studied by several groups.[22-24] The formation of heteropoly blues appears to involve the stepwise reduction of d^0 M atoms to the d^1 oxidation state without a change in the structure of the anion.[10,25,26] It is noted here that the formation of heteropoly blue anions appears to be restricted to complexes with type I or type III structures.[27] Thus, each of the type I structures listed in Table I is known to be reducible,[28] but there are no instances of the reduction of type II anions.[29] As far as type III structures are concerned, although the 12-paratungstate ion has such a structure in the solid state, there is little evidence for other than the hexatungsto (type II?) form in most solutions,[30] and there have been no reports of a paratungstate "blue." On the other hand, the demonstrated reducibility[31] of $\mathrm{PW_{11}O_{39}}^{7-}$, $\mathrm{SiW_{11}O_{39}}^{8-}$, and $\mathrm{P_2W_{17}O_{61}}^{10-}$ is consistent with the view of these complexes as type III species.

Conclusions regarding the structures of poly anions not listed in Table I may be drawn from considerations of their redox behavior. Recent polarographic investigations of the isopoly "pseudometatungstate"[32] and "polytungstate-Y"[33] anions indicate that these complexes are easily reduced, from which it may be inferred that they have type I (or type III) structures.[34] Since the true formulas of these complexes are not known at present, further speculation is inappropriate. In molybdate solutions, the isopoly anions which are the predominant solute species at pH 3-5, *viz.*, $\mathrm{Mo_7O_{24}}^{6-}$ and $\mathrm{Mo_8O_{26}}^{4-}$, are not reducible, although more acidic solutions of Mo(VI) are easily reduced to blue species. The anion responsible for the blue color in such solutions has been formulated[35] as $\mathrm{Mo_6O_{18}}^{2-}$. Recent work[36] shows that this species is better written as $\mathrm{H_2Mo^V{}_2Mo_4O_{19}}^{2-}$, a reduced form of the type I hexamolybdate anion, first reported by Fuchs and Jahr.[37]

Most of the approximately 75 anions representing the structures listed in Table I are tungstates and molybdates. At present count, all poly anions containing octahedral vanadium, niobium, or tantalum have type I structures.[38] This is to be expected for electrostatic reasons; type II structures for pentavalent atoms would tend to have high overall charges. Among molybdates and tungstates there appears to be a tendency for the former to adopt type II structures and the latter, type I structures. Thus, the only type I molybdates are a few 1:12 and 2:18 complexes with central atoms that strongly favor tetrahedral coordination ($\mathrm{P^V}$, Si, etc.), together with the hexamolybdate anion, $\mathrm{Mo_6O_{19}}^{2-}$. Type II tungstates are even less common than type I molybdates and are based on "octahedral" central atoms $\mathrm{I^{VII}}$, $\mathrm{Te^{VI}}$, $\mathrm{Ni^{II}}$, and $\mathrm{N^{IV}}$.[39] In this connection, the structues of the 10-tungstolanthanates, $\mathrm{Ln^{III}W_{10}O_{35}}^{7-}$, recently described by Peacock and Weakley[40] will prove interesting. Since no observations of heteropoly blue formation were made, it is possible that these complexes have type II structures. Further discussion of the significance or even the existence of the tungstate-type I *vs.* molybdate-type II dichotomy must therefore await the results of more structural studies.

Acknowledgments.—Helpful discussions with Professor L. C. W. Baker and Drs. C. M. Flynn, Jr., and H. So are gratefully acknowledged.

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[22] P. Souchay, "Ions Minéraux Condensés," Masson et Cie, Paris, 1969, pp 326-339; R. Massart and G. Hervé, *Rev. Chim. Miner.*, **5**, 521 (1968).

[23] M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

[24] P. Stonehart, J. G. Koren, and J. S. Brinen, *Anal. Chim. Acta*, **40**, 65 (1968).

[25] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).

[26] M. T. Pope, D. P. Smith, J. J. Altenau, and J. Bender, *Proc. Int. Conf. Coord. Chem., 13th*, **1**, 127 (1970).

