CHAPTER 2

BONDING IN CONDENSED (MACROPOLYHEDRAL) BORANES
2.0. INTRODUCTION

Polyhedral boranes have provided excitement in all branches of chemistry.\(^1\) Aesthetically pleasing structures, path breaking bonding characteristics, unusual physicochemical properties, promising materials for the future, Boron Neutron Capture Therapy,\(^1\) membrane specific spherical structures,\(^1\) templates for catalysis\(^1\) - the range of areas spanned by boranes is indeed vast.\(^1\) Several condensed polyhedra with borane structures are known in literature. Wade's rule, which has been successful in explaining the bonding in monopolyhedral boranes is inapplicable to assess the electronic requirements of condensed systems. Recently, a n+m skeletal electron pair count has been formulated for macropolyhedral boranes where condensation involves sharing of more than one vertex among m cages.\(^2\) \(\text{B}_{20}\text{H}_{16}\) with four atoms in common serves as the best example for this rule.\(^3\) Face sharing polyhedral skeletons are found in extended solids.\(^4\) The majority of the known macropolyhedral boranes are either edge-shared open cages or they share a single vertex.\(^5\) We conducted a thorough survey of all macropolyhedral borane skeletons characterized experimentally so far that resulted in a generalized electron counting scheme, which is applicable to all aromatic systems including metallaboranes, polydecker sandwiches and any combination of these structural motifs. The generalizations and illustrations of the rule are discussed in the first section followed by a justification considering various modes of fusion. The second part also demonstrates the importance of the electron counting rule as a guiding tool, specifically taking an experimentally reported macropolyhedral borane, the molecular formula of which is estimated erroneously.
2.1. A GENERALIZED ELECTRON COUNTING mno RULE

In recent years, it is increasingly felt that there are several common features among two-dimensional aromatic organic molecules and three-dimensionally aromatic polyhedral boranes. There are also attempts to merge another thriving area viz., organometallics with boranes through the intermediary of metallaboranes and metallocenes. A generally applicable electron counting rule should help in this process. We provide here such a generalization that brings polyhedral boranes, polycondensed polyhedral boranes and metallocenes under the same umbrella.

The variety of bonding patterns exhibited by polyhedral boranes was explored by Lipscomb (styx), Wade, Williams and many others in the second half of the last century. A major breakthrough came from William's perception that the experimentally isolated arachno and nido boranes can be viewed as being derived from the nearest closo structures by the removal of a vertex rather than as fragments of icosahedral B$_{12}$H$_{12}$ skeleton. Wade's n+1 electron pair rule for a polyhedron exhibiting a closo pattern (B$_{12}$H$_{12}^+$, Figure 1) where n is the number of vertices was derived simultaneously. Application of the rule generated a Paradigm for the Electron Requirements of Clusters (PERC approach) by Rudolph. The often reproduced chart of Rudolph gave a mnemonic way to correlate the different cluster patterns both by the debor approach and the seco approach and has been text book material for years. According to the debor approach, a nido cluster will have one BH group (one vertex) less with respect to its nearest closo form. The seco approach treats a nido unit as derived from its closo analogue by the removal of a bond pair. An arachno cluster can be differentiated from its
*nido* in a similar fashion. The Wade's rule was extended to include electron deficient clusters with capped vertices where each cap normally donates an electron pair.

In this treatment of polyhedral bonding all the boron atoms were treated as sp hybrids. One sp hybrid radiates away from the center of the sphere forming the *exo*-2e-2e bond with the hydrogen atom or other substituents. Another sp hybrid points towards the center of the cage. The two remaining unhybridized AOs are tangential to the sphere. Hence, each atom contributes three orbitals for skeletal bonding. The radial orbitals combine in phase to generate a strong core bonding molecular orbital (BMO). The tangential orbitals upon linear combination produce the remaining n surface BMOs. The n+1 electron pairs of a *closo* polyhedron occupy all BMOs so that a favorable structure results. The n+1 rule was justified using graph theory by King and Rouvray.\(^{12}\) Stone\(^{13}\) derived it using the Tensor Surface Harmonic Theory. Chemistry of boranes flourished along with this easily applicable electron-counting rule.\(^{1,10,14}\)

Early on there were examples of borane structures with condensed polyhedra. The first macropolyhedral borane, B\(_{20}\)H\(_{16}\), (2, Figure 1) was isolated as a neutral species in the sixties.\(^{3}\) It involves the sharing of four atoms between two icosahedra. This gave a clear indication that polycondensation of polyhedral boranes would reduce the electron requirement. Until then polyhedral boranes were known with negative charges and the neutrality of B\(_{20}\)H\(_{16}\) was a mystery. Condensed structures, where the delocalized electronic structure of the individual polyhedron is not disturbed, can be understood by the **Wade's n+1 electron pair rule**. For example, Structure 3 (Figure 1), may be visualized as a combination of two polyhedra where the electronic structure of the individual icosahedral units is retained. However there are many other ways in which the
condensation can take place (Figure 2). The absence of an electron-counting rule, which can be applied to all these condensed structures is immediately felt. An analysis on the nature of interaction between individual aromatic units of polyhedral boranes in all the possible modes has already resulted in an electron-counting scheme applicable to the whole range of main group elements. The rule gives the requirement of electron pairs as n+m for a closo macropolyhedral borane cluster, where m is the number of individual polyhedra involved in the condensation and n is the total number of vertices. For example the n+m electron pair count for B₂O₁₆ (2) is 20+2=22. The number of available electron pairs is also 22 (16 electron pairs from 16 BH groups and six from four boron atoms). Nido and arachno arrangements call for additional electron pairs.

