1. Introduction

Elemental boron forms diverse bulk allotropes with a variety of three-dimensional (3D) cage-like structural units, such as the B12 icosahedron, as building blocks to compensate for its electron deficiency.1-3 In contrast to bulk boron, systematic combined photoelectron spectroscopy (PES) and quantum chemistry studies in the past two decades have shown that the global-minimum (GM) structures of anionic boron clusters (Bn-) are planar or quasi-planar in an unexpectedly wide range of sizes (n = 3–30, 33–38).4-28 Chemical bonding analyses reveal that both localized peripheral two-center-two-electron (2c–2e) B–B σ-bonds and delocalized interior multicenter (mc-2e) σ- and π-bonds play important roles in stabilizing these two-dimensional (2D) Bn- clusters, giving rise to multiple aromaticity and antiaromaticity in boron clusters.6-8,29 Moreover, based on the similarity of π-bonding patterns between 2D boron clusters and polycyclic aromatic hydrocarbons (PAHs), the concept of all-boron analogues of PAHs has been proposed.6,11-14,19-22,29

All 2D Bn- clusters consist of B3 triangles, with tetragonal, pentagonal, or hexagonal vacancies appearing as defects at certain sizes. There is a tendency for the vacancy sizes to increase from tetragonal, pentagonal, to hexagonal as the cluster size increases. In the smaller size regime, Bn- (n = 11, 15, 17, 19) clusters6,12,13 were found to contain one or more tetragonal vacancies, while B20-, B21-, and B23–B25- all possessed pentagonal vacancies.9,14-17 The B36- clusters were the first quasi-planar boron clusters that contain a perfect central hexagonal vacancy, providing the first experimental evidence for the viability of extended two-dimensional all-boron sheets named borophenes.22 Following this work, the B101 cluster was found to be the first quasi-planar chiral boron cluster with two degenerate enantiomers possessing a relatively low conversion barrier.18 The smallest quasi-planar B10- with a hexagonal vacancy was B26-26 while 2D boron clusters with a double hexagonal vacancy (DHV) were observed in B35-, B37-, and B38-27 unveiling more flexible embryos for borophenes with adjacent hexagonal vacancies and different vacancy densities.20 Borophenes were recently successfully synthesized on an Ag(111) substrate.30,31

More intriguingly, the first experimental observation and characterization of all-boron fullerenes, B40-30,32 dubbed borospherenes,32 were reported in 2014. Although the B40- borosphere is slightly higher in energy than a 2D structure with a DHV, neutral B40 borosphere is overwhelmingly the GM on the potential energy surface. The first axially chiral borospherenes \( \text{C}_{1}/\text{C}_{2}\text{B}_{35-}^{39} \) were observed shortly after as well-defined GM structures.33 Seashell-like \( \text{C}_{3}\text{B}_{28-}^{38} \) and \( \text{C}_{4}\text{B}_{29-}^{39} \) borospherenes24,25 were also identified experimentally as minor isomers, which compete with a close-packed 2D \( \text{B}_{28-}^{30} \) and a stingray-shaped 2D \( \text{B}_{29-}^{30} \) with a pentagonal vacancy, respectively. Clearly, Bn- boron clusters in the size region of \( n = 26-38 \) exhibit a complicated structural landscape, featuring...
competition between 2D structures with a single hexagonal vacancy, 2D structures with a DHV, and 3D seashell-like low-lying isomers at \( n = 28 \) and 29. This situation presents a huge challenge in the characterization of \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) clusters, the last two anionic boron clusters that remain to be experimentally characterized to date in the size range \( n \leq 40 \), owing to their complex PES spectra and complicated potential energy surfaces. For them, 2D structures with a single hexagonal vacancy or a DHV, as well as 3D structures, all seem possible.

To fill in the gap and fully characterize all the \( \text{B}_{n}^{−} (n \leq 40) \) clusters, we present herein a joint investigation into the geometric and electronic structures of \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) using PES and first-principles calculations. Two degenerate quasi-planar chiral \( \text{C}_{1} \) enantiomers (I and II, \( ^{1}\text{A} \)) with a central hexagonal vacancy are identified as the GM structures of \( \text{B}_{31}^{−} \), with a \( \text{C}_{1} \) transition state located on the conversion pathway. Two degenerate boat-like chiral \( \text{C}_{2} \text{B}_{32}^{−} (\text{VI and VII,} \text{ }^{2}\text{A}) \) with a central hexagonal vacancy were also found as the GM structures of \( \text{B}_{32}^{−} \), along with a 2D chair-like local minimum \( \text{C}_{1} \text{B}_{32}^{−} (\text{VIII,} \text{ }^{2}\text{A}_{0}) \) as a minor isomer coexisting experimentally. Two degenerate \( \text{C}_{1} \) transition states as a pair of enantiomers are located between the observed \( \text{C}_{2} \) GM and the \( \text{C}_{1} \) isomer. The chiral conversions in quasi-planar \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) occur via the buckling of flexible molecular planes, making these species unique in 2D boron clusters.

