Nature of Bonding in Bowl-Like B₃₆ Cluster Revisited: Concentric $(6\pi + 18\pi)$ Double Aromaticity and Reason for the Preference of a Hexagonal Hole in a Central Location

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Abstract: The bowl-shaped $C_{6\nu}$ B₃₆ cluster with a central hexagon hole is considered an ideal molecular model for low-dimensional boron-based nanosystems. Owing to the electron deficiency of boron, chemical bonding in the B₃₆ cluster is intriguing, complicated, and has remained elusive despite a couple of papers in the literature. Herein, a bonding analysis is given through canonical molecular orbitals (CMOs) and adaptive natural density partitioning (AdNDP), further aided by natural bond orbital (NBO) analysis and orbital composition calculations. The concerted computational data establish the idea of concentric double π aromaticity for the B₃₆ cluster, with inner 6π and outer 18π electron counting,

which both conform to the (4n+2) Hückel rule. The updated bonding picture differs from existing knowledge of the system. A refined bonding model is also proposed for coronene, of which the B₃₆ cluster is an inorganic analogue. It is further shown that concentric double π aromaticity in the B₃₆ cluster is retained and spatially fixed, irrespective of the migration of the hexagonal hole; the latter process changes the system energetically. The hexagonal hole is a destabilizing factor for σ/π CMOs. The central hexagon hole affects substantially fewer CMOs, thus making the bowl-shaped $C_{6\nu}$ B₃₆ cluster the global minimum.

Introduction

Elemental boron clusters^[1-22] possess highly unusual structural and bonding properties owing to the intrinsic electron deficiency of boron. Systematic experimental and computational studies in the past 30 years have uncovered an unprecedented plethora of planar or quasi-planar (2D) boron clusters, up to 40 atoms for anions.^[9,21] Among notable 2D boron species is the B₃₆ cluster,^[17,18] which is bowl-shaped and triangularly closepacked with C_{6v} symmetry, featuring a hexagonal hole in the center as a "defect". It is widely considered to be a molecular model for low-dimensional boron nanomaterials, such as boron α sheets;^[23-25] borospherenes;^[20,21] and in particular borophenes,^[26-29] in which close-packed boron ribbons or sheets and hexagonal holes prevail. Given the importance of the B₃₆ cluster in the field, its structural, electronic, and bonding properties require analyses and understanding.

However, chemical bonding in boron clusters^[9,30] of such a size as B₃₆ turns out to be rather challenging for theoretical chemistry. With over 100 valence electrons, detailed and thorough analyses of canonical molecular orbitals (CMOs) can be a heroic effort, if not impossible. Newly developed tools, such as

Supporting information and the ORCID identification number(s) for the au-

adaptive natural density partitioning (AdNDP),^[31] are applicable, but the program is user-adapted and the interpretation of its output requires expertise. Consequently, we believe the exact nature of bonding in the B_{36} cluster has remained elusive, despite prior computational works.[17-19] Interestingly, Liu et al. recently raised a question with regard to bonding and energetics in the B₃₆ cluster:^[19] why does the hexagonal hole prefer to be located at a central position? To the best of our knowledge, this fundamental question is still unanswered.

Herein, we choose to address two critical open issues for the bowl-like B₃₆ cluster outlined above. What is the nature of bonding in the B₃₆ cluster? Why is the hexagonal hole situated in the center of the bowl in the B_{36} cluster? To this end, we have performed bonding analyses through CMOs and AdNDP, which are further aided by natural bond orbital (NBO)^[32] analysis and orbital composition calculations.^[33] Our computational data lead to a bonding picture of concentric double π aromaticity, with 6π and 18π electron counting for the inner and outer subsystems, respectively; both of them follow the (4n +2) Hückel rule. We briefly reason why the Hückel rule applies for the bowl-like B₃₆ cluster, although it is not a monocyclic system. We also uncover the reason behind the central position of the hexagonal hole in the $B_{\rm 36}$ cluster. The hexagonal hole turns out to be a destabilizing factor for surrounding CMOs. Although electron clouds associated with double π aromaticity are maintained and spatially fixed during migration of the hexagonal hole in a series of B₃₆ isomers, the central hexagonal hole manages to affect markedly fewer CMOs (that is, to minimize destabilization owing to the hexagonal hole). As a

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consequence, the bowl-shaped $C_{6\nu}$ B₃₆ cluster with a central hexagon hole becomes the global minimum (GM) of the system.

