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1. Introduction

As the light neighbour of carbon and the typical electrondeficient element in the periodic table, boron exhibits a strong propensity to form multi-center-two-electron (mc-2e) bonds in both bulk allotropes and polyhedral molecules.^{1,2} Major breakthroughs have been achieved in boron nanoclusters and lowdimensional boron nanomaterials in the past decade,³⁻¹² revealing a promising world of boron-based nanostructures parallel to that of carbon in both chemistry and materials science. Persistent joint photoelectron spectroscopy (PES) and first-principles theory investigations on small boron monoanions have established a rich landscape from planar or quasi-planar $B_n^{-/0}$ sheets (n = 3-30, 33-38) to cage-like borospherenes D_{2d} $B_{40}^{-/0}$ and C_3/C_2 B_{39}^{-} , which may serve as effective inorganic ligands with delocalized multi-center-two-electron (mc-2e) σ

Charge-induced structural transition between seashell-like B_{29}^- and B_{29}^+ in 18 π -electron configurations[†]

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Recent joint experimental and theoretical investigations have shown that seashell-like C_2 B₂₈ is the smallest neutral borospherene reported to date, while seashell-like C_s B₂₉⁻ (**1**⁻) as a minor isomer competes with its quasi-planar counterparts in B₂₉⁻ cluster beams. Extensive global minimum searches and first-principles theory calculations performed in this work indicate that with two valence electrons detached from B₂₉⁻, the B₂₉⁺ monocation favors a seashell-like C_s B₂₉⁺ (**1**⁺) much different from C_s B₂₉⁻ (**1**⁻) in geometry which is overwhelmingly the global minimum of the system with three B₇ heptagonal holes in the front, on the back, and at the bottom, respectively, unveiling an interesting charge-induced structural transition from C_s B₂₉⁻ (**1**⁻) to C_s B₂₉⁺ (**1**⁺). Detailed bonding analyses show that with one less σ bond than B₂₉⁻ (**1**⁻), C_s B₂₉⁺ (**1**⁺) also possesses nine delocalized π -bonds over its σ -skeleton on the cage surface with a $\sigma + \pi$ double delocalization bonding pattern and follows the $2(n + 1)^2$ electron counting rule for 3D spherical aromaticity (n = 2). B₂₉⁺ (**1**⁺) is therefore the smallest borospherene monocation reported to date which is π -isovalent with the smallest neutral borospherene C_2 B₂₈. The IR, Raman, and UV-vis spectra of B₂₉⁺ (**1**⁺) are computationally simulated to facilitate its spectroscopic characterization.

and π bonds.^{3-7,13-16} The borospherene family has been systematically expanded at FPT levels to include the cage-like B_n^q series (n = 36-42, q = n - 40) which are all composed of twelve interwoven boron double chains with a universal σ + π double delocalization bonding pattern.¹⁷⁻²⁰ B₃₆⁴⁻, B₃₇³⁻, B₃₈²⁻, B₃₉⁻, B_{40} , B_{41}^{+} , and B_{42}^{2+} therefore form a π -isovalent B_n^{q} series in different charge states (q = n - 40), which all have 12 multicenter-two-electron π -bonds (12 mc-2e π) over a σ -skeleton made up of n + 8 delocalized three-center-two-electron σ -bonds (n + 83c-2e σ).¹⁷⁻²⁰ Seashell-like $B_{28}^{-/0}$ and B_{29}^{-} clusters were also observed in PES measurements as minor isomers of the systems in gas phases, with B₂₈ and B₂₈⁻ being the smallest neutral borospherene and monoanionic borospherene reported to date, respectively.^{13,14,21} Ion-mobility measurements, on the other hand, showed that B_n^+ monocations in the size range of n = 16-25 possess double-ring tubular structures.²² A triple-ring tubular B₂₇⁺ has also been recently predicted at the density functional theory (DFT) level.²³ It is natural to ask at the current stage what is the smallest borospherene monocation at which cage-like boron monocations start to appear and what electronic structure and bonding pattern such a borospherene monocation may possess.

