



Rules for macropolyhedral boranes

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ABSTRACT

Based on extensive computational studies, rules to derive the thermodynamically most stable macropolyhedral borane for any formula between B_nH_{n-4} to B_nH_{n+8} were identified. Formally, the macropolyhedral boranes may be obtained by condensing regular convex borane clusters where as many BH_3 moieties are eliminated as vertexes are shared in the macropolyhedral framework. Macropolyhedral boranes consisting of two cluster fragments may be classified according to their general formulae ranging from B_nH_{n-4} to B_nH_{n+8} . For each of these formulae, various structure types are conceivable differing in the number of shared vertexes and in the types of combined cluster fragments. However, for each general formula, only one structure type is known experimentally and this one is also computationally found to be thermodynamically preferred! For each class of macropolyhedral B_nH_m boranes, a preferred number of shared vertexes is identified, and this determines the number of skeletal electron pairs. With this knowledge, the type of fused clusters, i.e. the most favourable framework, may be predicted. The concept of preferred fragments may be applied to even predict the distribution of vertexes among the fused fragments in the thermodynamically most stable isomers. When there is at least one *closo* fragment it has 12-vertexes. Without any *closo* fragment the most stable macropolyhedral borane has a *nido* 10-vertex cluster fragment.

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1. Introduction

Boron hydride chemistry was developed by Alfred Stock in the 1930s [1] but was intensively investigated not before the 1950s [2]. During the 1960s, more and more structures of boranes and carboranes became known [3] and intrigued chemists because of their nonclassical structures. Potential applications of boron cluster compounds [4] also inspired further research. With a considerable number of published examples available the underlying structural patterns were finally revealed and the bonding explained [5,6].

Due to three valence electrons a single boron atom is able to form three classical i.e. two center two electron (2c2e) covalent bonds. With its electron sextet and one remaining empty valence orbital, the center is electron deficient. The transition from classical to multicenter bonding is one way to alleviate the electron deficiency. The structural consequence is cluster formation, i.e. arrangement of boron atoms in polyhedra (usually with triangular faces, i.e. deltahedra) leading to higher coordination numbers (up to seven including the exo ligand which is generally bound through a classical 2c2e bond). Wade recognized that the type of polyhedron formed depends on the total number of so-called skeletal electrons available for the multicenter bonding in relation to the number of atoms involved in multicenter bonding, i.e. the cluster

atoms [7]. His rules became common textbook knowledge [8]. For n atoms, a number of $2n + 1$ electron pairs (n pairs are usually associated with external two center bonds) allows to fill all the multicenter bonding orbital combinations existing in a spherical deltahedron with n vertexes [8]. Such a cluster is termed “*closo*”. One skeletal electron pair (SEP) more ($2n + 2$) is perfect for a deltahedron with $n + 1$ vertexes. In the presence of n cluster atoms, however, one vertex remains unoccupied. The resulting type of polyhedra is called “*nido*” due to the nest like shape. Likewise, n atoms with $n + 3$ SEP occupy n vertexes of a deltahedron with $n + 2$ vertexes. In 1971, Williams pointed out that *nido*-polyboranes, *nido*-carboranes, and the *nido* carbocation $C_5H_5^+$ could be derived from *closo*-deltahedra by the removal of one high-coordinated vertex from each deltahedron and that the *arachno*-deltahedral fragments could subsequently be derived (from the *nido*-fragments) by the removal of one additional high-coordinated vertex from the open faces [9].

