Cluster Compounds

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π Aromaticity and Three-Dimensional Aromaticity: Two sides of the Same Coin?**

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In memory of Kenneth Wade

Abstract: *A bridge between classical organic polycyclic aromatic hydrocarbons (PAH) and closo borohydride clusters is established by showing that they share a common origin regulated by the number of valence electrons in an electronic confined space. Application of the proposed electronic confined space analogy (ECSA) method to archetypal PAHs leads to the conclusion that the 4n+2 Wade–Mingos rule for three-dimensional closo boranes is equivalent to the (4n+2)π Hückel rule for two-dimensional PAHs. More importantly, use of ECSA allows design of new interesting fused closo boranes which can be a source of inspiration for synthetic chemists.*

Closo-Borohydride (BH) clusters are anions with the general formula $[B_nH_n]^{2-}$ and have a structure of a polyhedron with triangular faces. They obey the Wade electron-counting rule,[1] which for the case of the *closo* boron clusters is $2n+2$ in where n represents the vertices of the polyhedron, or Mingos' rule which is $4n+2$.[2] Both rules are equivalent; Wade's rule refers to the skeletal electron pairs, whereas Mingos' rule also incorporates the exo electron pairs corresponding to the B–H bonds, thus referring to the total number of valence electrons (TNVEs). Mingos' rule is precisely Hückel's rule for aromaticity,[3] although the meaning of n is absolutely different. The Wade–Mingos rule does refer to the VE numbers needed to account for the high stability of *closo* boron clusters[4] but does not imply a character of aromaticity, most probably because this character was not obvious in BH clusters. A visual inspection of the structures of BH clusters shows that their shapes do not look at all like their organic counterparts, the hydrocarbons (HCs). The basic units of the BHs have three dimensions, for example, an icosahedron in $[B_{12}H_{12}]^{2-}$, whereas the basic units for the HCs are two-dimensional (e.g. C_6H_6) or one-dimensional (e.g. -CH_2-CH_2-). Moreover, and at variance with HCs, boron catenation in BHs is rare and boron prefers to form two- or three-dimensional hypercoordinate compounds.[5] Importantly, the bonding in HCs can be described by Lewis structures and resonance concepts, whereas this is not the case in BHs. For instance, in $[B_{12}H_{12}]^{2-}$ there are 42 atom-to-atom connecting lines but only 50 VEs. This shortage of pairs of electrons is what led the name "electron-deficient compounds". However, this nomenclature does not reflect their real stability. Something that is short of electrons implies frailness.[5d] But this is not the case for BH clusters, particularly those of the *closo* borane series. The high thermal stability is demonstrated with $Li_2[B_{12}H_{12}]$[6] and $Na_2[B_{12}H_{12}]$[7] which do not decompose below 600 °C.

The high stability of the $[B_nH_n]^{2-}$ clusters (especially for $n = 6$, 7, 10, and 12)[8] and their tendency to retain their molecular structure (with the exception of $[B_8H_8]^{2-}$ and $[B_{11}H_{11}]^{2-}$ which are fluxional)[9] led boron cluster chemists to think about these clusters as if they were aromatic. Indeed, already in 1959 Lipscomb et al. considered $[B_{12}H_{12}]^{2-}$ a super-aromatic molecule,[10] despite it not having unhybridized p orbitals in a continuous planar cyclic system to allow formation of an aromatic π system. Nowadays there is a wide consensus on the aromatic character of *closo* BH clusters. Nucleus-independent chemical shift (NICS) results,[8,11] bond-length alternation values,[8] and resonance energy calculations[12] support the aromatic character of $[B_nH_n]^{2-}$ clusters. The main aim of the present work is to demonstrate that the $4n+2$ Wade–Mingos rule followed by three-dimensional *closo* boranes and the $(4n+2)\pi$ Hückel rule applicable to two-dimensional monocyclic annulenes are related. This result differs from the similarities found by different authors between the π systems of some planar boron clusters and those of polycyclic aromatic hydrocarbons (PAHs) because our study refers to three-dimensional boron clusters.[5c,13]

We established[14] a link between the hydrocarbon and borohydride chemistries by showing that HCs and BHs have a common root regulated by the number of VEs in a confined space. Herein, we go one step further by applying the electronic confined space analogy (ECSA) method to bridge fundamental aromatic HCs and the analogous *closo* BH clusters. The steps are the following: 1) first we state the model organic compound; 2) next we define its confined

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space (*c*S) as the number of electrons enclosed in the ring of carbon atoms; 3) we transmute[15] each carbon atom into a boron atom and one electron (*e*T); 4) these extra electrons are replaced by sacrificial atoms (*s*A); and 5) finally we generate the new BH compound by structural relaxation (*s*R). Throughout the whole process, the number of valence electrons in the corresponding confined space remains unaltered. As sacrificial atoms H^+, B^{3+}, or $[BH]^{4+}$, among others, can be used. These cations have empty valence orbitals perfectly suited to form multicenter bonds. The following examples are illustrative of the procedure.