Attempts to modify the n+m rule to include the single vertex condensations as well, have paved the way for a new rule, which is christened as the mno rule. It unifies polycondensed polyhedral boranes, metallaboranes, metallocenes and any of their combinations. With the new parameter 'o' standing for the number of single vertex bridging, the rule states that m+n+o skeletal electron pairs are required for the stability of condensed polyhedral boranes involving closo arrangements.

A generalized electron counting rule, which also takes into account the open structures and capping vertices is given by N = m+n+o+p−q, where N is the skeletal electron pairs, m and n have the same implications as above, p is the number of missing vertices from its corresponding closo structure and q is the number of capping vertices. The electron-counting rule presented here is applied to a wide variety of boranes, heteroboranes and metallaboranes.
Representative examples (Structures 1-18) illustrating the mno rule are given.
A comparison of the variety of polyhedral bonding exhibited by simple polyhedral boranes and its polycondensed analogues. A correlation between closo, nido and arachno patterns of macropolyhedral borane systems are shown. The last set includes both the arachno and bisnido structures. At each level one structure is expanded. Others too branch off in a similar fashion as shown by dotted lines.

Condensation of polyhedra provides infinite variety. Figure 2 demonstrates this using two polyhedra with different modes of condensation. For simplicity the correlation has been drawn considering only an icosahedral fragment though it will be applicable to other polyhedral clusters in any possible combinations. Expansion of a macropolyhedral closo form to different nido patterns has been done only on a single cluster. The possibility of open structures starting with an icosahedron alone grows exponentially and hence only one structure is expanded at a given level of this tree-diagram. Similarly the
arachno and bisnido structures emerging from a single nido pattern have been shown. The branch at the extreme right hand side starting from the icosahedron indicates the closo, nido and arachno path for monopyhedral boranes discussed in the Rudolph diagram. Terminal hydrogens are omitted for clarity. The variety available in polycondensation is immediately obvious.

The success of any electron counting rule is in its applicability to a range of experimentally known systems and projections for the unknown. The generality of the mno rule by applying it to a large set of structures is demonstrated. Despite the success it is good to remember that electron-counting rules are just that - electron counting rules. Just as the \( B_nH_n \sim (n=5-12) \) exhibit varying stability, the detailed thermodynamic and kinetic stability of the favorable condensed structures depend on many factors and need to be studied individually. However, the evaluation of the number of cluster electrons from the constituent elements and its comparison with that predicted from the electron counting rules help in arriving at the charge of an unknown molecule, thus providing a tool for rationalizing data and exploring new avenues.

2.1.1. Illustration of the mno Rule

The icosahedron, \( B_{12}H_{12}^{2-} \) (1, Figure 1) can be a good starting point for illustrating the mno rule. Here the number of polyhedron \( m=1 \), the number of vertices \( n=12 \), and the number of single-vertex-sharing \( o=0 \), \( (m+n+o=13) \), so that the \( n+1 \) electron pair rule of Wade for single polyhedra is obtained. Each vertex with one terminal atom contributes all electrons for cluster bonding except one, which is involved in the exo covalent bond. Thus in the icosahedral \( C_2B_{10}H_{12} \), the BH groups donate one electron pair each and the CH contributes three electrons to the polyhedral bonding satisfying the mno
rule \((m=1, n=12, o=0)\). Simplest possible condensation is obtained by connecting two icosahedral fragments through a single bond as in Structure 3, represented by \((C_2B_{10}H_{11})_2\). The electron count is twice that of the single polyhedral system \((m+n+o=2+24+0)\). The structure has 26 skeletal electron pairs. Table 1 provides the number of electron pairs needed to satisfy the \(mno\) rule for structures discussed here.

Let us consider the condensation of two icosahedra through a single vertex to give 4 (Figure 1). The \(mno\) rule gives \(2+23+1=26\) electron pairs. For the Aluminacarborane, \([\text{(C}_2\text{B}_{9}\text{H}_{11})\text{Al(C}_2\text{B}_{9}\text{H}_{11})]\),\(^{15}\) with the overall structure 3, the \(mno\) electron count predicts a charge of \(-1\), since the electron pairs contributed from the various fragments amount only to 25.5 (BH groups - 18, CH groups - 6, Al - 1.5). The anionic structure is well-characterized.\(^{15}\) Compounds where Al is replaced by Fe, Co, Ni and Si are also known with appropriate charges.\(^{16}\) The transition metal sandwich complexes can be approximated to octahedral complexes so that the valence d orbitals of the transition metal is split into the “\(t_{2g}\)” and “\(e_g\) set”. The contribution of a transition metal in sandwich complexes towards skeletal bonding originates from this “\(e_g\) set”. This is usually found to be true except in cases such as the high spin species, ferrocenyl cation and cobaltocene.