Wade's rules apply for “small” boranes and heteroboranes with up to at least twelve cluster atoms. Larger boranes are also known, but their cluster shapes do not correspond to those predicted by Wade's rules but can be considered as composed of smaller fragments. When the fragments are intimately fused, i.e. share at least one atom, these *conjuncto* boranes are also called macropolyhedral boranes. Their cluster frameworks are concave. The building fragments correspond to cluster shapes of well known smaller boranes and as such conform to Wade's rules. The first macropolyhedral borane, $B_{18}H_{22}$, was reported in 1962 already and may be considered as

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a 10-vertex *nido* fragment sharing two vertexes of an open face edge with a 10-vertex *nido* fragment [10]. Two vertex sharing macropolyhedral boranes constitute by far the family with most experimentally known examples. Between one and four vertexes may be shared by the two cluster fragments in a macropolyhedron. Experimental examples include *arachno*(9)-[1]-*nido*(7)-B₁₅H₂₃ [11], *nido*(6)-[2]-*nido*(8)-B₁₂H₁₆ [12], *closo*(12)-[3]-*nido*(11)-B₂₀H₁₈²⁻ [13] and *closo*(12)-[4]-*closo*(12)-B₂₀H₁₆ [14] (see Fig. 1). Boron atoms occupying shared vertexes do not carry exo terminal substituents. Formally, macropolyhedral boranes may be obtained by condensation reactions from smaller Wade type boranes. In the formal condensation reaction as many BH₃ moieties (or isoelectronic species) are eliminated as vertexes are shared in the macropolyhedron (see Fig. 1).

Reports of theoretical treatment of macropolyhedral boranes are rare especially in comparison to smaller Wade type boranes and heteroboranes. Jemmis and coworkers presented the so-called mno rule [15] that among other species is applicable to macropolyhedral boranes [16]. According to the mno rule, the sum of the number of cluster fragments *m*, the number of vertexes *n*, the number of single vertex sharings *o* and the number of missing vertexes *p* is equal to the number of skeletal electron pairs, i.e. $m + n + o + p = n(\text{SEP})$. In order to apply the mno rule, however, the structure of a compound need to be known to derive the values of *m*, *o* and *p*. This rule e.g. was successfully applied to identify that a borate originally described as B₁₉H₂₀⁻ [17] actually has a B₁₉H₂₂⁻ composition [18]. With the help of the mno rule, some conceivable structures can be ruled out for a given compound. Let us consider the well known B₁₈H₂₂ as an example [19]. In *nido*(10)-[2]-*nido*(10)-B₁₈H₂₂, **A**, a 10-vertex *nido* fragment shares one edge with another one. It has $m = 2$, $n = 18$, $o = 0$ and $p = 2$ which gives

$m + n + o + p = 22$. Each of the 16 BH building units contributes two electrons to skeletal bonding, each bare B atom of the shared edge contributes three and each of the six additional H atoms one, which gives a total of 44 skeletal electrons. As $m + n + o + p = n(\text{SEP})$ the *nido*(10)-[2]-*nido*(10)-framework is a viable structure for B₁₈H₂₂. On the other hand, B₁₈H₂₂²⁺ and B₁₈H₂₂²⁻ have one SEP less and more, respectively. Therefore, according to the mno rule neither of them can have a *nido*(10)-[2]-*nido*(10)-structure. For the neutral B₁₈H₂₂, however, *nido*(10)-[2]-*nido*(10) is not the only framework that complies with the mno rule: The *closo*(10)-[1]-*nido*(9) isomer **B** has $m = 2$, $n = 18$ and $p = 1$ which sum up to a value of 21, matching $n(\text{SEP})$ (due to 17:BH, 1:B, 5H⁻). The *arachno*(10)-[3]-*nido*(11) isomer **C** (with 15:BH, 3:B⁻ and 7H⁻) is also a viable candidate based on the mno rule as both $m + n + p = 2 + 18 + 3$ and $n(\text{SEP})$ have values of 23. The computed relative energies are remarkably different: **B** and **C** are less stable than **A** by 60.0 and 57.3 kcal mol⁻¹, respectively [20]. In summary, the mno rule eliminates part of the structural candidates but also leaves some unfavourable choices as viable options. Here we present rules to predict the preferred macropolyhedral borane cluster for a given formula.