[27] The nonreducibility of type II anions is consistent with the observation that there are no authenticated examples of *cis*-$\mathrm{MO_2L_4}^{n-}$ complexes where M has a d^1 configuration: W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970). Griffith has suggested that this may be a consequence of the participation of the metal's t_{2g} orbitals in π bonding to the cis oxo groups.

[28] See ref 23-27 ($\mathrm{XM_{12}O_{40}}^{n-}$ and $\mathrm{X_2M_{18}O_{62}}^{6-}$); C. M. Flynn, Jr., H. So, and M. T. Pope, in preparation ($\mathrm{M_6O_{19}}^{n-}$); S. Ostrowetsky, *Bull. Soc. Chim. Fr.*, 1018 (1964) ($\mathrm{V_{10}O_{28}}^{6-}$).

[29] Although $\mathrm{Mo_7O_{24}}^{6-}$ cannot be chemically reduced without decomposition, γ irradiation of the ammonium salt produces $\mathrm{NH_3}^+$ and Mo(V) centers. Since the esr signal due to the latter species is isotropic at liquid nitrogen temperatues and shows superhyperfine structure, it is possible that the anion structure remains more or less intact following irradiation at these temperatures: I. Pascaru, O. Constantinescu, M. Constantinescu, and D. Arizan, *J. Chim. Phys.*, **62**, 1283 (1965).

[30] D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962); J. Aveston, *Inorg. Chem.*, **3**, 981 (1964); O. W. Rollins, Ph.D. Thesis, Georgetown University, 1965.

[31] P. Souchay and A. Tézé, *C. R. Acad. Sci., Ser. C*, **268**, 804 (1969).

[32] J. P. Launay, P. Souchay, and M. Boyer, *Collect. Czech. Chem. Commun.*, **36**, 740 (1971).

[33] F. Chauveau, M. Boyer, and B. Le-Meur, *C. R. Acad. Sci., Ser. C*, **268**, 479 (1969); F. Chauveau, private communication, 1971.

[34] Both of these anions are isolated from relatively acidic solutions. For this reason also, type I structures (since they contain fewer oxygen atoms per M atom than do type II) are likely.

[35] S. Ostrowetsky, *Bull. Soc. Chim. Fr.*, 1003 (1964).

[36] M. T. Pope, D. Ambruso, and D. J. Kenedy, in preparation.

[37] J. Fuchs and K. Jahr, *Z. Natursforsch. B*, **23**, 1380 (1968).

[38] The structure proposed for the (reducible) heteropolyvanadate $\mathrm{MnV_{13}O_{38}}^{7-}$ is type III, however: C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970).

[39] K. Eriks, private communication, 1970; H. H. K. Hau and K. Eriks, Abstracts, American Crystallographic Association Meeting, New Orleans, La., 1970, No. P10.

[40] R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A*, 1836 (1971).

[41] A sabbatical leave (1970-1971) spent in the Department of Inorganic Chemistry, Technical University of Vienna, was supported in part by a Type D grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Hückel-Type Rules and the Systematization of Borane and Heteroborane Chemistry

Sir:

This correspondence deals with some theoretical justification for two empirical concepts which in our opinion allow for a conceptually simple systematization of boranes, carboranes, and heteroboranes. One concept correlates the structures of the known boranes and heteroboranes to a "parent" series of closo molecules[1] whose geometries are closely approximated by regular deltahedra (Figure 1, column 1)[2] and from which the nido[1] and arachno[1] series can be derived (Figure 1, columns 2 and 3, respectively). The second concept

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[1] R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).

[2] A deltahedron is a polyhedron whose faces are equilateral triangles.

