Planar Tricyclic B₈O₈ and B₈O₈⁻ Clusters: Boron Oxide Analogues of s-Indacene C₁₂H₈

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S Supporting Information

ABSTRACT: Boron clusters and their oxides are electron-deficient species with (π and σ) aromaticity and antiaromaticity, enabling a structural and bonding analogy between them and the aromatic hydrocarbons. s-Indacene C12H8 is normally considered as a border system between the classes of aromatic and antiaromatic hydrocarbons. We show herein, via computer global-minimum searches and B3LYP and single-point CCSD(T) calculations, that boron oxide clusters D_{2h} B₈O₈ (1, ¹A_g) and D_{2h} B₈O₈ $(2, {}^{2}B_{2g})$ adopt planar tricyclic structures, which feature fused heterocyclic



 $B_3O_2/B_4O_2/B_3O_2$ rings and two boronyl (BO) terminals, a structural pattern analogous to the $C_5/C_6/C_5$ rings in s-indacene. Bonding analyses indicate that $B_s O_s(1)$ is a formally antiaromatic 12π system, the molecular orbitals of which are largely similar to those of s-indacene. Infrared and ultraviolet-visible spectra of B_8O_8 (1) neutral, as well as the photoelectron spectrum of $B_8 O_8^-$ (2) anion, are predicted computationally. The latter spectrum shows a sizable energy gap of 3.5 eV for 2, demonstrating the electronic robustness of 1. Our bonding analyses also shed critical light on the nature of bonding in s-indacene.

1. INTRODUCTION

Boron has a high affinity for oxygen, and the combustion of boron and boranes as highly exothermic processes has been actively pursued for the development of boron-based propellants over the past 60 years.¹ Boron oxide clusters are not only relevant to mechanistic understanding of the combustion processes at the molecular level but also exotic species in terms of molecular structures and chemical bonding, which are being extensively studied lately.²⁻³² Boron clusters are electron-deficient themselves, 33-47 and thus boron oxide clusters are anticipated to be even more electron-deficient, offering opportunities to explore novel chemical bonding. A main finding in boron oxide clusters is that boronyl (BO) serves as a robust ligand,^{2,7–9} which governs cluster structures in the gas phase and in synthetic compounds. Another finding is the analogy^{8,9,19,38,39,41-43} between boron-based clusters and hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs).

To facilitate such a chemical analogy, boron oxide clusters utilize electrons that would otherwise be merely O 2p lonepairs for delocalized π bonding within polygonal B–O rings (typically rhombic, pentagonal, or hexagonal).^{19,24,25,27-29} This bonding situation helps stabilize boron oxide clusters, as well as makes polygonal B-O rings the key structural units. For instance, boronyl boroxine, D_{3h} B₆O₆, was found to be a 6π system with a boroxol (B3O3) ring as the core and three boronyl groups as terminals, rendering it an inorganic analogue of benzene.¹⁹ The $C_{2\nu}$ B₅O₅^{+/0} clusters also feature a boroxol ring with two boronyl terminals and can be viewed as analogues of phenyl cation $(C_6H_5^+)$ and phenyl radical (C_6H_5) , respectively.²⁸ Furthermore, D_{2h} B₂O₂H₂ and D_{2h} B₄O₄ clusters^{25,27} were shown to have a rhombic B_2O_2 core, with two H atoms (or two boronyls) attached terminally. These two species are 4π systems with a four-center four-electron (4c-4e) π bond (that is, the so-called "o-bond"),^{24,27} in which two canonical molecular orbitals (CMOs) are in a nonbonding/ bonding combination, in contrast to antibonding/bonding in a typical 4π antiaromatic hydrocarbon such as cyclobutadiene (C_4H_4) . An o-bond system is considered aromatic despite its 4π electron-counting, because the upper π CMO is essentially nonbonding and should not be counted with respect to either aromaticity or antiaromaticity. The o-bond concept was reinforced lately in ternary $B_3S_2H_3^{0/-}$ and $B_3N_2H_5^{0/-/2-}$ clusters,^{48,49} in which a 4π (rather than 6π) species is electronically robust.

Up to now, a variety of boron-rich boron oxide clusters have been studied experimentally or computationally, indicating that boronyl dominates their structures.² Relatively little appears to be known about oxygen-rich $B_n O_m$ (n < m) clusters^{4,5,23,24} and those with equal content of boron and oxygen (n = m). As for the $B_n O_n$ clusters, two systems ($B_4 O_4^{0/-}$ and $B_6 O_6^{0/-/2-}$) were studied in our recent works.^{19,27,29} In these clusters, rhombic B_2O_2 and hexagonal B_3O_3 rings were shown to be structural cores, with the rest of the components being attached as boronyl terminals.

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What are the structures of larger $B_n O_n$ clusters? How do they grow with increasing size? Do the larger B_nO_n clusters possess multiple B-O rings, and do they show chemical analogy to PAHs? These remain the open questions to be addressed. Building upon existing knowledge in the field, the $B_8 O_8^{0/-}$ clusters are interesting targets for computational study, which have an equal content of boron and oxygen. Their globalminimum (GM) structures and nature of bonding are still unknown. We have undertaken a theoretical study on structures and bonding of $B_8 O_8^{0/-}$ clusters, making use of an array of computational tools: computer GM searches, electronic structure calculations at density-functional theory (DFT) and coupled-cluster theory (CCSD(T)) levels, natural bond orbital (NBO) analyses for Wiberg bond indices (WBIs) and natural atomic charges, and bonding analyses via CMOs and adaptive natural density partitioning (AdNDP).50

In this contribution, we shall report on the geometric structures and chemical bonding of $B_8O_8^{0/-}$ clusters using quantum chemical calculations, through which we firmly establish their planar, tricyclic GM structures. The structures consist of two pentagonal B_3O_2 rings and one hexagonal B_4O_2 ring, fused together by sharing two B_2 units and terminated by two boronyl groups. A proposal is put forward that $B_8O_8^{0/-}$ clusters are inorganic analogues of *s*-indacene $(C_{12}H_8)^{51-53}$ which all have the characteristic pentagon/hexagon/pentagon structural pattern, as well as six delocalized π CMOs that formally fulfill the 4*n* Hückel rule for antiaromaticity. Our analyses also shed light on the nature of bonding in *s*-indacene, a puzzling issue in the literature with "mixed aromatic and antiaromatic character".⁵² The $B_8O_8^{0/-}$ clusters complete the $(B_2O_2)_n^{0/-}$ series for n = 1-4, which follow a uniform growth pattern as suggested herein.