2. Discussion

2.1. For which cluster sizes are macropolyhedral structures to be expected?

First of all we should clarify for what formula we can expect a macropolyhedral structure at all. Undecaborane(15), B₁₁H₁₅ [21], is the largest among experimentally known homonuclear *nido*-boranes with a Wade type cluster. On the other hand, the smallest

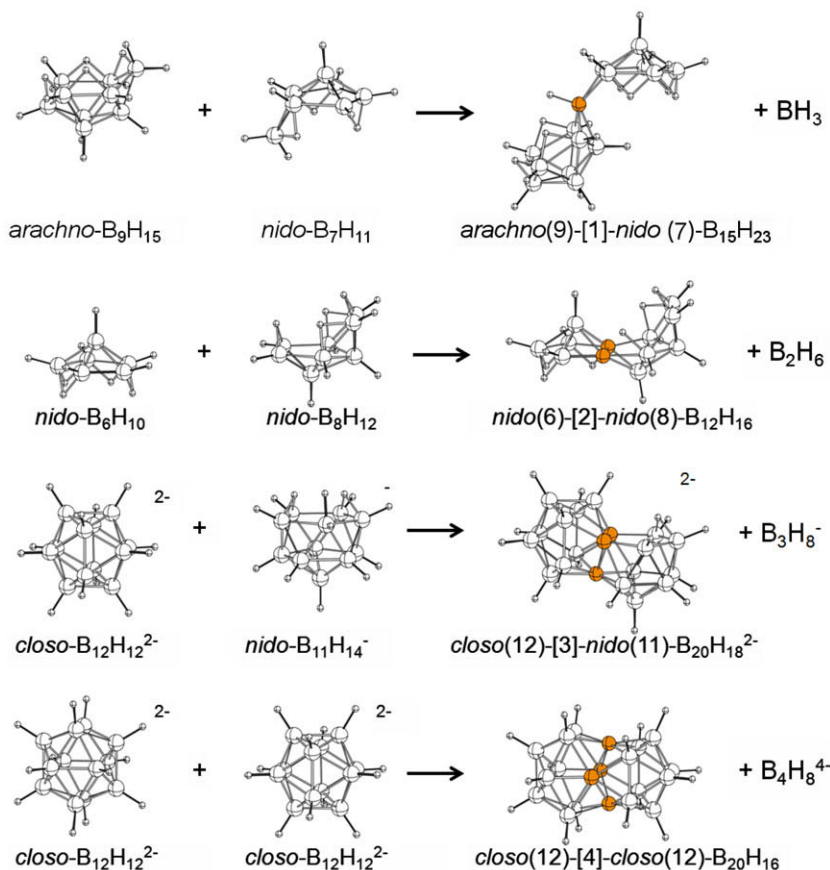


Fig. 1. Examples for formal condensation reactions leading to macropolyhedral boranes with different numbers of shared vertexes, $x = 1-4$.

macropolyhedra is *nido*(6)-[2]-*nido*(8)-B₁₂H₁₆ [12]. However, the latter was computed to be 3.9 kcal mol⁻¹ less stable than the *nido*-B₁₂H₁₆ isomer [22].

In order to determine the thermodynamic stability of macropolyhedra relative to convex Wade type clusters, we computed *nido*-B_nH_{n+4} boranes and *nido*-[2]-*nido*-isomers for increasing cluster size *n*. Only for *n* ≥ 12, *nido*-[2]-*nido*-structures could be found that were computed to be more stable than convex *nido*-borane clusters [22]. A similar comparison of *arachno*-[2]-*nido*- versus *arachno*-B_nH_{n+6} structures resulted in lower energies for the macropolyhedra for *n* ≥ 10 [23]. However, it was also found that the cluster size for which the macropolyhedra are clearly more stable increases to 17 and 15 vertexes, respectively, when borates are considered rather than neutral boranes [22,23]. In conclusion, for less than 10 cluster atoms macropolyhedra are not to be expected, and hence only for larger cluster sizes the shape of macropolyhedra need to be considered.