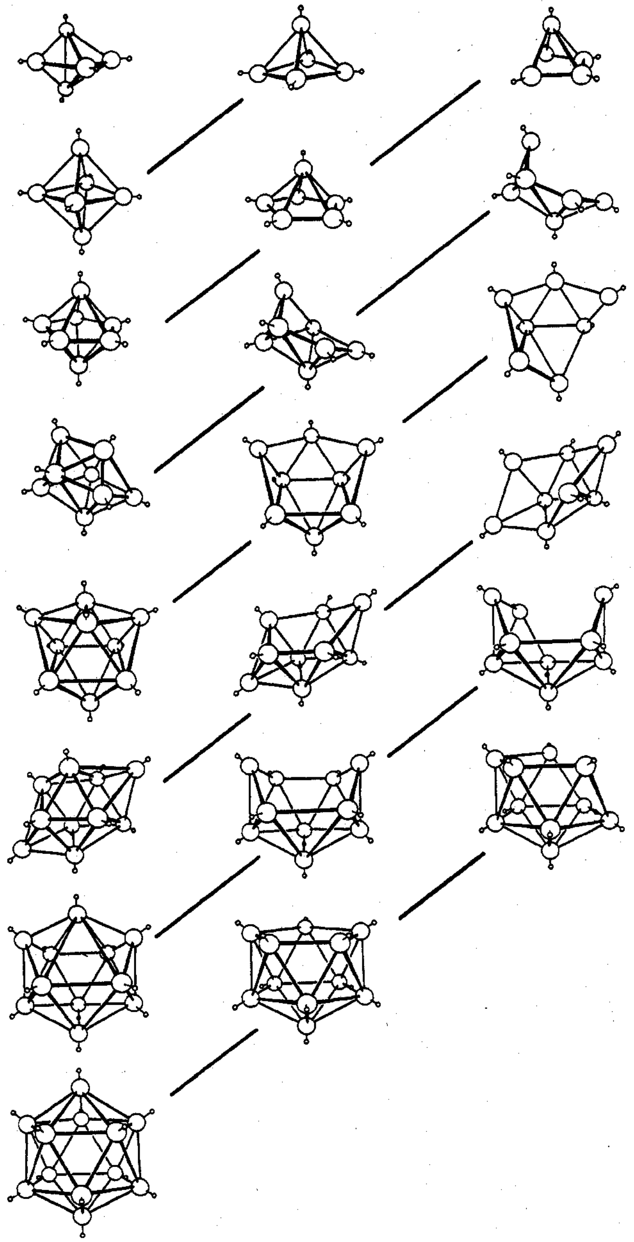

Figure 1.—Idealized structures for closo, nido, and arachno boranes and heteroboranes. From left to right, the vertical columns give the basic closo, nido, and arachno frameworks; bridge hydrogens and BH_2 groups are not shown, but when appropriate, they are placed around the open face of the framework in a manner which preserves the symmetry of the basic nido or arachno framework. Any nido or arachno structure can be derived from the appropriate deltahedron by ascending a diagonal from left to right; this progression generates the nido structure by removing the most highly connected vertex of the deltahedron; the arachno structure is generated by removing the most highly connected atom in the open face of the nido structure. Each horizontal row indicates the basic structural changes which occur as the number of framework electrons is varied from $2n + 2$ to $2n + 4$ to $2n + 6$. It appears that these correlations can be extended to include a 12-atom nido framework: G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 2541 (1971).

deals with the "magic" number of electrons which is required for the framework bonding in these molecules as inferred from various molecular orbital treatments.

Systematics in the chemistry of the boron hydrides and heteroboranes have been based on reaction chemistry,[3] topological rules,[4] and isoelectronic analogies.[4,5] Topological treatments of "electron-deficient" molecules describe their valence structures in terms of localized three-center and two-center bonds. Such localized bonding descriptions have been especially successful for open structures (nido and arachno) where localized two-center and three-center interactions can reflect the molecular symmetry. Still the "correct" topological description of a given molecule often requires computer assistance and/or the tedious interpretation of a large set of semiempirical rules.[4,6] In fact, in the case of the closo boranes and heteroboranes, localized-bonding treatments represent equivocations since for only one known closo molecule, $B_3C_2H_5$,[7] can localized bonds reflect the molecular symmetry.[8]