The magnetic property is an indicator of the electronic structure of such complexes. A search of Cambridge Crystallographic Database\(^{17}\) gave over 80 structures with this skeleton, most of which follow the electron count. Examples are known with the same skeleton as 4 having dative bonds, which affect the charge requirements.\(^{18}\) When an external bond is dative in nature, all the valence electrons on the vertex atom participate in the polyhedral bonding. Compounds are also isolated with bridging groups between two dicarbolide ligands.\(^{19}\)
Table 1. The Number of skeletal Electron pairs required according to the mno rule for the polyhedra (m=No. of polyhedra, n=No. of vertices, o=No. of single-vertex-bridge, p=No. of missing vertices, q=No. of capping vertices, a = No. of electrons from the metal, (3 = No. of electrons from a main group element other than boron, a = No. of electron pairs donated by bridging hydrogen atoms and b = No. of electron from a dative bond) and comparison with that provided from the constituent elements. Last column gives the references to experimental structures wherever available. * implies electron count ambiguous for various reasons described in the text.

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Structure 5 gives the skeleton of a slipped sandwich complex. The distorted skeleton is known with transition metals such as Ni, Cu, Au etc. All of them have one or more additional electron pairs than expected from the mno rule. Consider the slipped complex of nickel. Treating the structure as closo, it requires 26 electron pairs. Nickel donates its 2 electron pairs which along with the 24 electron pairs originating from the two dicarbollide ligands lead to an electron pair count of 26. An additional charge of -2 make the electron pair count to exceed the mno count for closo structures. Alternative is
obviously to have a nido arrangement. The detailed electronic structure study of the slipped structures and the occupancy of the metal-ligand antibonding orbitals that cause the distortion in these complexes have been well documented.\textsuperscript{21}

Next we consider two atoms (edge) sharing structures. Two closo structures condensed by an edge lead to severe steric crowding. The atoms represented in dark colors in 6 (Figure 1) are too close to each other. There is no example of this kind in the literature. However if one or more vertex is removed as it happens in the nido arrangements, edge sharing should be practical. For example B\textsubscript{18}H\textsubscript{20}\textsuperscript{2-} (7) is well characterized and adheres to the mno rule.\textsuperscript{22} The compound has 16 BH groups (16 electron pairs), two boron atoms (3 electron pairs) and four bridging hydrogens (2 electron pairs). The molecule achieves the mno electron count as a dianion. The steric interaction is reduced in a triangular face sharing (three atoms sharing) polyhedron, B\textsubscript{21}H\textsubscript{18} (8)\textsuperscript{2-} and the four atoms sharing polyhedral borane, B\textsubscript{20}H\textsubscript{16} (2),\textsuperscript{7} which is discussed earlier. In (8) m=2, n=21 and o=0 and hence 23 electron pairs are required. This is accounted from the 18 BH groups, 3 boron atoms and a negative charge.

The importance of the mno rule is obvious in its applicability to a variety of polyhedral boranes where condensation has taken place by any combination of one, two, three, or four atom sharing. Let us take the formidable looking structure 9, [Cp\textsuperscript{*}IrB\textsubscript{18}H\textsubscript{20}].\textsuperscript{24} With three nido arrangements, the mno rule leads to 31 electron pairs (m=3, n=24, o=1, p=3). The skeleton gets its electron pairs from 15 BH groups (15), 5 CH groups (7.5), 3 shared boron atoms (4.5), 5 bridging hydrogens (2.5), and Ir atom (1.5). The next structure we consider, [Cp\textsuperscript{*}IrB\textsubscript{18}H\textsubscript{19}S]\textsuperscript{+} (10) has an additional vertex in the form of a sulphur atom so that the number of electron pairs required is 32. Sulphur is

\[51\]
found to be a four-electron donor with two electrons remaining as a lone pair orienting outward from the cluster. Three bridging hydrogens, 16 BH, two boron atoms, 5 CH groups, the metal and four electrons from sulphur together contribute 31.5 electron pairs to the skeletal framework. Therefore the mno rule requires an additional electron, as indeed is observed.\textsuperscript{24} [Cp\textsubscript{2}Rh\textsubscript{2}B\textsubscript{17}H\textsubscript{19}] (11) requires 39 electron pairs (m=4, n=29, o=2, p=4) for stability taking into account the 4 nido structures. The complex has five bridging hydrogen atoms which enable it to attain the mno electron count and is found to be neutral.\textsuperscript{25} [Cp\textsubscript{2}Rh\textsubscript{2}S\textsubscript{2}B\textsubscript{15}H\textsubscript{14}(OH)] (12) is in perfect agreement with the mno electron count for a cluster with four nido structures and 42 skeletal electron pairs for stability.\textsuperscript{26} Metallocones can be easily included if one considers them as having two open (nido) faces. Taking the simplest case, ferrocene (13), the molecule has 16 electron pairs (15 from the ten CH groups and one electron pair from iron). The mno rule suggests the same count for a skeleton with two open faces (m=2, n=11, o=1, p=2).

