Abstract: The bonding environment of boron is usually thought about in terms of localized 2c–2e bonding (as in diborane) or completely delocalized polyhedral bonding (as in B\textsubscript{12}H\textsubscript{12}). Recently, a number of boron compounds having a rhomboidal B\textsubscript{4} framework have been synthesized; these show an amazing variation in their skeletal electron count, one that cannot be interpreted in familiar ways. In this report, we systematically explore the origin of the range of electron counts in these compounds. We find that four skeletal MOs are primarily responsible for keeping the B\textsubscript{4} skeleton together. As a subunit in a macrocyclic environment, termed rhombo-B\textsubscript{4}, such an arrangement of B atoms deviates from Wade’s rule by three electron pairs (if treated as a distorted arachno system derived from B\textsubscript{6}H\textsubscript{6}).

Aided by this analysis, we examine the nature of bonding in Na\textsubscript{3}B\textsubscript{20}, where the rhombo-B\textsubscript{4} unit forms linear chains fusing closo-B\textsubscript{7} units. Theory suggests that this structure requires one more electron per formula unit for optimal bonding. Finally, we study the nature of bonding in β-SiB\textsubscript{3}, where silicon atoms also adopt the rhomboid skeleton in such diverse environments.

Molecules with the geometry of a perfect square are rare for the main group elements. The exceptions are S\textsubscript{4}+, Te\textsubscript{2}+, Se\textsubscript{2}+, and P\textsubscript{2}− ions and some organic systems with exocyclic double bonds. A ring-puckering distortion of the square is common in saturated hydrocarbons such as cyclobutane and even in organic systems that should be aromatic by Hückel’s rule. Recently, a variety of electron-deficient, boron-containing molecules with characteristic, nearly planar rhombic rings and P\textsubscript{2}− ions have been synthesized. These systems appear to exist with a wide range of electron counts. The rhomboid is also found as a substructure in the recently characterized extended structures of Na\textsubscript{3}B\textsubscript{20} and β-SiB\textsubscript{3}. In this report, we explore the nature of bonding in these systems, probing the mystery behind the persistence of the rhomboid skeleton in such diverse environments.

Figure 1 shows some representative examples of experimentally characterized molecules with a B\textsubscript{4} rhomboid skeleton. Assuming 2c–2e (two-centered-two electron) exo-rhomboid bonds, molecule 1a\textsuperscript{b} has four electron pairs left for the bonding in the rhombus. Some related systems with a variety of substituents were also been reported.\textsuperscript{b,c} A similar assumption leads to three electron pairs for 1b\textsuperscript{d} and two electron pairs for 1c. Molecule 1d, B\textsubscript{2}B\textsubscript{18}H\textsubscript{18}, was synthesized 40 years ago;\textsuperscript{9a} several polyhedra contain this rhomboid B\textsubscript{4} skeleton. An interesting paradox in electron counting arises for B\textsubscript{20}H\textsubscript{18};\textsuperscript{9a} it can be formally constructed from two B\textsubscript{10}H\textsubscript{10}− molecules by removing two hydride ions. If we then allocate (n + 1) electron pairs, n = 10, for the individual closo-B\textsubscript{10} units, following Wade’s rules,\textsuperscript{10} we are left with the absurdity of having no electrons left to hold the two polyhedra together. It is clear that electrons in this system are delocalized over the entire skeleton. This rhomboidal framework is also observed in molecules where one or more boron atoms are replaced by isobolal transition-metal fragments.\textsuperscript{11}
**Computational Methodology**

The energies of the MOs for the molecules (as well as those of fragments) used in the interaction and correlation diagrams were derived from extended Hückel (eH) calculations. Geometrical optimizations of selected molecular systems were done using the Gaussian 98 suite of programs at the density functional based B3LYP/6-31G* level of theory; frequency calculations characterize the nature of the stationary points. For band structures and density of states for extended structures, we employ the eH-based YaHMO suite of programs.

Further, we have also used the DFT VASP program to optimize the structures and to produce the band structures for calibrating the eH results. In the VASP calculations, we chose ultrasoft pseudopotentials based on the projector-augmented-wave method using the local density approximation, which is ideal for arriving at equilibrium geometries.

All the calculations were well converged with respect to the chosen cutoff energy and k-point sampling, unless stated otherwise.

**Molecular Orbitals of Square (D_{4h}) and Rhombus (D_{2d}) B_{10}H_{4}**

To understand the nature of bonding in rhomboid systems, it will be useful to analyze the evolution of molecular orbitals (MOs) with a square-rhombus distortion. The MOs of $B_1$ ($D_{2d}$) can be constructed from the valence AOs of boron, oriented conveniently into radial ($p_r$), tangential ($p_t$), and the perpendicular ($p_s$) sets of $p$ orbitals ($p_l$), along with the $s$ orbital set. In $D_{2h}$ symmetry, both the $s$ and $p_l$ AOs transform as $a_1 + e + b_1$ while $p_s$ transform as $b_2 + e + a_2$. The degenerate $p_l$ orbitals will mix the most, including $s$, $p_t$, and $p_r$. The four MOs arising from $p_l$ orbitals transform as $a_1 + e + b_2 + b_3$ and will not mix with any of the other MOs. Figure 3 shows the $B_1^4$ ($D_{4h}$) MOs at left in schematic form, indicating the major contributions to the calculated MOs (at $B-B$ 1.65 Å). Note the expected orderings: $e$, $a_2$, $b_2$, and $b_3$ orbitals. In the resulting MO scheme for square $B_4H_4$, there are four levels very close in energy in the frontier region, with six electrons in them; this is recognizable as a typical first- or second-order Jahn–Teller situation. The distortion of a square to a rhombus will remove this approximate degeneracy.