The observation that seashell-like C_2 B₂₈ is the smallest neutral borospherene while seashell-like C_8 B₂₉⁻ (1⁻) is a minor

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Fig. 1 Charge-induced structural transition from seashell-like $C_{\rm s} B_{29}^{-} (\mathbf{1}^{-})$ to seashell-like $C_{\rm s} B_{29}^{+} (\mathbf{1}^{+})$ in the electron detachment process at the PBE0/6-311+G(d) level.

isomer in B₂₉⁻ cluster beams competing with its major quasiplanar counterparts¹⁴ present the possibility to form a highly stable cage-like B_{29}^{+} monocation which could be π -isovalent with neutral C_2 B₂₈,¹³ similar to the situation observed in the cage-like B_{41}^{+} monocation which is π -isovalent with the neutral borospherene B40.17 Extensive global minimum searches and first-principles theory calculations performed in this work well support the chemical intuition: with two electrons detached from B_{29}^{-} , a B_{29}^{+} monocation clearly favours a seashell-like $C_{\rm s} B_{29}^{+}(1^{+})$ which is overwhelmingly the global minimum (GM) of the system with three B7 heptagonal holes in the front, on the back, and at the bottom, respectively, exhibiting an obvious charge-induced structural transition from $C_{\rm s} \ {\rm B}_{29}^{-}$ (1⁻) to $C_{\rm s} B_{29}^{++}$ (1⁺) (Fig. 1). Detailed bonding analyses show that $C_{\rm s} \, {\rm B_{29}}^+ ({\bf 1}^+)$ indeed conforms to the 18-electron configuration with a $\sigma + \pi$ double delocalization bonding pattern and follows the $2(n + 1)^2$ electron counting rule for 3D spherical aromaticity (n = 2), similar to neutral seashell-like B_{28} .¹³ It thus forms the smallest aromatic borospherene monocation reported to date.

2. Theoretical procedure

Extensive GM searches were performed on B₂₉⁺ using the TGMin method^{24,25} with more than 2000 stationary points probed on the potential energy surface, in combination with manual structural constructions from the known low-lying isomers of $B_{29}^{-/0.14}$ The low-lying isomers thus obtained are fully re-optimized using the hybrid DFT-PBE0 functional²⁶ and the 6-311+G(d) basis set²⁷ implemented in the Gaussian 09 program,²⁸ with vibrational frequencies checked to make sure that all isomers reported are true minima of the monocation. More accurate relative energies for the 17 lowest-lying isomers and the first tubular isomer were calculated using the coupled cluster method with triple excitations $(CCSD(T))^{29,30}$ implemented in MOLPRO³¹ with the 6-311G(d) basis set at PBE0/6-311+G(d) geometries. Detailed bonding analyses on $C_8 B_{29}^{++}(1^+)$ (Fig. 3) were performed using the adaptive natural density partitioning (AdNDP) method developed by Zubarev and Boldyrev.^{32–34} The IR and Raman spectra of $C_8 B_{29}^+$ (1⁺) were simulated at the PBE0/6-311+G(d) level and the UV-vis absorption spectrum calculated using the time-dependent DFT-PBE0 approach³⁵ implemented in Gaussian 09. Extensive Born-Oppenheimer molecular dynamics simulations were performed for $C_{\rm s}$ B₂₉⁺ (1) at 500 K, 700 K, and 1000 K for 30 ps (Fig. S3, ESI†) using the software suite of CP2K.³⁶

