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Competition between quasi-planar and cage-like structures in the B<sub>29</sub><sup>-</sup> cluster: photoelectron spectroscopy and *ab initio* calculations<sup>†</sup>

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Size-selected boron clusters have been found to be predominantly planar or quasi-planar (2D) in the small size regime with the appearance of three-dimensional (3D) borospherene cages of larger sizes. A seashell-like  $B_{28}^{-}$  cluster was previously shown to be the smallest borospherene, which competes with a quasi-planar isomer for the global minimum. Here we report a study on the structures and bonding of the  $B_{29}^{-1}$ and B<sub>29</sub> clusters using photoelectron spectroscopy (PES) and first-principles calculations and demonstrate the continued competition between the 2D and borospherene structures. The PES spectrum of  $B_{29}^{-}$  displays a complex pattern with evidence of low-lying isomers. Global-minimum searches and extensive theoretical calculations revealed a complicated potential energy surface for  $B_{29}^{-}$  with five low-lying isomers, among which the lowest three were shown to contribute to the experimental spectrum. A 3D seashell-like  $C_s$  (2, <sup>1</sup>A') isomer, featuring two heptagons on the waist and one octagon at the bottom, is the global minimum for  $B_{29}^{-}$ , followed by a 2D  $C_1$  (3, <sup>1</sup>A) isomer with a hexagonal hole and a stingray-shaped 2D  $C_s$  (1, <sup>1</sup>A') isomer with a pentagonal hole. However, by taking into account the entropic effects, the stingray-shaped isomer 1 was shown to be the lowest in energy at room temperature and was found to dominate the PES spectrum. Isomers 2 and 3, which have lower electron binding energies, were also found to be present in the experiment. Chemical bonding analyses showed that isomer **1** is an all-boron analogue of benzo[ghi] fluoranthene ( $C_{18}H_{10}$ ), whereas the borospherene isomer 2 possesses  $18\pi$  electrons, conforming to the  $2(N + 1)^2$  electron counting rule for spherical aromaticity. For the B29 neutral cluster, the seashell-like borospherene isomer is the global minimum, significantly lower in energy than the stingray-shaped quasi-planar structure.

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† Electronic supplementary information (ESI) available: Alternative optimized lowlying structures of B<sub>29</sub><sup>-</sup> within 1 eV of the global minimum at the PBE0/6-311+G\* level, along with the relative energies for top five lowest-energy structures at the single-point CCSD(T) level (Fig. S1); simulated photoelectron spectra for the fourth and fifth isomers of B<sub>29</sub><sup>-</sup> (Fig. S2); a comparison of the simulated photoelectron spectra for top three isomers using two theoretical methods (Fig. S3); an alternative version of the bonding patterns of quasi-planar  $C_8$  B<sub>29</sub><sup>-</sup> and  $C_{2v}$  C<sub>18</sub>H<sub>10</sub> as revealed from adaptive natural density partitioning (AdNDP), with the Clar type  $\pi$  bonds (Fig. S4); comparisons of experimental VDEs of B<sub>29</sub><sup>-</sup> with those calculated at timedependent PBE0/6-311+G\* and ROVGF/6-311+G\* levels for isomers 1–5 (Table S1); and Cartesian coordinates of top three isomers of B<sub>29</sub><sup>-</sup> at the PBE0/6-311+G\* level (Table S2). See DOI: 10.1039/c6cp05420j

### 1. Introduction

Boron is a prototypical electron-deficient element and forms strong covalent bonds with itself and with other elements. However, unlike its neighbor carbon, boron sheets with a honeycomb lattice are unstable because of the electron deficiency. Bulk boron is dominated by icosahedral  $B_{12}$  building blocks covalently bonded to each other, and boranes and many boron alloys also possess three-dimensional (3D), cage-like structural units. Over the past decade, a large body of experimental and theoretical works<sup>1–21</sup> has unraveled the structural evolution of anionic boron clusters up to  $B_{28}^-$ , which have all been found to possess unique planar or quasi-planar (2D) structures as their global minima. Beyond  $B_{28}^-$ , a number of larger clusters, such as  $B_n^-$  (n = 30, 35, 36, 39, 40), have also been also elucidated, <sup>13,14,22–25</sup> extending the 2D boron clusters to as large as  $B_{36}^{-}$ .<sup>23,24</sup>