2.2. Why do Wade's rule not work for macropolyhedral boranes?

The prediction of the shape of a small borane cluster by Wade's rule is not only simple and straightforward but also pretty failsafe. Why does a similar approach not exist for macropolyhedra? In small boranes each cluster atom has an exo ligand (or an exo lone pair) consuming one valence electron in a 2c2e exo bond (or two in a lone pair). The total number of valence electrons available for cluster bonding is therefore well defined. In macropolyhedra, however, there are shared cluster atoms that do not bear an exo ligand. When a usual BH vertex (contributing two electrons to cluster bonding) is transformed into a shared vertex, *n*(SEP) increases by one as both the B and H atoms contribute all their valence electrons (a total of four) to cluster binding. Hence the total number of skeletal electrons in a macropolyhedral borane depends not only on the formula but also on the number of vertexes shared by the fused cluster fragments. In order to calculate *n*(SEP) of a macropolyhedral borane (e.g. to apply the mno rule), the structure has to be known! That is why we first have to address the question what fusion modes are possible and which of them are preferred (if any) for a given formula.

2.3. What fusion modes are possible?

Let us start considering a general B_nH_n compound. As a convex cluster made up of *n* BH units, this would have *n* SEP. However, a *closo* cluster needs *n* + 1 SEP. As a one vertex sharing macropolyhedron, the number for B_nH_n would increase to *n* + 1 as one :BH unit is transformed to a :B· and a H·. This number of skeletal electrons would be adequate for one *closo* cluster, but in a macropolyhedron at least two fragments have to be combined. Therefore, one shared

vertex does not provide enough skeletal electrons to generate two suitable cluster fragments. When two vertexes are shared *n*(SEP) becomes *n* + 2 which suffices to have two *closo* clusters. So, *closo*-[2]-*closo* is the first viable macropolyhedral framework for a B_nH_n borane. For even more shared vertexes, the number of skeletal electrons increases further. The extra skeletal electrons will cause opening of the cluster fragments. With three shared vertexes, B_nH_n has *n* + 3 SEP available and will combine one *closo* with one *nido* fragment. Four vertexes may be shared by two *nido* or one *closo* and one *arachno* fragment. Four vertexes is the largest number that may be shared between two convex deltahedra for geometrical reasons. It is straightforward to derive the possibilities for other general formula: e.g. B_nH_{n-2} has one SEP less than B_nH_n, so *closo*-[3]-*closo* is the first viable option, while B_nH_{n+2} has one SEP more than B_nH_n for which *closo*-[1]-*closo* is already feasible. Table 1 lists the possible macropolyhedral frameworks for B_nH_{n-4} to B_nH_{n+10} [20]. Going down one line i.e. increasing the formula by two hydrogen atoms increases *n*(SEP) by one while going one column left, i.e. reducing the number of shared vertexes by one reduces *n*(SEP) by one. The diagonal entries correspond to the same general number of skeletal electrons, e.g. *n*(SEP) = *n* + 2 for the entries between *closo*-[1]-*closo*-B_nH_{n+2} and *closo*-[4]-*closo*-B_nH_{n-4} or *n*(SEP) = *n* + 6 between *arachno*-[1]-*arachno*-B_nH_{n+10} and *arachno*-[4]-*arachno*-B_nH_{n+4}.

2.4. Are there preferred fusion modes in macropolyhedral boranes?

Having identified possible fusion modes for macropolyhedral boranes in general (see Table 1), the obvious question is which of these types are actually realized in experimentally known examples. Are all of the possible frameworks equally likely to be realized or are some types preferred over others?

Examination of macropolyhedral borane examples reported in the literature leads to the discovery that for each general formula, only one type of cluster fusion has been found so far. These types are printed in bold face in Table 1. Is the fact, that for any general formula only one type of macropolyhedral framework has been realized experimentally so far just coincidence? Fig. 2 shows representative examples for B_nH_{n-2} to B_nH_{n+8} and compares computed relative energies of experimentally known examples (highlighted) with isomers of viable macropolyhedral frameworks according to Table 1.