2. Methods

2.1 Photoelectron spectroscopy

The experiments were carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic source. Details of the experimental setup have been described elsewhere.\(^ {19,34} \) Briefly, boron anion clusters (\( \text{B}_{n}^{−} \)) were generated by the laser vaporization of a hot-pressed \( ^{10}\text{B} \)-enriched boron disk target using He carrier gas seeded with 5% Ar. The cooling of the clusters was controlled by the time delay between the pulsed valve and the vaporization laser, as well as by the residence time of clusters in the nozzle.\(^ {19} \) Negatively charged boron clusters were extracted perpendicularly from the molecular beam and analyzed using a time-of-flight mass spectrometer. The \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) clusters were mass selected and decelerated before photodetachment by the 193 nm (6.424 eV) radiation from an ArF excimer laser. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectrum was calibrated using the known spectrum of Bi\(^ {−} \) and the resolution of the PES apparatus was \( \Delta E_{B}/E_{B} \approx 2.5\% \), that is, \( \sim 25 \) meV for 1 eV kinetic energy electrons.

2.2 Theoretical methods

The GM searches were performed on \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) clusters using the TGMin code\(^ {35,36} \) at the DFT level, in conjunction with manual structural constructions based on the known planar, cage-like, and tubular boron cluster motifs. By running TGMin searches from independent initial structures, we obtained more than 5400 and 4000 structures for \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \), respectively. Low-lying isomers were then fully optimized at the PBE0/6-311+G(d) level.\(^ {37,38} \) Vibrational frequencies were calculated to ensure that the reported isomeric structures are true minima on the potential energy surfaces. Single-point energies of the five lowest-lying isomers were further refined at PBE0 geometries using the coupled cluster CCSD(T) method\(^ {39−41} \) implemented in MOLPRO 2012.\(^ {42} \) The vertical detachment energies (VDEs) for excited states were calculated using time-dependent DFT (TD-DFT)\(^ {43} \) with the PBE0 functional. Bonding analyses were performed using the adaptive natural density partitioning (AdNDP) approach at the PBE0/6-31G(d)/PBE0/6-311+G(d) level.\(^ {44} \) All optimizations were performed using the Gaussian 09 package.\(^ {45} \)

3. Experimental results

The PES spectra of \( \text{B}_{31}^{−} \) and \( \text{B}_{32}^{−} \) at 193 nm are shown in Fig. 1a and 2a, respectively, compared to the simulated spectra of their respective GM structures. The observed spectral bands are labelled with the letters (X, A, B, ...). The lowest binding energy band (X) corresponds to the transition from the ground state of \( \text{B}_{n}^{−} \) to that of the corresponding neutral, whereas the higher binding energy bands (A, B, C, ...) correspond to detachment transitions to excited states of the neutral species. All measured VDEs and adiabatic detachment energies (ADEs) are listed in Tables S1 and S2 in the ESI,\(^ {†} \) where they are compared with the calculated VDEs and ADEs at the PBE0 level.

![Fig. 1](image-url)
3.2 Photoelectron spectrum of B32

The 193 nm PES spectrum of B32 consists of six relatively broad bands, labelled as X and A-E (Fig. 2a). The lowest binding energy band X gives the first VDE at 3.82 eV and an estimated first ADE at 3.65 eV from its onset. There is a weak shoulder X′ (VDE: 3.57 eV) at the low binding energy side, which may come from a minor isomer of B32. Band A (VDE: 4.30 eV) is well separated from band X. Following a large gap, two intense and closely spaced bands B (5.04 eV) and C (5.17 eV) are observed. Above 5.5 eV, the spectrum is congested, and bands D (~5.8 eV) and E (~6.1 eV) are tentatively labelled for the sake of discussion.