Computational Details

Isomeric structures I, II, and III of the B₃₆ cluster were constructed based on data from the literature,^{117–19]} followed by full reoptimizations by means of density functional theory (DFT) at the PBE0 level^[34] with the 6-311 + G(d) basis set.^[35] Vibrational frequencies were calculated at the same level to ensure that all three isomers were true minima on the potential-energy surfaces. Chemical bonding in the B₃₆ isomers and their polycyclic aromatic hydrocarbon (PAH) analogue, coronene (C₂₄H₁₂), were elucidated through CMO analysis and AdNDP, which dealt with all valence electrons, both σ and π . Because AdNDP analysis was not sensitive to the level of theory or basis sets used, we chose to perform calculations at the PBE0/6-31G level by using the AdNDP program.^[31]

NBO analysis^[32] was performed to obtain natural atomic charges and Wiberg bond indices (WBIs), whereas natural atomic orbital (NAO) calculations^[33] were performed to analyze orbital compositions. All electronic structure calculations were accomplished by using the Gaussian 09 software package.^[36] Orbital compositions were calculated by using the Multiwfn^[33] package. Visualization of the AdNDP results was realized by using Molekel.^[37] Cluster structures and their CMOs were visualized by using GaussView 5.0.9.^[38]

Results and Discussion

Structures and Energetics of Isomers I, II, and III of the B_{36} Cluster

Three isomers of the B_{36} cluster (I, II, and III), as optimized at the PBE0 level, are illustrated in Figure 1. Structure I has a perfect bowl shape with C_{6v} symmetry. For the sake of clarity, we define herein that the cluster is composed of three concentric boron rings, which are labeled from core to periphery as the *first* (B₆), *second* (B₁₂), and *third* (B₁₈) rings, respectively. We fur-



Figure 1. Optimized bowl-shaped isomers I–III of the B₃₆ cluster at the PBE0/ 6-311 + G(d) level: a) GM structure I (C_{6w} ¹A₁), which consists of concentric B₆/B₁₂/B₁₈ rings from the inner core to outer periphery that are defined as the first, second, and third boron rings, respectively; b) local minimum (LM) II (C_{sr} ¹A'); and c) LM III (C_{sr} ¹A'). Relative energies are shown in kcalmol⁻¹ for isomers II and III, for which the hexagonal hole is located at the first and second boron rings, respectively.

ther define that the first and second boron rings make an *inner* boron double ring (BDR) ribbon, whereas the second and third boron rings form an *outer* BDR ribbon. The inner BDR ribbon has 18 atoms, relative to 30 atoms for the outer ribbon. As shown below, essential bonding elements in isomers I–III are all clouded on the BDR ribbons, rather than on specific boron rings.

Structure I is the GM of the B_{36} cluster,^[17-19] which features ideal inner and outer BDR ribbons. It also has a characteristic hexagonal hole^[20,21,23-28] at the center. Six apex boron atoms in the third boron ring are tricoordinated, and the remaining 12 edge boron atoms tetracoordinated. For comparison, the 6 and 12 boron atoms in the first and second boron rings have penta- and hexacoordination, respectively. The different coordination environments indicate that each kind of boron site may participate in chemical bonding in distinct ways (see below).

Overall, GM I is about 40 and 61 kcal mol⁻¹ below isomers II and III, respectively (Figure 1). These values are virtually identical to those reported by Liu et al. at the PBE0/def2-TZVP level.^[19] Structures I–III differ only in the position of the hexagonal hole: at the center of the first boron ring in I, on the first boron ring in II, and on the second boron ring in III. As a result, the inner BDR ribbon in II is not closed, owing to a defect, and yet it also has a filled and imperfect "disk" center. Notably, similar pentacoordinate boron motifs were previously observed in B_{24}^- and B_{25}^- clusters.^[39,40] In contrast, neither the inner nor outer BDR ribbons in III are closed, owing to the defect, although it has a perfect hexacoordinate B₇ disk at the center.