The mno rule is necessary to account for the skeletal electron pairs of structures 14 and 15 because the metal platinum is sandwiched between two polyhedral boranes of which either one or both are condensed to one more subcluster.\textsuperscript{27} \textsuperscript{28} A transition metal with external ligands is related to its BH analogue with appropriate charges when it occupies an unshared site. Otherwise it is replaced by boron equivalent. This is done applying the concepts of isolobal analogy\textsuperscript{29} followed by deprotonation\textsuperscript{29}. Thus, the d\textsuperscript{10} ML\textsubscript{2} fragment at a nonshared position in 15 is isolobally equivalent to a CH2 fragment and in turn to BH\textsuperscript{2n}. Hence it is a three orbital - four electron donor. The number of electron pairs in 14 and 15 is 45 and 35 respectively. The mno rule suggests an electron pair count of 44 and 34 respectively for a skeleton with two absent vertices. The extra
electrons lead to a slipped geometry around the metal as is found in the nickel complex, 5. The highly mixed up organometallaborane skeleton, 16, finds its 32 electron pairs in \([\text{Cp}^*\text{Ru}(\text{B}_4\text{H}_{10})\text{Ru}(\text{B}_4\text{H}_{10})\text{RuCp}^*])\). The non-bonding interactions expected in single vertex sharing polyhedra become prominent when the shared vertex is a boron atom. The smaller size of the central atom results in the shortening of the distance between the neighboring ring atoms, which are bridged by a single vertex. This raises the energy of some of the BMOs where the antibonding interactions become significant. As a result the number of BMOs will be fewer than \(m+n+o\) and such systems deviate from the electron counting rule. To achieve a boron atom sandwiched borane the size of the ring has to be reduced. Even with four-membered ring the interactions are significant enough to cause deviations as has been observed in octahedral aluminium clusters. No isolated molecule is experimentally characterized with this framework though this pattern is observed in solid state for aluminum clusters of the type \(\text{AeM}_2\text{Al}_9\) (\(\text{Ae}=\text{Ba, M}=\text{Fe, Co, Ni}; \text{Ae}=\text{Sr, M}=\text{Co}; \text{Ae}=\text{Ca, M}=\text{Co}\)) and \(\text{CaNiAl}_9\). With heavier elements in the ring such a possibility has been suggested. The only known structure with a sandwich type bonding to boron is found as part of the \(\text{B}_{10}\text{-B}_{10}\) unit of the \(\beta\)-rhombohedral boron unit cell where the \(mno\) rule is successfully applied to account for its bonding.4 The mismatch between a bridged atom and the ring size is seen in simple multidecker sandwiches where a single five membered ring bridges two metals. They are exceptions to the \(mno\) rule in the sense that complexes are known with a range of electronic requirements including the ones dictated by the \(mno\) rule. When the shared metal is of smaller size there will be the usual nonbonding interactions mentioned earlier.
If the metal atom is of bigger size there is a tendency towards metal-metal bond formation. Both these are factors which bring in additional interactions than what is considered in the formulation of the \( mno \) rule. Molecules with the \( mno \) electron count as in the example, \([C_{23}H_{42}B_6CoRh]^3 \) (17) and with less and more electrons are known. The requirement of 24 electron pair in 17 is met with the building fragments of the polyhedral cluster.

Compounds are known with fewer electrons than the Wade's electron count and are called 'hypercloso' or 'isocloso' compounds. They are well-debated structures and have been studied theoretically. Similarly isonido and isoarachno structures also exist where they are stable with \( n+1 \) and \( n+2 \) electron pair count respectively. The hypothetical \(\text{closo}\) eleven vertex \(B_{11}H_{11}^2\) species is found to be highly fluxional suggesting other open structures for the complex. Results of Mingo's calculations on two models of \(B_{10}H_{10}^2\), a spherical deltahedron and a polar deltahedron gave a clear MO picture. A deltahedra, which can be approximated to a sphere has equal number of bonding and antibonding \(\pi\) MOs, whereas once it is distorted a \(n\) and a \(n^*\) orbital become approximately non bonding and are at the frontier range. Obviously the nonbonding MO need not be filled so that the molecule prefers one electron pair fewer than the Wade's \(n+1\) count. When this anomalous behavior is extended to condensed clusters many of the apparently anomalous structures can be accounted for. Structure 18 \([\text{Cp}^\prime\text{RhB}_9(\text{SMe}_2)\text{H}_1\text{RhB}_9\text{H}_7(\text{SMe}_2)_2]\), is a case in point. This compound consists of a \(\text{closo}\) \(B_9\text{Rh}\) unit conjoined through rhodium atom to an open \(\text{RhB}_9\) unit. Considering Cp ligand as part of the cluster, the total electron requirement is 32 electron pairs (\(n=25\),
m=3, o=2, p=2). But the electron pairs obtained by the skeletal fragments are only 31. Thus the open part has some isonido characteristics.\textsuperscript{40}

Considering the plethora of structures known, the selection of the structures given in Table 1 is arbitrary. Attempts were made to cover one example, each involving different modes of fusion and then to present representative examples with any combinations of the possible fusion modes. Emphasis is given to bring out structures that have ambiguities. We have applied the rule to all the experimental structures obtained by searching the CSD;\textsuperscript{17} only structures with differing structural patterns are listed in table 1.

