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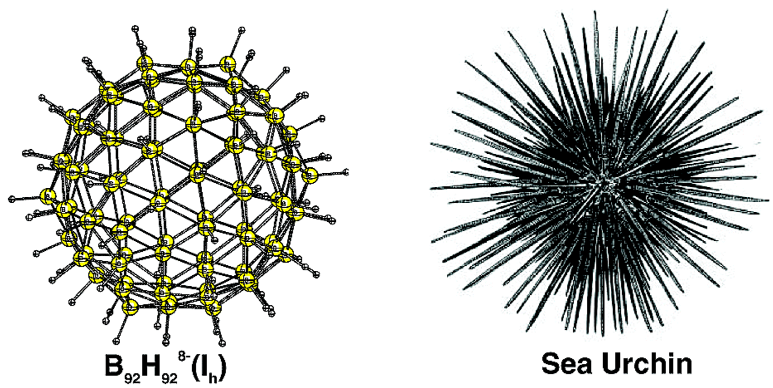

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A "Sea Urchin" Family of Boranes and Carboranes: The $6m + 2n$ Electron Rule

Zhi-Xiang Wang and Paul von Ragué Schleyer*

Center for Computational Quantum Chemistry, Computational Chemistry Annex, University of Georgia, Athens, Georgia 30602-2525

Received April 10, 2003; E-mail: schleyer@chem.uga.edu

The aesthetically pleasing structures of polyhedral boranes,[1] as well as their nonclassical bonding characteristics and potential in material and medical applications, continue to intrigue scientists. The Wade[2]−Mingos[3] electron count rules for stabile borane have led to the successful preparation of new boranes.[4] Jemmis and Balakrishnarajan[5] recently proposed a more general *mno* rule, which can be applied widely, for example, to condensed boranes and metallocenes. We here report our computational prediction[6] of a new family of related boranes and carboranes, which follow another electron counting rule, $6m + 2n$. The globular shapes and protruding hydrogens, especially of the larger members of this family, remind one of sea urchins.

The design of these new compounds starts from organic polyhedranes such as the [N] prismanes ($N = 3$, 4, 5, and 6) and $C_{20}H_{20}$.[7] All of the carbons in these $(CH)_p$ cages are first replaced conceptually by borons. These resulting open polyhedral $(BH)_p$ cages with triangular, rectangular, pentagonal, and hexagonal faces do not have sufficient bonding electrons to sustain the polyhedral framework and usually are not minima. If only two additional electrons are added, collapse to more compact forms, that is, the well-known $B_pH_p^{2-}$ boranes, would occur. To preserve the open polyhedral $(BH)_p$ framework, more electrons are needed. This can be accomplished by adding BH and CH "caps" on all faces larger than triangular and adding electrons. The $6m + 2n$ rule governs the number of BH versus CH caps chosen and the overall charge. Furthermore, all degenerate sets of MOs must be fully occupied, and the resulting compounds should have appreciable HOMO−LUMO gaps.

Applying this strategy to the [N] prismanes ($N = 3$ (**1C**), 4 (**2C**), 5 (**3C**), and 6 (**4C**)) (all molecules with suffix **C** are shown in the Supporting Information, SI.1) results in the polyhedral cages (**1B**$^{1-}$−**4B**) with prismatic $(BH)_p$ substructures. Compounds **1B**$^-$, **2B**$^{2-}$, and **3B**$^-$ are minima; the lowest frequencies are appreciable (Table 1). Although the relatively large HOMO−LUMO gap indicates **4B** to be favorable electronically (as are **1B**$^-$, **2B**$^{2-}$, and **3B**$^-$ in this regard), it has eight small imaginary frequencies. A CH cap is too small (i.e., the orbital radial extensions are insufficient) to fit a six-membered ring. This geometric mismatch distorts **4B** away from D_{6h} symmetry slightly.

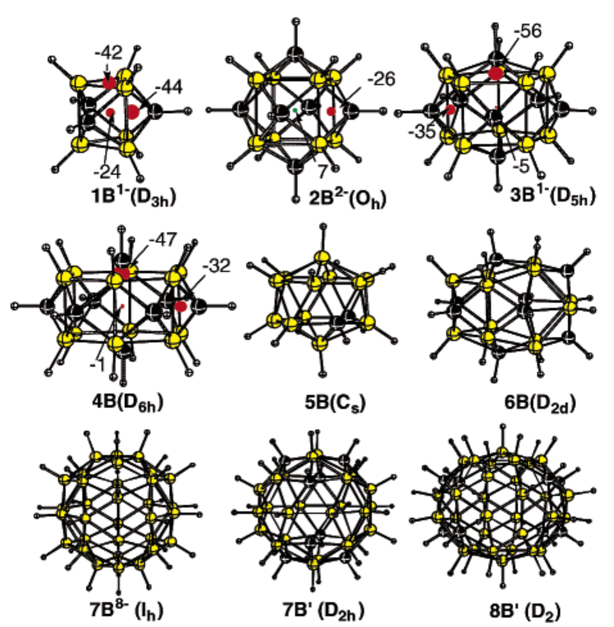
The skeletal electron counts (excluding the BH and CH e's) of **2B**$^{2-}$ (36e), **3B**$^-$ (42e), and **4B** (48e) correspond to $6m$, where m is the number of faces (larger than triangular) in the original prismanes, that is, **2C**, **3C**, and **4C**, 6, 7, and 8, respectively. The $6m$ value of **1B**$^-$ (and **1C**) is 18, but 22 skeletal electrons are required to assign two pairs to the two uncapped BBB triangular faces and provide stabilizing 3c−2e bonding. Unlike **2B**$^{2-}$, **3B**$^-$, and **4B**, with borons linked to three CH caps, the borons in **1B**$^-$ are connected to two CH caps. Because of the 3c−2e bonding, the equatorial B−B bond lengths (1.764 Å) in **1B**$^-$ are shorter than the equatorial B−B bonds (>2.0 Å) in **2B**$^{2-}$, **3B**$^-$, and **4B**.

The general $6m + 2n$ electron counting rule follows from this discussion of **1B**$^-$−**4B**: Starting from polyhedranes $(CH)_p$ with m faces larger than triangles and n triangles, the open polyhedral $(BH)_p$ cages, generated by replacing carbons in $(CH)_p$ cages by borons, can be stabilized by using CH and BH groups to cap all faces larger than triangles. The total skeletal electrons required for stabilization are $6m + 2n$.

Table 1. Number of Imaginary Frequencies (Nimag), Smallest Frequencies (in Parentheses, cm^{-1}), and HOMO−LUMO Gaps (Gap, in eV) at B3LYP/6-31G*, Actual Skeletal Electron Counts (Sec), Numbers of Faces Larger than a Triangle (m), and Numbers of Triangular Faces (n) in the Corresponding Polyhedranes

	Pg	Nimag	gap	Sec[a]	m	n
$C_3B_6H_9^{1-}$ (**1B**$^{1-}$)	D_{3h}	0(279)	6.6	22	3	2
$C_6B_8H_{14}^{2-}$ (**2B**$^{2-}$)	O_h	0(311)	6.4	36	6	0
$C_7B_{10}H_{17}^{1-}$ (**3B**$^{1-}$)	D_{5h}	0(176)	6.6	42	7	0
$C_8B_{12}H_{20}$ (**4B**)	D_{6h}	8(373i)	5.0	48	8	0
$C_2B_{12}H_{14}$ (**5B**)	C_s	0(288)	6.1	30	4	3
$C_8B_{12}H_{20}$ (**6B**)	D_{2d}	0(195)	6.9	48	8	0
$B_{32}H_{32}^{8-}$ (**7B**$^{8-}$)	I_h	0(164)	3.3	72	12	0
$C_8B_{24}H_{32}$ (**7B′**)	D_{2h}	0(228)	5.2	72	12	0
$B_{32}H_{32}^{2-}$ (**7B″**$^{2-}$)	I_h	5(3966i)	1.0	66[b]	12	0
$B_{38}H_{38}^{8-}$ (**8B**$^{8-}$)	D_{6d}	2(90i)	2.7	84	14	0
$C_8B_{30}H_{38}$ (**8B′**)	D_2	0(211)	5.0	84	14	0
$B_{16}H_{16}$ (**9B**)	T_d	0(341)	4.0	32	4	4
$C_6B_{12}H_{18}^{2+}$ (**10B**$^{2+}$)	C_{3v}	0(237)	6.2	40	6	2
$C_4B_{14}H_{18}$ (**10B′**)	C_s	0(224)	5.4	40	6	2
$C_9B_{14}H_{23}^{1+}$ (**11B**$^{1+}$)	D_{3h}	0(228)	6.9	54	9	0
$C_{10}B_{16}H_{26}^{2+}$ (**12B**$^{2+}$)	C_{4v}	0(207)	6.9	60	10	0
$C_8B_{18}H_{26}$ (**12B′**)	C_{4v}	0(152)	5.6	60	10	0
$B_{92}H_{92}^{8-}$ (**13B**$^{8-}$)[c]	I_h	0(147)	9.1	192	32	0
$C_8B_{84}H_{92}$ (**13B′**)[c]	D_{2h}	0(150)	8.7	192	32	0
$B_{92}H_{92}^{2-}$ (**13B″**$^{2-}$)[c]	I_h	3(844i)	2.0	186[d]	32	0

[a] All Secs are equal to the numbers predicted by the $6m + 2n$ rule except for **7B″**$^{2-}$ and **13B″**$^{2-}$. [b] The $6m + 2n$ value is 72. [c] Computed at HF/STO-3G. [d] The $6m + 2n$ value is 192.



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The magic numbers 6 and 2 in this $6m + 2n$ rule are offshoots of the 6 interstitial electron rule[8] for compounds such as pyramidal C_{4v} $(CH)_5^+$ and the 3c−2e delocalized electrons for deltahedra structures such as H_3^+ and $(CH)_3^+$. These compounds combine aromatic pyramidal and triangular units: each pyramidal unit in **1B**$^-$−**4B** and the BBB triangles in **1B**$^-$ have large negative NICS values[9] (see structures). The small negative NICS values at the centers of **2B**$^{2-}$−**4B** are quite different from the large negative NICS values at the centers of closo-boranes and carboranes, which are true three-dimensional aromatics.[10] Thus, our new set of compounds only has the local aromaticity associated with the faces. The large negative NICS at the center of **1B**$^-$ is due to its proximity to the aromatic deltahedral faces.

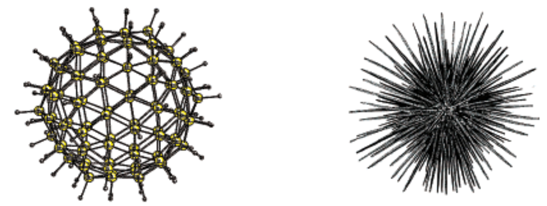
The $6m + 2n$ rule can be extended to construct many new boranes and carboranes. The C_{3v} polyhedrane $C_{10}H_{10}$ (**5C**) has three pentagons, one hexagon ($m = 4$), and three triangles ($n = 3$). The required 30 skeletal electron count is met by the 12 BH and the 2 CH groups in **5B**. The skeletal electron count of **5B** also obeys Wade's rule for a 14 vertex borane. Hence, the $6m + 2n$ rule sometimes overlaps with Wade's rule. The D_{2d} $C_{12}H_{12}$ (**6C**) has four rectangles and four pentagons ($m = 8$); therefore, 48 skeletal electrons are predicted. These are offered by the 8 CH and 12 BH caps in **6B**.

Lipscomb and co-workers[11] proposed $B_{32}H_{32}^{2-}$ as the second icosahedral borane following I_h $B_{12}H_{12}^{2-}$. Although $B_{32}H_{32}^{2-}$ obeys Wade's rule with 33 electron pairs, it has five very large degenerate imaginary frequencies (3965*i* at B3LYP/6-31G*). On the basis of our strategy, the same 32 vertex borane cage can be built from I_h $C_{20}H_{20}$ (**7C**). With $m = 12$ and $n = 0$, the $6m + 2n$ rule requires 72 skeletal electrons for stabilization. The octaanion, $B_{32}H_{32}^{8-}$ (**7B**$^{8-}$), is more promising than the $B_{32}H_{32}^{2-}$ dianion. Indeed, $B_{32}H_{32}^{8-}$ is an icosahedral minimum. The HOMO−LUMO gap of $B_{32}H_{32}^{8-}$ is 3 times larger than that of $B_{32}H_{32}^{2-}$ and is larger than the C_{60} gap, 2.8 eV (Table 1). The neutral $C_8B_{24}H_{32}$ (**7B′**) minimum (smallest frequency 228 cm^{-1} and a 5.2 eV gap) is even better. The optimal use of bonding orbitals in the octaanion is beneficial energetically. Our recent computational studies show that large closo-borane dianions are much less stable than their "conjunto" isomers[5c] due to increasing strain in the larger closo-cages.[12] While closo-$C_2B_{30}H_{32}$ (C_i) is 238 kcal/mol less stable the conjuncto-CB_9H_{12}−$B_{12}H_8$−CB_9H_{12} (C_{2v}), closo-$C_8B_{24}H_{32}$ is only 14 kca/mol less stable than conjuncto-$C_3B_7H_{12}$−$C_2B_{10}H_8$−$C_3B_7H_{12}$ (C_{2v}). Hence, our new, large closo-cages may be easier to achieve than large closo-borane dianions.