2. METHODS

The GM structural searches for B_8O_8 were conducted using the coalescence kick $(CK)^{54-56}$ and basin hopping $(BH)^{57}$ algorithms, aided with manual structural constructions. Full structural optimizations and frequency calculations were carried out for the low-lying isomers using the hybrid B3LYP method^{58,59} with the 6-311+G(d,p) basis set, as implemented in Gaussian 09.⁶⁰ Top structures identified for B_8O_8 were used as the initial structures for $B_8O_8^-$ during their structural searches. To check for consistency, relative energies were also calculated using the PBE1PBE functional with symmetry constraints.⁶¹ Furthermore, the energetics were refined for low-lying isomers using single-point CCSD(T) calculations⁶²⁻⁶⁵ at the B3LYP geometries, that is, at the CCSD-(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level.

Chemical bonding in B_8O_8 , $B_8O_8^-$, and their relevant PAH species (*s*-indacene, $C_{12}H_8$) was elucidated using the CMO analyses and AdNDP.⁵⁰ The NBO 5.0 program⁶⁶ was used to calculate the WBIs and natural atomic charges. Adiabatic and vertical detachment energies (ADE and VDEs) of the $B_8O_8^-$ anion cluster were calculated using the time-dependent DFT (TD-B3LYP) method.^{67,68} Multiwfn⁶⁹ was used to perform the orbital composition analyses.

3. RESULTS

3.1. Potential Energy Surfaces and Isomeric Structures. The GM structures of B_8O_8 neutral and $B_8O_8^-$ anion were established, via global searches and B3LYP/6-311+G(d,p) and single-point CCSD(T) calculations, to be 1 $(D_{2\mu}, {}^{1}A_{\nu})$ and

2 (D_{2h} , ${}^{2}B_{2g}$), respectively, as illustrated in Figure 1. Alternative low-lying structures of $B_8O_8^{0/-}$ at B3LYP are shown in Figure 2



Figure 1. Global-minimum structures of (a) $D_{2h} B_8 O_8$ (1, ${}^{1}A_g$), (b) $D_{2h} B_8 O_8^-$ (2, ${}^{2}B_{2g}$), and (c) $C_{2h} C_{12}H_8$ (3, ${}^{1}A_g$) at the B3LYP/6-311+G(d,p) level. Also shown is a transition-state structure (d) $D_{2h} C_{12}H_8$ (4, ${}^{1}A_g$) at the same level. Bond distances are labeled in angstroms. Red color represents the O atoms.

and in the Supporting Information (Figure S1), in which their relative energies at the B3LYP and CCSD(T) levels are documented, along with complementary data at PBE1PBE/6-311+G(d,p); the latter serve to check for consistency of the B3LYP method.

As shown in Figures 2 and S1, the low-lying structures of B_8O_8 and $B_8O_8^-$ clusters are dominated by a polygonal B–O ring, or fusion of two to three polygonal B–O rings, as the structural core. The B–O rings consist of from four up to eight atoms, with B_3O_2 , B_4O_2 , and B_3O_3 being the most popular. Heptagonal B_4O_3 and octagonal B_4O_4 rings are present in a number of isomers, but these are typically quite high in energy. Rhombic B_2O_2 ring also appears in one isomer. The existence of B–O polygons governs the planar geometries of these isomers, which also hints that π bonding owing to O 2p electrons plays a crucial role in stabilizing the systems.



Figure 2. Alternative low-lying isomeric structures of the B_8O_8 cluster at the B3LYP/6-311+G(d,p) level. Relative energies with zero-point energy (ZPE) corrections are shown in eV, at the B3LYP/6-311+G(d,p), PBE1PBE/6-311+G(d,p) (in *italic*), and single-point CCSD(T)//B3LYP/6-311+G(d,p) (in **bold**) levels, respectively. Red color represents the O atoms.



Figure 3. Wiberg bond indices (WBIs) and natural atomic charges in lel of (a and b) D_{2h} B_8O_8 (1) and (c and d) C_{2h} $C_{12}H_8$ (3).

In all isomers, polygonal B—O rings as the structural core are attached by B—O terminals. Among the terminals, boronyl (a monovalent σ radical with a B \equiv O triple bond)² is frequently observed and it normally makes the structures low in energy. The BO group can also be attached to the core via the O site, which leads to an isomer that is markedly higher in energy. The BO₂ group is present in a couple of isomers, albeit those are not competitive with the GM structure. Lastly, a dangling O ligand is observed in one isomer.

3.2. Global-Minimum Structures: $B_8O_8 \mathbf{1} (D_{2hr} {}^1A_g)$ and $B_8O_8^- \mathbf{2} (D_{2hr} {}^2B_{2g})$. The energetics at all three levels of theory are consistent with each other, suggesting that the GM structures of $B_8O_8^{0/-}$ (1 and 2; Figure 1a and b) are reasonably well-defined on their potential energy surfaces.⁷⁰ At CCSD(T), our highest level of theory, structures 1 and 2 are 0.48 and 0.21 eV, respectively, lower in energy than their nearest competitors.

GM 1 is perfectly planar. It is a tricyclic system with two B_3O_2 pentagons and one B_3O_3 hexagon, which are fused together by sharing two B_2 units. The tricyclic core is terminated by two BO groups at the far ends. The overall shape has D_{2h} symmetry, which is significantly elongated, in particular with respect to the D_{4d} isomer (Figure 2).¹⁴ For the bond distances in 1 (Figure 1a), terminal B—O groups are 1.20

Å and can be assigned as B \equiv O triple bonds (that is, boronyls).² The latest recommended covalent radii⁷¹ give the upper bound of B–B single, B \equiv B double, and B \equiv B triple bonds as 1.70, 1.56, and 1.46 Å, respectively. Thus, the B–B distances in 1 (1.68 and 1.70 Å) are close to single bond. The B–O distances within tricyclic rings fall in the regime of 1.38–1.40 Å, which are quite uniform. These values are in between single (1.48 Å) and double (typical distance,²⁴ 1.28 Å; upper bound,⁷¹ 1.35 Å) bonds, suggesting a delocalized ring system in addition to B–O σ single bonds.

The GM of $B_8O_8^-$ anion cluster, **2** $(D_{2h}, {}^2B_{2g})$, is remarkably similar to B_8O_8 (**1**). They differ only in slight variations of bond distances. Terminal B \equiv O bonds expand by 0.01 Å from **1** to **2**, and 8 out of 12 B-O bonds in the tricyclic core also expand by 0.01–0.02 Å. In contrast, B-B bonds shrink by 0.02–0.04 Å. The above data indicate that cluster **2** is similar to **1** in terms of bonding and the extra charge in **2** enhances the B-B bonding within four B₂ units.

4. DISCUSSION

4.1. Planar Tricyclic $D_{2h} B_8 O_8^{0/-}$ Clusters, Wiberg Bond Indices, and Natural Atomic Charges. As shown in Figure 1, $B_8 O_8$ and $B_8 O_8^-$ clusters have similar D_{2h} GM structures: (1,

 ${}^{1}A_{g}$) and (2, ${}^{2}B_{2g}$). Both species exhibit an elongated tricyclic core (with a pentagon/hexagon/pentagon pattern), which is terminated by two boronyls. Four B₂ units are present in each cluster. According to analyses in section 3.2, the classical Lewis bonding elements in 1 and 2 are rather simple and straightforward. First, each O atom has one 2s/2p lone-pair, collectively consuming 16 electrons. Second, two B=O triple bonds localize 12 electrons. Third, 12 B-O single bonds in the tricyclic core consume 24 electrons. And fourth, four B-B single bonds use eight electrons. These Lewis elements consume 60 electrons in total. Since cluster 1 has 72 valence electrons and 2 has 73, the delocalized π bonding in 1 and 2 only involves 12 and 13 electrons, respectively.

