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Boron Hydride Valence Structures. A Topological Approach

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A topological approach to boron hydride three-center valence structures is presented. The method differs from earlier ones in that, on the basis of SCF-localized orbital results, open BBB bonds are excluded. Most of the boron frameworks for molecules, ions, and intermediates which are known or thought to be among the more stable species give rise to more allowed valence structures than do hypothetical topologies. A new, simpler topological computer program is described. Several charge distribution dependent weighting schemes for population analyses are considered. New structures are predicted, and use of the method in elucidating reaction pathways and more stable isomers is illustrated.

I. Introduction

The success of the three-center bond formalism[2] in describing the valence structures of the boron hydrides and of related electron-deficient molecules is now well established. The three-center, two-electron bond has played an important role in molecular orbital calculations, both semiempirical[3] and *ab initio*.[4] Its use has also served as a theoretical framework for the analysis of experimental results. Recent calculations[5] employing self-consistent field (SCF) wave functions and the localized molecular orbital (LMO) formulation[6] have put the ideas of three-center bonding on a firm quantitative footing.

One of the most interesting applications of the three-center bond formalism has been the topological or "semitopological" approach to boron hydride valence structures, developed by Dickerson and Lipscomb.[7] Capable of extension to a vast array of systems, the topological generation of boron hydride valence structures offers promise of providing a simple, systematic, pictorial description of boron hydride chemistry similar to that afforded by the dot and line drawings[8] so familiar to organic chemists. The efforts of Hoffmann and Lipscomb[3b] to program high-speed digital computers to generate boron hydride valence structures yielded a number of promising results. However, the problem is complicated, both computationally and conceptually, by the existence of two topologically distinct types of three-center boron-boron-boron bonds (see Figure 1). The SCF-LMO calculations noted, above,[5a,c,d] as well as LMO calculations[9] performed with other types of wave functions, fail to show any evidence so far for the existence of the open three-center BBB bond, Figure 1c, in the boron hydrides studied. Reformulation of the topological theory with only a single type of three-center BBB bond allows for great simplification. In this paper we describe a new computer program for the generation of all allowable boron hydride valence structures given a topological arrangement of the boron and hydrogen nuclei.

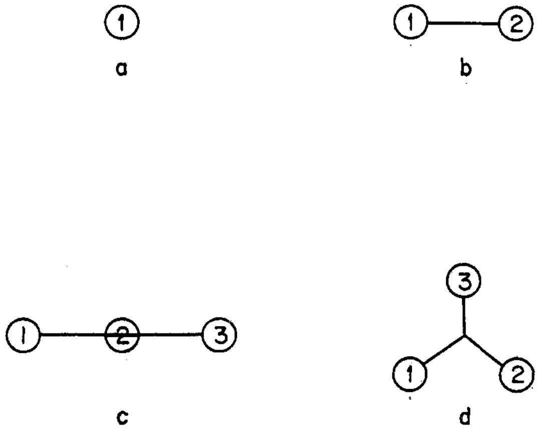

Figure 1.—Topological diagrams of orbital types found in boron hydrides.

We discuss briefly the topological approach and its application to electron-deficient molecules in general. A description of the program, with emphasis on the difference between the present version and earlier topological programs, is followed by a summary of results obtained for a number of boron hydride molecules and ions. The concluding section contains a discussion of the chemical significance and of possible extensions, modifications, and limitations of this approach.

II. The Topological Approach

If we look at molecules topologically—*i.e.*, in terms only of the connections between atoms, regardless of their identity or the distance between them (so long as we regard them as connected)—then, for our present purposes, we need to consider only the four types of orbitals shown in Figure 1. Of course, there are a few examples in which one may have to be somewhat arbitrary in deciding which atoms are connected to each other. Nevertheless, for most molecules, the complete set of connections or bonds is given by chemical or geometrical intuition. If necessary one can set up quantitative criteria such as a maximum interatomic distance (dependent upon the types of atoms involved) for two atoms to be deemed "connected." The orbitals we discuss here are *idealized* charge distributions. Localized one-, two-, and three-center orbitals always

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[1] National Science Foundation Predoctoral Fellow.

[2] W. H. Eberhardt, B. Crawford, and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[3] (a) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

[4] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2361 (1966).

[5] (a) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969); (b) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 3837 (1970); (c) E. Switkes, W. N. Lipscomb, and M. D. Newton, *ibid.*, **92**, 3847 (1970); (d) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971).

[6] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963); *J. Chem. Phys.*, **43**, S97 (1965).

[7] R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 212 (1957).

[8] M. A. Couper, *C. R. Acad. Sci.*, **46**, 1157 (1858).

[9] M. D. Newton, private communication.

contain contributions from other centers which may amount to several per cent of the total electron density in the orbital.[5] A recent experimental study[10] suggests that the distinction between the two types of three-center bond (Figure 1c, d) is not nearly so clearcut as might have been thought.