4. Computational results

We searched for the GM and low-lying isomers of B31\textsuperscript{−} and B32\textsuperscript{−} by employing the TGMIn code. The resulting isomers were then re-optimized at the PBE0/6-311+G(d) level. The lowest 20 structures of B31\textsuperscript{−} and B32\textsuperscript{−} at PBE0 are shown in Fig. S1 and S2\textsuperscript{†} respectively. All the structures were determined to be true minimum without imaginary frequencies. Low-lying isomers of B31\textsuperscript{−} and B32\textsuperscript{−} within 0.5 eV at PBE0 were further refined at the single-point CCSD(T) level. The five lowest-lying structures of B31\textsuperscript{−} and B32\textsuperscript{−} are shown in Fig. 3(a) and (b) and the Cartesian coordinates are given in Table S3\textsuperscript{†}.

4.1 Global minima and low-lying isomers of B31\textsuperscript{−}

We found that the GM structures of B31\textsuperscript{−} are two degenerate quasi-planar ones, I and II (C\textsubscript{1h}, 1A\textsuperscript{′}; Fig. 3a), which are a pair of chiral enantiomers with a central hexagonal vacancy. Both structures are composed of seventeen peripheral and fourteen interior atoms with an out-of-plane buckling of 1.52 Å. They can be obtained by removing two edge atoms of the previously observed GM for B\textsubscript{13}\textsuperscript{−}\textsuperscript{28} The third isomer III (C\textsubscript{2v}, 1A) is a 3D seashell-like cage structure similar to the B\textsubscript{28} and B\textsubscript{29} borospheres\textsuperscript{24,25} which lie slightly higher (by 0.08 eV) than the GM structures at the CCSD(T) level. The fourth isomer IV (C\textsubscript{3v}, 1A) with a DHV is found to be 0.12 eV higher in energy at CCSD(T), and it is related to the experimentally identified 2D B\textsubscript{15} cluster\textsuperscript{20} by removing a row of four edge atoms at the bottom. The 2D isomer V (C\textsubscript{1v}, 1A) is calculated to be 0.17 eV above the GM at CCSD(T). Among the lowest 20 isomers of B31\textsuperscript{−} shown in Fig. S1\textsuperscript{†} 12 are quasi-planar and 8 are seashell-like, indicating that there is a competition between the 2D structures and 3D cages at this size.

4.2 Global minimum and low-lying isomers of B32\textsuperscript{−}

The GM structures of B32\textsuperscript{−} are also a pair of quasi-planar degenerate chiral enantiomers with a boat-like shape and a
central hexagonal vacancy, VI and VII (C_2, 3A) in Fig. 3b. A chair-like isomer VIII (C_{18}, 9A), which is 0.13 eV higher in energy at CCSD(T), can be viewed as a conformational isomer of boat-like VI and VII, similar to the chair- and boat-like cyclohexanes. These three isomers are all related to the second isomer of the B_{27} cluster^{21} by adding a B_2 double chain along one of the tetrameric edges. The structural differences between boat and chair conformers lie in the buckling within the molecular plane. Both boat-like VI and VII enantiomers possess an out-of-plane buckling of 1.55 Å. Quasi-planar IX, X (C_{18}, 9A) lie 0.29 eV and 0.35 eV above the GM structures of B_{27} at CCSD(T), respectively. These higher lying isomers also contain a central hexagonal vacancy, but with different structural arrangements compared to boat- and chair-like B_{27}. The top five isomers all consist of eighteen peripheral atoms and fourteen interior atoms. A tubular isomer (D_{18}, 3A; Fig. S2†) is 0.36 eV higher in energy at the PBE0 level. Different from the B_{27} cluster, the potential energy surface of B_{32} is entirely dominated by 2D structures, as reflected by the fact that the top 20 lowest-lying isomers of B_{32} are all quasi-planar, except the tubular one.

5. Discussion

5.1 Comparison between experiment and theory

The PES spectrum can be viewed as an electronic fingerprint for the underlying anionic cluster. In order to confirm the GM structures of B_{31} and B_{32}, the VDEs of the predicted low-lying isomers of B_{31} (I–V) and B_{32} (VI–VIII) were calculated using TD-DFT with the PBE0 functional and they are compared with the experimental VDEs in Tables S1 and S2, respectively. The computed VDEs are used to produce the simulated spectra by fitting each VDE with a unit-area Gaussian, which are compared with the experimental spectra in Fig. 1, 2 and S3.†