The first system addressed is $[C_4H_4]^{2-}$, an aromatic dianion with six π electrons. We start defining the confined space with TNVE = 22 and after electronic transmutation from C to B^-, we get $[B_4H_4]^{6-}$ as a minimum with C_{2h} symmetry. Then, we can introduce $[BH]^{4+}$ as a sacrificial group to yield the D_{3h} trigonal bipyramidal $[B_5H_5]^{2-}$. The electronic transmutation can be represented in the layout with one dot near to each substituted atom (Figure 1). The

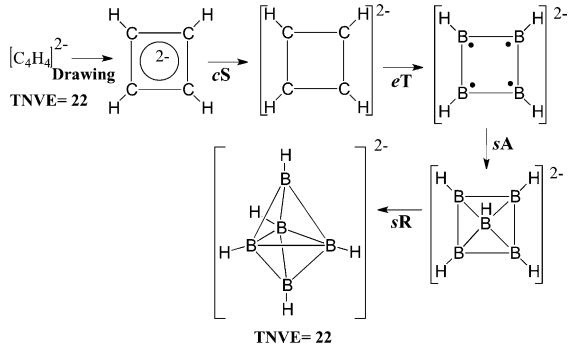

Figure 1. The ECSA method applied to $[C_4H_4]^{2-}$.

four dots representing four electrons are electronically equivalent to a [BH] group. Thus, they can be geometrically replaced by this entity on the right place to satisfy all four transmuted atoms. This replacement can only be on top of the existing square face. The final result after structural relaxation is the D_{3h} $[B_5H_5]^{2-}$ *closo* borane cluster. For years, many boron chemists have associated the stability and reactivity of *closo* boranes with their three-dimensional aromatic character.[16] The connection between aromatic $[C_4H_4]^{2-}$ and $[B_5H_5]^{2-}$ supports this view. Not unexpectedly, $NICS(0)_{zz}$ values (the axial axis of the polyhedron was taken as the z direction to calculate the $NICS(0)_{zz}$ value) of planar $[B_4H_4]^{-6}$ and pyramidal and trigonal bipyramid $[B_5H_5]^{2-}$ are quite different (Table 1). However, NICS(0) values are comparable. While resonance energies calculated by Aihara indicate that $[B_5H_5]^{2-}$ is not aromatic,[12] the relatively low bond-length alternation (difference between the longest and shortest B–B bond distance in the cluster) value of 0.15 Å and NICS(0) value seem to support the aromatic character of this *closo* borane.[8] As a whole, the aromatic nature of $[B_5H_5]^{2-}$ is somewhat controversial and this may offer an explanation of why this cluster has not been synthesized yet.

The cyclopentadienyl anion is the smallest all-carbon cycle with 6π electrons (TNVE = 26 electrons) and has

Table 1: Calculated NICS values [ppm] and bond length alternation Δ*r* [Å] of the compounds under analysis derived from monocyclic and polycyclic hydrocarbons.

Compound	Ring	NICS(0)	$NICS(0)_{zz}$	Δ*r*
$C_4H_4^{2-}$	4-MR	−6.3	6.8	0.00
$B_5H_5^{2-}$	3-MR	−26.1	−33.3	0.15
$C_5H_5^-$	5-MR	−12.7	−16.6	0.00
$B_6H_6^{2-}$	4-MR	−31.0	−31.0	0.00
C_6H_6	6-MR	−8.1	−14.6	0.00
$B_7H_7^{2-}$	5-MR	−22.8	−38.7	0.17
$C_{10}H_8$	6-MR	−8.5	−13.4	0.06
$B_{12}H_{10}^{2-}$	5-MR	−15.9	−33.0	0.26
$C_{14}H_{10}$/Anthracene	6-MR terminal	−7.3	−9.8	0.07
	6-MR central	−11.4	−19.1	
$B_{17}H_{13}^{2-}$	5-MR terminal	−16.0	−30.5	0.31
	5-MR central	−9.1	−20.4	

MR = membered ring.