2.2. JUSTIFICATION AND APPLICATIONS OF THE MNO RULE

Macropolyhedral boranes that are formed by the interaction of two or more monomeric units can be broadly classified into two categories. The first category involves the \textit{exo}-interactions where the individual units are connected together by localized bonds. The latter category involves the sharing of one or more atoms between the individual units giving rise to condensed polyhedral boranes. Among the condensed polyhedral boranes, the single vertex sharing systems are treated separately, as their electronic requirements are different from the rest of the condensed systems. To illustrate the various possible modes of interactions, we describe the study of two generalized closo-polyhedral boranes by bringing them together from a non-interacting distance to form condensed systems, varying the distance periodically. Exo-polyhedral interactions arise as the first case, followed by condensed systems.

As an illustration of the applications of the rule, we present the structural error reported experimentally in one of the macropolyhedral boranes. The compound, reported
with a molecular formula of $\text{B}_{19}\text{H}_{20}^{1-}$ exhibits an edge-sharing pattern with two \textit{nido} faces \textit{trans} to each other. Our analysis of their MOs using extended Hückel theory and higher level theoretical calculations found all indications that the reported $\text{B}_{19}\text{H}_{20}$ to be a stable species only as a tri-anion. The formulation presented for $\text{B}_{19}\text{H}_{20}^{1-}$ requires two additional electrons and hence the correct structure is predicted to be $\text{B}_{19}\text{H}_{22}^{1-}$. Based on the above results the mechanism for the formation of $\text{B}_{19}\text{H}_{22}^{1-}$ is also explained.

2.2.1. Justification for the \textit{mno} Rule

\textbf{i. Exo-Polyhedral Interactions}

Let us assume that one B-H bond each of the two \textit{closo}-polyhedral boranes $\text{B}_x\text{H}_x^{2-}$ and $\text{B}_y\text{H}_y^{2-}$ are brought along a line of interaction. With the decrease in distance, the nonbonding interactions dominate (Figure 3, A), giving a doubly bridging structure (Figure 3, B) as a possibility. The resulting structure is very similar to that of diborane ($\text{B}_2\text{H}_6$), but, unlike diborane, has only one hybrid orbital on each bridging boron. It is not sufficient to generate two stable levels. The charge requirements remain the same as four electrons. The electrons that are earlier involved in the exo-B-H bonds are enough to stabilize the one 4c-2e bond. The second pair of electrons necessarily goes to a less stable level resulting in an unstable system. But this shortcoming is alleviated when any one of these two boron atoms is replaced with transition metals, which have diffused orbitals to lower the unstable level. It is even possible with a main group element where the bridging hydrogens are replaced by groups like CO or -CH$_3$ with unoccupied $\pi^*$ or pseudo $\pi^*$ orbitals to stabilize the antibonding level. An example which illustrates this type of interaction is ($\text{Be}($B$_3\text{H}_8$)CH$_3$)$_2$ (1, Figure 4).\textsuperscript{41} This linkage can also be viewed as the equivalent of the doubly protonated C$_2$H$_4$, the neutral analogue being B$_2$H$_6$. 

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Different modes of interaction (A-J) between two polyhedra ranging from exopolyhedral to condensed ones are depicted. All patterns except G is known experimentally. Structural pattern G is observed in the unit cell of $\beta$-rhombohedral boron and also when the central boron atom is replaced by heavier elements.

Another way to arrive at a stable structure from B (Figure 3) is to remove one of the hydrogen atoms, which leads to structure C (Figure 3). Here, the two sp-hybridized
orbitals of boron and the s-orbital of hydrogen will interact together to form a stable BMO and two antibonding MOs. Three electrons are available, one with each atom involved in the three-center interaction. As only two electrons are required for this 3c-2e bond, one electron has to be expelled from the system, which reduces the charge to (3-). This pattern is a fairly stable mode of interaction provided the nonbonding interactions between adjacent B-H groups are minima. \((B_{10}H_3)_2H\) involves a protonated B-B linkage between two of its B_{10} units and exemplifies such type of linkage\(^{42}\) \((B_{20}H_{19}^{+3}, 2).\)

![Figure 4](image)

Representative examples illustrating exopolyhedral interactions between two polyhedra.
Removal of a proton from C leads to the most familiar form of condensation, resulting in a new 2c-2e B-B bond (Figure 3, D). Here the electron count is the sum of the electron counts for two polyhedral systems. Thus $B_{12}H_{11}-B_{12}H_{11}$ requires $m+n+o$ $(2+24+0=26)$ electron pairs supporting the anticipated four negative charges. With several arms ready for condensation, dendrimers are a natural extension as is found experimentally.\(^{43}\) These systems have got rid of the unfavorable enhanced charge requirement by replacing borons by carbons.\(^{43}\) Two $B_{10}$ units are known to have this type of linkage exhibiting closo or nido patterns (3, 4).\(^{44}\)