The rhomboid distortion involves the movement of two diagonal boron atoms ($B_a$, $B_b$, $B_c$, and $B_d$) toward each other, to a bonding contact (taken as $B_a-B_b$ 1.65 Å for the calculation shown). The molecule is still planar but the symmetry is reduced from $D_{4d}$ to $D_{2h}$. The reduction in symmetry splits the MOs $B_1^4$ ($D_{4h}$), all four MOs that have predominant $s$ character are filled and lie very low in energy. The all-bonding combinations of the $p_l$ orbitals are also low-lying. On interaction with four $H^+$ ions, as depicted in the first to second column in Figure 4 (the MOs of the fourth $H^+$ span the same irreducible representation as those of boron $s$ and $p_l$) all the orbitals with substantial radial character are stabilized, as expected—their overlaps with external hydrogen atoms are largest. This is seen in the $e$, $a_2$, and $b_2$ orbitals. In the resulting MO scheme for square $B_4H_4$, there are four levels very close in energy in the frontier region, with six electrons in them; this is recognizable as a typical first- or second-order Jahn–Teller situation. The distortion of a square to a rhombus will remove this approximate degeneracy.

For a subset of these species, 1a and 1b, a neat explanation of the bonding based on ideas of $\sigma$ and $\pi$ aromaticity is at hand.

**Figure 1.** Some discrete molecular systems containing a rhomboid $B_4$ skeleton. Boron atoms and boron–boron bonds are indicated in green.

**Figure 2.** Rhombic geometry exhibited by (a) $B_4$ units in Na$_3$B$_{20}$ and (b) Si$_4$ units in $\beta$-SiB$_3$.
The degeneracy of the \( e_u \) and \( e_g \) MOs. The \( B_4H_4 \) frontier \( e_u \) (which has near equal mixing of both \( p_t \) and \( p_r \)) splits strongly into \( b_{2u} \) and \( b_{1g} \); the radial contribution to \( e_u \) is behind this substantial splitting. For \( B_4H_4(D_2h) \), the higher member of the set (\( b_{2u} \)) is vacated, and the all-bonding tangential MO (\( b_{2g} \)) is filled. As a whole, this distortion results in a \( B_4H_4 \) framework that has a reasonable \( \text{HOMO} (b_{3g}) - \text{LUMO} (b_{2u}) \) gap. However, the gap is not large enough to ensure stability. With hydrogens as substituents, calculations indicate that neither square nor rhombus systems are minima on the potential energy surface\(^{20} \) as they move toward bridging positions distorting planarity. However, the HOMO–LUMO gap can be increased (with it, likely the stability) by substitution strategies. As shown in Figure 4a, \( \pi \)-donors at \( B_L \) would be stabilized by the LUMO and tangential \( \pi \)-acceptor \( - \)NMe\(_2\) groups across the longer diagonal (\( B_L - B_L \)) for tangential \( \pi \)-donation and appropriately oriented \( -BH_2 \) groups (p orbital in the \( B_4 \) plane) across the shorter diagonal (\( B_S - B_S \)) as the tangential \( \pi \)-acceptor. The size of the substituents is kept small to allow us to explore the system at a good level of theory. The resulting \( D_{2h} \) symmetric \( B_4(BH_2)_2F_2 \) (Figure 4b) is a minimum on its potential energy surface at the B3LYP/6-311+G** level.

To substantiate this reasoning, we substituted fluorine atoms across the longer diagonal (\( B_L - B_L \)) for tangential \( \pi \)-donation and appropriately oriented \(-BH_2 \) groups (p orbital in the \( B_4 \) plane) across the shorter diagonal (\( B_S - B_S \)) as the tangential \( \pi \)-acceptor. The size of the substituents is kept small to allow us to explore the system at a good level of theory. The resulting \( D_{2h} \) symmetric \( B_4(BH_2)_2F_2 \) (Figure 4b) is a minimum on its potential energy surface at the B3LYP/6-311+G** level.

Are the deduced requirements for stabilization consistent with the molecules known in this class?\(^{4} \) Reasonably so; for example, the system studied by Siebert and co-workers,\(^{4} \) \( B_4(NMe_2)_2(B(NMe_2)_2)_2 \) (Figure 1a), has a nearly \( D_{2h} \)-symmetric \( B_4 \) skeleton stabilized by the tangential \( \pi \)-acceptor \(-\) \( (NMe_2)_2 \) groups across the shorter diagonal and \( \pi \)-donor \(-\) \( NMe_2 \) groups across the longer diagonal of the \( B_4 \) ring. The \( B_4 \) substituents are experimentally slightly out of plane, but the external

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NBN groups are indeed oriented for \(\pi\)-acceptance (roughly perpendicular to the ring). The donor dimethylamino substituents, however, are not optimally oriented for \(\pi\)-donation, for their CNC plane is observed to be roughly in the \(\text{B}_4\) plane. There could still be some \(\pi\)-type donation from \(\text{C} = \text{N} = \text{C}\) \(\sigma\)-orbitals. Model calculations point to a variable degree of distortion of the substituents away from the \(\text{B}_4\) plane.