"Magic" Numbers $(2n + 2)$.—The bonding in closo heteroboranes has been nicely described as delocalized by various molecular orbital treatments.[9,4a,10–12] The compact, highly "connected" structures and delocalized bonding in such closo structures extrapolate easily to give them the label of "superaromatic" molecules.[12,13] In keeping with the concepts of delocalized bonding and "superaromaticity" in closo heteroboranes, we prefer to characterize these molecules in terms of the number of electrons which they require for framework bonding. The Hückel rule states that $(4q + 2)\pi$ electrons lead to aromaticity[14,15] and a special stability deriving from the presence of a closed shell; the rule has been a concept of special value in discussions of the chemistry of cyclic organic molecules. Likewise, electron counting rules are implicit in the isoelectronic analogies often used to compare boron hydrides and carboranes.[4,5] A more explicit statement of these rules would be that closo boranes and heteroboranes in deltahedral framework geometries (Figure 1, column 1) require $2n + 2$ framework electrons for a closed shell [n = 5–12 framework atoms; the electrons contributed by cage atoms to exodeltahedral bonds (B–H, C–H, etc.) or lone pairs are not considered in the count of framework electrons]. The representative closo boranes and heteroboranes listed in Table I can be adduced in support of the $2n + 2$ rule if the rather arbitrary scheme of electron accounting shown there is followed. For example, the molecule $(C_6H_5)B_{11}H_{10}S$,

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(3) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

(4) For example, see (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (b) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971); (c) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(5) (a) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970; (b) R. E. Williams, *Progr. Boron Chem.*, **2**, 37 (1970).

(6) For example, the molecule B_5H_9 has possible solutions of 4120, 3211, and 2302 for the equations of balance.[4a] The 2302 structure (C_s) satisfies the rules but apparently collapses to the observed C_{4v} structure which is satisfactorily represented by appropriately weighting all the canonical structures possible for the 4120 solution.[4c]

(7) I. Shapiro, C. D. Good, and R. E. Williams, *J. Amer. Chem. Soc.*, **84**, 3837 (1962).

(8) S. F. A. Kettle and V. Tomlinson, *J. Chem. Soc. A*, 2002 (1969).

(9) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc., Ser. A*, **224**, 336 (1954); **230**, 110 (1955).

(10) E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(11) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); **37**, 2872 (1962).

(12) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3489 (1962).

(13) E. L. Muetterties and W. H. Knoth, *Chem. Eng. News*, **44**, 88 (May 9, 1966).

(14) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **76**, 628 (1932); **83**, 632 (1933).

(15) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

TABLE I

REPRESENTATIVE EXAMPLES OF THE $2n + 2$, $2n + 4$, AND $2n + 6$ RULES

	Framework electron contributions					
Compound	Boron[a]	Carbon[a]	Other hetero-atom[a]	Charge	Total	Ref
	$2n + 2$ Systems					
$B_3C_2H_5$	3 (2)	2 (3)		0	12	*c*
$(B_6H_6)^{2-}$	6 (2)			2	14	*d*
$(CH_3)GaC_2B_4H_6$	4 (2)	2 (3)	1 (2)	0	16	*e*
$(B_8H_8)^{2-}$	8 (2)			2	18	*c*
$B_7C_2H_9$	7 (2)	2 (3)		0	20	*f*
$(B_9CH_{10})^-$	9 (2)	1 (3)		1	22	*g*
$B_9C_2H_{11}$	9 (2)	2 (3)		0	24	*h*
$(C_6H_5)B_{11}H_{10}S$	11 (2)		1 (4)	0	26	*i*
$B_9C_2H_{11}Sn$	9 (2)	2 (3)	1 (2)	0	26	*j*
$B_{10}CH_{11}P$	10 (2)	1 (3)	1 (3)	0	26	*k*
	$2n + 4$ Systems					
$B_3C_2H_7$	3 (2)	2 (3)		2[b]	14	*l*
$B_3C_3H_7$	3 (2)	3 (3)		1[b]	16	*m*
$B_2C_4H_6$	2 (2)	4 (3)		0	16	*n*
$B_9H_{11}S$	9 (2)		1 (4)	2[b]	24	*i*
$(B_9CH_{10}P)^{2-}$	9 (2)	1 (3)	1 (3)	2	26	*k*
	$2n + 6$ Systems					
B_5H_{11}	5 (2)			6[b]	16	*o*
$B_7C_2H_{13}$	7 (2)	2 (3)		4[b]	24	*p*
$B_9H_{12}S-$	9 (2)		1 (4)	4[b]	26	*i*