All 2D  $B_n^-$  clusters are shown to consist of a periphery and one or more interior atoms. The periphery of all the 2D boron clusters is bonded by classical two-center two-electron (2c-2e)

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B-B  $\sigma$  bonds, whereas delocalized bonding (both  $\pi$  and  $\sigma$ ) is found in the interior of the 2D boron clusters, giving rise to the concepts of aromaticity and antiaromaticity in boron clusters.<sup>6,7,11,12,21</sup> On the basis of  $\pi$  bonding, a close analogy has been established between 2D boron clusters and polycyclic aromatic hydrocarbons (PAHs).<sup>8,9,12-14,26-29</sup> The interior of the 2D boron clusters is mainly composed of B<sub>3</sub> triangles, decorated by tetragonal, pentagonal, or hexagonal holes. For example, the  $B_n^-$  (n = 20, 21, 23-28) series of clusters<sup>10,15-19</sup> were shown to contain one or two pentagonal holes, whereas  $B_{30}^{-}$ ,  $B_{35}^{-}$ , and  $B_{36}^{-}$  all contain hexagonal holes. The discovery of the 2D B<sub>36</sub> cluster with a central hexagonal hole provided the first indirect evidence of the viability of 2D boron monolayers, dubbed borophene.<sup>23</sup> The subsequent finding of the  $B_{35}^{-}$  cluster with two adjacent hexagonal holes provided an even more flexible building block for borophenes.<sup>13</sup> Recently, borophenes have been synthesized on Ag substrates,<sup>30,31</sup> representing a milestone in boron chemistry. Another key discovery is the observation of the  $B_{40}^{-}$  borospherene,<sup>14</sup> which is the first freestanding all-boron hollow cage, analogous to the C60 buckyball (albeit with substantially different structures and bonding). Shortly after that, the  $C_3/C_2$   $B_{39}^{-}$  clusters were characterized as chiral borospherenes.<sup>25</sup> Very recently, the seashell-like  $C_2$   $B_{28}^{-}$ , which competes with the 2D  $C_2$   $B_{28}^-$  for the global minimum, was observed as the smallest borospherene.<sup>19,20</sup>

The  $B_{29}^{-}$  cluster has thus far eluded us, because of its rather complex PES spectra and the challenges for global optimizations. What is the global minimum structure of  $B_{29}^{-?}$ ? Is it planar? Does it possess a pentagonal or hexagonal hole? Is the seashell-like cage structure present for  $B_{29}^{-?}$ ? A computational study on  $B_{29}^{-}$  has appeared,<sup>32</sup> suggesting that its global-minimum structure is 2D with a hexagonal hole and  $C_1$  symmetry. As our experimental and theoretical data will show, the  $B_{29}^{-}$  anion cluster has several competitive low-lying structures, contributing to the complicated PES spectra observed. Both a stingray-shaped 2D  $C_s(\mathbf{1}, \mathbf{A}')$  structure and a seashell-like  $C_s$  (2, <sup>1</sup>A') borospherene are found to be low-lying isomers, whose relative stabilities are found to be governed by entropy. At around room temperature, the 2D isomer 1 dominates, with the borospherene isomer 2 being slightly higher in energy. However, at 0 K, 2 is calculated to be the most stable and 1 is 0.21 eV higher in energy at the PBE0 level. In between isomers 1 and 2, there appears to be a third, 2D isomer:  $C_1$  (3, <sup>1</sup>A). Isomers 1, 2, and 3 are shown to coexist in the experimental PES spectrum. For the B<sub>29</sub> neutral, the seashell isomer is the most stable, with the stingray isomer being 0.90 eV higher in energy at PBE0. Bonding analyses show that 1 is an inorganic analogue of benzo[ghi]fluoranthene  $(C_{18}H_{10})$ , whereas 2 exhibits three-dimensional aromaticity, with  $18\pi$ electrons conforming to the  $2(N + 1)^2$  electron-counting rule for spherical aromaticity.33