The Lewis elements (30 of them) largely define the structural skeleton of clusters 1 and 2. This is understandable using a simple argument. Under the assumption that O and B are in their formal charge states of O^{2-} versus B^{3+} and the B/O atoms are interconnected via terminal B==O triple or bridging B–O single bonds, the B_8O_8 cluster should have eight excess electrons on B centers. These electrons thus form four B–B single bonds, dictating GM structure 1. The same argument is true for $B_8O_8^-$ (2), except for one extra delocalized electron.

NBO analyses provide quantitative data on the WBIs and natural atomic charges in clusters 1 and 2 (see Figure 3, Figure S2, and Table S1). Three general observations can be made. First, the B and O atoms in 1 and 2 carry a substantial amount of charges. Specifically, B has a positive charge of +0.7 to 0.8 lel in 1, whereas O is negative (-0.7 to -0.8 lel). Intramolecular charge transfers appear to be rather local processes. Second, the B-O bonding is of mixed covalent and ionic character, resulting in relatively low WBIs for single B-O (WBI: 0.87-0.90) and triple B≡O (WBI: 1.83–1.96) bonds in 1 and 2. In contrast, the B-B single bonds are nearly perfect (WBI: 0.95-1.02). Third, going from 1 to 2, WBIs increase only for B-B bonds (by 0.03-0.04) and those of B \equiv O/B-O bonds either decrease or stay unchanged. Note that, with the addition of an extra electron, the amount of positive charge on eight B centers collectively drops by 0.74 lel from 1 to 2, suggesting that the extra charge in 2 primarily contributes to the B-B bonding (vide infra).

4.2. Chemical Bonding in D_{2h} $B_8O_8^{0/-}$ **Clusters: Boron Oxide Analogues of s-Indacene.** The nature of bonding in clusters 1 and 2 can be further elucidated using the CMO and AdNDP analyses.⁵⁰ Since 1 and 2 are similar in structures and bonding, we focus on cluster 1 only. As mentioned earlier, the classical Lewis elements are conceivable solely on the bases of cluster geometries and bond distances (Figure 1). Such 30 Lewis elements in 1 are elegantly recovered via the AdNDP analysis (Figure 4), including 1 lone-pair for each O center (8 in total), 2 B \equiv O triple bonds (6 bonds in total), 12 B-O single bonds, and 4 B-B bonds.

The delocalized bonding in 1 relies on a set of six π CMOs (Figure 5a). Orbital component analyses (Table 1) indicate that the π CMOs are dominated by O 2p components, from 69.1% in HOMO–18 up to 99.5% in HOMO–6. In total, O 2p contributes to approximately 84% of these π CMOs, with B balancing the remaining 16%. Thus, at zeroth order, the π framework stems from six O 2p_z lone-pairs (one from each O center), which extend and combine to form six delocalized π CMOs. Actually, O 2p_z lone-pairs can be roughly traced back to the CMOs. For example, HOMO–12 has a major component from the constructive combination of O 2p_z from O1 and O2 in the central B₄O₂ hexagon (56%, including 3.5% from B),



Figure 4. Lewis bonding elements of $D_{2h} B_8 O_8$ (1) as recovered from adaptive natural density partitioning (AdNDP). (a) O lone-pairs, one for each O center. (b) Two terminal B=O triple bonds. (c) Peripheral B=O σ single bonds within the tricyclic core. (d) Four B-B σ single bonds. Occupation numbers (ONs) are shown.

whereas HOMO-15 has a 77.5% contribution from the hexagon (including 15.5% from B) and yet in a destructive combination between O1 and O2. The constructive/destructive pair helps recover the main portion of two O 2p₂ lone-pairs on O1 and O2 (of course, other CMOs such as HOMO-6 and HOMO-18 also make nonnegligible contributions, if one wants to fully recover the lone-pairs). Likewise, HOMO-18 and HOMO-17 may recombine to generate a pair of completely bonding π bonds on two B₃O₂ pentagons, and HOMO-6 and HOMO-7 for their corresponding pair of partially bonding/antibonding π bonds. In this way, each pentagon has a bonding π bond and a partially bonding/ antibonding one, which further recombine to recover the O 2p_z lone-pairs on O7/O8/O9/O10. The above analysis suggests that the $B_3O_2/B_4O_2/B_3O_2$ rings each have a (moderately delocalized) 4π system, conforming to the 4n Hückel rule for antiaromaticity.

The elongated shape, pentagon/hexagon/pentagon pattern, and 12π electron-counting of cluster 1 are reminiscent of sindacene ($C_{12}H_8$), one of the PAHs. Similar to a prior report,⁵² our calculations at B3LYP/6-311+G(d,p) indicate that the C_{2h} (3) structure of s-indacene is more stable than D_{2h} (4) (Figure 1); the latter is a transition state $(336.4i \text{ cm}^{-1})$. However, in terms of bonding, D_{2h} (4) and C_{2h} (3) are essentially the same. Indeed, the C—C distances in 3 and 4 differ by only 0.00–0.03 Å. All peripheral C—C distances in 3 (1.38–1.44 Å) are close to that in benzene (1.39 Å) and yet deviate significantly from C-C single (1.54 Å) and C=C double (1.33 Å) bonds. In particular, the "longer" C—C bonds in C_{2h} (3) are 1.42–1.45 Å (Figure 1c), well in between typical single and double bonds. The calculated WBIs and natural atomic charges of 3 and 4 are presented in Figures 3 and S3; it is stressed that WBI values for the "shorter" C-C links are far less than double bonds. For reference, benzene has WBIs of 1.44 for C—C links at the same



Figure 5. Illustration of π canonical molecular orbitals (CMOs) of (a) D_{2h} B₈O₈ (1), compared with (b and c) their selected AdNDP schemes. (b) Five-center two-electron (5c-2e) and 6c-2e π bonds, 4π electrons for each pentagon or hexagon. (c) Delocalized 12c-2e π bonds. Parts b and c are equivalent to each other. ONs are shown.