3. Results and discussion

3.1. Structures and stabilities

As shown in the configurational energy spectrum of B_{29}^{+} at the CCSD(T) level in Fig. 2, the seashell-like $C_{s} B_{29}^{+}(1^{+})$ is overwhelmingly the GM of the monocation lying at least 0.17 eV lower than other low-lying isomers. B_{29}^{+} appears to have a complicated potential energy surface with at least 17 low-lying isomers lying within ~ 0.7 eV above the GM B_{29}^+ (1⁺), which possesses three B7 heptagonal holes in the front, on the back, and at the bottom, respectively. Its HOMO-LUMO energy gap of $\Delta E_{\text{gap}} = 2.55$ eV calculated at PBE0/6-311+G(d) is higher than the corresponding values of ΔE_{gap} = 2.10 eV in seashell-like C_2 B_{28}^{13} and $\Delta E_{gap} = 2.25$ eV in cage-like $D_{2h} B_{38}^{37}$ and lower than that of $\Delta E_{gap} = 3.13$ eV in $D_{2d} B_{40}^{7}$ at the same theoretical level. More alternative low-lying isomers within 1 eV above the GM at the PBE0 level are summarized in Fig. S1 (ESI⁺). The second lowest-lying cage-like $C_s B_{29}^+$ (2⁺) which lies +0.17 eV higher than $C_s B_{29}^+$ (1⁺) at CCSD(T) contains a B_{11} tetragonal unit atop a distorted B₁₈ double-chain tube at the bottom. The third highsymmetry isomer $C_{2v} B_{29}^{+}(3^{+})$ which contains two B_7 heptagonal holes at two sides and two B₅ pentagonal holes at the bottom appears to be 0.20 eV less stable than the GM. To check the reliability of these results, isomers 1-3 were further optimized at the CCSD/6-31G(d) level which turn out to have almost the same geometries as that optimized at PBE0/6-311+G(d), with isomers 2 and 3 possessing the CCSD(T)/CCSD relative energies of +0.17



Fig. 2 Configurational energy spectrum of B_{29}^+ at the CCSD(T)/6-311G(d)// PBE0/6-311+G(d) level. Black and red horizontal lines represent cage-like and quasi-planar structures, respectively. Relative energies are given in eV.

and 0.15 eV, respectively, supporting the corresponding CCSD(T)/ PBE0 values shown in Fig. 2. It should also be noted that the seashell-like $C_s B_{29}^+$ (6⁺), which has the same geometry as the observed seashell-like $C_{\rm s} B_{29}^{-}$ (1⁻) with two heptagons on the waist and one octagon at the bottom,¹⁴ turns out to lie 0.23 eV higher than $C_{s} B_{29}^{+}(\mathbf{1}^{+})$ at CCSD(T). We also observe that the ten lowest-lying isomers of B_{29}^{+} within 0.33 eV are all cage-like (Fig. S1, ESI[†]), with the quasi-planar stingray-shaped $C_s B_{29}^+$ which has the same geometry as the observed $C_{\rm s} B_{29}^{-14}$ lying much higher (by 1.62 eV) than $C_{s} B_{29}^{+}(1^{+})$ at PBE0/6-311+G(d). The results obtained above as shown in Fig. 2 and Fig. S1 (ESI⁺) indicate that with two valence electrons detached from B_{29}^{-} , the B_{29}^{+} monocation favours cage-like structures overwhelmingly over their quasi-planar counterparts and there exists a clear charge-induced structural transition from the seashell-like $C_{\rm s}$ $B_{29}^{-}(\mathbf{1}^{-})$ to $C_{s} B_{29}^{+}(\mathbf{1}^{+})$ in the electron detachment process.

Extensive molecular dynamics (MD) simulations were also performed on B_{29}^+ (1⁺) to check its dynamical stabilities at various temperatures. As shown in Fig. S2 (ESI⁺), B_{29}^+ (1⁺) is dynamically stable at both 500 K and 700 K during MD simulations in 30 ps, with the small root-mean-square-deviation and the maximum bond length deviation values (on average) of RMSD = 0.08 Å and 0.09 Å and MAXD = 0.23 Å and 0.29 Å, respectively. However, it starts to hop between the two lowest-lying isomers $C_s B_{29}^+$ (1⁺) and $C_s B_{29}^+$ (2⁺) in concerted mechanisms with low energy barriers. The structural transformations involve synergetic bond breakage and formation. It is the bonding fluctuation that leads to the geometrical fluctuations in cagelike borospherenes.^{7,13,14,18-20}

3.2. Bonding pattern analyses

The high stability of $B_{29}^{+}(1^*)$ originates from its unique electronic structure and bonding pattern. As an extension of the popular natural bond orbital (NBO) method,³⁸ AdNDP analyses^{32–34} reveal both the localized and delocalized bonds in the systems, providing a relatively simple bonding picture for complicated molecular structures. Detailed AdNDP analyses indicate that $C_s B_{29}^+(1^*)$ possesses 34 3c-2e σ bonds with occupation numbers (ONs) greater than 1.79 |e| on the cage surface. Over the σ -skeleton, there exist 9 delocalized 5c-2e π bonds with ON > 1.80 |e|, including 4 5c-2e π bonds at the bottom (Fig. 3). $B_{29}^+(1^*)$ thus possesses a $\sigma + \pi$ double delocalization bonding pattern. With one less delocalized 6c-2e σ bond than $C_s B_{29}^+(1^-)$ on the top, ¹⁴ $B_{29}^+(1^+)$ has the same number of delocalized π bonds as $B_{29}^+(1^-)$.¹⁴ With 18 delocalized π -electrons, it conforms to the