# 2. Experimental and theoretical methods

#### 2.1. Anion photoelectron spectroscopy

The photodetachment experiment of the  $B_{29}^{-}$  cluster was carried out using a magnetic-bottle PES apparatus equipped

with a laser vaporization source, details of which can be found elsewhere.34 Briefly, boron clusters were produced by laser vaporization of an isotopically enriched <sup>10</sup>B (96%) target. Clusters were entrained by a He carrier gas containing 5% Ar and underwent a supersonic expansion to form a collimated beam using a skimmer. The size distribution and cooling of the clusters were controlled by the time delay between the pulsed valve and the vaporization laser, as well as by the resident time of clusters in the nozzle.35,36 Negatively charged boron clusters were extracted perpendicularly from the molecular beam and analyzed using a time-of-flight mass spectrometer. The B<sub>29</sub><sup>-</sup> cluster was mass-selected and decelerated before being intercepted by a 193 nm (6.424 eV) laser beam 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 Au<sup>-</sup> and the resolution of the PES apparatus was  $\Delta E_k/E_k \approx 2.5\%$ , that is, ~25 meV for 1 eV kinetic energy electrons.

#### 2.2. Computational methods

Global-minimum searches for the  $B_{29}^{-}$  cluster were accomplished using the Minima Hopping (MH) algorithm,<sup>37</sup> as well as the TGmin code developed based on the Basin Hopping (BH) algorithm,<sup>22,23,38</sup> at the density-functional theory (DFT) level. Manual structural constructions were also done based on the known planar, cage-like, and tubular boron cluster motifs to aid the structural searches. By running the MH and TGmin searches from independent initial structures, we obtained about 4100 and 1200 structures, respectively. All isomers within ~1 eV of the global minimum were reoptimized at the PBE0/6-311+G\* level.<sup>39,40</sup> Vibrational frequencies were calculated to ensure that the reported isomeric structures are true minima on the potential energy surface. A set of five neutral  $B_{29}$  structures, which correspond to the top five lowest-lying isomers of  $B_{29}^{-}$ , were also optimized and calculated at the PBE0/6-311+G\* level.

For more accurate assessment of the relative energies for the isomers of  $B_{29}^{-}$ , single-point CCSD(T)<sup>41–43</sup> calculations were carried out for the top five isomers with the 6-311+G\* basis set, at their corresponding PBE0/6-311+G\* geometries. The first vertical detachment energy (VDE) for an isomer was computed by the energy difference between the anion and the neutral at the respective anion geometry. The higher VDEs, corresponding to the excited states of the neutral, were calculated using two methods: the time-dependent DFT (TD-DFT)<sup>44</sup> and the outer valence Green's function (OVGF).<sup>45–47</sup> Bonding analyses were performed using canonical molecular orbitals (CMOs) at the PBE0/6-311+G\* level, as well as adaptive natural density partitioning (AdNDP)<sup>48</sup> at the PBE0/6-31G level. The AdNDP results were visualized using the Molekel 5.4.0.8 program.<sup>49</sup> All calculations were performed using the Gaussian 09 package.<sup>50</sup>

### 3. Experimental results

The PES spectrum of  $B_{29}^{-}$  at 193 nm is shown in Fig. 1(a). It displays a complex spectral pattern with reasonably well-defined



**Fig. 1** Photoelectron spectrum of  $B_{29}^{-}$  at 193 nm (a) and comparison with simulated spectra of isomers **1** (b), **2** (c), and **3** (d) at the time-dependent PBE0/6-311+G\* (TD-PBE0) level. The simulations were done by fitting the calculated VDEs (vertical bars), with unit-area Gaussian functions of 0.05 eV half-width. *I*<sub>rel</sub> represents the relative intensity.

spectral features beyond 4.2 eV, labeled as X and A–E. The spectrum also shows a long, low binding energy tail down to ~3.2 eV. These weak signals could be due to vibrational hot bands, but the extent of the energy range of these weak signals suggests that they are most likely due to contributions from weakly populated low-lying isomers. Band X should correspond to the transition from the ground state of (the dominant isomer of)  $B_{29}^{-}$  to that of the corresponding neutral  $B_{29}$ , with a VDE of  $4.37 \pm 0.03$  eV. This VDE value is quite high

for boron clusters beyond n = 24,<sup>21</sup> suggesting that B<sub>29</sub><sup>-</sup> is closed-shell. Since no vibrational structure is resolved for band X, the adiabatic detachment energy (ADE) is estimated by drawing a straight line along the leading edge of band X and then adding the experimental resolution to the intersection with the binding energy axis. The ADE so evaluated is  $4.15 \pm 0.05$  eV, which also represents the electron affinity (EA) of the corresponding neutral B<sub>29</sub> cluster. Among the low binding energy weak signals originated from minor isomers, two bands are tentatively labeled, X' (~3.4 eV) and X'' (~3.9 eV), for the sake of discussion. The measured VDEs for B<sub>29</sub><sup>-</sup> are collected in Table S1 in the (ESI<sup>+</sup>), where they are compared with the computational data.