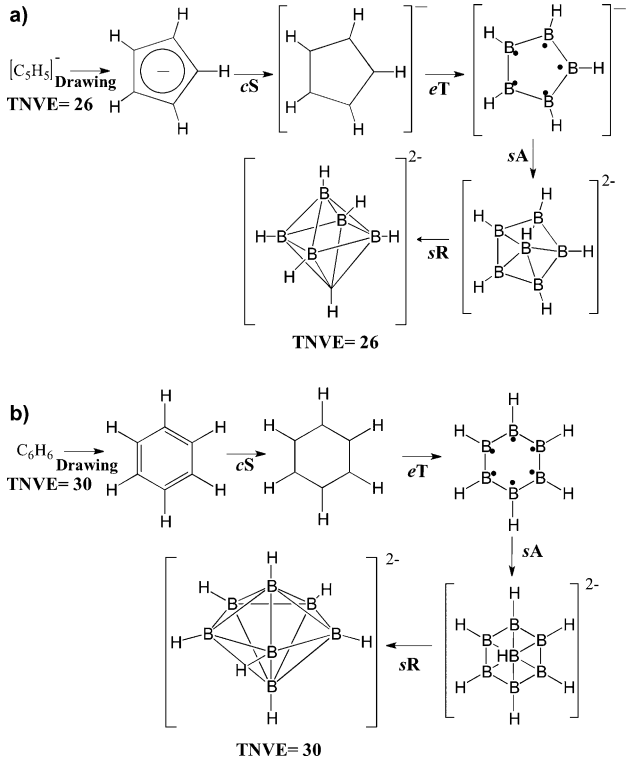

Figure 2. The ECSA method applied to a) $[C_5H_5]^-$ and b) C_6H_6.

a recognized stability for further reactions. The process of conversion into a borane is as before (Figure 2a). The first stages lead to $[B_6H_6]^{2-}$ in a pentagonal pyramidal geometry, however its stability competes with that of trigonal prismatic or octahedral polyhedra. The concept of a higher number of coordination to reach the octet prevails and the octahedron structure is favored over the pentagonal pyramid. The well-known octahedral geometry for the $[B_6H_6]^{2-}$ *closo* borane[17] is 62.3 kcal mol^{-1} lower in energy than the pentagonal pyrami-

dal geometry. Values in Table 1 seem to indicate that octahedral $[B_6H_6]^{2-}$ is even more aromatic than the cyclopentadienyl anion. As for $[C_5H_5]^-$, all bonds share the same bond distance in $[B_6H_6]^{2-}$. Among the smallest *closo* boranes $[B_nH_n]^{2-}$ ($n=5$–12), $[B_6H_6]^{2-}$ was the most aromatic with the largest resonance energy per face[12] and the most negative NICS value.[8]

Benzene is the archetype of the aromatic molecule. Therefore, it was stimulating to find its partner in BH clusters (Figure 2b). In this case, we have TNVE = 30 in the confined space. The electronic transmutation with B^- drives us to $[B_6H_6]^{6-}$ with chairlike symmetry. The planar structure of $B_6H_6^{-6}$ can be achieved by adding six Li^+ counterions, although the $Li_6B_6H_6$ obtained has D_{2h} symmetry.[18] The sacrificial group is again $[BH]^{4+}$, thus leading to the hexagonal pyramid $[B_7H_7]^{2-}$ which is not a minimum, but relaxes to a pentagonal bipyramid $[B_7H_7]^{2-}$, as experimentally found.[19] NICS(0) again points out that $[B_7H_7]^{2-}$ is at least as aromatic as benzene. The relatively low bond-length alternation value of 0.17 Å seems to confirm the aromatic character of this *closo* borane. Resonance energies per face as calculated by Aihara[12] indicate that $[B_7H_7]^{2-}$ is the most aromatic *closo* borane $[B_nH_n]^{2-}$ ($n=5$–12) after $[B_6H_6]^{2-}$. Interestingly, by using a different procedure to count the TNVE, McGrady linked C_6H_6 to non-isoelectronic $[B_6H_6]^{2-}$.[20]

Once having observed the parallelism between monocyclic aromatics and monodeltahedron *closo* boranes, we aimed at extending the prospective new molecules to derivatives of bi- and polycyclic organic compounds. So we moved to acenes. The smallest acene species is naphthalene, $C_{10}H_8$, a bicyclic aromatic species with 10π electrons which obeys Hückel's rule with $n=2$. It has a TNVE equal to 48. If the ECSA method is applied in the bicycle and one takes into account the structural relaxations described in Figure 3a, by which