The one-center orbitals (Figure 1a) are inner shells or lone pairs. The latter make important contributions to the properties of molecules containing "electron-rich" atoms, such as nitrogen or oxygen, which have more valence electrons than available bonding orbitals.

Figure 1b shows the two-center or "normal" bond which, for many chemists, constitutes *the* chemical bond. One motivation behind our work on the boron hydrides has been the feeling that a deeper understanding of chemical bonding requires insight into the "anomalous" cases as well as the more familiar ones.

When three centers are to be linked by a single orbital, there exist two topologically distinct possibilities. We can connect them in the "open" manner of Figure 1c, in which the two end atoms are neighbors[11] of the middle one but not of each other. This is the type of bonding found in boron hydride bridge bonds (BHB), with two borons and hydrogen linked by an electron pair. Alternatively one can have a "central" three-center bond (Figure 1d), in which all three atoms are pairwise neighbors and are topologically equivalent.

The original topological formulation of boron hydride valence theory[7] allowed both types of three-center BBB bond. The starting point of our new approach is the requirement, based on our recent SCF-LMO calculations,[5] that all BBB bonds be of the central type.

Given the number of boron and hydrogen atoms in a molecule and a topological picture of how they are to be connected, the problem is to find all possible valence structures for the molecule which satisfy our topological rules. The presence of only central BBB bonds permits us to work with a somewhat simpler set of rules than that used by earlier investigators.[3b,7] We may dispense with the notions of excess connectability and connectivity,[7] and we need no longer worry about possible awkward hybridizations[3b] engendered by the crossing of two-center and open three-center bonds. We now set down our rules simply in terms of connections, orbitals, and electrons. (1) Every pair of boron atoms which are neighbors[11] must be connected by at least one B-B, BHB, or BBB bond. (2) No boron framework bond may include a pair of nonneighbor borons. (3) Each boron, since it has four valence atomic orbitals, must participate in $4 - n_i - m_i$ boron framework bonds, where n_i is the number of terminal hydrogens and m_i the number of bridge hydrogens bonded to the boron (i) in question. (4) Since each boron contributes three valence electrons and four valence orbitals, the molecule B_pH_{p+q} must have $(s - q)/2$ B-B and $p - s$ BBB bonds, where s is the total number of BHB bridges in the molecule. (5) No two borons may be bonded by both a two-center and a three-center (BBB or BHB) bond. Parenthetically, we comment that these rules for boranes are to be modified for carboranes.

The assumptions here are consistent with the "extended valence theory" of Lipscomb[12,13] in which borons may be bonded to zero, one, or two terminal hydrogens. Ionic species may be included by modifying rule 4 to allow for the appropriate number of electrons in the molecule.[14] "Heteroatoms" such as carbon or nitrogen may also be introduced by modifying rule 4. For example, the topological problem for the octahedral carborane $B_4C_2H_6$[15] is equivalent to that for the $B_6H_6^{2-}$ octahedron. Although we shall not do so here, one can also allow for multiple bonding and π donation in boron hydrides by relaxing restriction 5.[5d]

III. Computer Program

The first Hoffmann-Lipscomb topological program[3b] for computerized generation of boron hydride valence structures was modified and improved by Simpson[16] in his studies of $B_{18}H_{22}$. In its most elaborate form, Simpson's program was able to investigate many thousands of structures and to find about 425 acceptable structures per minute. Hoffmann's combinatorial subprograms were written in machine language. Simpson's later program was in FORTRAN but was longer than Hoffmann's and about 5 times the length of our present version. Simpson appears to have accepted Hoffmann and Lipscomb's hypothesis[3b] that specifying the two-center and open three-center bonds suffices to fix uniquely the remaining central three-center bonds. In Appendix I we show by (a rare) counterexample that this conjecture is false. No errors, however, appear to have resulted in earlier calculations from this assumption.

Our present program is extremely simple. It is written entirely in FORTRAN and has minimal storage requirements. Thus it can easily be used on nearly any computer. Input for a molecule consists simply of the number of borons and hydrogens, the charge, and a list of topological connections. This list is divided into B-H (B bonded to no, one, or two hydrogens and BHB groups) and B-B framework subsections.

From the input, the program calculates how many two- and three-center boron framework bonds are required for a valid structure (rule 4 above). It also constructs a canonically ordered list of allowed two- and three-center bonds. The search procedure consists in testing each possible combination of framework bonds to see if it satisfies rules 1, 3, and 5. The program operates by assembling allowable combinations of two-center bonds first and then matching them with three-center combinations. In this way, one need test only a fraction of the theoretically possible structures, since eliminating one two-center combination eliminates all possible three-center combinations with it. Our program turns out about as many acceptable structures per minute as Simpson's,[16] but it has to test far fewer.