Band A corresponds to the first excited state of neutral  $B_{29}$  associated with the main anion isomer. Band A with a VDE at 4.84 eV is separated from band X by an energy gap of 0.47 eV. Band B at a VDE of 4.97 eV is overlapped with band A. Band C is measured with a VDE of 5.44 eV, following an energy gap of 0.47 eV from band B. Beyond band C, two additional bands D (5.70 eV) and E (6.04 eV) are labeled. All the observed PES bands are broad, due to either large geometric changes between the anion and the neutral, or multiple detachment transitions.

#### Theoretical results

#### 4.1. Global minimum searches for B<sub>29</sub><sup>-</sup>

The MH and BH searches for  $B_{29}^{-}$ , in combination with manual structural constructions, generated about 5300 stationary points on the potential energy surface. The reoptimized low-lying structures at the PBE0/6-311+G\* level are presented in the ESI† (Fig. S1). As many as 97 structures were identified within 1 eV of the global minimum, about 25 of them being within 0.5 eV. The top five isomers were further refined at the single-point CCSD(T) level. The low-lying isomers of  $B_{29}^{-}$  are dominated by 2D structures, although a couple of 3D cage-like structures are also observed to be among the low-lying isomers.

The top five lowest-lying isomers of  $B_{29}^{-}$  at the PBE0 and single-point CCSD(T) levels are shown in Fig. 2(a), along with the relative energies at CCSD(T) with corrections for Gibbs free energies at 298 K. These isomers are labeled as 1, 2, 3, 4, and 5, according to their Gibbs free energies at room temperature. Isomers 1, 2, and 3 are essentially degenerate at room temperature, which are critical for the interpretation of the experiment at finite temperatures. At 298 K, isomers 1–5 span a narrow energy range of 0.11 eV, and none could be ruled out without comparison with the experiment.

Note that the energy order of the isomers varies at the PBE0 and single-point CCSD(T) levels (at 0 K). Both levels of theory indicate that isomer 2 is the global minimum, followed by 3. Isomer 1 is predicted to be 0.21 and 0.13 eV higher in energy at PBE0 and CCSD(T), respectively. The global minimum reported previously<sup>32</sup> corresponds to isomer 4 ( $C_1$ , <sup>1</sup>A), which occurs as the fourth low-lying isomer at both levels of theory, even with consideration of the entropic effect.



**Fig. 2** The top five lowest-lying structures (**1–5**) for  $B_{29}^{-}$  at the PBE0/6-311+G\* level, along with their relative energies (in eV) at three levels of theory: PBE0/6-311+G\*, single-point CCSD(T) at PBE0/6-311+G\* geometries (in parentheses), and CCSD(T) with corrections for Gibbs free energies at 298 K (in square brackets). The PBE0 and CCSD(T) data are corrected for zero-point energies at PBE0. Gibbs free energies are calculated at the PBE0/6-311+G\* level. The same set of low-lying isomers for  $B_{29}$  (**6–10**) at the PBE0 level are also shown.

#### 4.2. The top five lowest-lying structures of $B_{29}$

Isomer 1  $(C_s, {}^{1}A')$  is quasi-planar with a central pentagonal hole. It has a stingray-like shape with an out-of-plane distortion of 2.15 Å. Isomer 1 may be constructed from the seventh isomer of the  $B_{30}^{-}$  cluster<sup>22</sup> via the removal of one B atom from a hexagon, or from the ninth isomer of the  $B_{28}^{-}$  cluster<sup>19</sup> by inserting one B atom into the heptagon. Isomer 2  $(C_s, {}^{1}A')$  is a seashell-like cage, similar to the seashell B<sub>28</sub><sup>-</sup> borospherene.<sup>19</sup> It consists of two quasi-planar B<sub>15</sub> triangular sheets, being fused together by sharing one apex atom at the top and forming two B<sub>2</sub> interlaces at the bottom. Isomer 2 has two heptagons on the waist and one octagon at the bottom. The overall dimensions of the  $B_{29}^{-}$  seashell are 3.95, 6.13, and 5.65 Å, for its thickness, length, and width, respectively. Isomer 3  $(C_1, {}^{1}A)$  is also quasi-planar, containing a hexagonal hole and a filled pentacoordinate B atom. The Cartesian coordinates of the three lowest-lying structures (1-3) are given in Table S2 (ESI<sup>+</sup>).