Table 1. Orbital Composition Analysis for the π Canonical Molecular Orbitals (CMOs) in B₈O₈ (1, D_{2h}, ¹A_e) Cluster

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CMO ^{<i>a,b</i>}	01/02	O7/8/9/10	O total ^c	B3/4/5/6	B11/12	B total
НОМО-6	26.7	72.8	99.5			
HOMO-7		93.0	93.0	6.7		6.7
HOMO-12	52.5	32.8	85.3	3.5	8.8	12.3
HOMO-15	62.0	22.3	84.3	15.5		15.5
HOMO-17		74.2	74.2	10.6	14.0	24.6
HOMO-18	26.1	43.0	69.1	23.4	6.9	30.3

^{*a*}Only those components greater than 1% per B or O atom are included. All numbers are in percentages (%). ^{*b*}Atoms are labeled as in Figure 1a. ^{*c*}Shown in **bold** are collective contributions from six O centers in the tricyclic core.



Figure 6. π CMOs of (a) D_{2h} $C_{12}H_8$ (4) and (b and c) their selected AdNDP schemes. (b) The "hybrid" 3c-2e/8c-2e π scheme; two 8c-2e π bonds are delocalized within two pentagons and cannot be further localized. (c) Delocalized 12c-2e π bonds. Parts b and c are equivalent to each other. ONs are shown.

level of theory (as compared to the formal bond order of 1.50). In short, both 3 and 4 should be considered "delocalized" systems. The notion of C_{2h} (3) being localized with alternative single and double bonds is an oversimplified picture for *s*-indacene. We thus choose to present the bonding of *s*-indacene using D_{2h} (4), for the sake of simplicity.

According to Figure 6a, the bottom five π CMOs of D_{2h} (4) show one-to-one correspondence to those of B_8O_8 (1) (Figure

Sa). The only difference between 4 and 1 is the top π CMO: HOMO–6 for 1 (Figure 5a) versus HOMO for 4 (Figure 6a). The former CMO is formally *antibonding* in the three rings with electron clouds orienting perpendicular to the boronyl groups, whereas the latter is *bonding* in this direction. This difference has an important consequence in the nature of bonding; see section 4.3. Other than this, B_8O_8 (1) and $B_8O_8^-$ (2) should be viewed as inorganic analogues of *s*-indacene.

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4.3. AdNDP π Schemes of D_{2h} B₈O₈ (1) and D_{2h} C₁₂H₈ (4) and Chemical Bonding of s-Indacene Revisited. AdNDP offers an in-depth understanding of bonding in D_{2h} B_8O_8 (1) and s-indacene. One advantage of AdNDP is the flexibility to partition natural density into *n*-center two-electron (nc-2e) bonds, where value n can be varied manually to produce different AdNDP schemes: from the more localized ones to the completely delocalized one. Comparison of these schemes allows the capture of bonding essence in a molecular system. For D_{2h} B₈O₈ (1), the 12 π system is readily partitioned into at least four AdNDP schemes (Figures 5 and S4): (i) six 1c-2e O 2p_z lone-pairs; (ii) six 3c-2e B-O-B π bonds; (iii) three sets of 5c-2e or 6c-2e π bonds, that is, a 4π subsystem for each B–O ring; (iv) the 12c-2e π scheme. Scheme i is the extreme, localized version, and yet its occupation numbers (ONs) are reasonably high (1.65–1.68 lel; Figure S4a), which confirms that the π framework is indeed derived from six O 2p_z lone-pairs. To the other extreme, scheme iv is delocalized, giving perfect ONs (2.00 lel; Figure 5c) and yet the least insight into bonding.

In between the extremes, schemes ii and iii offer somewhat localized views, showing that three B–O rings in 1 each have 4π electrons, which form 5c-4e/6c-4e subsystems, or equivalently two 3c-2e π bonds for each ring (Figures 5b and S4b). Note that a 5c-4e π bond is similar to the "o-bond" in rhombic B₂O₂ systems;^{24,25,27,31} the key to the o-bond is that the upper bond has little antibonding overlap and is essentially nonbonding. For polycyclic systems such as 1 and 2, it is more complex to assess whether the upper bond is nonbonding or antibonding and thus the o-bond concept is somewhat fuzzy here. Nevertheless, HOMO–6 and HOMO–7 (Figure 5a) are closer to nonbonding between the O centers,⁷² hinting that two pentagons can be o-bond subsystems. These rings thus have local aromaticity despite the 4π electron-counting.^{25,31}

Surprisingly, the π framework in C₁₂H₈ (4) is challenging for AdNDP analyses (Figures 6 and S5). We have attempted to generate a number of schemes: (i) six localized 2c-2e π bonds, which represent one of two equivalent resonance structures; (ii) mixed 3c-2e/4c-2e π bonds; (iii) isolated 5c-2e/6c-2e π bonds for triple rings; (iv) the "hybrid" $3c-2e/8c-2e \pi$ scheme; (v) the ultimate 12c-2e π scheme. Schemes i–iii are less than ideal, with certain ON values being low (<1.5 lel). On the basis of our understanding of s-indacene, we prefer schemes iv and v; see Figure 6b and c. A key point is that, of the six π CMOs in 4 (Figure 6a), only HOMO-5/HOMO-11 and HOMO-2/ HOMO-3 roughly form constructive/destructive pairs. These CMOs can be islanded as two 5c-2e π bonds (one completely bonding bond on each pentagon) and two 6c-2e π bonds (on the hexagon: one completely bonding and one partially bonding/antibonding, in the spirit of 4π antiaromaticity). In contrast, HOMO and HOMO-1 do not form a genuine constructive/destructive pair, which in principle cannot be islanded and have to be delocalized in AdNDP. With this argument, localized schemes ii and iii are distorted from true bonding in s-indacene. The only reasonable, localized AdNDP scheme is iv, which is "hybrid" due to the above argument. Note that scheme iv is a reasonable approximation of v. The formal 12c-2e bonds in v indeed show a certain degree of localization as reflected in iv.

s-Indacene is an elusive molecule, with "mixed aromatic and antiaromatic character".⁵² Its π CMOs have never been fully analyzed, to our knowledge. This is perhaps the reason why the bonding of s-indacene has remained a puzzling issue. On the

basis of the above analyses, we shall propose a simple bonding picture (Figure 7). Briefly, we consider that π CMOs of *s*-



Figure 7. Schematic of a bonding model of *s*-indacene ($C_{12}H_8$), using the D_{2h} $C_{12}H_8$ (4) structure. The hexagon in part a inherits two π orbitals from a C_6 hydrocarbon (such as C_6H_6), with a slight reverse in energy order due to interactions with two pentagons. The left and right panels in part b show that the $\pi^2 \pi^{*1} \pi^{*1}$ configurations from two C_5 hydrocarbons (triplet $C_5H_5^+$) combine to generate four π orbitals in *s*-indacene (central panel), which are associated with two pentagonal rings. This picture explains why *s*-indacene has mixed aromatic and antiaromatic character; see text for details.

indacene are inherited from hexagonal and pentagonal complexes (for example, C_6H_6 and $C_5H_5^+$). The C_6 ring contributes 4π electrons via a completely bonding π orbital and a partially bonding/antibonding one. The shapes of these π orbitals are maintained in *s*-indacene, but their relative energies reverse due to interactions with two pentagons (Figure 7a). On the other hand, each C_5 ring offers four π electrons via three orbitals: two electrons from a completely bonding orbital and one electron from each of a pair of partially bonding/antibonding orbitals, sort of in the spirit of a $\pi^2 \pi^{*1} \pi^{*1}$ triplet configuration (Figure 7b). Two "triplet" C_5 rings then couple to form four π CMOs of *s*-indacene, including two kinds of π^* CMOs (HOMO versus HOMO-1; Figure 6).

