the deeply occupied inner shells to unoccupied frontier orbitals (HOMO-14 \rightarrow LUMO+5 (47%) + HOMO-22 \rightarrow LUMO (20%)) (Table S1, ESI†).

The other strong absorptions at 323 ($^{1}A_{u}$), 360 ($^{1}A_{u}$), 406 ($^{1}B_{u}$), 450 ($^{1}A_{u}$) and 512($^{1}B_{u}$) nm correspond to S0 \rightarrow S303, S0 \rightarrow S220, S0 \rightarrow S160, S0 \rightarrow S125, and S0 \rightarrow S81 excitations, respectively. The three broad bands with lower excitation energies at 694, 738, and 832 nm originate basically from HOMO-2 \rightarrow LUMO+1 (74%), HOMO-LUMO+6 (74%), HOMO-2 \rightarrow LUMO (76%) transitions, respectively.

Similar UV-vis spectra exist for C_2 B₅₄ (I) in Figure 4 and $C_{2\nu}$ B₆₂ (2) in Figure S4.

Two-dimensional B₃₄ bilayer boron allotrope

A 2D B₃₄ (Pmm2) bilayer boron sheet is derived from B₅₄ (I), B₆₀ (II), and B₆₂ (III) in Figure 5a. It has the optimized lattice parameters a=8.55 Å and b=4.97 Å and average binding energy per atom of 6.09 eV at PBE+D3 level. This 2D bilayer structure lies 0.01, 0.03, 0.03, and 0.24 eV/atom more stable than the previously reported boron α -sheet,^[26,27] χ_3 , β_{12} , and δ_3 monolayers,^[48,49] respectively, though it is slightly less stable (by 0.11 eV/atom) than the 2D bilayer boron sheet proposed by Zhao and coworkers.^[37] As shown in Figure 5b, a few dispersive bands go across the fermi level in its calculated band structure and projected density of states (PDOS), indicating that the 2D B₃₄ bilayer borophene is metallic in nature.



Figure 5. Optimized structure of 2D B_{34} bilayer boron sheet (Pmm2) and its projected densities of states (PDOS) at PBE+D3 level.

Summary

Based on extensive GM searches and manual structural constructions, we have presented in this work three highly stable bilayer B_n nanoclusters C_2 B_{54} (I), $C_{2h} B_{60}$ (II), and $C_1 B_{62}$ (III) as the GMs of the systems, expanding the bilayer structural pattern to a larger size range in boron nanoclusters. Such 3D aromatic bilayer clusters follow the σ + π double delocalization bonding pattern observed in cage-like borospherenes. They are further stabilized by three or four interlayer 2c-2e B-B σ bonds between inward-buckled B atoms in the bilayer systems. Supported borophenes have been characterized on metal substrates.[24,25] However, monolayer borophenes have not been successfully separated from metal substrates to date due to their high reactivity. The bilayer structural pattern developed in

Ref.32 and this work provides the possibility to produce bigger bilayer boron nanoclusters or even free-standing bilayer borophenes. Breaking the bottleneck in boron nanomaterials deserves further theoretical and experimental investigations in this direction.

Theoretical procedure

Extensive GM searches were peformed on B₅₄, B₆₀, and B₆₂ using the TGMin program^[50-52], in conjuction with manual structural constructions based on related Bn-/0/+ clusters, [38-41] with more than 2000 stationary points probed on their potential energy surfaces. Low-lying isomers were firstly optimized at the level of PBE0/6-31G(d), with vibrational frequencies checked to ensure that all isomers obtained were true minima on the potential energy surface. To achieve more reliable relative energies, the twenty lowest-lying isomers of B54, B60, and B62 were further re-optimized at the hybrid DFT-PBE0^[42] and DFT-TPSSh^[44] levels with the basis set of 6-311+G(d)^[43], respectively. Detailed bonding analyses on $C_2 B_{54}$ (I) and $C_{2h} B_{60}$ (II) were carried out using the adaptive natural density partitioning (AdNDP)^[45,46] method at the PBE0/6-31G level. The IR and Raman spectra of $C_2 B_{54}$ (I), $C_{2h} B_{60}$ (II) and C_{2v} B₆₂ were simulated at PBE0/6-311+G(d) level and their UV-vis absorption spectra calculated using the time-dependent density functional method (TD-DFT-PBE0).^[53,54] All the calculations in this work were performed using the Gaussian 16 program.[55] Extensive Born-Oppenheimer molecular dynamics (BOMD) simulations were peformed on the prototypical C_2 B₅₄ (I) at 1000 K, and C_{2h} B₆₀ (II) at 300 K and 500 K for 30 ps, using the software suite CP2K^[56] with the GTH-PBE pseudopotential and DZVP-MOLOPT-SR-GTH basis set. Two-dimensional bilayer boron structures were designed and optimized using DFT within the Perdew-Burke-Ernzerhof (PBE)^[57] exchange correlation functional of generalized gradient approximation (GGA) and projector-augmented wave (PAW)^[58,59] method, as implented in the Vienna Ab initio Simulation Package (VASP) code.[60,61] A plane-wave basis set with an energy cutoff of 500 eV was used. Both lattice parameters and atomic positions were optimized using conjugate gradient method, and a large vacuum spacing (more than 15 Å) was taken to prevent mirror interactions. The Brillouin zones were sampled with $2\pi \times 0.02$ Å⁻¹ spacing in reciprocal space by the Monkhorst-Pack scheme.[62] Grimme's DFT-D3 van der Waals (vdW) corrections with the Becke-Jonson (BJ) damping^[63,64] was employed.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21720102006 and 21973057 to S.-D. Li and 21803037 to W.-Y. Zan)

Keywords: Boron • Bilayer structure • Density functional calculations • Chemical bonding

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