Isomer 4 is also quasi-planar ( $C_1$ ), featuring a hexagonal hole. Isomer 5 is another seashell-like structure, differing from isomer 2 by the orientation of the two B<sub>2</sub> interlaces. Isomer 4 was reported in a recent theoretical study as the global minimum for B<sub>29</sub><sup>-,32</sup> whereas isomers 1–3 and 5 were not reported previously.

#### 4.3. The B<sub>29</sub> neutral cluster

For the neutral  $B_{29}$  cluster, the same set of five isomers corresponding to the anion isomers **1–5** are optimized at the PBE0/6-311+G\* level, as shown in Fig. 2(b) (6–10). The energetic order of the neutral isomers differs from that of the anion at the PBE0 level of theory. Apparently, both seashell-like isomers **6** ( $C_s$ , <sup>2</sup>A') and 7 ( $C_2$ , <sup>2</sup>B) are favored in the neutral, while the 2D structures become notably higher in energy. In particular, the stingray-like isomer **10**, which corresponds to the anion isomer **1**, becomes 0.90 eV higher in energy for the neutral ion.

### 5. Discussion

## 5.1. Comparison between experiment and theory and the effects of finite temperatures

We calculated the VDEs for isomers 1-5 of the  $B_{29}^{-}$  cluster using TD-DFT and compared the simulated PES spectra with the experimental data. The simulated PES spectra of isomers 1, 2, and 3, obtained by fitting unit Gaussians of width 0.05 eV to the computed VDEs, are compared with the measured PES spectrum in Fig. 1. Isomers 1-3 give distinct first VDEs of 4.17, 3.54, and 3.89 eV, respectively, at the PBE0 level. The computed first VDE of 4.17 eV for isomer 1 agrees well with the experimental band X. The computed ADE, or EA, of 4.06 eV for isomer 1 is also in excellent agreement with the measured ADE for band X (4.15  $\pm$  0.05 eV). Furthermore, the higher VDE bands in the simulated spectrum of isomer 1 are also consistent with the major observed PES bands. In particular, the observed energy gaps between bands X and A, as well as between bands B and C, are well reproduced in the simulated spectrum of isomer 1.

The lower first VDEs for isomers 2 (3.54 eV) and 3 (3.89 eV) are consistent with the observed weak low binding energy features of X' (~3.4 eV) and X'' (~3.9 eV), respectively, suggesting that isomers 2 and 3 are weakly populated in the  $B_{29}^{-}$  cluster beam. The simulated spectra for isomers 4 and 5 are given in Fig. S2 (ESI†). The two isomers also have low first VDEs.

While their contributions to the extended low binding energy tail in the experimental spectrum cannot be completely ruled out, populations of these isomers are expected to be minimal, if any.

To further confirm the simulated PES spectra at the TD-PBE0 level, we also computed the VDEs for isomers 1–3 using OVGF, as compared with the PBE0 results in Fig. S3 (ESI†). The OVGF data are generally similar to those of TD-PBE0. Overall, the theoretical results are in good agreement with the experimental observation, lending considerable credence for the identified global minimum and low-lying isomers for  $B_{29}^{-}$ .

Clearly, temperature plays an important role in the relative population of the isomers. Isomer 1 is not the global minimum at 0 K. But its Gibbs free energy becomes the lowest at about room temperature (Fig. 3). Even though the temperature of the clusters is not known exactly in the experiment, our previous experience suggests that clusters in this size range should be at about room temperature or sub-room temperature.<sup>35,36</sup> Fig. 3 shows the relative Gibbs free energies for the top five isomers as a function of temperature. At 0 K, the seashell isomer 2 is the lowest in energy, followed by the quasi-planar 3 and seashelllike 5 at 0.07 and 0.08 eV, respectively, as also shown in Fig. 2(a). With increasing temperature, the Gibbs free energy of the seashell isomer 5 increases slightly relative to that of isomer 2, whereas those for isomers 1, 3, and 4 all decrease. In particular, the stingray isomer 1 displays the sharpest drop. Thus, at room temperature, isomers 1-3 become virtually isoenergetic, in agreement with their coexistence experimentally. The Gibbs free energy curves in Fig. 3 predict the region where isomers 1-3 may coexist and reproduce the observed relative distributions. Considering the uncertainty of the computational methods in terms of energetics, we think that the prediction