Alternatively, structural pattern C (Figure 3) can be bent to have more than one interacting centers, by the linking of two or more adjacent centers with a 3c-2e or 2c-2e bond as in pattern F. In the case of 3c-2e linkages, every such bond will reduce the total charge by one, whereas the 2c-2e bonds keep the charge requirements constant. Such multiple linkages are quite possible even with pure borane clusters. Occasionally, atoms other than hydrogen may also bridge the two aromatic units by forming 2c-2e bonds on both the sides. It is fairly easy to recognize and evaluate the electron requirement in these cases as they seldom form 3c-2e bonds. Cases where two $B_{10}$ units interact through this type of multiple linkage, have been experimentally characterized (5).\(^{45}\)

Conversely, if one of the boron atoms in pattern D is brought closer so that two adjacent boron atoms of the other borane unit are within bonding distance as represented in E, the nature of interaction dramatically changes. This interaction gives rise to the capping of an edge by a boron atom, where the two exo-hydrogens of the boron atoms that are connected by the concerned edge are still retained. Since capping interactions will not add any BMOs than that is already present in the polyhedra, the extra electron
available on boron atom can be used to fill up the BMOs of the polyhedra. These types of interactions occur pairwise, if the cluster geometry is favorable, where one boron atom from each borane unit caps an edge of the other boron, as depicted in E. These systems exhibit true macropolyhedral skeleton, as localized bonds do not separate these interacting borane units anymore. This pattern depicts the intermediate skeletal nature between connected and condensed polyhedral boranes, as they neither share any vertices nor are separated by localized bonds. Many examples are known with this type of bonding. One among them is \( \text{B}_{20}\text{H}_{18}^{2-} \).\(^{46}\) Capping interaction should be differentiated from 3c-2e interactions where none of the edges of the 3c-2e bond are common with the individual polyhedral units formed during the interaction. The interactions discussed so far are all exo-polyhedral and seldom affect the nature of the skeletal bonding of both the polyhedra. All these patterns were observed experimentally, in varying numbers. The careful identification of the nature of these interactions is necessary before employing the electron counting rules. In the following section, interactions where the interacting borane units share one or more vertices is considered, a situation that is entirely different from what was discussed so far.

ii. Condensed Polyhedral Boranes

Though the structures discussed so far may be categorized as products of condensation, here those structures where the process of condensation has reduced at least one vertex in comparison to the isolated polyhedra is discussed. As in the previous section, the number of vertices that are shared will be systematically increased, considering all the possibilities of condensation.
The first mode of condensation is through a single vertex (G, Figure 3) leading to a sandwich. The BMO pattern and hence the electronic requirement is very much dependent on the distance between the two polyhedral fragments when they are allowed to share a single vertex. When the distance between the non-bonded vertices is reasonably large, the number of BMOs remains the same. This is achieved by replacing the central atom by atoms larger than boron. The electron count here depends on the central atom. While assigning the charge of (-5) to the system G (Figure 3) it was assumed that the nonbonding interactions were absent. With smaller central atom the nonbonding interactions involving B-H groups on neighboring polyhedra raise some of the BMOs. The details of these destabilizing interactions and the consequent reduction in the negative charge to (-1) are discussed below. In these sandwich systems the central atom is assumed to be sp hybridized. The two sp hybridized orbitals of the central atom are ideally directed towards the center of each cluster that is shared. One of the sp hybrid interacts with the inwardly pointing sp hybrids of the other boron atoms in one cage to form a single strongly bonding MO, as in the case of mono-polyhedral boranes. One more strongly bonding MO is formed by the interaction with the other cage AOs. So the number of core orbitals formed by the overlap of the radial orbitals on each vertex equals the number of cages in the polycondensed system, m. The two tangential orbitals on the shared vertex are mutually perpendicular to each other and they contribute to the surface BMOs. Each sub cluster retains its electronic requirement. If the number of vertices on each sub-cluster of a two polyhedra condensed complex, excluding the shared atom are 'a' and 'b' respectively such that a+b+1=n, the total number of vertices, then the bonding surface MOs formed from the tangential orbitals on each sub-cluster will be a+1
and \( b+1 \) respectively. The total amounts to \( n+1 \) which when generalized gives \( n+o \), where \( o \) is the total number of single vertex condensations. So the total bonding MOs is \( m+n+o \), which is the basis of the rule.

The electronic requirements of single vertex sharing can also be rationalized using a fragment molecular orbital approach, starting with a ring-cap division used in explaining the relative stability of closo borane isomers. This approach simplifies the problem by reducing the number of BMOs to be considered.

![Molecular orbital diagram](image)

*Figure 5*

A molecular orbital diagram of sandwich complexes correlating main group sandwiches and corresponding transition metal systems.
The ring atoms are considered as sp² hybrids, interacting with a sp hybrid cap. The frontier MOs of the ring will be the n molecular orbitals formed by the linear combination of the unhybridised p orbitals similar to conjugated hydrocarbons. Figure 3 gives a correlation between the simplified MO pattern of both main group sandwich complex and transition metal complex.