This unique feature distinguishes *s*-indacene from $B_8O_8^{0/-}$ (1 and 2), despite the fact that their overall π pattern looks similar. A $\pi^2 \pi^{*1} \pi^{*1}$ triplet system is aromatic according to the reversed 4n Hückel rule for aromaticity.⁷³ Thus, while pentagon/hexagon/pentagon rings each have 4π electrons, the pentagons are aromatic (at least formally) and the hexagon is antiaromatic. By manually adding four electrons to B_8O_8 (1), the $D_{2h} B_8O_8^{4-}$ tetraanion becomes well-behaved for AdNDP analysis, yielding a perfect, islanded $6\pi/4\pi/6\pi$ pattern in tricyclic rings (Figure S6). We believe this understanding shall solve the puzzle with regard to bonding in *s*-indacene.⁵²

4.4. Predicted Electronic Properties of D_{2h} **B**₈**O**₈^{-/0} **Clusters.** To aid future experimental characterizations of D_{2h} **B**₈**O**₈ (1) and D_{2h} **B**₈**O**₈⁻ (2), we predict their electronic properties. The ionization potential (IP) of B₈**O**₈ (1) is

calculated to be 11.01 and 11.15 eV at the B3LYP/6-311+G(d,p) and CCSD(T)//B3LYP levels, respectively. At the same levels, IP values of *s*-indacene C_{2h} $C_{12}H_8$ (3) are 7.22 and 7.23 eV, respectively, suggesting that D_{2h} B₈O₈ (1) is a relatively stable species. The calculated infrared (IR) and ultraviolet–visible (UV–vis) spectra of B₈O₈ (1) are shown in Figure 8. The intensities of most IR modes are weak. The main



Figure 8. Predicted infrared (IR) and ultraviolet-visible (UV-vis) spectra of D_{2h} B₈O₈ (1).

features are four characteristic IR peaks at 1255 (b_{1u}), 1389 (b_{1u}), 1222 (b_{2u}), and 1168 (b_{1u}) cm⁻¹, which are all associated with the tricyclic core. For the UV–vis spectrum, there are two strong absorptions in the UV region: 283 and 213 nm.

Photoelectron spectroscopy (PES) is a powerful tool to characterize anion clusters. Ground-state ADE and VDE of $B_8O_8^-(2)$ are calculated to be 2.04 and 2.11 eV, respectively, at the B3LYP level, where the first value is the electron affinity of neutral B_8O_8 (1) cluster. Higher VDEs for excited-state transitions are also predicted using TD-B3LYP (Table S2). A simulated PES spectrum is presented in Figure 9, which features an energy gap of 3.49 eV. This is an indication of a remarkably robust neutral cluster, B_8O_8 (1). The HOMO of 1 is primarily O based (56%) and completely bonding between six bridging O atoms, whereas the LUMO is B based (92%) and formally antibonding between four B_2 units. A large HOMO–LUMO gap is therefore anticipated for B_8O_8 (1), as reflected from the simulated anion PES spectrum.

4.5. Growth Pattern of the $(B_2O_2)_n$ (n = 1-4) Series. The geometries of $(B_2O_2)_n^{0/-}$ (n = 1, 2) clusters were studied earlier.⁷⁴⁻⁷⁶ We performed a PES and computational study on $B_4O_4^{0/-}$ clusters more recently.²⁷ A D_{3h} B₆O₆ cluster as a boron oxide analogue of boroxine and benzene was also reported.¹⁹ The present study thus completes the $(B_2O_2)_n$ (n = 1-4)cluster series. Figure 10 presents a proposed growth pattern, as well as the cohesive energies, of these clusters. The clusters evolve from linear, rhombic, hexagonal, to tricyclic structures. Here we consider that all $(B_2O_2)_n$ (n = 1-4) clusters are constructed from B2O2 units, which were observed in low temperature matrixes.⁴ Polar π bonds in boronyl groups make B_2O_2 reactive and facilitate the growth of $(B_2O_2)_n$ clusters. The processes are driven by the formation of two B–O σ bonds and a delocalized π system (using O 2p lone-pairs) in each step, in exchange of the conversion of one boronyl to a B-O single bond, which is overall exothermic. The cohesive energies, with respect to isolated B_2O_2 units, are evaluated to be -25.71, -91.84, and -141.27 kcal mol⁻¹ for B_4O_4 ($D_{2h\nu}$ ¹ A_g), boronyl boroxine, and D_{2h} B₈O₈ (1), respectively, at the B3LYP level.

5. CONCLUSIONS

We have reported on theoretical predictions of cluster structures of $B_8 O_8^{0/-}$ via computational global searches and electronic structure calculations at the B3LYP and single-point CCSD(T) levels. It is shown that these boron oxide clusters adopt perfectly planar, tricyclic geometries: $B_8 O_8$ (1, D_{2h} , 1A_g)



Figure 9. Simulated photoelectron spectrum of the $D_{2h} B_8 O_8^-(2)$ anion cluster using time-dependent B3LYP (TD-B3LYP) calculations. Labeled electronic transitions correspond to the ground state and excited states of $D_{2h} B_8 O_8(1)$ neutral. Also depicted are the HOMO and LUMO of $D_{2h} B_8 O_8(1)$ that define the energy gap in the simulated spectrum.

Article



Figure 10. Proposed growth pattern of the $(B_2O_2)_n$ (n = 1-4) series of clusters, in which B_2O_2 is used as the basic structural unit. Calculated cohesive energies for $(B_2O_2)_n$ with respect to $n B_2O_2$ units are shown in kcal mol⁻¹ at the B3LYP level.

and $B_8O_8^-$ (2, D_{2h} , ${}^2B_{2g}$). Both clusters exhibit an elongated tricyclic core and two terminal boronyl groups, in which the structural core consists of two B_3O_2 rings and one B_4O_2 ring that are fused together via sharing two B_2 units. In terms of bonding, these are 12π delocalized systems, similar to (albeit not identical with) *s*-indacene. An updated bonding model is also proposed for *s*-indacene. The present finding of structural and bonding analogy between boron oxide clusters and *s*-indacene shall encourage further exploration and rational design of novel boron oxide clusters, using the strategy of isolobal analogy.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b12479.