With the movement of the hexagonal hole from the center of the bowl out, the energetics of the B₃₆ cluster elevates gradually and monotonously, which demonstrates the preference of the hexagonal hole for the central location, as revealed initially by Liu et al.^[19] This observation is intriguing and should be rationalized on the basis of bonding analyses. Indeed, a prerequisite is that the bonding analyses need to be complete and correct, which are not a trivial task, despite numerous prior attempts.^[17–19] This is understandable considering the size of the system, as well as the nature of electron deficiency and multifold (σ and π) aromaticity in planar boron clusters.^[9,41]

Bonding in the B_{36} Cluster Revisited: Concentric Inner 6π Plus Outer 18π Double Aromaticity

We focus on the bonding in the bowl-like B_{36} (I) cluster, the complete set of π CMOs are shown in Figure 2a. As a starting point for discussion, for a polygonal *n*-membered molecular system, each specific atomic orbital (AO) can, in principle, combine into a set of *n* CMOs, which have 0, 1, 2, ..., nodal planes from the bottom up.^[42–44] When all *n* CMOs are fully occupied, they can be transformed into localized Lewis elements, either two-center two-electron (2c–2e) bonds or lone pairs. Otherwise, they form a delocalized system that leads to aromaticity or antiaromaticity, according to the Hückel electron-counting rules.

The bowl-like $B_{36}\left(I\right)$ cluster has a total of 108 valence electrons. To form a primitive molecular skeleton, the first and

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Figure 2. Pictures of the π CMOs of a) GM I (C_{6w} ¹A₁) of B₃₆ cluster and b) coronene C₂₄H₁₂ (D_{6hv} ¹A₁).

third boron rings use 12 and 36 electrons, respectively, for localized 2c–2e σ bonds,^[45] this has been established to be routine for planar boron clusters.^[9,41] Indeed, a set of six σ CMOs with zero, one (degenerate), two (degenerate), and three nodal planes are readily identified for the first boron ring. Similarly, along the third boron ring, a full set of 18 σ CMOs can be found.^[46] AdNDP analyses recover these 6+18 σ bonds, which are presented as 2c–2e/3c–2e σ bonds in Figure 3a.^[18] See ref. [45] for a clarification of the 2c–2e versus 3c–2e issue.

Other than those mentioned above, 18 σ CMOs, as depicted in Figure S1 in the Supporting Information, are located on the inner and outer BDR ribbons. The 12 CMOs in Figure S1 b in the Supporting Information are primarily clouded on the outer ribbon (by 72–94% based on orbital component analysis), with the deeper six also having secondary contributions from the inner ribbon. These CMOs strictly follow the building principle with 0 to 6 nodal planes, which, owing to C_{6v} symmetry, can be effectively "islanded" as 12 σ bonds (upon destructive/constructive combination with the six CMOs in Figure S1a in the Supporting Information). The most reasonable scheme is 12 rhombic 4c–2e σ bonds along the outer BDR ribbon (Fig-



Figure 3. Bonding patterns based on AdNDP for a) $B_{36} I (C_{6\nu} {}^{1}A_{1})$ and b) $C_{24}H_{12} (D_{6h\nu} {}^{1}A_{1})$. Occupation numbers (ONs) are indicated. The π clouds in I are spatially split into two regimes: an inner BDR ribbon made of the first and second boron rings versus an outer BDR ribbon made of the second and third boron rings. In a), six 2c-2e σ bonds in the middle of the edges (with ONs of 1.71 |e|) can be expanded as 3c-2e bonds, but that does not make a marked difference, except for slightly larger ONs of 1.95 |e|. The third boron center contributes only 12%.

ure 3 a). Here, each apex atom in the third boron ring is associated with two 4c-2e σ bonds. It is stressed that this scheme is an approximation because σ delocalization is known to be crucial in boron clusters.^[47-49] People would even argue that the

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most important contribution to electron delocalization comes from σ electrons. However, the occupation numbers (ONs) are close to ideal (1.89–1.95 |e|). Likewise, the six CMOs shown in Figure S1 a in the Supporting Information have 54–70% contributions from the inner BDR ribbon. They can combine constructively/destructively with the bottom six CMOs in Figure S1b in the Supporting Information to obtain a set of σ bonds on the inner ribbon, which have zero to three nodal planes and correspond to six 4c–2e σ bonds (see AdNDP data in Figure 3 a).