After having realized that obviously for each general macropolyhedral borane formula B_nH_n there is one considerably preferred type of cluster fragment fusion (i.e. number of shared vertexes), we may derive the number of skeletal electrons. Table 2 lists the preferred number of shared vertexes *x* for each formula, the resulting *n*(SEP) and corresponding structure. The remaining *n* - *x* cluster atoms are distributed to the fused cluster fragments.

Table 1
Viable fusion modes in macropolyhedra with general formula B_nH_{n-4} to B_nH_{n+10}.^a

Formula	Number of shared vertexes			
	One	Two	Three	Four
B _n H _{n-4}				closo-[4]-closo
B _n H _{n-2}			closo-[3]-closo	<i>closo</i> -[4]- <i>nido</i>
B _n H _n		<i>closo</i> -[2]- <i>closo</i>	closo-[3]-nido	<i>nido</i> -[4]- <i>nido</i> ^b
B _n H _{n+2}	<i>closo</i> -[1]- <i>closo</i>	closo-[2]-nido	<i>nido</i> -[3]- <i>nido</i> ^b	<i>arachno</i> -[4]- <i>nido</i>
B _n H _{n+4}	<i>closo</i> -[1]- <i>nido</i>	nido-[2]-nido ^b	<i>arachno</i> -[3]- <i>nido</i>	<i>arachno</i> -[4]- <i>arachno</i>
B _n H _{n+6}	<i>nido</i> -[1]- <i>nido</i> ^b	arachno-[2]-nido	<i>arachno</i> -[3]- <i>arachno</i>	
B _n H _{n+8}	arachno-[1]-nido	<i>arachno</i> -[2]- <i>arachno</i>		
B _n H _{n+10}	<i>arachno</i> -[1]- <i>arachno</i>			

^a Types for which examples are known experimentally are in bold face.

^b Ref. [24].