D_{6d} $C_{24}H_{24}$ (**8C**), with $m = 14$ and $n = 0$, points to D_{6d} $B_{38}H_{38}^{8-}$ (**8B**) and to neutral $C_8B_{20}H_{38}$ (**8B′**) which meet the $6m + 2n$ rule. The latter is a minimum with a smallest frequency of 211 cm^{-1} and a 5.0 eV HOMO−LUMO gap. The geometries of **9B**−**12B′**, minima obeying the $6m + 2n$ rule, are given in the Supporting Information (SI.2). All of these compounds are minima obeying the $6m + 2n$ rule.

We also can build boranes and carboranes from carbon cluster cages (without hydrogens) like the fullerenes. After replacing the carbons by BH groups, the $6m + 2n$ rule guides the capping of polygon faces with CH and BH groups. For example, starting from C_{60}, we first replace the carbons by BH's. The 12 pentagons and 20 hexagons require 192 skeletal electrons. If only BH caps are used, the sea-urchin-like $B_{92}H_{92}^{8-}$ (**13B**$^{8-}$) is predicted. It is an icosahedral minimum at the HF/STO-3G level. The eight charges may be neutralized as in D_{2h} $C_8B_{84}H_{92}$(**13B′**), which is a minimum at HF/STO-3G. In contrast, $B_{92}H_{92}^{2-}$, which obeys Wade's rule, is not a minimum at this level. Furthermore, the HOMO−LUMO gaps of **13B**$^{8-}$ and **13B′**, which follow the $6m + 2n$ rule, are much larger than that of **13B″**$^{2-}$.

The recently synthesized cubic carbaalane,[13] analogous to **2B**$^{2-}$, obeys the $6m + 2n$ rule. Other carbaalane cages can be predicted. Investigations of endohedral derivatives of these new compounds, similar electron counting rules for nido- and arachno- forms, and transition metal applications are underway.



13B^{8-} **(Ih)** **sea urchin**

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Supporting Information Available: The structures of **1C**−**13C** (SI.1) and **10B**−**13B″** (SI.2), and the B3LYP/6_31G* Cartesian coordinates of compounds listed in Table 1 (SI.3) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Cotton, F. A.; Murillo, C. A.; Bochmann, M.; Grimes, R. N. *Advanced Inorganic Chemistry*, 6th ed.; John Willey & Sons: New York, Singapore, Toronto, 1999. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Woburn, MA, 1997.

(2) (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, *792*. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (c) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(3) (a) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (b) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.

(4) (a) Burke, A.; Ellis, D.; Giles, B. T.; Hondson, B. E.; Macgregor, S. A.; Rosair, G. M.; Welch, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 225. (b) Grimes, R. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1198. (c) King, R. B. *Chem. Rev.* **2001**, *101*, 1119.

(5) (a) Balakrishnarajan, M. M.; Jemmis, E. D. *J. Am. Chem. Soc.* **2000**, *122*, 4516. (b) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4313. (c) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. *Chem. Rev.* **2002**, *102*, 93−144.

(6) All compounds were computed and characterized at B3LYP/6-31G* except for the 92 vertex cages using Gaussian 98 (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998).

(7) (a) Earley, C. W. *J. Phys. Chem.* **2000**, *104*, 6622. (b) Mehta, G.; Padma, S. In *Carbocyclic Cage Compounds: Chemistry and Applications*; Osawa, E., Yonemitsu, O., Eds.; VCH: New York, 1992.

(8) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 1538. (b) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 7017.

(9) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(10) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3455.

(11) (a) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 3443. (b) Gindulyte, A.; Krishnamachari, N.; Lipscomb, W. N.; Massa, L. *Inorg. Chem.* **1998**, *37*, 6546. (c) Dadashev, V.; Gindulyte, A.; Lipscomb, W. N.; Massa, L.; Squire, R. In *Structures and Mechanics: from Ashes to Enzymes.* Eaton, G. R., Wiley, D. C., Jardetzky, O., Eds.; ACS Symposium Series 827; American Chemical Society: Washington, DC, 2002; p 79.

(12) (a) Moran, D.; Wang, Z.-X.; McKee, M. L.; Schleyer, P. v. R.; Schaefer, H. F., in preparation. (b) Schleyer, P. v. R.; Najafian, K.; Mebel, A. M. *Inorg. Chem.* **1998**, *37*, 6765. (c) McKee, M. L.; Wang, Z.-X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2000**, *122*, 4781.

(13) (a) Stasch, A.; Ferbinteanu, M.; Prust, J.; Zheng, W.; Cimpoesu, F.; Roesky, H. W.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Am. Chem. Soc.* **2002**, *124*, 5441. (b) Uhl, W. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley: Europe, 2002; pp 239.

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