In brief, we have reasoned above in full detail, through CMO analyses, that cluster I has 6 and 18 2c-2e/3c-2e σ bonds on the first and third boron rings, respectively, as well as 6 and 12 4c-2e island σ bonds on the inner and outer BDR ribbons, respectively. These σ bonds cover the whole cluster surface almost uniformly and collectively consume 42 pairs of electrons. The σ framework^[17,18] is elegantly summarized in the AdNDP Scheme (Figure 3 a, top row).

The π framework seems to be simpler and relatively straightforward in terms of CMOs (Figure 2a); see also Figure S2 in the Supporting Information for isomer II and Figure 4 for isomer



Figure 4. Pictures of the π CMOs of artificially flattened $C_{2\nu}$ B_{36} associated with LM III.

III. However, it turns out to be challenging to reach an essential bonding picture from the π CMOs for a number of reasons. First, it is fundamental and open whether the (4n + 2) and 4n Hückel rules apply for polycyclic clusters, such as I–III. Second, if they do, how? Third, is a system with 12 π CMOs (that is, 24 π electrons) in line with the 4n Hückel rule? Is it aromatic or antiaromatic? Fourth, how does the user-adapted AdNDP program^[31] help in the elucidation of such a complex π -bonding system?

The π CMOs (Figure 2a) are composed of B 2 p_z AOs, following the building principle mentioned above for the σ framework. These can be divided spatially into two subsets: three π CMOs for the inner BDR ribbon (HOMO-1, HOMO-1', and HOMO-5; with secondary components from the third ring by 48–49%) and the remaining nine CMOs for the outer ribbon. Of course, there is mixing between inner and outer ribbons for certain CMOs. Indeed, the bottom three CMOs for the outer

ribbon (HOMO-17, HOMO-17', and HOMO-18) contain 21–29% from the first ring; these combine constructively/destructively with those of the inner ribbon to fully recover three π CMOs for the inner BDR ribbon. Their corresponding destructive/constructive combination leads to three "purified" π CMOs clouded on the outer ribbon, which, along with six higher π CMOs (HOMO, HOMO', HOMO-3, HOMO-6, HOMO-10, and HOMO-10'), form an extensive series with zero to four nodal planes, including four pairs of degenerate CMOs. Note that for π bonds, the intrinsic nodal plane associated to p_z AO is not counted, as routine. The inner and outer π subsystems are perfectly recovered in AdNDP analysis (Figure 3 a).

The π system in the inner BDR ribbon (Figure 3a, second row) is exactly analogous to the π sextet in benzene, except that the former is clouded on a BDR ribbon, instead of a single boron ring. The reason for this is that boron is electron deficient, with respect to carbon, so that BDRs collectively function as a single carbon ring.^[50-52] Such a π sextet cannot be localized, even in a single C₆ ring in benzene. In B₃₆ (I), the inner π sextet is 18-centered in nature and intrinsically delocalized, which renders π aromaticity for the cluster according to the Hückel rule.

For the outer BDR ribbon, a π subsystem with nine CMOs is identified (Figure 2a, second and third rows). Their corresponding AdNDP bonds are shown in Figure 3a, which are slightly modified with respect to CMOs and become strictly 30c-2e in nature (rather than global). These π bonds are located on the outer ribbon, following a regular pattern of zero to four nodal planes, which is a genuine and complete series and cannot be arbitrarily divided, segmented, islanded, or localized. With this understanding, the 18π electron counting again conforms to the (4*n*+2) Hückel rule, thus rendering double π aromaticity for the cluster. Therefore, our CMO analyses firmly establish a concentric, doubly π aromatic system, with 6π electron counting for the inner BDR ribbon and 18π for the outer one. AdNDP data fully reproduce this bonding picture (Figure 5a), which differs fundamentally from prior knowledge of the system.^[17,18] Specifically, Chen et al. stated inner and outer π sextets.^[18] Piazza et al. reached a "global" 12π electron system, without the spatial distinction between inner and outer BDR ribbons,^[17] the electron counting of which presumably satisfied the 4n Hückel rule. The 12π system^[17] exhibits 0, 1, 3, and 4 nodal planes in AdNDP, which is not a complete series of bonds that follow the construction principle. In particular, only one AdNDP bond has three nodal planes, in contrast to two AdNDP bonds with four nodal planes.