The L.H.S. of the Figure 5 shows the MO pattern for a main group sandwich where the central atom is larger than boron. It is correlated with the transition metal compound on the R.H.S. The mno rule can be well understood from the BMO pattern of (B₆H₆)₂M where M=A1, Si etc. An extension of any rule to transition metal complexes usually results in additional terms to account for the d-orbitals. But it can be seen from Figure 5 that the BMOs which have a major contribution from the polyhedral skeleton remain the same whether M is a main group or a transition metal and hence the constancy in the rule.

There are no major changes in the BMO pattern of the two correlated systems except in the "e_g" and "e_u" set. The "e_g" set of the first system do not have a proper match from the orbitals of the main group element and is the highest among the occupied levels. It is this "e_g" set which is affected when a larger central atom is replaced by boron leading to a charge of (-1) instead of (-5) as given in Figure 3, G. This, in addition to other repulsive interactions, makes the existence of single boron bridged condensation unlikely. The dₓz and dᵧz orbitals of transition metals are of proper symmetry to interact with these particular orbitals and hence stabilize the "e_g" set, bringing it below the "e_u" set (Figure 5, RHS). The LUMO of the second system is doubly degenerate. When the number of electrons exceeds the mno count, this antibonding MO has to be occupied. The resulting
antibonding interactions can be reduced with slipping. The distortion provides some bonding character to the otherwise antibonding orbital. This explains the additional requirement of the slipped sandwiches, which results in excess electrons than that required according to the rule.$^{21}$

One more atom at the shared position between two monomeric units leads to an edge shared polyhedron (H, Figure 3). As discussed earlier the closo form is not practical for these systems. The core BMOs of this polycondensed polyhedron that are formed by the strongly bonding interaction of the inward pointing sp hybrid orbitals remain unchanged. But, the two surface BMOs are shared between both the units since they share more than one atom. Edge sharing allows the existence of hamiltonian circuits$^{12}$ that span the entire macropolyhedral framework which enables the stabilization of exactly the same number of surface bonding orbitals as to the number of vertices in the system. A similar effect is observed in the three and four vertex sharing macropolyhedral systems (I, J, Figure 3). But the sp hybrids of the boron atoms in these systems, unlike in the case of single vertex sharing systems, will not be ideally oriented towards each polyhedron. This necessitates a rehybridization of the shared boron to have more p character to relieve strain and essentially reduces the s orbital contribution. The core BMOs of these systems are stabilized by rehybridization due to the increased overlap. In some very condensed systems like $\text{B}_{26}\text{H}_{21}^{1+}$ which is found in J3-rhombohedral boron, the p character of the hybrid orbitals of the central atom sharing the three polyhedra are close to sp$^2$ hybridization, since three radial orbitals are required. Polycondensation by sharing five atoms leads to boron nanotubes. This arrangement makes the system cylindrical in shape with a uniform radius of curvature. Such a system emerges as a single polyhedra
the rule can be applied. Higher fusions are not possible due to the poor ring-cap
compatibility of boron.

All the various types of fusions discussed here starting from structures B to I
(Figure 3) are isolated experimentally. All-borane structures are lacking only for B and , the reasons for which have been discussed. Theoretical calculations on the same
stems (B-I) with the predicted charge by mno rule also provide reasonably fair HOMO-UMO gap supporting the qualitative explanations given in the above section.

2.2. Application of mno Rule for Edge Shared Macropolyhedral Boranes

When two B₁₂ units are forced to share an edge, the proximity between the non-
sharing boron atoms of the two polyhedra is very small as illustrated in 7 (Chart 1) .
With the experimental B-B distances of B₁₂H₁₂²⁻, the distance between the boron atoms
presented by dark spheres is less than 1.5 Å. This distance is not improved even in
dge sharing octahedra. But these steric interactions caused by condensation will be
relieved by the removal of one or more vertices near the shared atoms leading to nido
structures. An additional electron pair is required for compensating every vertex that is
moved from the non-adjacent positions. Hence these molecules acquire bridging
hydrogens between two adjacent borons at the open face to acquire extra electrons or else
they must be anions with appropriate charges.