5.1.1 B_{31}. As shown in Table S1,† isomer I of B_{31} and its chiral enantiomer II have the same electronic structure, giving a set of entirely identical VDEs. The first and second VDEs of I/II, resulting from the removal of an electron from HOMO (47a) and HOMO–1 (46a), are calculated to be 3.89 eV and 4.07 eV, respectively. These two VDEs are close to each other, agreeing with the observed adjacent bands X (4.07 eV) and A (4.24 eV), which are separated by 0.17 eV. The calculated ADE of I/II is 3.76 eV, in excellent agreement with the experimental ADE of 3.74 eV. Electron detachment from HOMO–2 (45a) and HOMO–1 (24a), resulting from the removal of an electron from HOMO, are calculated to be 3.89 eV and 4.07 eV, in excellent agreement with the experimental ADE (3.65 eV). The next two detachment channels come from removal of an electron from HOMO–1 (24a), producing both triplet and singlet final states. The computed VDEs of 4.12 and 4.38 eV for these two channels, respectively, are in good agreement with the broad band A at 4.30 eV. In the regime of 4.71 to 5.22 eV, there are six detachment channels, which are responsible for the intense and overlapping bands B (5.04 eV) and C (5.17 eV). There are also numerous detachment channels at the higher energy side, consistent with the broad bands E and F (Fig. 2b and Table S2†).

The chair-like C_{18} VIII lies only 0.13 eV higher in energy than the boat-like VI/VII. Its calculated first VDE of 3.77 eV (Table S2†) appears to be slightly lower than that of VI/VII (3.78 eV). In the experimental spectrum, there is a weak shoulder peak X′ at 3.57 eV. Since there exist no other low-lying isomers between VII and VIII, isomer VIII is the only possible species contributing to peak X′ (Fig. 2c). Isomers IX and X can be safely ruled out from the experiment because of their relatively high energies. Hence, we conclude that the degenerate boat-like chiral pair C_{18} VII/VIII are the main isomers in the cluster beam of B_{32}, while the slightly higher lying chair-like VIII isomer is present as a minor species.

5.2 Chemical bonding

To understand the stability of the GM structures of B_{31} (I/II; C_{18}, 9A) and B_{32} (VI/VII; C_{24}, 5A), we analyze their chemical bonding using AdNDP.44 The AdNDP analyses were done on the closed-shell systems, C_{1} B_{31}, C_{2} B_{32}, and C_{2} B_{32}^{2−}, as shown in Fig. 4, 5, and S4,† respectively.

As shown in Fig. 4a, B_{31}^{−} possesses 17 2c–2e σ bonds on the peripheral B_{17} ring, 6 3c–2e σ bonds around the inner B_6 hexagon, and 14 4c–2e σ bonds between the interior and peripheral rings. In addition, our AdNDP analyses of B_{31}^{−} uncovered ten multi-center π bonds, which include 2 4c–2e π bonds, 4 5c–2e π bonds, and 4 6c–2e π bonds. The π bonding pattern of B_{31}^{−} exhibits a one-to-one correspondence to the ten π bonds of the PAH C_{18}H_{11}^{−} (Fig. 4b). In fact, this π-bonding pattern is identical to that of B_{31}^{−} although B_{31} contains three fewer σ bonds. Therefore, B_{31}^{−} is the second all-boron analog of C_{18}H_{11}^{−}, further reinforcing the analogy between 2D boron clusters and PAHs.6–8,11–14,19–22,29
As shown in Fig. 5a, there are also three types of \( \sigma \) bonds in \( \text{C}_2 \text{B}_{32} \), including 18 peripheral 2c–2e bonds, 6 3c–2e bonds around the hexagonal vacancy, and 14 4c–2e bonds in the molecular framework. The remaining 20 electrons form 10 multi-centre \( \pi \) bonds (2 4c–2e \( \pi \) bonds, 6 5c–2e \( \pi \) bonds, and 2 6c–2e \( \pi \) bonds). The \( \pi \) bonding pattern is analogous to that of PAH perylene (\( \text{C}_{20}\text{H}_{12} \)), as shown in Fig. 5b. Hence, the \( \text{B}_{32} \) cluster presents another all-boron analogue of PAHs. With two extra electrons, the closed-shell \( \text{C}_2 \text{B}_{32}^{2-} \) dianion possesses one more 8c–2e \( \pi \) bond than neutral \( \text{C}_2 \text{B}_{32} \) (Fig. S4†). All other \( \sigma \) and \( \pi \) bonds in \( \text{C}_2 \text{B}_{32}^{2-} \) are the same as in neutral \( \text{C}_2 \text{B}_{32} \).