We add a few comments here: 1) B₃₆ I is a polycyclic cluster, rather than monocyclic. Nonetheless, once it is viewed as a concentric cluster with inner and outer BDR ribbons and consists of spatially separated double π subsystems, each BDR ribbon (and π subsystem) is equivalent to a monocyclic system because a BDR ribbon is equivalent to a carbon single chain.^[50–52] Thus, the (4*n*+2) and 4*n* Hückel rules, which many people believe to be valid for monocyclic systems only, apply for the bowl-shaped B₃₆ (I) cluster. 2) Cluster I is doubly π aromatic, despite the fact that it has a total of 24 π electrons. This π framework needs to be subdivided into 6 π versus 18 π sub-

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Figure 5. Concentric double π aromaticity, as revealed from the CMO and AdNDP analyses, for a) B₃₆ I (C_{64} , $^{1}A_{1}$) and b) $C_{24}H_{12}$ (D_{6h} , $^{1}A_{1}$). The inner 6π and outer 18 π electron counting in the bowl-like B₃₆ cluster is established herein for the first time, whereas the bonding model for $C_{24}H_{12}$ also differs from that reported in the literature.^[53,54]

systems because they are spatially independent from each other and should be counted separately. 3) AdNDP analysis is user-adapted and the data should be examined with caution. In fact, for the outer BDR ribbon in I cluster, prior analysis generated six island 4c-2e π bonds on apex sites and three global 36c–2e π bonds (that is, the outer π sextet),^[18] which differed from the scheme in Figure 5 a. The reason is that AdNDP automatically, and indeed arbitrarily, segments the nine π CMOs (Figure 2a, second and third rows) into two parts, so that the lower six are islanded as six 4c–2e π bonds, with the three of higher energy (HOMO, HOMO', and HOMO-3) remaining delocalized because it was simply not possible to localize them. Such a scheme is actually "hybrid" and arbitrary. It is stressed that the π sextet is abnormal, with the lowest energy bond having as many as three nodal planes. As stated earlier, such a bond should normally be completely delocalized and completely bonding. 4) Similar, unreasonable AdNDP schemes have been reported in the literature for other clusters as well, which motivated us to undertake the present study. We believe our analysis will benefit the field.

A Refined Bonding Model for Coronene

The circular shape of cluster I and its π -bonding pattern are reminiscent of coronene (C₂₄H₁₂); the latter contains C–C bonds for the hub, rim, flank, and spoke. Such an analogy was first recognized by Chen et al.^[18] Indeed, both I and C₂₄H₁₂ possess 108 electrons. Their π CMOs amount to 12 for both species, showing one-to-one correspondence (Figure 2). Being described through some 20 resonance structures or by three mobile Clar sextets, coronene itself is of interest in chemical bonding and aromaticity.^[53–55] Boldyrev and co-workers recently proposed a bonding model on the basis of AdNDP analysis, which features six 2c–2e C–C π bonds on the rim, three 6c–2e π bonds on the C₆ hub, and three 24c–2e π bonds on all carbon centers.^[53,54] Kumar et al. subsequently conducted a comparative study between the Clar sextet model and the AdNDP model.^[55]

The Boldyrev model, as appealing as it looks, has certain aspects that need refinement. We have performed a CMO analysis on coronene because CMOs are fundamental in chemical bonding. The π framework is presented in Figure 2b, the 12 CMOs of which show close correspondence to I. Thus, in light of the comprehensive analysis presented above for I, the bonding in coronene is relatively easy to understand. Briefly, coronene also possesses concentric double π aromaticity, with 6π and 18π electrons for the hub and rim/flank, respectively. This overall picture is also borne out from our AdNDP analysis (Figure 3b; see also Figure S3 in the Supporting Information). Here, the inner 6π subsystem is primarily situated on the C₆ hub, which can be slightly expanded to the spokes (Figure 3b, second row). Specifically, the hub contributes to ONs by 1.67-1.87 |e|; that is, 84–94%. The outer 18 π subsystem is completely delocalized on the C₁₈ ring (rim and flank; Figure 3b, third and fourth rows), which is intrinsically aromatic and should not be localized or segmented. As an independent support, we also performed nucleus-independent chemical shift (NICS)^[56] calculations. The NICS(1) values at the PBE0 level, calculated at 1 Å above the hole center, is -5.00 ppm for coronene, as compared to -10.38 ppm for benzene. For the artificially flattened D_{6h} B₃₆ bowl cluster, NICS(1) amounts to -15.98 ppm. These values are all negative, in line with π aromaticity in the systems. In the Boldyrev model, the outer 18π subsystem of coronene is segmented into six 2c–2e π bonds, with the remaining three π CMOs being treated as global 24c– 2e π bonds. Notably, these 24c–2e π bonds have 3 or 4 nodal planes. This is against the building principle for an aromatic system, which requires that the bottom bond be completely bonding (and normally with zero nodal plane).