![Chart 1](image-url)
Several molecules (Chart 2, 9-14) are known to exhibit this edge-sharing nido pattern and all of them require \( n+m \) electron pairs for stability. The charge requirement for all these structures is evaluated in Table 1. For example, the isomers of \( \text{B}_{18}\text{H}_{22} \) (13, 14) have 18 boron atoms distributed over two nido-cages.\(^{50}\) Hence \( n=18 \), \( m=2 \) and two more electron pairs are needed to compensate the two absent vertices. The polyhedral skeleton requires \( (n+m+2) \) electron pairs. The 16 B-H groups give 16 electron pairs and six bridging hydrogen atoms give 3 electron pairs to the skeletal bonding. Two shared boron atoms each give three electrons (all its valence electrons as there is no exo-2c-2e bond) to make the total electron pairs 22. All the other structures can be worked out in a similar way (Table 2).
A recently reported edge sharing condensed polyhedral borane $\text{B}_{19}\text{H}_{20}$ does not fit the $mno$ electron counting rule. Here we point out an alternative to this structure. As per the $n+m$ rule, this structure requires $(n=19$ and $m=2)$ $19+2+2=23$ electron pairs taking into account of the two nido fragments. However, $\text{B}_{19}\text{H}_{20}$ is reported to be a mono anion having $17 + 3 + 2 (3\text{H} + 1\text{e}) = 22$ electron pairs. In the absence of electron count, there were no guidelines to estimate the number of electrons. The number of hydrogen atoms was therefore assumed to be 20 and their initial positions were generated from the skeletal geometry for the X-ray structure analysis. During the refinement of diffraction data, the number of hydrogens was unaltered as there were no bonding considerations to do so. The MALDI mass-spectra of the ions showed two additional mass units consistently. The authors prefer a different interpretation for the two additional mass
units, which is not convincing. The mechanistic schemes that gave rise to the $\text{B}_{19}\text{H}_{20}^{1-}$, with two hydrogen atoms less than necessary are also not convincing. One of them required an elimination of one mole of $\text{H}_2$, while the maximum observed was 0.13 mol only. The other two pathways had improbable mechanistic steps.

We have calculated the energy levels at the extended Hückel\textsuperscript{55} and B3LYP/6-31G* levels\textsuperscript{56,57} and found all indications for the reported $\text{B}_{19}\text{H}_{20}$ to be a stable species only as a tri-anion. Frequency calculations at the same level characterized the structure $\text{B}_{19}\text{H}_{20}^{3-}$ as minima on the potential energy surface. But the same structure with -1 charge failed to converge. The formulation presented for $\text{B}_{19}\text{H}_{20}^{1-}$ requires two additional electrons and hence most likely the correct structure is $\text{B}_{19}\text{H}_{22}^{1-}$. The authors discounted this fact, as they assumed that the additional two hydrogen atoms would lead to *arachno* structures.

Based on the above results the mechanism for the formation of $\text{B}_{19}\text{H}_{22}^{1-}$ can be explained. The reaction of $\text{B}_{18}\text{H}_{20}^{2-}$ with $(\text{CH}_3)_2\text{SBH}_2\text{Cl}$ results in the formation of $\text{B}_{19}\text{H}_{22}^{1-}$ in which, a $\text{BH}_2^+$ caps the triangular face of $\text{B}_{18}\text{H}_{20}^{2-}$ skeleton. In the case of $(\text{CH}_3)_2\text{SBHC_1}_2$, the equivalent intermediate is $\text{B}_{19}\text{H}_{21}\text{Cl}^-$ where the cap is $\text{BHX}^+$ instead of $\text{BH}_2^+$. It has been proved that a capping B-H or BH$_2^+$ group in a polyhedral skeleton\textsuperscript{11} does not alter the electronic requirement of the polyhedral skeleton and the number of electron pairs for this skeleton, (18+2+2) 22, remain the same as that of $\text{B}_{18}\text{H}_{22}$. The migration of the BH$_2$ or BHX groups from the capping position to the polyhedral skeleton results in the final $\text{B}_{19}\text{H}_{22}^{1-}$. In the process one of its *exo*-hydrogen atom is moved to the bridging position to satisfy the increased requirement of 23 electron pairs of $\text{B}_{19}\text{H}_{22}^{1-}$. In the case of $\text{B}_{19}\text{H}_{21}\text{Cl}^-$, migration of BHCl group takes place in a similar manner followed
by the substitution of hydrogen in the place of chlorine. The importance of an electron-counting rule in exploring the chemistry of macropolyhedral boranes, is thus obvious.

2.3. CONCLUSIONS

A unifying electron counting rule - the mno rule - explains the bonding patterns exhibited by single and condensed polyhedral borane clusters. According to this mno rule, m+n+o electron pairs are necessary for a closo polycondensed polyhedral system. Here m= number of polyhedral clusters, n=number of vertices, o=single vertex fusions. Wade’s n+1 rule is a special case of mno rule where m=1 and o=0. Similarly the m+n rule is a special case with o=0. The rule can also be extended to metallocenes, which can be merged with the borane systems. The rules of condensation envisage infinite possibilities. A glimpse of the dimension of the problem is seen in Figure 2, which treats condensation of icosahedral fragments alone. There are endless mixing and matching possible. The mno rule will be a useful guide to achieve the different goals wherein efforts are made to unify the two fields.

A justification based on MOT is provided for the mno rule. The variety of bonding patterns observed in terms of the modes of condensation of macropolyhedral boranes are accounted for. Application of the rule to rectify an error in a recently reported edge sharing macropolyhedral borane, B\textsubscript{19}H\textsubscript{20}\textsuperscript{1-} illustrates the importance of the mno rule in the further exploration of polyhedral borane chemistry. The mechanism for the formation of the structure with the exact molecular formula, B\textsubscript{19}H\textsubscript{22}\textsuperscript{1-} is also revised based on the mno rule.
REFERENCES


57. B3LYP is Becke's three parameter hybrid method with LYP correlation functional: