Missing Hydrogens in $B_{19}H_{20}{}^-$? Application of Electron Counting Rule for Edge-Sharing Macropolyhedral Boranes

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Recently we had provided an electron counting rule to predict and to explain the electronic requirements of polycondensed polyhedral boranes.[1] According to this rule, a condensed polyhedral borane with n vertexes and m individual polyhedra sharing two, three, or four vertexes requires $n + m$ electron pairs for skeletal bonding. Thus, the polyhedral boranes $B_{12}H_{12}$ (**1**, I_h), $B_{21}H_{18}$ (**2**, D_{3h}),[2] and $B_{20}H_{16}$ (**3**, D_{2d})[3] exist with −2, −1, and 0 charges, respectively. A recently reported edge-sharing macropolyhedral borane $B_{19}H_{20}{}^-$ does not fit the electron counting rule.[4] We predict that the structure should have two additional hydrogens to attain electron sufficiency.

A skeleton containing two *closo*-boranes sharing two vertexes is not realizable because of the increased nonbonding interactions between the adjacent B−H vertexes of the shared atom. This is illustrated in **4** (Chart 1), where two B_{12} units are forced to share an edge. With the experimental B−B distances of $B_{12}H_{12}{}^{2-}$, the distance between the boron atoms represented by dark spheres is less than 1.5 Å. This distance is not improved even in edge-sharing octahedra.[5] But these steric interactions caused by condensation will be relieved by the removal of one or more vertexes near the shared atoms leading to *nido* structures. An additional electron pair is required for compensating every vertex that is removed from the nonadjacent positions.[6] 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.

Several molecules (Chart 2, **6**−**11**) 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 $B_{18}H_{22}$ (**10**) have 18 boron atoms distributed over two *nido* cages.[7] Hence $n = 18$, $m = 2$, and two more electron pairs are needed to compensate the two absent vertexes. The polyhedral skeleton requires $(n + m + 2)$ $18 + 2 + 2 = 22$ electron pairs. The 16
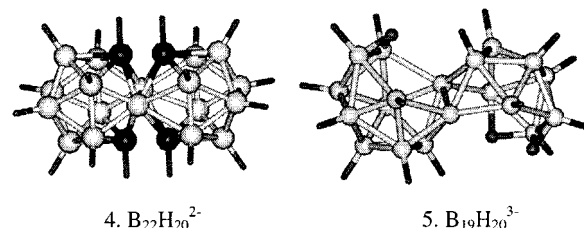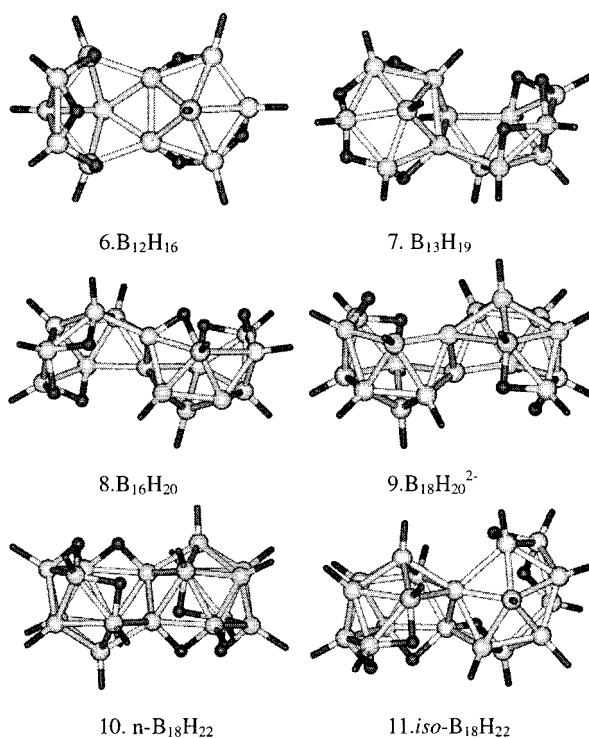
Chart 1