According to our understanding, the Boldyrev model, as illustrated,^[53] should imply that the rim C–C links in coronene possess a formal bond order of slightly greater than two: one 2c–2e σ bond, one 2c–2e π bond, plus extra contribution from three "global" 24c–2e π bonds. A C–C bond in hydrocarbons, if indeed 2c–2e in nature, is anticipated to have a nearly ideal bond order of one. However, our calculated WBI values for

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these C–C links are only 1.58 at the PBE0/6-311+G(d) level. For calibration, benzene has a calculated WBI of 1.44, compared to a formal value of 1.50. To further ensure this, we also calculated WBIs at the B3LYP/6-311+G(d) level, and the values are 1.57 for coronene and 1.44 for benzene. In short, the PBE0 and B3LYP data are highly consistent. This indicates that the actual bond order for the C–C rim in coronene is far lower than that illustrated in the Boldyrev model, which appears to be a con for the latter. Bond lengths give a similar picture.^[57] In contrast, the current model (Figure 5b) is consistent with all data and represents a refinement of the Boldyrev model.

As noted by one reviewer, chemical bonding model for coronene is not trivial, in principle, and cannot be described by only one model. This fact is nicely exemplified by numerous models created by a number of groups worldwide. The reviewer specifically stated that our current bonding model (Figure 5b) is no exception; this opinion we fully respect. Nonetheless, we would like to offer slightly more detail on how our model interprets the uneven C-C bonds in the outer C₁₈ ring in coronene. The primary reason is that coronene has an overall D_{6h} symmetry only (rather than 9- or 18-fold symmetry, such as D_{18h}), owing to its inner C₆ core. The carbon centers in the outer C₁₈ ring are split into two types: 12 for the rim versus 6 for the flank. As a consequence, the 18 C-C links in the outer C₁₈ ring are not equivalent and do not participate completely equally in π delocalization, resulting in slightly uneven WBI values (1.58 for the rim and 1.27 for the flank at the PBEO level). However, such unevenness is relatively moderate (as compared to the "double" versus "single" bonds in the Boldyrev model).^[53] Notably, the WBI for the flank C–C bond is markedly greater than one and that for the rim C-C bond markedly smaller than two, which effectively smooths the difference between double and single C-C bonds; this is consistent with the outer 18π delocalization in our bonding model. We thus conclude that the uneven C-C distances in the outer C₁₈ ring in coronene are not a con for our updated bonding model. On the contrary, the quantitative WBI data fully support our model.

We can construct a model $C_{18}H_{18}$ monocyclic ring cluster, which indeed has D_{18h} symmetry upon optimization at the PBE0/6-311 + G(d) level. Its nine π CMOs (Figure S4 in the Supporting Information) show exact one-to-one correspondence to those of coronene or cluster I, further supporting the idea that the latter two species have an outer 18π -electron aromatic subsystem (rather than 6π). The D_{18h} $C_{18}H_{18}$ cluster has a uniform WBI of 1.40 for all C–C bonds, which lies in between those of the rim (1.58) and flank (1.27) in coronene because the model $C_{18}H_{18}$ cluster has an ideally delocalized 18π system (compared to the less-than-ideal outer 18π subsystem for coronene, owing to its lower D_{6h} symmetry; see above). For I, the B–B distance in the third ring (B₁₈) is also split between the 12 apex B–B links and 6 edge ones. However, this does not contradict the outer 18π aromatic subsystem.^[58, 59]



Figure 6. AdNDP bonding patterns of LM structures II and III of the B₃₆ cluster. The ONs are indicated. The concentric double π aromatic subsystems are essentially the same as those of GM I, irrespective of the position of hexagonal hole.

Why Does the Hexagonal Hole in the B₃₆ Cluster Prefer to Be in the Central Position?