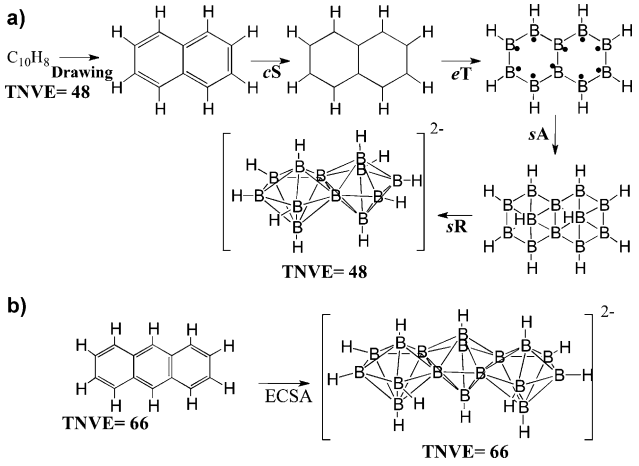

Figure 3. The ECSA method applied to a) naphthalene and b) anthracene.

a six-membered ring (6-MR) converts into a pentagonal bipyramid, then two bipyramids sharing one edge are generated for a molecule with the formula $[B_{12}H_{10}]^{2-}$. This fused *closo* borane species is a stable species. Similarly, anthracene ($C_{14}H_{10}$) is a polycyclic aromatic hydrocarbon with 14π electrons and obeys the $(4n+2)\pi$ Hückel rule for $n=3$. If the ECSA method is applied (Figure 3b), three pentagonal bipyramids, the central sharing two edges with the peripheral bipyramids, are generated for a molecule with the formula $[B_{17}H_{13}]^{2-}$. It is worth noting that the same fused *closo* borane is achieved starting from phenanthrene. Finally, Table 1 shows similar NICS for the above mentioned acenes and the analogous yet to be discovered fused *closo* boranes. Bond-length alternation values, however, are larger for fused *closo* boranes than acenes.

As a whole, molecules have to satisfy a certain number of electrons to be stable. Above and below this number the molecule is unstable or highly reactive. Thus, chemists are used to managing electron counting rules to predict the preferred electron count for molecules. Examples are the octet rule,[21] 18-electron rule,[22] Hückel's rule,[3] and the $2(n+1)^2$ Hirsch's rule.[23] Wade's rule has been extremely significant for interpreting structures which could not be explained by two-center-two-electron bonding, and has found wide application in boranes, carboranes, heteroboranes, and low-valent transition-metal clusters, among others.[4] Wade's rule was extended to condensed polyhedral borane clusters by Jemmis and Balakrishnarajan, thus leading to the mno rule[24] which can interpret clusters such as $B_{20}H_{16}$.[25] These are electron counting rules which stand by themselves. They are applied to one molecule and do not require a reference type. A different concept is the isolobal analogy[26] and as its name indicates, relates the structure of organic and inorganic molecular fragments to predict bonding properties of organometallic compounds. Thus, it has a reference organic compound.

The method deployed in this paper is also an analogy model based on a reference organic compound. The analogy is electronic and based on maintaining the same number of electrons of reference compound in the derivative. However, it is also structural, although the final structure may not look, at first glance, similar to the reference one. The preservation of the number of electrons occurs in a confined space, which is not identical but similar to that of the reference compound. The method has the advantage that it starts from a monocyclic hydrocarbon reference compound which is highly stable, either fulfilling the Lewis structures for covalently bound molecules or the $(4n+2)\pi$ Hückel electron rule, and is transformed into a monodeltahedron BH cluster, which obeys the $4n+2$ Wade–Mingos rule. Noticeably the value of n has a different meaning in each equation. In the $(4n+2)\pi$ Hückel rule n can be any integer and has no direct relationship with the structure. Conversely in the $4n+2$ Wade–Mingos rule n is structure dependent and refers to the number of vertices occupied by boron atoms. Also the TNVE value is kept constant throughout the process. It is interesting to note that the TNVE value has no indication of aromaticity in the reference compound but ends up following the $4n+2$ Wade–Mingos rule. Conversely the $(4n+2)\pi$ Hückel rule is obeyed in the organic reference compound but has no meaning at the derived borane cluster (see Table S1 in the Supporting Information). Figure S4 shows the molecular orbitals (MOs) of monodeltahedron $[B_7H_7]^{2-}$ as an example. As in conjugated annulenes of D_{nh} symmetry, there is an all-bonding MO

first and then the rest come by pairs, except the last one for even n value. Placing $(4n+2)\pi$ electrons in these MOs leads to a closed-shell electronic structure which provides the extra stability typical of classical aromatic organic compounds. The same structure is repeated in *closo* $[B_nH_n]^{2-}$ boranes for σ and π orbitals and this explains the origin of the $2n+2$ (or $4n+2$ if we include the B–H exo bonds which are not responsible for aromaticity in *closo* boranes) Wade–Mingos rule. It turns out that when starting from a conventional aromatic compound which obeys the $(4n+2)\pi$ Hückel rule, and applying the ECSA method, a three-dimensional deltahedron which follows the $4n+2$ Wade–Mingos rule is generated and is in turn aromatic. This correlation is a clear indication that the two types of aromaticity (two- and three-dimensional) are nothing but the two sides of the same coin.