(300 K or slightly larger) is quite good in comparison to the experiment (around room temperature, or slightly lower).<sup>35,36</sup>

## 5.2. The stingray-shaped $C_s(1)$ isomer of $B_{29}^-$ as an analogue of benzo[*ghi*]fluoranthene

The chemical bonding in the stingray-shaped isomer **1** is analyzed using both the CMOs and the AdNDP approach. Since this  $C_s$  isomer is quasi-planar, we flatten it to a planar  $C_{2v}$ species in the chemical bonding analyses in order to gain a clearer view of the  $\sigma$  and  $\pi$  bonding. The CMOs of isomer **1** show nine completely delocalized  $\pi$  bonds (Fig. 4(a)), suggesting an aromatic  $\pi$  system.<sup>51</sup> More interestingly, we have found that the  $\pi$  bonding in isomer **1** is analogous to that in benzo[*ghi*]fluoranthene ( $C_{1s}H_{10}$ ), as shown in Fig. 4(b). The  $\pi$ CMOs in the two systems exhibit remarkable similarities, suggesting that the stingray-like  $C_s$  (**1**) isomer of  $B_{29}^{-}$  can be considered as an all-boron analogue of  $C_{18}H_{10}$ .

Alternatively, the bonding in the  $C_{\rm s}$  B<sub>29</sub><sup>-</sup> (1) and benzo[ghi]fluoranthene may be understood on the basis of AdNDP analyses.<sup>48</sup> In AdNDP, the bonding of a molecular system is represented in terms of *n*-center two-electron (*n*c-2e) bonds, with the value of *n* ranging from one to the total number of atoms in the system. AdNDP thus recovers not only the classical Lewis elements (lone-pairs and 2c-2e bonds), but also delocalized multi-center bonds.

Even though the solutions from AdNDP are not unique, one guiding principle for the bonding analyses should be to obtain a chemically intuitive bonding picture for such a complex cluster system. Our AdNDP results for  $C_s B_{29}^-$  (1) are presented in Fig. 5(a). There are thirty-six B<sub>3</sub> triangles and one pentagon in  $B_{29}^-$ , with forty-four pairs of valence electrons. For the  $\sigma$  framework, we find the familiar 2c-2e  $\sigma$  bonds for the seventeen peripheral B–B bonds, as well as five 3c-2e  $\sigma$  bonds around



Fig. 3 Relative energies of the top five isomers (1–5) of  $B_{29}^{-}$  at the single-point CCSD(T) level, with Gibbs free energy corrections at PBE0/6-311+G\* as a function of temperature from 0 to 400 K. The energies are plotted relative to that of the seashell-like  $C_s$  (2) structure.

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 $17 \times 2c-2e \sigma$  bonds  $5 \times 3c-2e \sigma$  bonds  $13 \times 4c-2e \sigma$  bonds ON = 1.76-1.93 |e| ON = 1.88-1.93 |e| ON = 1.87-1.95 |e|



 $4 \times 4c-2e \pi$  bonds ON = 1.80-1.84 |e|



2 × 5c-2e π bonds ON = 1.75 |e|



ON = 1.70 |e|

2 × 7c-2e π bonds ON = 1.67 |e|



Fig. 5 Results of AdNDP bonding analyses for (a) the  $C_s$  (1) isomer of  $B_{29}^-$  and (b) the  $C_{18}H_{10}$  PAH at the PBE0/6-31G level. Occupation numbers (ONs) are shown.

the inner  $B_5$  hole and thirteen 4c-2e  $\sigma$  bonds. As anticipated, the nine  $\pi$  CMOs of  $C_s B_{29}^{-}(1)$  have been transformed into nine delocalized  $\pi$  bonds: four 4c-2e, three 5c-2e, and two 7c-2e  $\pi$ bonds (Fig. 5a, second row). This  $\pi$  bonding scheme is referred to as being of the Kekule type. A similar bonding analysis for benzo[*ghi*]fluoranthene is shown in Fig. 5(b), again demonstrating the close analogy between the  $\pi$  bonding in the  $C_s B_{29}^{-}(1)$ and benzo[*ghi*]fluoranthene.  $\pi$  bonding can also be represented in the Clar-type schemes, as shown in Fig. S4 (ESI†) for the  $C_s$  $B_{29}^{-}(1)$  and benzo[*ghi*]fluoranthene, which also reveals the analogy in  $\pi$  bonding between the two systems.