WBIs and natural atomic charges of D_{2h} GM structures of B_8O_8 (1) and $B_8O_8^-$ (2) and their calculated HOMO– LUMO energy gaps at the B3LYP/6-311+G(d,p) level (Table S1); calculated VDEs for $B_8O_8^-$ (2) at the TD-B3LYP level (Table S2); alternative low-lying isomeric structures of the $B_8O_8^-$ anion cluster at B3LYP (Figure S1); WBIs and natural atomic charges of $B_8O_8^-$ (2) and D_{2h} $C_{12}H_8$ (4) (Figures S2 and S3); and alternative AdNDP π schemes for D_{2h} B_8O_8 (1) (Figure S4), D_{2h} $C_{12}H_8$ (4) (Figure S5), and a model cluster D_{2h} $C_{12}H_8^{4-}$ (Figure S6) (PDF)

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Notes

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REFERENCES

(1) Bauer, S. H. Oxidation of B, BH, BH_2 , and B_mH_n species: Thermochemistry and kinetics. *Chem. Rev.* **1996**, *96*, 1907–1916.

(2) Zhai, H. J.; Chen, Q.; Bai, H.; Li, S. D.; Wang, L. S. Boronyl chemistry: The BO group as a new ligand in gas-phase clusters and synthetic compounds. *Acc. Chem. Res.* **2014**, *47*, 2435–2445.

(3) Wenthold, P. G.; Kim, J. B.; Jonas, K. L.; Lineberger, W. C. An experimental and computational study of the electron affinity of boron oxide. *J. Phys. Chem. A* **1997**, *101*, 4472–4474.

(4) Burkholder, T. R.; Andrews, L. Reactions of boron atoms with molecular oxygen. Infrared spectra of BO, BO₂, B₂O₂, B₂O₃, and BO₂⁻ in solid argon. *J. Chem. Phys.* **1991**, *95*, 8697–8709.

(5) Peiris, D.; Lapicki, A.; Anderson, S. L.; Napora, R.; Linder, D.; Page, M. Boron oxide oligomer collision-induced dissociation: Thermochemistry, structure, and implications for boron combustion. *J. Phys. Chem. A* **1997**, *101*, 9935–9941.

(6) Drummond, M. L.; Meunier, V.; Sumpter, B. G. Structure and stability of small boron and boron oxide clusters. *J. Phys. Chem. A* **2007**, *111*, 6539–6551.

(7) Zhai, H. J.; Wang, L. M.; Li, S. D.; Wang, L. S. Vibrationally resolved photoelectron spectroscopy of BO⁻ and BO₂⁻: A joint experimental and theoretical study. *J. Phys. Chem. A* **2007**, *111*, 1030–1035.

(8) Zhai, H. J.; Li, S. D.; Wang, L. S. Boronyls as key structural units in boron oxide clusters: $B(BO)_2^-$ and $B(BO)_3^-$. J. Am. Chem. Soc. **2007**, 129, 9254–9255.

(9) Li, S. D.; Zhai, H. J.; Wang, L. S. $B_2(BO)_2^{2-}$ – diboronyl diborene: A linear molecule with a triple boron-boron bond. *J. Am. Chem. Soc.* **2008**, *130*, 2573–2579.

(10) Tai, T. B.; Nguyen, M. T. Structure and electron delocalization of the boron oxide cluster $B_3(BO)_3$ and its anion and dianion. *Chem. Phys. Lett.* **2009**, 483, 35–42.

(11) Nguyen, M. T.; Matus, M. H.; Ngan, V. T.; Grant, D. J.; Dixon, D. A. Thermochemistry and electronic structure of small boron and boron oxide clusters and their anions. *J. Phys. Chem. A* **2009**, *113*, 4895–4909.

(12) Tai, T. B.; Nguyen, M. T.; Dixon, D. A. Thermochemical properties and electronic structure of boron oxides B_nO_m (n = 5-10, m = 1-2) and their anions. J. Phys. Chem. A **2010**, 114, 2893–2912.

(13) Shao, C. B.; Jin, L.; Ding, Y. H. A theoretical survey on the structures, energetics, and isomerization pathways of the B_5O radical. *J. Comput. Chem.* **2011**, 32, 771–777.

(14) Zhang, Z.; Pu, L.; Li, Q. S.; King, R. B. Pathways to the polymerization of boron monoxide dimer to give low-density porous materials containing six-membered boroxine rings. *Inorg. Chem.* **2015**, *54*, 2910–2915.

(15) Zubarev, D. Y.; Boldyrev, A. I.; Li, J.; Zhai, H. J.; Wang, L. S. On the chemical bonding of gold in auro-boron oxide clusters Au_nBO^- (n = 1-3). *J. Phys. Chem. A* **2007**, *111*, 1648–1658.

(16) Zhai, H. J.; Miao, C. Q.; Li, S. D.; Wang, L. S. On the analogy of B–BO and B–Au chemical bonding in $B_{11}O^-$ and $B_{10}Au^-$ clusters. *J. Phys. Chem. A* **2010**, *114*, 12155–12161.

(17) Zhai, H. J.; Guo, J. C.; Li, S. D.; Wang, L. S. Bridging η^2 -BO in $B_2(BO)_3^-$ and $B_3(BO)_3^-$ clusters: Boronyl analogs of boranes. ChemPhysChem **2011**, 12, 2549–2553.

(18) Chen, Q.; Zhai, H. J.; Li, S. D.; Wang, L. S. Probing the structures and chemical bonding of boron-boronyl clusters using photoelectron spectroscopy and computational chemistry: $B_4(BO)_n^-$ (n = 1-3). J. Chem. Phys. **2012**, 137, 044307.

(19) Li, D. Z.; Bai, H.; Chen, Q.; Lu, H. G.; Zhai, H. J.; Li, S. D. Perfectly planar boronyl boroxine D_{3h} B₆O₆: A boron oxide analog of boroxine and benzene. *J. Chem. Phys.* **2013**, *138*, 244304.

(20) Chen, Q.; Zhai, H. J.; Li, S. D.; Wang, L. S. On the structures and bonding in boron-gold alloy clusters: $B_6Au_n^-$ and B_6Au_n (n = 1-3). J. Chem. Phys. **2013**, 138, 084306.

(21) Zhai, H. J.; Chen, Q.; Bai, H.; Lu, H. G.; Li, W. L.; Li, S. D.; Wang, L. S. Pi and sigma double conjugations in boronyl polyboroene nanoribbons: $B_n(BO)_2^-$ and $B_n(BO)_2$ (n = 5-12). J. Chem. Phys. 2013, 139, 174301.

(22) Bai, H.; Zhai, H. J.; Li, S. D.; Wang, L. S. Photoelectron spectroscopy of aromatic compound clusters of the B_{12} all-boron benzene: $B_{12}Au^-$ and $B_{12}(BO)^-$. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9646–9653.

(23) Tian, W. J.; Xu, H. G.; Kong, X. Y.; Chen, Q.; Zheng, W. J.; Zhai, H. J.; Li, S. D. Photoelectron spectroscopy of lithium and gold alloyed boron oxide clusters: Charge transfer complexes, covalent gold, hyperhalogen, and dual three-center four-electron hyperbonds. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5129–5136.