[a] Number of atoms multiplied by (electrons contributed to the framework). [b] In this case charge is used in only a formal sense. Actually the "charge" is balanced by protons, often resulting in bridge hydrogens and BH_2 groups in $2n + 4$ and $2n + 6$ systems, *viz.*

$$B_9C_2H_{11}{}^{2-} \xrightarrow{H^+} B_9C_2H_{12}{}^- \xrightarrow{H^+} B_9C_2H_{13}$$

[c] Reference 7. [d] Reference 25. [e] R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, **91**, 6498 (1969). [f] P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969). [g] W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274 (1967). [h] F. N. Tebbe, P. M. Garret, and M. F. Hawthorne, *ibid.*, **86**, 4222 (1964). [i] Reference 16. [j] R. L. Voorhees and R. W. Rudolph, *ibid.*, **91**, 2173 (1969). [k] Reference 17. [l] D. A. Franz and R. N. Grimes, *ibid.*, **92**, 1438 (1970). [m] Reference 5. [n] Reference 29. [o] K. Borer, A. B. Littlewood, and C. S. G. Phillips, *J. Inorg. Nucl. Chem.*, **15**, 316 (1960). [p] P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2008 (1969).

i.e., $B_{11}H_{11}S$,[16] has the 26 electrons requisite for framework bonding if two of the six valence electrons of sulfur are assigned to a single exodeltahedral lone pair. Conversely, if sulfur has two exodeltahedral lone pairs, the count of framework electrons is not $2n + 2$ but only $2n$. In order to substantiate the electron accounting scheme of Table I, we have performed LCAO–MO calculations on the hypothetical thiaboranes B_4H_4S [trigonal bipyramid; S both axial (C_{3v}) and equatorial (C_{2v})] and B_9H_9S [bicapped square antiprism; S both axial (C_{4v}) and equatorial (C_s)], the known carbaphosphaborane 1,7-$B_{10}CH_{11}P$[17] [icosahedron (C_s)], and the unknown icosahedral tricarbaboranes 1,7,9-$B_9C_3H_{12}{}^+$ (C_{3v}) and 1,7,9-$B_9C_3H_{11}$ (C_s). Off-diagonal terms were taken as $H_{ij} = K \cdot S_{ij}(H_{ii} + H_{jj})/2$ with $K = 1.75$ as originally suggested by Wolfsberg and Helmholtz.[18] Slater-type atomic orbitals were used as a basis set with exponents of 1.30 (B 2s and 2p),[4a] 1.625 (C 2s and 2p),[4a] 1.20 (H 1s),[19] 1.817 (S 3s and 3p),[19] 1.20 (S 3d),[19] 1.60 (P 3s and 3p),[19] and 1.10 (P 3d).[19] The diagonal elements H_{ii} were chosen in the usual way as the corresponding valence-state ionization potentials with H_{ii}: (H 1s) = −13.6,[19] (B 2s) = −15.36,[4a] (B 2p) = −8.63,[4a] (C 2s) = −21.34,[19] (C 2p) = −11.27,[19] (S 3s) = −23.06,[19] (S 3p) = −10.36,[19] (S 3d) = −2.50,[19] (P 3s) = −20.3,[19] (P 3p) = −11.00,[19] (P 3d) = −2.50 eV.[19] Regular geometries were assumed with the B–H distance constant at 1.10 Å, the B–B and B–C distances in the 1.70–1.77-Å range, and the B–S and B–P distances set nominally at 1.90 Å, respectively. Although a test calculation on B_4H_4S showed that the inclusion of sulfur d orbitals in the basis set did not markedly affect the results, 3d orbitals were included in all other calculations involving phosphorus and sulfur heteroboranes. In all cases the energy level diagram showed a rather smooth energy progression and filling of all degenerate levels until the entire set of valence electrons was accommodated and then a sizable gap (nominally 4–6 eV).[20] In all cases inspection of the eigenvector matrix for those MO's below the energy gap showed the requisite number of very low-lying B–H (C–H) bonding orbitals and a single, rather high-lying, exodeltahedral "sp hybrid" on the sulfur, phosphorus, or unique carbon in $B_9C_3H_{11}$. The remaining occupied orbitals were best described as framework MO's and held $2n + 2$ electrons (n = number of framework atoms) in agreement with the previously stated rule for deltahedral heteroboranes with 5 to 12 framework atoms.