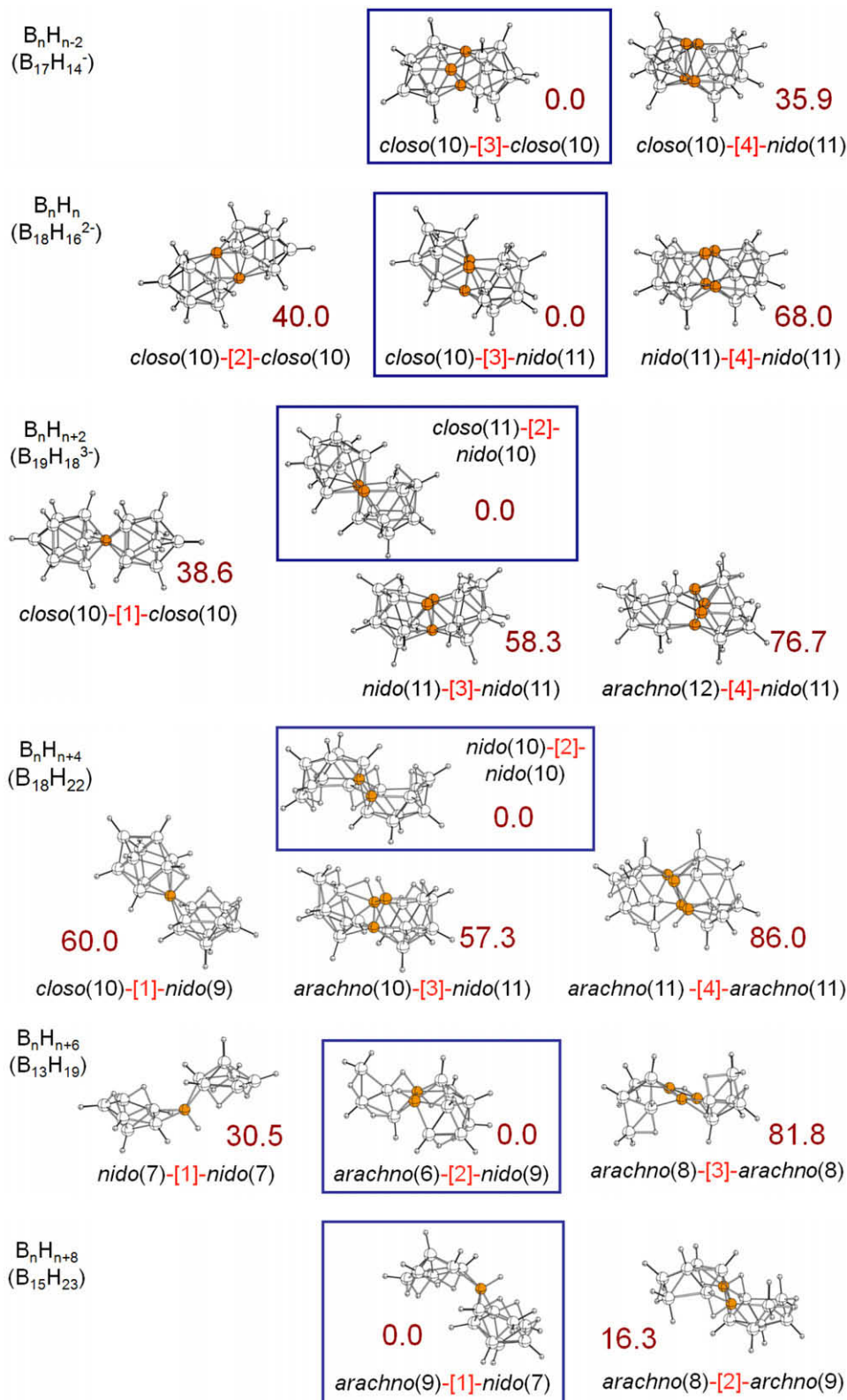


Fig. 2. Computed structures of representative macropolyhedral boranes and the relative energies of viable isomers in comparison to the experimentally realized structures.

2.5. Are some cluster fragments preferred over others?

We may go even one step further and ask if we can also make predictions about the cluster sizes in the preferred macropolyhedral framework. To investigate this, we computed the relative energies of isomeric macropolyhedral boranes only differing in

the size of the cluster fragments combined but neither in the number of shared vertexes nor in the cluster fragment types. Among the *closo*-[4]-*closo*- B_nH_{n-4} , the most stable isomers are *closo*(10)-[4]-*closo*(12)- $B_{18}H_{14}$, *closo*(9)-[4]-*closo*(12)- $B_{17}H_{13}$, *closo*(8)-[4]-*closo*(12)- $B_{16}H_{12}$, *closo*(7)-[4]-*closo*(12)- $B_{15}H_{11}$, *closo*(6)-[4]-*closo*(12)- $B_{14}H_{10}$, *closo*(5)-[4]-*closo*(12)- $B_{13}H_9$ [20]. In each of these,

Table 2

The preferred number of shared vertexes, x , in macropolyhedral boranes with general formula from B_nH_{n-4} to B_nH_{n+8} and as a consequence, the resulting number of skeletal electron pairs, $n(\text{SEP})$, the cluster structure and the thermodynamically most stable framework.