Liu et al. recently observed that isomers I–III of the B_{36} cluster successively gain stability as the hexagonal hole moves from the second boron ring to the first and eventually to the center of the bowl (see Figure 1).^[19] These authors made an effort to rationalize this trend through AdNDP analysis. Nonetheless, the bonding pictures for isomers II and III did not seem to be

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correct, owing to the complex nature of the systems. Thus, we believe that Liu et al. did not succeed in answering the question as to why the hexagonal hole in the B_{36} cluster prefers to be in the central position.

We have carried out chemical bonding analyses for isomers II and III, through CMOs and AdNDP. The σ framework appears to be easy to model with the aid of AdNDP, resulting in 2c-2e/ $3c-2e^{[45]}$ and island $4c-2e \sigma$ bonds that almost uniformly cover the whole surface (Figure 6). The above AdNDP data are similar to those of Liu et al., [19] with minor discrepancies, which are not crucial. For the π framework, our key observation from CMOs is that the two spatially separated π subsystems (6 π versus 18π) persist in II and III. Remarkably, the center of the π subsystems is fixed at the cluster center and does not migrate with the hexagonal hole. As an example, the complete set of π CMOs of isomer III are presented in Figure 4, which show correspondence to isomer I (Figure 2a). The AdNDP π schemes of II and III are illustrated in Figure 6. As clearly revealed herein, the π patterns in I–III are largely the same for both CMOs (Figure 4 and Figure S2 in the Supporting Information) and the AdNDP schemes.^[60] All ON values in AdNDP are reasonable, except for one 29c–2e π bond in III (1.47 |e|; Figure 6b). The latter is due to participation of the core in this specific bond, which can be traced back to the HOMO (Figure 4). Expansion of this bond to 36c-2e fully recovers the ON value to 2.00 |e| (Figure S5 in the Supporting Information).

The similarity of π -bonding patterns in isomers I–III is not sufficient enough to differentiate the three isomers for energetics, despite efforts by Liu and co-workers (Figure S6b in the Supporting Information).^[19] To rationalize the trend in energetics (Figure 1), it is crucial to examine how a hexagonal hole affects orbital energies for different isomers. A few examples are shown in Figure 7 for isomers I and III, which have the largest difference in energetics. For isomer I, HOMO-30, HOMO-5, HOMO-17, and HOMO-3 are chosen; the corresponding CMOs in isomer III are HOMO-49, HOMO-16, HOMO-24, and HOMO-3, respectively.



Figure 7. a) The central hexagonal hole in GM I of the B₃₆ cluster is a penalty for certain CMOs, such as HOMO-30 (σ) and HOMO-5 (π), with respect to their corresponding CMOs in isomer **III** (shown in the bottom panels). b) For some CMOs, the hexagonal hole in GM I serves as a relative stabilizer. All CMO energies are given in eV.

The CMOs of I and III in Figure 7 a have major contributions from the inner core, which occurs as a hexagonal B₆ ring in I (with a prototypical hexagonal hole) versus a filled hexagonal B₇ disk in III (with elimination of the hexagonal hole). Energetically, HOMO-30 (σ) in I has an orbital energy that is 3.52 eV less stable than its counterpart in III, despite the fact that the former looks more symmetric and more delocalized. Similarly, HOMO-5 (π) in I is 1.44 eV less stable than its counterpart in III. This effect is unexpected and seems odd, but it is completely understandable. Here, the hexagonal hole of I is not important, nor is its high symmetry. It is the spatial position of electron clouds, as well as the spatial match/mismatch between the hexagonal hole and electron clouds, that matter. The hexagonal hole is a con for a CMO that is positioned on it, whereas a filled hexagon hardens the disk and stabilizes a CMO, either π or σ .

Likewise, HOMO-17 and HOMO-3 in I, for example, are primarily located on the outer BDR ribbon, with little electron cloud on central hexagon hole. In these cases, the central hexagonal hole does not affect these CMOs very much. On the contrary, the migration of the hexagonal hole to the outer BDR ribbon in III effectively destabilizes their corresponding CMOs (HOMO-24 and HOMO-3), which cover the new hexagonal hole. Specifically, HOMO-24 is destabilized by 0.31 eV with respect to isomer I and HOMO-3 by 0.44 eV. Because there are substantially more CMOs around the outer BDR ribbon in the B₃₆ cluster than that at the vicinity of the bowl center (approximately 39 versus 15 for isomer I; see Figure 3a), it is better to situate the hexagonal hole at the center of the bowl. This sort of arrangement destabilizes far fewer σ/π CMOs, which effectively makes isomer I of the $B_{\rm 36}$ cluster more stable than that of its rivals.