 $\begin{array}{c} 34 \times 3c - 2e \ \sigma \ bonds \\ ON = 1.79 - 1.97 \ |e| \end{array} \begin{array}{c} 2 \times 5c - 2e \ \pi \ bonds \\ ON = 1.94 \ |e| \end{array} \begin{array}{c} 2 \times 5c - 2e \ \pi \ bonds \\ ON = 1.80 \ |e| \end{array} \begin{array}{c} 5 \times 5c - 2e \ \pi \ bonds \\ ON = 1.81 \ |e| \end{array}$

Fig. 3 σ and π AdNDP bonding patterns of $C_{\rm s}$ B₂₉⁺ (**1**⁺), with the occupation numbers (ONs) indicated.



Fig. 4 Simulated IR and Raman spectra of $C_s B_{29}^+$ (1⁺) at PBE0/6-311+G(d).

 $2(n + 1)^2$ electron counting rule for 3D spherical aromaticity (*n* = 2), as evidenced by the negatively calculated nucleus-independent chemical shift³⁹ of NICS = -34.01 ppm at the cage center.

3.3. Spectral simulations

Infrared photodissociation (IR-PD) has proven to be a powerful approach to characterize novel cluster monocations.^{40,41} As shown in Fig. 4, the simulated IR and Raman spectra of B_{29}^+ display numerous active absorption peaks which encompasses 19 IR (5a' + 14a'') and 62 Raman (38a' + 24a'') active modes. However, intensities of most of the IR and Raman active modes are very weak. The major IR peaks of $C_s B_{29}^+$ (1⁺) lie between 1100 and 1400 cm⁻¹, with five strong IR peaks at 1295 cm⁻¹ (a''), 1291 cm⁻¹ (a'), 1249 cm⁻¹ (a''), 1231 cm⁻¹ (a'), and 1168 cm⁻¹ (a''), which may serve as fingerprints to characterize the monocation. The major Raman active peaks of B_{29}^+ (1⁺) occur at 1337 cm⁻¹ (a'), 1156 cm⁻¹ (a''), 736 cm⁻¹ (a'), and 514 cm⁻¹ (a'), respectively, with main contributions originated from the a' symmetrical vibrational modes.

The main UV-vis absorption bands at 216, 234, 252, 286, 302, 372, 422, and 679 nm mainly originate from electron excitations involving the deep-lying inner shells of the monocation, while excitations from $S_0(^1A')$ to $S_4(^1A')$ and from $S_0(^1A')$ to $S_2(^3A')$ mainly originating from HOMO \rightarrow LUMO transitions are predicted to be at 822 nm and 925 nm with low intensities, respectively.

4. Conclusions

In summary, we have performed in this work an extensive firstprinciples theory investigation on B_{29}^{+} monocations and analysed



Fig. 5 Simulated UV-vis absorption spectrum of $C_{\rm s}$ B₂₉⁺ (**1**⁺) at PBE0/6-311+G(d).

the charge-induced structural transition from seashell-like B_{29}^{-} (1⁻) to B_{29}^{+} (1⁺). The results obtained show that with two valence electrons detached from B_{29}^{-} , B_{29}^{+} takes a seashell-like groundstate structure $C_s B_{29}^{+}$ (1⁺) which is much different from the experimentally observed seashell-like $C_s B_{29}^{-}$ (1⁻). Detailed bonding analyses indicate that $C_s B_{29}^{+}$ (1⁺) conforms to the 18-electron configuration with a $\sigma + \pi$ double delocalization bonding pattern and exhibits 3D spherical aromaticity. B_{29}^{+} was firstly detected in time-of-flight mass spectroscopy in the gas phase in 1992.⁴² The results obtained in this work will help facilitate its spectroscopic characterization in the future (Fig. 5).

Conflicts of interest

There are no conflicts to declare.

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