4. $B_{22}H_{20}{}^{2-}$ 5. $B_{19}H_{20}{}^{3-}$

Chart 2

6. $B_{12}H_{16}$ 7. $B_{13}H_{19}$

8. $B_{16}H_{20}$ 9. $B_{18}H_{20}{}^{2-}$

10. n-$B_{18}H_{22}$ 11. *iso*-$B_{18}H_{22}$

B−H groups give 16 electron pairs, and six bridging hydrogen atoms give three electron pairs to the skeletal bonding. Two shared boron atoms each give three electrons (all its valence electrons

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Table 1. Skeletal Electron Pairs for Edge Sharing *nido*-Boranes[8−11]

Borane	Electron pairs required by rule				Skeletal Electron pairs contributed by fragments				q	Ref.
	n	m	p	Sum	BH	B[a]	b-H	Sum		
$B_{12}H_{12}$	20	1	0	13	12	0	0	12	-2	(2)
$B_{20}H_{16}$	20	2	0	22	16	6	0	22	0	(2)
$B_{21}H_{18}$	21	2	0	23	18	4.5	0	22.5	-1	(3)
$B_{22}H_{20}$	22	2	0	24	20	3	0	23	-2	
$B_{12}H_{16}$	12	2	2	16	10	3	3	16	0	(8)
$B_{13}H_{19}$	13	2	2	17	12	1.5	3.5	17	0	(9)
$B_{16}H_{20}$	16	2	2	20	14	3	3	20	0	(10)
$B_{18}H_{20}$	18	2	2	22	16	3	2	21	-2	(11)
$B_{18}H_{22}$[b]	18	2	2	22	16	3	3	22	0	(7)
$B_{19}H_{20}$[c]	19	2	2	23	17	3	1.5	21.5	-3	(4)

[a] Boron atoms at the shared position. [b] Two isomers. [c] The species observed must be $B_{19}H_{22}^-$. p is the number of missing vertexes, b-H bridging hydrogens, and q the net charge.

because 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 1).

A recent report of a condensed polyhedral borane[4] (Chart 1, **5**) seems to be an exception. As per the *n* + *m* rule, this structure requires (*n* = 19 and *m* = 2) 19 + 2 + 2 = 23 electron pairs, taking into account the two *nido* fragments. However, $B_{19}H_{20}$ is reported to be a monoanion having 17 + 3 + 2 (3H + e⁻) = 22 electron pairs. In the absence of an electron counting rule, 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 because 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 $B_{19}H_{20}^-$, with two hydrogen atoms less than necessary are also not convincing. One of them required an elimination of 1 mol of H_2, which was discounted by the authors themselves, and the other two pathways had improbable mechanistic steps.

We have calculated the energy levels at the extended Huckel[12] and B3LYP/6-31G* levels[13−14] and found all indications for the reported $B_{19}H_{20}$ to be a stable species only as a trianion. Frequency calculations at the same level characterized the structure $B_{19}H_{20}^{3-}$ as minima on the potential energy surface. But the same structure with −1 charge failed to converge. The formulation presented for $B_{19}H_{20}^-$ requires two additional electrons, and hence, most likely the correct structure is $B_{19}H_{22}^-$. The authors discounted this fact because they assumed that the additional two hydrogen atoms would lead to *arachno* structures.

On the basis of the above results, the mechanism for the formation of $B_{19}H_{22}^-$ can be explained. The reaction of $B_{18}H_{20}^{2-}$ with $(CH_3)_2SBH_2Cl$ results in the formation of $B_{19}H_{22}^-$ in which a BH_2^+ caps a triangular face of a $B_{18}H_{20}^{2-}$ skeleton. In the case of $(CH_3)_2SBHCl_2$, the equivalent intermediate is $B_{19}H_{21}Cl^-$ where the cap is BHX^+ instead of BH_2^+. It has been proved that a capping B−H or BH_2^+ group in a polyhedra does not alter the electronic requirement of the polyhedral skeleton[15] and the number of electron pairs for this framework, (18 + 2 + 2) 22, remain the same as that of $B_{18}H_{22}$. The migration of the BH_2 or BHX groups from the capping position to the polyhedral skeleton results in the final $B_{19}H_{22}^-$. 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 $B_{19}H_{22}^-$. In the case of $B_{19}H_{21}Cl^-$, migration of the 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.

Supporting Information Available: Total energy and Cartesian coordinates of the optimized geometry of $B_{19}H_{20}^{3-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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