Formula	x	$n(\text{SEP})$	Structure	Most stable framework
B_nH_{n-4}	4	$n+2$	<i>closo</i> -[4]- <i>closo</i>	<i>closo</i> ($n-8$)-[4]- <i>closo</i> (12)
B_nH_{n-2}	3	$n+2$	<i>closo</i> -[3]- <i>closo</i>	<i>closo</i> ($n-9$)-[3]- <i>closo</i> (12)
B_nH_n	3	$n+3$	<i>closo</i> -[3]- <i>nido</i>	<i>closo</i> (12)-[3]- <i>nido</i> ($n-9$)
B_nH_{n+2}	2	$n+3$	<i>closo</i> -[2]- <i>nido</i>	<i>closo</i> (12)-[2]- <i>nido</i> ($n-10$)
B_nH_{n+4}	2	$n+4$	<i>nido</i> -[2]- <i>nido</i>	<i>nido</i> ($n-8$)-[2]- <i>nido</i> (10)
B_nH_{n+6}	2	$n+5$	<i>arachno</i> -[2]- <i>nido</i>	<i>arachno</i> ($n-8$)-[2]- <i>nido</i> (10)
B_nH_{n+8}	1	$n+5$	<i>arachno</i> -[1]- <i>nido</i>	<i>arachno</i> ($n-6$)-[1]- <i>nido</i> (7) ^a

^a This class was not studied extensively by computations, but the two experimentally known examples, *arachno*(8)-[1]-*nido*(7)- $B_{14}H_{22}$ and *arachno*(9)-[1]-*nido*(7)- $B_{15}H_{23}$ [11], both include a *nido*(7) cluster fragment.

one fragment is a *closo* 12-vertex fragment. It therefore seems to be the strongly favoured fragment for this class of macropolyhedra. The same conclusion can be drawn from an analysis of *closo*-[3]-*closo*- B_nH_{n-2} , *closo*-[3]-*nido*- B_nH_n and *closo*-[2]-*nido*- B_nH_{n+2} [20]. So, whenever there is a *closo* fragment present in the preferred macropolyhedral structure, the most stable isomer will have one *closo*(12) fragment incorporated. When there is no *closo* fragment present, i.e. in *nido*-[2]-*nido*- and *nido*-[2]-*arachno*-macropolyhedra a *nido*(10) fragment turns out to be the predominantly favourable fragment [22]. Its preference, however, cannot compete with that of the *closo*(12) fragment. Assigning increments for cluster fragments designed to reproduce the thermodynamic stability order of *nido*-[2]-*nido*- and *nido*-[2]-*arachno*-macropolyhedral isomers gives a quantitative estimate: *nido*(6)-, *nido*(8)-, *nido*(11)-, *nido*(5)-, *nido*(9)-, *nido*(7)-, are disfavoured against the *nido*(10)-fragment by 10.8, 11.2, 17.8, 19.4, 21.6, and 28.0 kcal mol⁻¹, respectively [25]. With the identification of *closo*(12) and *nido*(10) as preferred building blocks with the former predominating we can specify completely the most stable macropolyhedral framework for any general formula (last column in Table 2).

3. Conclusions

Macropolyhedral boranes can be formally constructed by sharing one to four vertexes between simple boron hydride clusters and are conceivable for more than ten vertexes. The total number of skeletal electrons in a macropolyhedral borane depends not only on the formula but also on the number of vertexes shared by the fused cluster fragments. Assignments of fusion modes in macropolyhedra with general formulae ranging from B_nH_{n-4} to B_nH_{n+10} results in 20 different classes of macropolyhedral boranes. For each general formula only one type of cluster fusion has been found to be known experimentally. Computationally it could be demonstrated that these are really considerably preferred based on relative thermodynamic stabilities. Thus the number of conceivable macropolyhedral borane classes reduces to eight. For each class and its single preferred number of shared vertexes, the number of skeletal electrons is determined. With this knowledge, the type of fused clusters, i.e. the most favourable framework, may be derived. Intensive computational investigations have shown some cluster fragments to be significantly preferred over others. The concept of preferred fragments may therefore be applied to even predict the distribution of vertexes among the fused fragments in the thermodynamically most stable isomers.

Many macropolyhedral boranes incorporate heteroboranes. This increases the number of possible structures per framework. For Wade type convex clusters, we have shown that the relative stability of various isomers may be estimated by increments due to certain structural features [26]. A similar approach should be working for heterosubstituted macropolyhedra as well.

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