(24) Chen, Q.; Lu, H. G.; Zhai, H. J.; Li, S. D. Chemical bonding in electron-deficient boron oxide clusters: Core boronyl groups, dual 3c-4e hypervalent bonds, and rhombic 4c-4e bonds. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7274–7279.

(25) Li, D. Z.; Zhang, L. J.; Ou, T.; Zhang, H. X.; Pei, L.; Zhai, H. J.; Li, S. D. Ternary $B_2X_2H_2$ (X = O and S) rhombic clusters and their potential use as inorganic ligands in sandwich-type $(B_2X_2H_2)_2N_i$ complexes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 16798–16804.

(26) Li, D. Z.; Bai, H.; Ou, T.; Chen, Q.; Zhai, H. J.; Li, S. D. Planar dicyclic B_6S_{69} , $B_6S_{6}^{-}$, and $B_6S_{6}^{2-}$ clusters: Boron sulfide analogues of naphthalene. *J. Chem. Phys.* **2015**, *142*, 014302.

(27) Tian, W. J.; Zhao, L. J.; Chen, Q.; Ou, T.; Xu, H. G.; Zheng, W. J.; Zhai, H. J.; Li, S. D. Photoelectron spectroscopy of $B_4O_4^-$: Dual 3c-4e π hyperbonds and rhombic 4c-4e o-bond in boron oxide clusters. *J. Chem. Phys.* **2015**, *142*, 134305.

(28) Tian, W. J.; You, X. R.; Li, D. Z.; Ou, T.; Chen, Q.; Zhai, H. J.; Li, S. D. A first-principles study on the $B_5O_5^{+/0}$ and $B_5O_5^{-}$ clusters: The boron oxide analogs of $C_6H_5^{+/0}$ and $CH_3Cl.$ *J. Chem. Phys.* **2015**, 143, 064303. (29) Ou, T.; Tian, W. J.; You, X. R.; Wang, Y. J.; Wang, K.; Zhai, H. J. On the structure and bonding in the $B_4O_4^+$ cluster: A boron oxide analogue of the 3,5-dehydrophenyl cation with π and σ double aromaticity. *Phys. Chem. Chem. Phys.* **2015**, *17*, 29697–29706.

(30) Wang, W.; Chen, Q.; Wang, Y. J.; Bai, H.; Gao, T. T.; Li, H. R.; Zhai, H. J.; Li, S. D. Boronyl as a terminal ligand in boron oxide clusters: Hexagonal ring $C_{2\nu}$ B₆O₄ and ethylene-like D_{2h} B₆O₄^{-/2-}. *Phys. Chem. Chem. Phys.* **2015**, *17*, 19929–19935.

(31) Zhao, L. J.; Tian, W. J.; Ou, T.; Xu, H. G.; Feng, G.; Xu, X. L.; Zhai, H. J.; Li, S. D.; Zheng, W. J. Structures and chemical bonding of $B_3O_3^{-/0}$ and $B_3O_3H^{-/0}$: A combined photoelectron spectroscopy and first-principles theory study. *J. Chem. Phys.* **2016**, *144*, 124301.

(32) Li, D. Z.; Zhang, S. G.; Dong, C. C. Binary B_4S_4 rhombic clusters as promising inorganic ligands for triple-decker sandwich complexes. *Eur. J. Inorg. Chem.* **2016**, 2016, 1103–1107.

(33) Hanley, L.; Whitten, J. L.; Anderson, S. L. Collision-induced dissociation and ab initio studies of boron cluster ions: Determination of structures and stabilities. *J. Phys. Chem.* **1988**, *92*, 5803–5812.

(34) Oger, E.; Crawford, N. R. M.; Kelting, R.; Weis, P.; Kappes, M. M.; Ahlrichs, R. Boron cluster cations: Transition from planar to cylindrical structures. *Angew. Chem., Int. Ed.* **2007**, *46*, 8503–8506.

(35) Aihara, J. I.; Kanno, H.; Ishida, T. Aromaticity of planar boron clusters confirmed. J. Am. Chem. Soc. 2005, 127, 13324–13330.

(36) Fowler, J. E.; Ugalde, J. M. The curiously stable B_{13}^+ cluster and its neutral and anionic counterparts: The advantages of planarity. *J. Phys. Chem. A* **2000**, *104*, 397–403.

(37) Boustani, I. Systematic LSD investigation on cationic boron clusters: B_n^+ (n = 2-14). Int. J. Quantum Chem. **1994**, 52, 1081–1111.

(38) Zhai, H. J.; Alexandrova, A. N.; Birch, K. A.; Boldyrev, A. I.; Wang, L. S. Hepta- and octacoordinate boron in molecular wheels of eight- and nine-atom boron clusters: Observation and confirmation. *Angew. Chem., Int. Ed.* **2003**, *42*, 6004–6008.

(39) Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. Hydrocarbon analogues of boron clusters – Planarity, aromaticity and antiaromaticity. *Nat. Mater.* **2003**, *2*, 827–833.

(40) Kiran, B.; Bulusu, S.; Zhai, H. J.; Yoo, S.; Zeng, X. C.; Wang, L.
S. Planar-to-tubular structural transition in boron clusters: B₂₀ as the embryo of single-walled boron nanotubes. *Proc. Natl. Acad. Sci. U. S. A.* 2005, *102*, 961–964.

(41) Sergeeva, A. P.; Zubarev, D. Y.; Zhai, H. J.; Boldyrev, A. I.; Wang, L. S. A photoelectron spectroscopic and theoretical study of B_{16}^{-1} and B_{16}^{-2} : An all-boron naphthalene. *J. Am. Chem. Soc.* **2008**, *130*, 7244–7246.

(42) Huang, W.; Sergeeva, A. P.; Zhai, H. J.; Averkiev, B. B.; Wang, L. S.; Boldyrev, A. I. A concentric planar doubly π -aromatic B₁₉⁻ cluster. *Nat. Chem.* **2010**, *2*, 202–206.

(43) Li, W. L.; Chen, Q.; Tian, W. J.; Bai, H.; Zhao, Y. F.; Hu, H. S.; Li, J.; Zhai, H. J.; Li, S. D.; Wang, L. S. The B₃₅ cluster with a doublehexagonal vacancy: A new and more flexible structural motif for borophene. *J. Am. Chem. Soc.* **2014**, *136*, 12257–12260.

(44) Wang, Y. J.; Zhao, X. Y.; Chen, Q.; Zhai, H. J.; Li, S. D. B₁₁⁻: A moving subnanoscale tank tread. *Nanoscale* **2015**, *7*, 16054–16060.

(45) Wang, Y. J.; Zhao, Y. F.; Li, W. L.; Jian, T.; Chen, Q.; You, X. R.; Ou, T.; Zhao, X. Y.; Zhai, H. J.; Li, S. D.; Li, J.; Wang, L. S. Observation and characterization of the smallest borospherene, B_{28}^- and B_{28} . J. Chem. Phys. **2016**, 144, 064307.