Opening of the Deltahedron ($2n + 4$; $2n + 6$).—It has been noted empirically that a progressive framework opening accompanies the formal addition of electron pairs to a closo molecule and gives the nido and arachno structures for $2n + 4$ and $2n + 6$ framework electrons, respectively.[1,21] The nature of these structural changes is illustrated across any row of Figure 1. It should also be noted that the "charge" of the added electrons is often "compensated" for by the formation of B–H–B gridge bonds and/or BH_2 groups around the open face of the molecule. Thus, in a formal sense at least, bridge hydrogens and BH_2 groups represent the addition of protons to a $2n + 4$ or a $2n + 6$ electron bonding framework.[22–24] Examples of known nido and arachno boranes and heteroboranes are given in Table I.

In order to explore the theoretical basis for such empirical relationships between structure and the number of framework electrons, we have used EHMO calculations to evaluate the total energy of the mole-

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(16) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

(17) L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969).

(18) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

(19) L. S. Bartell, L. S. Su, and H. Yow, *Inorg. Chem.*, **9**, 1903 (1970) We thank L. S. Bartell for use of the EHMO computer program.

(20) Even when the d orbitals were set at −5.0 eV for B_4H_4S, the energy gap was 3 eV.

(21) As stated by K. Wade, *J. Chem. Soc. D*, 792 (1971), the rules note *electron pair* requirements ($n + 1$, $n + 2$, and $n + 3$ for closo, nido, and arachno, respectively).

(22) This formalism has considerable chemical basis as illustrated by reactions such as[23]

$$(B_9C_2H_{11})^{2-} \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} (B_9C_2H_{12})^- \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} B_9C_2H_{13}$$

or[24]

$$B_5H_8{}^- \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} B_5H_9$$

(23) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

(24) D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 3375 (1967).