Two more molecules synthesized by Berndt’s group fall in this class\(^{18,19}\) (Figure 5). In molecule 5a, the \(\text{NMe}_2\) groups of 1a are replaced by \(-\text{NEt}_2\) and \(-\text{B(NMe}_2)\), groups at the longer diagonal \(\text{B}_L\).\(^{20}\) Here, the \(\pi\)-donor \(-\text{B(NMe}_2)\) rotates out of plane so that the \(\text{NBN}\) plane is approximately perpendicular (\(-81^\circ\)) to the \(\text{B}_4\) plane. In molecule 5b, all the four substituents are replaced by alkyl groups.\(^{21}\) Calculations (not reported here) show that these substitutions increase the HOMO–LUMO gap sufficiently so as to ensure stability.

The \(\text{B}_4\) system is very rich in its geometrical possibilities. The planar rhomboid actually occurs in a minority of the structures studied to date. \(\text{B}_4\) with \(R = \text{Cl},\text{CMe}_3\), and \(\text{tmp}\) (2,2,6,6-tetramethylpiperidiner) are tetrahedral. Interesting in this context is \(\text{B}_4\) \((\text{i-Pr}_2\text{N})_4\), with a folded \(\text{B}_2\) ring between planar and tetrahedral.\(^{22}\) The rearrangement of rhomboidal \(\text{B}_4\) to tetrahedral \(\text{B}_4\) is symmetry forbidden, just like square-\(\text{B}_4\) to rhomboid \(\text{B}_4\). The later, popularly known as diamond-square-diamond rearrangement (DSD) has been repeatedly studied theoretically,\(^{23,24}\) ever since it was first proposed by Lipscomb.\(^{25}\) Braunstein et al. have studied the rearrangement of the rhomboid to a tetrahedron in transition-metal complexes.\(^{26}\)

**Evolution of the Skeletal MOs of the Rhomboid upon Increased exo-Substitution.** We now move on to more complex substitution patterns. To simplify things, we leave the four most bonding MOs of \(\text{B}_4\) at the bottom (Figure 3) out of consideration. These MOs span the same irreducible representation as those subduced by four \(\text{B}-\text{H}\) bonds and we will take the lowest four orbitals primarily as such (though we are well aware that \(\text{B}-\text{B}\) and \(\text{B} - \text{H}\) bonding are mixed; more on this below). We begin then in the second column of Figure 6, and proceed to add hydrogens stepwise. \(\text{D}_{2h}\) symmetry was maintained for all of the model systems.

Consider first adding a hydrogen atom to each \(\text{B}_L\) of \(\text{B}_4\) (Figure 6) to form planar \(\text{B}_4\) \((\text{D}_{2h})\). In this process, two more electrons are brought to the system. The two incoming hydrogens form symmetric and antisymmetric combinations, which will interact strongly with orbitals having tangential character at \(\text{B}_1\). One can see this in the stabilization of \(b_{3u}\) and \(b_{2u}\) as one moves from the second to the third column in Figure 6, resulting in a substantial HOMO–LUMO gap. Though \(\text{B}_4\) has two more \(\text{B} - \text{H}\) bonds than \(\text{B}_4\), only one additional MO is getting filled. Hence, we need to count \(b_{3u}\) along with \(b_{2u}\) as part of the \(\text{B} - \text{H}\) bond set, to fit a localized \((2c - 2e)\) \(\text{B} - \text{H}\) bond description. This leaves only three MOs \((a_g, b_{1u}, \text{and } b_{3u})\) for formal bonding in the \(\text{B}_4\) skeleton.

Does the reduced number of framework MOs signal the weakened bonding in the rhombus? To probe this, we computed the Mulliken overlap population (OP); the results are shown in Table 1.

While moving from \(\text{B}_4\) to \(\text{B}_4\), the OP between \(\text{B}_5 - \text{B}_5\) decreases, as expected. But, surprisingly, the OP increases across \(\text{B}_5 - \text{B}_5\), despite filling an additional MO \((b_{2u})\) which, on the face of it, is antibonding in this region. To understand this anomaly, we probed the contributions to the OP for \(\text{B}_5 - \text{B}_5\) for every individual skeletal MO (Table 2).

The OP values indicate that the antibonding interaction across \(\text{B}_5 - \text{B}_5\) is actually very small in \(b_{2u}\) for \(\text{B}_4\). The bonding interactions between \(\text{B}_5 - \text{B}_5\) in \(b_{1u}\) and \(a_g\) are slightly increased while the

![Figure 5](Image)

**Figure 5.** Two experimentally characterized \(\text{B}_4\) \(\text{R}_4\) molecules. The Me, Et, H, and SiMe\(_3\) substituents are indicated schematically by a single “atom”.

![Figure 6](Image)

**Figure 6.** Correlation of the skeletal \(\text{B}_4\) \((\text{D}_{2h})\) MOs with the addition of \(\text{exo}\) substituents. MOs of dissimilar symmetries are shown with distinct colors.
Table 1. Overlap Population between Boron Atoms in the B₄ Skeleton Obtained from eH Calculations for an Assumed Idealized Geometry (B–B = 1.65 Å, B–H = 1.2 Å)

<table>
<thead>
<tr>
<th>no.</th>
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<th>Bₛ–Bₛ</th>
<th>Bₛ–Bₐ</th>
<th>Bₐ–Bₐ</th>
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<tr>
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<td>B₄H₄</td>
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<td>2</td>
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<tr>
<td>3</td>
<td>B₄H₁₀</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B₄H₁₂</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>B₄H₁₆</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Table 2. Overlap Population between Bₛ–Bₛ for the Skeletal MOs in B₄H₄ and B₄H₆

<table>
<thead>
<tr>
<th>MO</th>
<th>Symm</th>
<th>BₛH₄</th>
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<td>0.194</td>
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<tr>
<td>b₁₄</td>
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<tr>
<td>b₂₂</td>
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<tr>
<td>b₂</td>
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<td>−0.159</td>
<td>−0.011</td>
</tr>
</tbody>
</table>

*Not filled in B₄H₆.

Figure 7. b₁₄ MO of the rhombus skeleton in (a) B₄H₄ and (b) B₄H₆.

antibonding in b₂₂ is substantially decreased. Figure 7 shows the shape of the b₁₄ in B₄H₄ and B₄H₆. What a difference! The incoming hydrogens induce extensive second order mixing with high-lying b₃g orbitals, essentially removing the Bₛ contribution (and thus Bₛ–Bₛ antibonding in b₃g is substantially decreased. Figure 7 shows the shape of the b₃g in B₄H₄ and B₄H₆. What a difference! The incoming hydrogens induce extensive second order mixing with high-lying b₃g orbitals, essentially removing the Bₛ contribution (and thus Bₛ–Bₛ antibonding in this MO). There is an analogous effect in the b₂u orbital.

Figure 8. Two MOs of diborane which are involved in three-center B–H–B bonding.

How can there be any B–B bonding if there are no B–B bonding orbitals left? Clearly, the conceptual separation of localized B–H bonding around the rhombus B₄ ring fails at this point; a delocalized description is inevitable. An orbital-by-orbital analysis of the contributions to these overlap populations (Table 3) shows that some of the MOs which we have called B–H bonding are also B–B bonding. This is especially true for the a₂ and b₁₄ orbitals. However, there is a general reduction of the overlap population values (Table 1) in the Bₛ framework of B₄H₁₀ compared to B₄H₆.

This situation—B–H bonding orbitals that are also B–B bonding—is to be expected. Recall the classical three-center bonding picture in diborane. The two MOs involved in the three-center bonding are shown in Figure 8. It is clearly seen that even as they are B–H bonding, they are also B–B bonding. In the boranes, multicenter B–B and B–H bonding separations are never clean. This is what happens in B₄H₁₀, where the simple counting of framework orbitals eventually breaks down.

Base Adducts of B₄H₄. The experimentally isolated system with the B₄H₄ framework (Figure 1b) is reported to form an adduct with pyridine, at one of its Bₛ position, the pyridine coming in approximately perpendicular to the Bₛ plane (Figure 9).³

Though there are four positions where one or more pyridine molecules can—in principle—attach to the B₄H₄ skeleton, only one monooadduct at Bₛ is reported to be formed, even when treated with excess pyridine. What happens to the MOs on stepwise addition of pyridine?

(22) The bond distances of the experimental compound (Bₛ–Bₛ = 1.633, Bₛ–Bₐ = 1.605, 1.632, and Bₛ–B = 1.691) are comparable to our computed values for the model compound BₓFₓ(BₓHₓ) (Bₛ–Bₛ = 1.60, Bₛ–Bₐ = 1.62, and Bₛ–B = 1.62).
Lewis bases, here modeled by hydride ions ($H^-$), is illustrated in Figure 10 for addition at $B_8$. The full $D_{3h}$ symmetry is lowered as one adds bases and is restored only at $B_8H_{10}^{4-}$.

The general effect is of lowering the energy of the $b_{2g}$ and $a_u$ orbitals. But look at where the biggest electron gap is found! Adding one hydride ion (a model for pyridine) at a $B_3$ leads to a nice gap for $B_8H_8^{2-}$ (a model for $B_8H_4$(pyridine)). Adding two hydrides, the gap would be large not for $B_8H_6^{2-}$, but for the neutral $B_8H_8$ a model for $B_8H_4$ (pyridine)$^{+}$. The same situation prevails on the addition of three and four bases. This explains why only a single pyridine is observed to add to the compound (Figure 1b) made by Berndt and co-workers [5].

In the next step, we add two more hydrogen atoms to the $B_8H_{10}$ system, to model the bonding environment of $Si_4$ chains in $Si-SiB_4$ (Figure 2b). The $MO$s of $B_8H_2$ are shown in the last column of Figure 6. Now there are four hydrogens on each side of the $B_8$ plane, bonded to all the four boron atoms. This results in the stabilization of all the $\pi$-MOs of the $B_8$ ring, of which two were initially unfilled ($b_{2g}$ and $b_{3u}$). Four more electrons are required to reach a good HOMO–LUMO gap; only two come with the hydrogens, so one needs to add two more electrons ($B_8H_4^{2+} + 2B_8H_4^{2-}$). The all-bonding radial $MO$ ($a_g$) is stabilized, while the antibonding tangential $MO$ ($b_{3g}$) is empty. Filling of all $\pi$ orbitals essentially cancels out all the stabilization from the $p_{xy}$ set to the rhombus $B_8$ skeleton. The HOMO–LUMO gap for $B_8H_8$ is comparatively smaller than the gap between LUMO and LUMO $+1$. The stabilization of $B_3$ in this ligand environment might be achieved either by (a) stabilizing $b_{2g}$ and filling it by adding two more electrons or (b) raising $b_{3g}$ in energy to increase the HOMO–LUMO gap of the neutral species. Our attempts to stabilize the all-bonding tangential $MO$ $b_{3g}$ with various substituents at $B_3$ such as $-BH_3, -BF_3, etc.$ proved futile—such substituents brought in additional levels in the frontier region, reducing the HOMO–LUMO gap. However, destabilization of the $b_{3g}$ by $\pi$-donating substituents such as fluorine at $B_8$ increases the HOMO–LUMO significantly, as shown in the third column of Figure 11.

DFT calculations on $B_8F_4H_2$ show two small imaginary frequencies for the $D_{3h}$ structure; the energy minimum corresponds to a slightly puckered structure (dihedral angle $156^\circ$) with $C_2v$ symmetry, about 1.2 kcal lower in energy than the planar form (Figure 12). The origin of this puckering is not clear; the energetic preference is anyway small. The long-known $B_8F_4H_2$ [29] whose structure was solved recently [6] (Figure 1c) has a similar skeleton to our model $B_8F_4H_2$ (where the hydrogen atoms are replaced by $-BF_2$ groups) but has a low symmetry ($C_1$) geometry, possibly due to the flat potential surface arising from the puckering.

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loose torsional modes of the BF₂ substituents. An eH calculation on the experimentally observed geometry of B₈H₁₂ gives a nice gap of 2.59 eV.

The MOs Essential for Rhomboid Bonding. The OP values within the B₄ ring decrease steadily with the addition of hydrogens, with the exception of B₄H₆ (Table 3). In our level evolution diagram (Figure 5), all these systems have four occupied MOs in common. These are the all-bonding combination of the radial (a₉), tangential p₉ (b₃g), and π p₉ (b₁u) and b₁u. The contribution of these four MOs to the net overlap population of the two B–B bonds is given in Table 4. Though we have sometimes labeled the MOs in this set as B–B bonding and sometimes as B–H bonding orbitals, it is clear from their contributions that these MOs are responsible for well over half of B–B and B–H bonding. We take this as an indication that the occupation of just these four MOs is required for a stable rhomboid ring.

A Rhomboid B₄ Unit as Part of a Macropolyhedral Borane. We now turn to the systems where a rhomboid B₄ ring fuses two polyhedral units, as in B₂₀H₁₈²⁻ (Figure 1d). To count electrons in these polyhedral systems, the special electronic requirement of rhombo-B₄ (D₂h) needs to be related to the usual and successful formalism of polyhedral electron counting rules. The B₄H₄ skeleton can be reached from closo-B₆H₆²⁻ by the removal of two capping B–H groups leaving the electrons they used in the skeletal bonding behind, i.e., B₆H₆²⁻ → 2(BH)²⁻ + B₄H₄⁶⁻.

B₄H₄⁶⁻ is also isoelectronic with cyclobutadiene dianion C₄H₄²⁻ (D₄h). As we have seen earlier, the distortion of square B₄H₄⁶⁻ to a rhombus leads to a good gap for a rhomboidal system (rhombo-B₄) with six electrons less (see Figure 3). So the rhombo-B₄H₄⁶⁻when considered as a distorted arachno system derived from closo-B₆H₆²⁻—deviates from Wade’s rule by three electron pairs. We can take this as an adjustment of electron counting rules for macropolyhedral systems containing a rhombo-B₄ unit; we apply this “correction” in the sequel every time we encounter such a unit.

Table 3. Overlap Populations between Specified Atoms in the Frontier MOs of B₄H₁₀²⁻

<table>
<thead>
<tr>
<th>MO</th>
<th>Symmetry</th>
<th>B₃-B₅</th>
<th>B₃-B₆</th>
<th>B₃-H</th>
<th>B₃-H₂</th>
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</thead>
<tbody>
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<td>b₁a</td>
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<td>0.000</td>
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<td>a₉</td>
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<td>0.069</td>
<td>0.154</td>
<td>0.028</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>b₁g</td>
<td>-0.011</td>
<td>0.028</td>
<td>0.000</td>
<td>0.161</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>b₁d</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.205</td>
<td>0.155</td>
<td></td>
</tr>
<tr>
<td>b₂a</td>
<td>0.013</td>
<td>0.027</td>
<td>0.000</td>
<td>0.000</td>
<td>0.155</td>
<td></td>
</tr>
</tbody>
</table>

Figure 11. Interaction of MOs between the B₄ ring (D₂h) with eight hydrogens in the D₃h symmetric environment (middle). The last column shows the effect of substituting hydrogens by fluorines at B₃. MOs of dissimilar symmetries are shown in distinct colors.

Figure 12. DFT-optimized geometries of planar (D₃h) and puckered (C₂ᵥ) B₄H₄F₄.
There is an alternative formulation that was suggested to us by Walter Siebert. This is to consider the rhombo-B₄ structural element as a “hyper-closo” 2n electron species instead of “distorted arachno”. We see several problems in this formulation: (1) the term “closo” is traditionally understood as a skeleton that is homeomorphic to a sphere. Hence, the four vertex closo system is tetrahedral not rhomboid. (2) The hypo-closo-B₄ notation will raise potential confusion with the tetrahedral B₄ skeleton that is observed in molecules such as B₄Cl₄, B₄(B₁-Br₄), etc., which are also, unfortunately, 2n electron species. For some unknown reasons, these molecules are sometimes referred to as hyper-closo, meaning super-closo, even for systems such as B₄Cl₄ and B₄Cl₆, though electronically these systems are hype rather than hyper. It is enough to make a chemist go into advertising! (3) The term “hypo” also has the potential to be confused with “hypso”, which refers to the electron-rich polyheda that have three missing vertices (2n + 6 species). (4) rhombo-B₄, though experimentally known as a subsystem from the 1960s, has so far never been referred to as either hypo or closo.

To summarize, though derivation of electron count for rhombo-B₄, as hypo-closo 2n electron species looks easier, we think it is inconsistent with the definition of closo. And this terminology is confusing, in relation to the molecules having tetrahedral-B₄ units, which are also 2n electron species.

Nomenclature in this field clearly engenders debate. So Russell Grimes, long active in this field, in a comment on this section of the paper says, “I would question whether Wade’s rule is really applicable to planar-B₄H₄, because it is not a fragment of a closo-polyhedron (delatrahedron). In other words, when you distort square B₄H₄ to rhombo-B₄H₄ you are leaving Wade’s country behind. In contrast, bent B₄H₄ (an octahedron minus two adjacent vertices) is a Wade structure—and in B₄H₂₀ has six additional electrons (from the six added hydrogen atoms) and in agreement with Wade’s rules.” We would say that rhombo-B₄ unit leaves Wade’s country, but still prefers to live in the neighborhood.

According to a recently formulated and quite general electron-counting scheme, a macrocyclic boronate having n vertices and m


- Figure 13. Schematic deduction of skeletal electron pair counting for B₄H₄ (D₃h).

<table>
<thead>
<tr>
<th>molecule</th>
<th>B₂–B₄ overlap population</th>
<th>net B₂–B₄ overlap population</th>
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</thead>
<tbody>
<tr>
<td>B₄H₄</td>
<td>0.232</td>
<td>0.514</td>
</tr>
<tr>
<td>B₄H₄⁺</td>
<td>0.536</td>
<td>0.702</td>
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<tr>
<td>B₄H₁₂⁺</td>
<td>0.220</td>
<td>0.364</td>
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<tr>
<td>B₄H₁₂⁺</td>
<td>0.170</td>
<td>0.329</td>
</tr>
</tbody>
</table>

- Table 4. Contribution from the Four Skeletal MOs (a₁g + b₃g + b₃u + b₁u) to the Net B–B Overlap Populations in Different Exocyclic Environments of the B₄ Ring

- Figure 14. Structure of the B₂₅H₁₈⁻ (a) with a rhombo-B₄ ring flanked between two B₁₀ polyedra and (b) its photoisomer-.
an isomer shown in Figure 14b. In this isomer, one has a “normal” structure of two B10 polyhedra linked by two \( \text{B}^-\text{H}^-\text{B}^-\) three-center two-electron bridges. Using this reasoning, the rhomboïdal connection of the two B10 units in structure 14a can also be viewed as being made up of two 3c–2e bonds. The mechanism of interconversion between these isomers is not simple, as it involves not just the movement of two hydrogen atoms to the bridging positions, but a positional shift in the boron polyhedra.

In concluding our discussion of discrete molecular systems, we should mention that we have not looked at rhomboïdal systems with bridging hydrogens. These deserve discussion, but even though they are common in borane chemistry in general, except for the \( \text{B}_2\text{O}_2\text{H}_2\text{O}^- \) isomer, they have not been seen for the rhomboïd geometry.

**Rhomboïd Connections in Extended Systems:** \( \text{Na}_3\text{B}_{20} \). \( \text{Na}_3\text{B}_{20} \) is a recently characterized alkali metal boride,\(^7\) found in a structural refinement of a sodium boride that was incorrectly assigned a composition of \( \text{Na}_6\text{B}_6 \) earlier.\(^{28}\) The orthorhombic \( \text{Cmmn} \) structure was solved by X-ray powder diffraction and neutron diffraction. The structure has layers of alternating octahedral \( \text{B}_6 \) units and trigonal-bipyramidal \( \text{B}_7 \) units, seen from a “top” perspective in Figure 15. While the \( \text{B}_6 \) units are connected to the adjacent polyhedra by regular two-center bonds, the adjacent \( \text{B}_7 \) units are fused by the now familiar rhomboïd-\( \text{B}_7 \) unit, similar to the fusion of the \( \text{B}_{10} \) units in the molecular \( \text{B}_{20}\text{H}_{18}^+ \). In forming infinite chains of \( \text{B}_7\text{B}_7 \) units, the topological arrangement is such that the \( \text{B}_7 \) units share a unique single vertex. \( \text{Na}_3\text{B}_{20} \) is reported to be an insulator.\(^{7b}\)

The orthorhombic unit cell of \( \text{Na}_3\text{B}_{20} \) \((Z = 2)\) can be conceptually divided into \( (\text{Na})_6(\text{B}_6)_2(\text{B}_7)_4 \) units for the purpose of electron counting. While the two electron requirement of \( \text{B}_6 \) can be directly deduced from Wade’s rule, the \( \text{B}_7 \) units which are fused by rhomboïd-\( \text{B}_7 \) units require the application of the mno rule. Each \( \text{B}_7 \) chain has two \( \text{B}_7 \) and two \( \text{B}_3 \) units in the unit cell. Hence \( n = 14, m = 2, \) and \( o = 2 \), which gives a total of 18 electron pairs per chain or an anticipated count of nine electron pairs per \( \text{B}_7 \) unit. For every repeat unit of the \( \text{B}_7 \) chain, there are four boron atoms with \( \text{exo}-2\text{c}–2\text{e} \) bonds connecting the other polyhedra. These boron atoms formally contribute one electron pair each to skeletal electron count. The remaining three boron atoms of the \( \text{B}_7 \) unit have no \( \text{exo}-2\text{c}–2\text{e} \) bonds, and they together contribute 4.5 electron pairs (3 × 3 valence electrons) to skeletal bonding. We thus have a situation where a \( \text{B}_7 \) unit has 17 electrons (8.5 electron pairs) but by the mno rule requires 18 electrons for stability. The \( \text{B}_7 \) unit should then acquire an extra electron from the rest of the lattice for stability, as \( \text{B}^{15+} \). The charge assignment of individual units in \( \text{Na}_3\text{B}_{20} \)

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**Figure 15.** Structure of \( \text{Na}_3\text{B}_{20} \).

**Figure 16.** Band structure of \( \text{Na}_3\text{B}_{20} \) from eH calculations.

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1.4 eV. This indicates substantial inter-unit cell interaction in the frontier MOs of this polymer.

Returning to Na$_3$B$_{20}$, we studied the electron deficiency of the neutral structure with DFT calculations, optimizing the primitive unit cell ($Z$ = 1) with +1, 0, and −1 charges. We used a plane-wave cutoff energy of 400 eV with a $k$-point separation of about 0.04 Å$^{-1}$ (9 × 9 × 12 mesh). Our repeated attempts to obtain the converged geometry for neutral and +1 charged unit cell by using increased cutoff energy, and $k$-point sampling proved futile. However, the system with a −1 charge converged rapidly. The optimized primitive unit cell of Na$_3$B$_{20}$ ($a$ = 9.771 Å, $b$ = 4.090 Å, $c$ = 4.090 Å; $a$ = $b$ = 90.0°, $c$ = 146.43°; cell volume = 215.919 Å$^3$) is in reasonable agreement with the experimentally reported unit cell parameters ($a$ = 9.757 Å, $b$ = 4.14 Å, $c$ = 4.14 Å; $a$ = $b$ = 90.0°, $c$ = 146.09°; cell volume = 220.347 Å$^3$) from neutron diffraction.

The band structure of Na$_3$B$_{20}$ obtained from eH calculations using the DFT-optimized geometry is given along with the DFT bands in Figure 20. The band structures appear similar, except that the band gap of ~1 eV obtained from eH calculations vanishes in the DFT band structure, which shows a zero band gap, near special point Y (~0.5, 0.5, 0) in the Brillouin zone.

We have a problem: (1) electron counting and our calculations point to Na$_3$B$_{20}$ needing more electrons, and (2) it is hard to see how Na$_3$B$_{20}$ with an odd number of electrons in a primitive unit cell (as found) can be insulating. Insulating behavior due to localization of states (a Mott transition) seems to be improbable, due to the steep nature of the bands from B$_7$ chains in the frontier region. One can think of two possible mechanisms by which the system can get its extra electrons: (a) partial occupancies or (b) interstitial atoms. Sodium vacancies, i.e., partial occupancy of sodium sites, moves the electron count in the wrong direction. Even partial occupancy of boron sites in this system will increase the electron deficiency, as it will give rise to partially open “nido” structures, which demand more electrons. The possibility of having interstitial Na$^+$ ions is also unlikely, due to the compact packing. The heptagonal channels in the boride network already contain sodium atoms with nearest Na–Na contacts ~4.14 Å.

We suggest that there are in this structure some interstitial boron atoms, capping the faces of the polyhedra. Such capping boron atoms are known to provide additional electrons to the framework without modifying the electron count, in structures such as β-rhombohedral...
boron. The mechanism has been described by Mingos et al. as the “capping principle.” Since there are many three-membered ring faces available in the unit cell, the capping atoms may be randomly distributed in different faces. This would make their experimental detection by diffraction methods difficult. In summary, further structural investigation of this phase is indicated; the electronics argue strongly against a simple Na$_3$B$_{20}$ stoichiometry.