Conclusions

The bowl-shaped B₃₆ cluster is an interesting molecular model for low-dimensional boron-based nanosystems, such as borophenes. We report a revised chemical bonding model for the $B_{36}\xspace$ cluster on the basis of CMO analysis and AdNDP. The cluster features concentric double π aromaticity with spatially independent inner 6π and outer 18π subsystems, each following the (4n+2) Hückel rule. This bonding picture differs from that reported in prior studies on the system. We also show that the electron clouds of concentric 6π and 18π system are spatially fixed, irrespective of the migration of hexagonal hole. The latter is revealed to be a destabilizing factor for σ/π CMOs clouding the hole. The preference for the central location of the hexagonal hole in the B₃₆ cluster lies in the fact that substantially fewer CMOs are present around the bowl center, thus resulting in much less collective destabilization. In other words, minimizing the destabilization from the hexagonal hole (rather than maximizing stability) governs the GM of the bowllike C_{6v} B₃₆ cluster.

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Conflict of interest

The authors declare no conflict of interest.

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- [57] The C–C bond lengths in coronene correlate roughly with their WBI values. At PBE0, the C–C distances of the outer C₁₈ ring in coronene are 1.37 (for the rim) and 1.42 Å (for the flank), respectively, and that in D_{18h} C₁₈H₁₈ model cluster is 1.42 Å. These three values correspond to the calculated WBIs of 1.58, 1.27, and 1.40, respectively. We believe that, in this case, WBI is a slightly better indicator for C–C bonding. For comparison, typical C–C, benzene, and C=C bonds are 1.54, 1.40, and 1.34 Å, respectively. Clearly, the rim and flank C–C bonds in coronene are in the vicinity of benzene (and D_{18h} C₁₈H₁₈) in terms of either bond orders or distances. For example, the rim and flank C–C distances are within ±0.03 Å of benzene. In particular, the flank C–C bonds are not single bonds. All of the above data concertedly point to a delocalized outer π subsystem in coronene, which largely smears the "C=C" versus "C–C" bonds in the Boldyrev model.^[53]
- [58] As reasoned throughout this paper, there is no doubt that the outer BDR ribbon in the B₃₆ (I) cluster supports a 18π aromatic subsystem. This is particularly convincing in light of a close comparison with the model C₁₈H₁₈ cluster (Figure S4 in the Supporting Information). We shall offer herein an argument for the unevenness of apex versus edge B–B links in the third boron ring in B₃₆ (I). Two types of boron centers are present in the third boron ring (tricoordinate apex sites versus tetra-coordinate edge sites). Their distinct coordinate environments are the

primary reason for the unevenness in B–B distances, which differ in σ bonding. For the σ framework, an apex B–B link is associated to both 2c-2e σ and island 4c-2e σ bonds, whereas an edge B–B link is bound by a 2c-2e σ bond only^[45] (Figure 3a, first row). In other words, an apex B–B link is twofold σ bound and an edge link is onefold σ bound. Therefore, the unevenness of B–B distances in the third ring is not a con for the outer 18 π aromatic subsystem in B₃₆ (I).

- [59] Furthermore, the outer BDR ribbon in B_{36} (I) does not have 9- or 18-fold symmetry owing to the $C_{6\nu}$ structure of the cluster, nor does the outer ribbon contain 18 rhombic B_4 units (Figure 1a). In this case, each B_4 rhombus, B_3 triangle, or B–B link can contribute differently to the outer 18 π aromatic subsystem. However, such unevenness is not a con to the 18 π aromaticity. This argument is in the spirit of that for coronene.
- [60] Again, Liu et al. relied on the AdNDP program to produce π schemes for isomers II and III.^[19] In their schemes, the inner 6π subsystem is destroyed and occurs randomly in space, which are inconsistent with CMOs. Note that even the number of inner π bonds can be varied in AdNDP; an example^[19] of which is shown in Figure S6b in the Supporting Information.

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