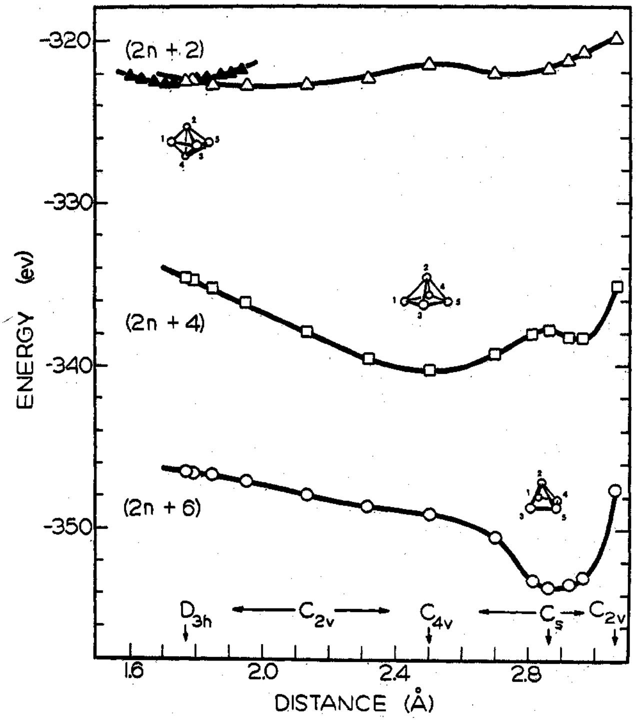

Figure 2.—Total energy as a function of geometry and electron count. The total energy is plotted on the vertical axis in electron volts. The horizontal axis gives the variation of the [B(3)–B(4)] distance as the polyhedron is deformed. For the D_{3h} to C_{4v} deformation one equatorial distance [B(3)–B(4)] was extended to 2.50 Å and the axial distance [B(1)–B(5)] shortened to 2.50 Å, while maintaining all other B–B distances at 1.77 Å and the B–H distances at 1.10 Å. For the C_{4v} to C_s deformation one basal distance [B(1)–B(3)] was extended while maintaining all other nearest B–B distances at 1.77 Å. The energies calculated for the $2n + 2$, $2n + 4$, and $2n + 6$ cases are given by △, □, and ○, respectively. The additional consideration of an axial deformation involving the B(1)–B(5) distance of the D_{3h} structure is given by shaded points, ▲. The arrows below D_{3h}, C_{4v}, and C_{2v} designate the B(3)–B(4) distance for the regular trigonal-bipyramidal, square-pyramidal, and planar structures, respectively. Upon deformation from D_{3h} to C_{4v} the framework symmetry is C_{2v}; from C_{4v} to C_{2v} it is C_s; the arrow below C_s designates the B(3)–B(4) distance for a framework corresponding to a nonplanar fragment of a regular pentagonal pyramid.

cule as a function of both oribital occupancy and molecular geometry for the case of a five boron atom framework. The results of these calculations are plotted in Figure 2.

The 12-electron case ($2n + 2$) is not very sensitive to molecular geometry, but there is a slight minimum for a trigonal bipyramid (D_{3h}) compressed along the threefold axis. Thus, although the calculations slightly favor a D_{3h} closo structure over the C_{4v} nido or C_s arachno structures, the barrier to rearrangement appears to be low; *i.e.*, the total energy varies by a nominal value of only 1.5 eV. By comparison, for $B_8H_8^{2-}$ the range is nominally 4.5 eV over structures of D_{4d}, C_{2v}, D_{2d}, O_h, D_{3d}, and D_{3h} symmetry.[25]

The 14- and 16-electron cases ($2n + 4$, $2n + 6$) show definite energy minima (Figure 2) at the nido and arachno structures, respectively, in agreement with the empirical correlations previously cited.

It should also be noted that the deformation of these various five-atom frameworks is predicted by symmetry rules.[26] Since the LUMO of $(B_5H_5)^{2-}$ (D_{3h}) is of e′ symmetry (the next MO is a$_2$′ and 4.5 eV higher), addition of two electrons to one of the e′ levels (singlet state) would give rise to first-order Jahn–Teller instability and spontaneous deformation.[26] Consider also the corresponding triplet state. Since the direct product of e′ and a$_2$′ in the D_{3h} group is E′, the molecule with one electron in each of the degenerate e′ orbitals might deform in the second order to a lower energy state *via* an E′ bending motion.

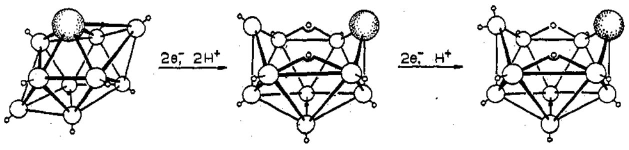

Figure 3.—Conversion of the hypothetical B_9H_9S to $B_9H_{11}S$ and $B_9H_{12}S^-$. Even the $B_9H_{11}S$ and $B_9H_{12}S^-$ structures are tentative (ref 16). The equatorial placement of the sulfur in B_9H_9S is consistent with a least motion closing of the $B_9H_{11}S$ cage. However, the isomer of B_9H_9S with an axial sulfur (a lower coordination position) is probably more stable based on empirical considerations: R. E. Williams, private communication.