Not only monodeltahedron but also polydeltahedron BH clusters can be designed by applying the ECSA method to PAHs. It is remarkable that the polydeltahedron derivatives of the PAHs all have a formula $[B_nH_{(n-2se)}]^{2-}$ (se = number of shared edges) which is very much like the $[B_nH_n]^{2-}$ formula for all *closo* borane species which are also aromatic. Particularly noticeable is that all structures keep the negative charge of two electrons independent of the number of fused deltahedra. This feature is remarkable because in the interpretation of the original Wade rule with $n+1$ skeletal electron pairs, the $n+1$ MOs to produce the closed-shell are the consequence of one highly stabilized orbital made up with of inner sp-atomic orbitals from each boron atom and n peripheral molecular orbitals made with the n p-atomic orbitals from the n boron atoms. As each boron atom contributes to the boron cluster skeleton with $2\,e^-$, it was visualized that "these" electrons were for the n peripheral MOs, and that the $2\,e^-$ from the negative charge were for the highly stabilized MO originating from sp. However, for the polydeltahedron boranes the MO, visualization is not so easy as only a $2\,e^-$ negative charge exists irrespective of the number of fused deltahedra. As an example, Figure S5 depicts the MOs of $[B_{12}H_{10}]^{2-}$. As in the case of naphthalene, there are no degenerate orbitals which can justify the $4n+2$ rule of Wade–Mingos for closed-shell electronic structures.

The $4n+2$ Wade–Mingos rule is not followed in fused *closo* boranes. This aspect can be observed for the ECSA application to benzene to produce $[B_7H_7]^{2-}$, a $4n+2$ ($n=7$) electron count (Wade–Mingos rule), to naphthalene to produce $[B_{12}H_{10}]^{2-}$, a $4n$ ($n=12$) electron count, to antracene to produce $[B_{17}H_{13}]^{2-}$, a $4n-2$ ($n=17$) electron count, or to tetracene to produce $[B_{22}H_{16}]^{2-}$, a $4n-4$ ($n=22$) electron count. Systematically, the number of electrons as a function of the number of vertices n decreases with an increasing number of fused deltahedra, thus resulting in the formula $4n+2(1-se)$ in which se accounts for the number of shared edges. Therefore, the $4n+2$ Wade–Mingos rule has to be generalized to the $4n+2(1-se)$ rule if we want to apply it to yet to be discovered fused *closo* boranes.

Finally, it is worth mentioning that a direct connection between the *nido* or the *arachno* borane clusters and the hydrocarbon chemistry is not as straightforward as the one reported here between *closo* boranes and classical organic compounds, although we have found some correlations. Moreover, it remains to be investigated whether the ESCA approach could be applied to heteroaromatic species and to relate other clusters (such as the Zintl clusters) to analogous hydrocarbons or fullerenes. Further research is underway to explore these possibilities.

Experimental Section

All calculations were performed with the Gaussian09 package[27] by using the B3LYP[28] hybrid density functional and the 6-311++G(d,p) basis set.[29] The geometry optimizations were performed without symmetry constraints, and analytical Hessians were computed to confirm that the optimized structures are indeed minima (zero imaginary frequencies). Aromaticity was evaluated by the nucleus-independent chemical shift (NICS).[30] More details on the method of calculation together with Table S2 with values obtained at the OPBE/TZ2P level can be found in the Supporting Information.

The Supporting Information contains complete computational methods, complete Ref. [27], complete Table 1, Figures S1, S2, and S3 with the ECSA method applied to $[C_4H_4]^{2+}$, $[C_7H_7]^{+}$, and tetracene, respectively, Figures S4 and S5 with the molecular orbitals of $[B_7H_7]^{2-}$ and $[B_{12}H_{10}]^{2-}$, respectively, Table S1 with the equivalence in terms of TNVE between hydrocarbons and the corresponding *closo* borane derivatives, Table S2 with computed values of Table 1 at OPBE/TZ2P for comparison, and Table S3 with the optimized Cartesian coordinates of all studied species.

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