## 5.3. Chemical bonding in the seashell-like $C_s$ (2) borospherene of $B_{29}^{-}$

The bonding in the seashell-like  $B_{29}^{-}C_s(2)$  isomer was analyzed *via* AdNDP only, because the CMOs are simply too complicated for the low symmetry 3D species. The AdNDP results are shown in Fig. 6. The  $C_s(2)$  borospherene has thirty-eight  $B_3$  triangles, of which sixteen are on each  $B_{15}$  sheet and six are situated at the interface of the two  $B_{15}$  sheets (two for each of the three corners). The AdNDP analyses give rise to thirty-four 3c-2e  $\sigma$  bonds, plus one 6c-2e  $\sigma$  bond involving two  $B_3$  triangles on the two  $B_{15}$  sheets. The  $\sigma$  framework involves thirty-five delocalized  $\sigma$  bonds, leaving eighteen electrons for the  $\pi$  framework.

π bonding is relatively simple (Fig. 6, second row): each B<sub>15</sub> sheet has three 5c-2e π bonds, and the remaining three π bonds are situated at the three corners, involving both B<sub>15</sub> sheets. Note that all the σ and π bonds in the B<sub>29</sub><sup>-</sup> borospherene are delocalized, similar to the B<sub>40</sub> borospherene.<sup>14</sup> The 18π electrons in B<sub>29</sub><sup>-</sup> also conform to the 2(N + 1)<sup>2</sup> electron counting rule for spherical aromaticity (N = 2). Indeed, the calculated nuclear independent chemical shift (NICS)<sup>52</sup> at the cage center is -21.27 ppm

at the PBE0/6-311+G\* level, which is highly negative, and consistent with spherical aromaticity.

Finally, it should be pointed out that different isomer ordering between the  $B_{29}^{-}$  anion and the  $B_{29}$  neutral is similar to that observed previously for  $B_{40}^{-}/B_{40}$  and  $B_{28}^{-}/B_{28}^{-14,19}$  In each case, reordering is related to the EA of a given isomer, which determines the stability of the anion. In the case of  $B_{40}^{-}$ , the extremely low EA of the cage isomer makes the borospherene anion less stable relative to the planar one. In the case of  $B_{29}^{-}$ , the calculated EA of 4.06 eV for 1 is much higher than the value of 3.37 eV for 2 at the PBE0 level. Consequently, upon detachment of the extra electron from the anions, the stingray-shaped neutral isomer (10) becomes substantially destabilized with respect to the seashell isomer (6).

### 6. Conclusions

In conclusion, we have studied the structures and chemical bonding of the  $B_{29}^{-}$  cluster using anion photoelectron spectroscopy and quantum chemical calculations and found a rather complicated potential landscape for the medium-sized boron cluster. A quasi-planar stingray-shaped  $C_s$  (1) isomer and a seashell-like borospherene  $C_s$  (2) isomer are shown to be nearly degenerate and are observed to coexist in the size-selected anion PES experiment. The third quasi-planar  $C_1$  (3) isomer is also low in energy and makes minor contributions to the observed PES spectrum. Entropies are shown to be important for determining the relative stabilities of different isomers at finite temperatures. While at 0 K isomer 2 is the most stable, followed by 3 and 1, with increasing temperature isomer 1 becomes more stable with respect to 2 and is the major isomer observed experimentally. For neutral  $B_{29}$ , the seashell borospherene isomer



Fig. 6 Results of AdNDP bonding analyses for the seashell-like  $C_s$  (2) isomer of  $B_{29}^{-}$ . Occupation numbers (ONs) are shown.

is the global minimum and the stingray-shaped isomer becomes a higher energy species. Chemical bonding analyses reveal that the quasi-planar  $C_{\rm s} B_{29}^{-}$  (1), featuring nine delocalized  $\pi$  bonds, is an all-boron analogue of benzo[*ghi*]fluoranthene (C<sub>18</sub>H<sub>10</sub>). The seashell-like  $C_{\rm s} B_{29}^{-}$  (2) represents a new member of the borospherene family. All its  $\sigma$  and  $\pi$  bonds are delocalized and its  $18\pi$  electrons conform to the  $2(N + 1)^2$  electron-counting rule for spherical aromaticity.

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