A reviewer has suggested that there might be a carbon substituting the boron leading to the composition Na$_3$B$_{19}$C. However, the analytical data in the original work seems to exclude the presence of any other atom other than boron and sodium.

dangling bonds of the B\textsubscript{12} polyhedra. Both experimental measurements and DFT band structure calculations characterize the compound as a semiconductor with a definite band-gap.\textsuperscript{8} The bonding in B\textsubscript{12}Si\textsubscript{3} remains unexplored. The band structure obtained from eH calculation for B\textsubscript{12}Si\textsubscript{3} is given in Figure 22a.

For calibrating the parameters employed in eH calculations, we also performed a DFT optimization of Si\textsubscript{3} using a plane wave cutoff energy of 400 eV with a 5 x 5 x 5 k-point set. The band structure obtained from DFT calculations is given alongside the eH bands as Figure 21b. There is a direct band-gap of \~1.5 eV observed in both calculations, in good agreement with the earlier reports.

For the purpose of electron counting, we divide the orthorhombic unit cell of B\textsubscript{12}Si\textsubscript{3} (Z = 16) into (B\textsubscript{12})\textsubscript{4} (Si\textsubscript{4})\textsubscript{4}. Since each B\textsubscript{12} unit requires two electrons, the Si\textsubscript{4} unit has to be assigned a +2 charge.\textsuperscript{8} We can relate the environment of the Si\textsubscript{4} units to the neutral rhomboidal B\textsubscript{4}H\textsubscript{12} model discussed earlier. Each Si\textsubscript{4} unit differs somewhat from B\textsubscript{4}H\textsubscript{12}, as two of the four axial hydrogen atoms are missing on one side. So the appropriate model will be the doubly deprotonated B\textsubscript{4}H\textsubscript{10}\textsuperscript{2−}, which is isoelectronic to Si\textsubscript{4}H\textsubscript{10}\textsuperscript{2+}. To confirm the electronic requirement, we carried out DFT calculations on the discrete Si\textsubscript{4}H\textsubscript{10}\textsuperscript{2−} molecule with a C\textsubscript{2v} symmetric constraint. Frequency calculations indicate that Si\textsubscript{4}H\textsubscript{10}\textsuperscript{2−} (C\textsubscript{2v}) is not a minimum on its potential energy surface; the axial hydrogens at the longer diagonal are trying to move toward the bridging positions, breaking the symmetry. The replacement of axial hydrogens with −SiH\textsubscript{3} groups will simulate an ideal model for the environment around Si\textsubscript{4} units in B\textsubscript{12}Si\textsubscript{3}, but the loose torsional modes of −SiH\textsubscript{3} in practice will complicate the computations, due to the flat potential energy surface they engender. Hence, we decided to replace the two axial hydrogens with fluorine atoms. The resulting Si\textsubscript{4}H\textsubscript{8}F\textsubscript{2}\textsuperscript{2+} (Figure 23) is a minimum. The bond length variation is more pronounced in Si\textsubscript{4}H\textsubscript{8}F\textsubscript{2}\textsuperscript{2+} compared to the observed distances in B\textsubscript{12}Si\textsubscript{3}, presumably due to the higher electronegativity of fluorine.

Since the eH method gives a band structure very similar to that of the quantitatively more accurate DFT calculations on B\textsubscript{12}Si\textsubscript{3}, it is easy to test the effect of chain formation in Si\textsubscript{4} units on its charge. Figure 24 shows the band structure and density of states for the one-dimensional Si\textsubscript{4}H\textsubscript{8} polymer with a +2 charge per unit cell. There is a substantial band gap (\~5 eV), confirming that the linking of Si\textsubscript{4}\textsuperscript{2+} units does not alter the charge requirements.

The bonding in B\textsubscript{12}Si\textsubscript{3} thus can be conveniently interpreted as built up from B\textsubscript{12}\textsuperscript{2−} polyhedra and novel nonclassical Si\textsubscript{4}\textsuperscript{2+} units, analogous to boron rhomboids.

Conclusion

The electronic requirements of systems exhibiting the rhombohedron geometry, quite diverse, are explained using molecular orbital theory. There are four MOs which are primarily responsible for skeletal bonding. A bridge is built between molecular rhombo-B\textsubscript{4} systems and polyhedral extended structures with an analogous building block. We think the recently
reported structure of Na$_3$B$_{20}$ (which contains the rhombo-B$_4$ units) is electron deficient and requires one more electron per formula unit to explain the observed insulating behavior; we suggest there may be interstitial boron atoms in this structure. We have also related the bonding in $\beta$-SiB$_3$, which contains rhomboid Si$_4$ units, to that of molecular and extended rhombo-B$_4$ structures.

Acknowledgment. Our work was generously supported by the National Science Foundation through research grant CHE-0204841. We are grateful to Armin Berndt, Russell Grimes, Walter Siebert, and the reviewers for their comments on our paper.

Supporting Information Available: Cartesian coordinates for relevant molecules optimized at B3LYP/6-31G* level and fractional coordinates for relevant extended structures optimized with DFT based LDA/PAW calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0467420