Our chosen deformation from D_{3h} to C_{4v} is an extended E′ bend. The energies obtained from the EHMO calculations for the latter deformation drop linearly (Figure 2, $2n + 4$ case) indicating a first-order Jahn–Teller effect.[26]

For the C_{4v} framework containing $2n + 4$ electrons the LUMO is b$_1$, and, therefore, the addition of two electrons has no first-order Jahn–Teller consequences. However, the next MO has e symmetry and is only 3 eV higher. The direct product of e and b$_1$ contains E; an extended E bending motion was used for the deformation from C_{4v} to (C_s intermediate) C_{2v} (planar) shown in Figure 2.

Extension of such symmetry considerations to other closo boranes indicates that deformation of the deltahedron would occur if two electrons were added to the $2n + 2$ frameworks. The deltahedral molecules $B_6H_6^{2-}$ (O_h), $B_7H_7^{2-}$ (D_{5h}), $B_{10}H_{10}^{2-}$ (D_{4d}), and $B_{12}H_{12}^{2-}$ (I_h) all have degenerate LUMO's [t$_{2u}$, e$_2$″, e$_3$, and g$_g$, respectively].[4a] The contouring of the energy surfaces for the latter borane anions is not as straightforward as for $B_5H_5^{2-}$ but is under investigation.

One other feature of the total energy curve for the $2n + 4$ case is noteworthy (Figure 2). In addition to the deep minimum corresponding to the ground-state framework geometry of B_5H_9 (C_{4v}), note the shallower minimum at a geometry corresponding to a nonplanar fragment of a pentagonal pyramid for the boron framework. The latter minimum corresponds to a suggested intermediate form of B_5H_9.[4,6]

The use of these Hückel-type concepts to systematize the chemistry of boranes and hereroboranes emphasizes the oxidation–reduction aspects of much of their chemistry. Thus, the pyrolysis of the nido molecule $B_9C_2H_{13}$ ($2n + 4 = 26$) results in the loss of two "framework" electrons by the evolution of H_2 and the concomitant formation of the closo molecule $B_9C_2H_{11}$ ($2n + 2 = 24$).[23] The loss of two framework electrons

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(25) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

(26) For example, see L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

can also be effected when $B_9C_2H_{11}^{2-}$ ($2n + 4 = 26$) is treated with $SnCl_2$ to give $B_9C_2H_{11}$ and Sn.[27]

Although few closo heteroboranes other than carboranes have been reported for deltahedra other than the icosahedron, others should prove isolable. The hypothetical B_9H_9S would be the $2n + 2$ parent of the known thiaboranes $B_9H_{11}S$ and $B_9H_{12}S^-$ [16] [$2n + 4$ and $2n + 6$, respectively (Table I)]. Two successive additions of electron pairs to the B_9H_9S bicapped square antiprism ($n = 10$), with a corresponding opening[1,21] of the deltahedron and addition of protons to approach electrical neutrality, give $B_9H_{11}S$ and $B_9H_{12}S^-$ (Figure 3). Reversal of the latter sequence leads us to suspect that the action of a mild oxidizing agent on $B_9H_{11}S$ will lead to the isolation of B_9H_9S.

A molecule such as B_5CH_7[28] may appear to be an exception to the $2n + 2$ rule until it is realized that this neutral molecule is the conjugate acid of $B_5CH_6^-$ ($2n + 2 = 14$).[28] Another particularly intriguing application of such electron counting rules involves $B_2C_4H_6$[1,5,29] and related 16-electron, 6-atom frameworks which should fall into the nido classification. A nido structure is observed for $B_2C_4H_6$; however, $C_4H_4B_2F_2$, a molecule related to the latter by substitution of B–F groups for B–H groups, provides a clear exception to the subject systematics. Spectroscopic data for $C_4H_4B_2F_2$[30] point to a planar 6-membered ring with para B–F moieties. With fluorine and other halogens attached to boron there is of course the possibility of π bonding.[30] It appears that the "electron deficiency" of boron can in some cases be ameliorated by back-donation rather than by the multicenter bonding afforded in a cage framework. Thus, we anticipate that the majority of the exceptions to the systematics outlined here will occur where back-donation is possible.

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