(46) Guo, J. C.; Feng, L. Y.; Wang, Y. J.; Jalife, S.; Vasquez-Espinal, A.; Cabellos, J. L.; Pan, S.; Merino, G.; Zhai, H. J. Coaxial triple-layered versus helical $Be_6B_{11}^-$ clusters: Dual structural fluxionality and multifold aromaticity. *Angew. Chem., Int. Ed.* **2017**, *56*, 10174–10177. (47) Zhai, H. J.; Zhao, Y. F.; Li, W. L.; Chen, Q.; Bai, H.; Hu, H. S.; Piazza, Z. A.; Tian, W. J.; Lu, H. G.; Wu, Y. B.; Mu, Y. W.; Wei, G. F.; Liu, Z. P.; Li, J.; Li, S. D.; Wang, L. S. Observation of an all-boron fullerene. *Nat. Chem.* **2014**, *6*, 727–731.

(48) Li, D. Z.; Li, R.; Zhang, L. J.; Ou, T.; Zhai, H. J. Planar $B_3S_2H_3^-$ and $B_3S_2H_3$ clusters with a five-membered B_3S_2 ring: Boron–sulfur hydride analogues of cyclopentadiene. *Phys. Chem. Chem. Phys.* **2016**, *18*, 21412–21420.

(49) Li, D. Z.; Feng, L. Y.; Pei, L.; Zhang, L. J.; Wu, S. G.; Zhai, H. J. Pentagonal five-center four-electron π bond in ternary $B_3N_2H_5$ cluster: An extension of the concept of three-center four-electron ω bond. *Phys. Chem. Chem. Phys.* **2017**, *19*, 2479–2486.

(50) Zubarev, D. Y.; Boldyrev, A. I. Developing paradigms of chemical bonding: Adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* 2008, 10, 5207–5217.

(51) Hertwig, R. H.; Holthausen, M. C.; Koch, W.; Maksic, Z. B. s-Indacene: A delocalized, formally antiaromatic 12 π electron system. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1192–1194.

(52) Nendel, M.; Goldfuss, B.; Houk, K. N.; Hafner, K. s-Indacene, a quasi-delocalized molecule with mixed aromatic and anti-aromatic character. J. Mol. Struct.: THEOCHEM 1999, 461–462, 23–28.

(53) Soriano Jartin, R.; Ligabue, A.; Soncini, A.; Lazzeretti, P. Ring currents and magnetic properties of s-indacene, an archetypal paratropic, non-antiaromatic molecule. *J. Phys. Chem. A* **2002**, *106*, 11806–11814.

(54) Sergeeva, A. P.; Averkiev, B. B.; Zhai, H. J.; Boldyrev, A. I.; Wang, L. S. All-boron analogues of aromatic hydrocarbons: B_{17}^{-} and B_{18}^{-} . J. Chem. Phys. **2011**, 134, 224304.

(55) Saunders, M. Stochastic search for isomers on a quantum mechanical surface. J. Comput. Chem. 2004, 25, 621–626.

(56) Bera, P. P.; Sattelmeyer, K. W.; Saunders, M.; Schaefer, H. F.; Schleyer, P. v. R. Mindless chemistry. *J. Phys. Chem. A* 2006, *110*, 4287–4290.

(57) Wales, D. J.; Doye, J. P. K. Global optimization by basinhopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms. J. Phys. Chem. A **1997**, 101, 5111–5116.

(58) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. **1993**, 98, 5648-5652.

(59) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(60) Frisch, M. J.; et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

(61) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(62) Cizek, J. On the use of the cluster expansion and the technique of diagrams in calculations of correlation effects in atoms and molecules. *Adv. Chem. Phys.* **2007**, *14*, 35–89.

(63) Scuseria, G. E.; Schaefer, H. F., III Is coupled cluster singles and doubles (CCSD) more computationally intensive than quadratic configuration interaction (QCISD)? *J. Chem. Phys.* **1989**, *90*, 3700–3703.

(64) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III An efficient reformulation of the closed-shell coupled cluster single and double excitation (CCSD) equations. *J. Chem. Phys.* **1988**, *89*, 7382–7387.

(65) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic configuration interaction. A general technique for determining electron correlation energies. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

(66) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; University of Wisconsin: Madison, WI, 2001.

(67) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular excitation energies to high-lying bound sates from time dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold. *J. Chem. Phys.* **1998**, *108*, 4439–4449.

(68) Bauernschmitt, R.; Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Lett.* **1996**, *256*, 454–464.

(69) Lu, T.; Chen, F. W. Calculation of molecular orbital composition. *Acta Chim. Sin.* 2011, 69, 2393–2406.

(70) Our GM structure 1 $(D_{2h'} {}^{1}A_{g})$ of $B_{8}O_{8}$ is overwhelmingly more stable than circular $B_{8}O_{8}$ $(D_{4d'} {}^{1}A_{1})$ (Figure 2) by 0.98 and 1.41 eV at the B3LYP and single-point CCSD(T) levels, respectively. The D_{4d} $({}^{1}A_{1})$ isomer was reported to be the lower energy of two typical structures of $B_{8}O_{8}$ in ref 14, which contains an eight-membered $B_{4}O_{4}$ ring and four terminal BO groups. However, the current data show that it is not competitive with the tricyclic GM 1. The previous computational work¹⁴ thus clearly missed GM structure 1.

(71) Pyykkö, P. Additive covalent radii for single-, double-, and triplebonded molecules and tetrahedrally bonded crystals: A summary. J. Phys. Chem. A 2015, 119, 2326–2337.

(72) The O–O distances are 2.40 and 3.35 Å within pentagonal and hexagonal rings in 1 and 2.39 and 3.31 Å in 2, respectively, which are far beyond an O–O single bond (1.48 Å). The O–O overlap should be negligible unless B atoms participate in delocalized bonding. Thus, HOMO–6 and HOMO–7 in 1 (Figure 5) are indeed "nonbonding" in nature within the pentagons, justifying the pentagonal "o-bond" in 1 and 2.

(73) Baird, N. C. Quantum organic photochemistry. II. Resonance and aromaticity in the lowest ${}^{3}\pi\pi^{*}$ state of cyclic hydrocarbons. *J. Am. Chem. Soc.* **1972**, *94*, 4941–4948.

(74) White, D.; Walsh, P. N.; Mann, D. E. Infrared emission spectra of $B_2O_3(g)$ and $B_2O_2(g)$. J. Chem. Phys. **1958**, 28, 508–509.

(75) Ruscic, B. M.; Curtiss, L. A.; Berkowitz, J. Photoelectron spectrum and structure of B_2O_2 . J. Chem. Phys. **1984**, 80, 3962–3968. (76) Doyle, R. J. High-molecular-weight boron oxides in the gas phase. J. Am. Chem. Soc. **1988**, 110, 4120–4126.