5.3 Chiral conversions via buckling in both \( \text{B}_{31}^- \) and \( \text{B}_{32}^- \)

The GM structures of both \( \text{B}_{31}^- \) and \( \text{B}_{32}^- \) are chiral due to their quasiplanarity. To better understand the chirality and stability of the enantiomers of \( \text{B}_{31}^- \) (\( \text{C}_1 \) I and \( \text{C}_1' \) II) and \( \text{B}_{32}^- \) (\( \text{C}_2 \) VI and \( \text{C}_2' \) VII), we perform extensive searches to locate possible transition states between the enantiomer pairs using the QST2 or QST3 method at the PBE0/6-311+G(d) level. The obtained reaction paths were verified by the intrinsic reaction coordination (IRC)46 calculations at the same level of theory (Fig. S5 and S6†). As shown in Fig. 6, an almost planar transition state \( \text{C}_1 \text{B}_{31}^- \) (TS1) with the imaginary vibrational frequency of 79i \( \text{cm}^{-1} \) and a small out-of-plane buckling of 0.84 Å is located on the pathway between the two enantiomers of \( \text{C}_1 \)

\( \text{B}_{31}^- \) (I) and \( \text{C}_1' \text{B}_{31}^- \) (II). The chiral conversion energy barrier (\( \Delta E_a \)) is found to be 5.93 kcal mol\(^{-1} \) at CCSD(T), which is similar to the barrier (6.2 kcal mol\(^{-1} \)) reported previously for the chiral \( \text{B}_{30} \) cluster.18 Such an energy barrier well preserves the two enantiomers of \( \text{B}_{31}^- \) under our experimental conditions at sub-room temperatures.

As shown in Fig. 7, the chiral conversion of \( \text{B}_{32}^- \) goes through an intermediate non-chiral local minimum (\( \text{C}_2 \text{B}_{32} \))
Two degenerate chiral transition states $C_1 B_{32}^−$ (TS2) and $C_1′ B_{32}^−$ (TS3) with an imaginary frequency of $53i$ cm$^{-1}$ are located on the pathways between $C_1 B_{32}^−$ (VI)$−C_1 B_{32}^−$ (VIII) and $C_1 B_{32}^−$ (VIII)$−C_1′ B_{32}^−$ (VII), with the forward conversion barriers of $\Delta E_a = 5.49$ and 2.41 kcal mol$^{-1}$, respectively (Fig. 7). It should be pointed out that there is evidence that the $C_1 B_{32}^−$ (VIII) isomer is present experimentally (Fig. 2), suggesting that the 2.41 kcal mol$^{-1}$ conversion barrier is sufficient to protect the local minimum under our experimental conditions.

The chirality of $B_{31}^−$ and $B_{32}^−$ is entirely due to the non-planarity of these clusters. Hence, the conversion between enantiomers only involves buckling within the molecular plane, while the positions of the central hexagon and the atomic connectivity remain unchanged along the pathways. The relatively low energy barriers are unique in boron clusters due to delocalization of $\sigma$ and $\pi$ bonding on the buckled molecular surfaces of $B_{31}^-$ and $B_{32}^-$. It is interesting to speculate whether chirality in nanoclusters can be extended in two dimensions to form chiral borophenes with distinct optical activities.

6. Conclusions

We report a joint photoelectron spectroscopy and first-principles theoretical investigation on the geometric and electronic structures of $B_{31}^-$ and $B_{32}^-$, completing the experimental characterization studies of $B_n^-$ clusters in the size range of 3–40 atoms. Two degenerate quasi-planar chiral $C_1$ enantiomers are confirmed to be the global minima of $B_{31}^-$, and two degenerate boat-like chiral $C_2 B_{32}^-$ (VI and VII, $^2A_g$) and one chair-like $C_1 B_{32}^-$ (VIII, $^2A_u$) low-lying isomers are found to coexist experimentally. The unique chiral conversions via buckling within the molecular planes of $B_{31}^-$ and $B_{32}^-$ are also investigated and relatively low chiral conversion barriers are revealed. The chair-like low-lying isomer of $B_{32}^-$ is found to be a local minimum along the conversion path of its chiral global minima.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The experimental work done at Brown University was supported by the National Science Foundation (Grant No. CHE-1763380 to L. S. W.). The theoretical work at Shanxi University was supported by the National Natural Science Foundation of China (21720102006 to S. D. L.; 21873058 and 21573138 to H. J. Z.).

Notes and references