To see the great savings brought about by the elimination of open BBB bonds, consider the decaborane molecule, $B_{10}H_{14}$. Each valence structure must have 2

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(10) R. Brill, H. Dietrich, and R. Dierks, *Acta Crystallogr.*, in press.

(11) We shall refer to two atoms as neighbors if our topological framework requires them to be connected. In general the topological and geometrical notions of "neighbor" will coincide.

(12) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **47**, 969 (1961).

(13) W. N. Lipscomb, *ibid.*, **47**, 1791 (1961).

(14) One then has $y - (s/2) - (3l/2)$ two-center and $p - y + l$ three-center bonds, where l is the total charge of the ion.

(15) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 7019 (1970).

(16) (a) P. G. Simpson, Ph.D. Thesis, Harvard University, 1963; (b) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963); (c) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **39**, 2339 (1963).

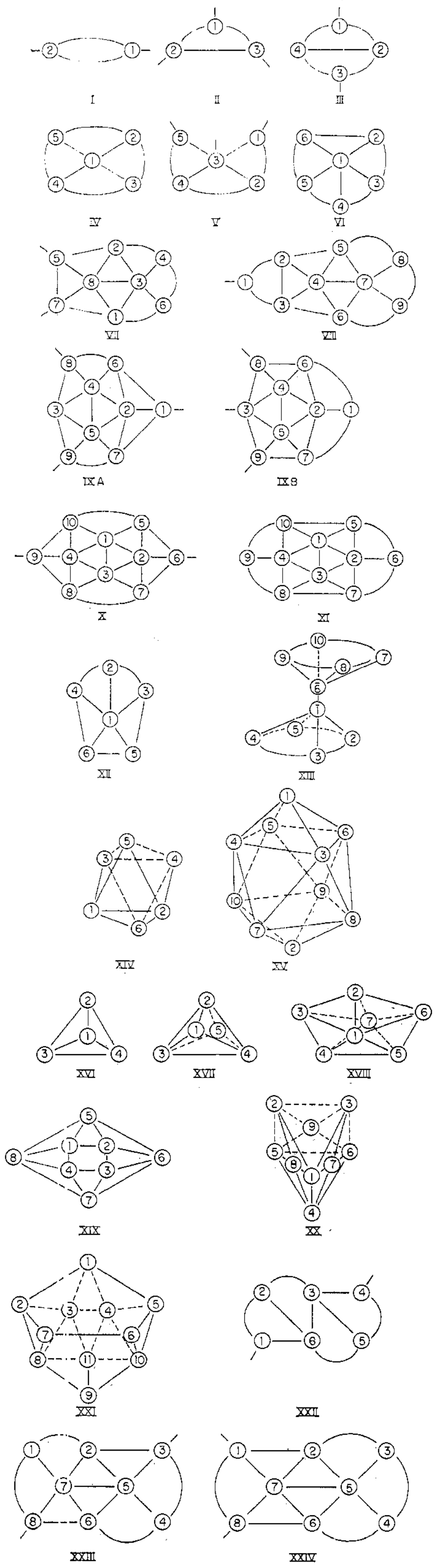

Figure 2.—Topological diagrams and numbering conventions for some known boron hydrides. ⓝ represents a BH group, ⓝ- a BH$_2$ group, and ⓝ a boron with no hydrogens attached. ⓝ⌒ⓜ indicates a B–H–B bridge, while ⓝ–ⓜ shows that borons *n* and *m* are neighbors in the topological sense of footnote 11.

two-center and 6 three-center boron framework bonds. There are 17 two-center, 12 central three-center, and 24 open three-center bonds topologically allowed. If we consider all possible three-center bonds, there are $[(17!)/(15!)(2!)] \times [(36!)/(30!)(6!)]$ or about 2.6×10^8 valence structures to test. Eliminating the open B–B–B bonds, as in the present program, reduces this number to $[(17!)/(15!)(2!)] \times [(12!)/(6!)(6!)]$ or about 1.3×10^5 possible structures. The savings generated are obvious. If one were willing to sacrifice the advantage of transferability among different computers, the speed could be increased even more by use of machine language combinatorial subprograms.

The final output of the program consists of a set of allowable valence structures, each one being specified by a list of its two-center and three-center bonds. The program also produces a population analysis, *i.e.*, charge and bond-order matrices obtained from the elementary distributions of Table I by averaging over all the valence structures obtained. Provision can also be made for the use of various weighting factors in the population analysis, as discussed below. The program, like its predecessors,[3b,16] makes no use of molecular symmetry, since independent generation of symmetry-equivalent valence structures provides an ideal check on the reliability of the search procedure. We recognize that there are difficulties in our averaging procedures arising from nonorthogonality of these valence structures.

Table I
Contributions of Boron–Hydrogen and Boron–Boron Orbitals to Population Analysis

	Electrons			B–B overlap population		
Bond type	1	2	3	2–3	1–3	1–4
1-center	2.0	...	...	...	...	...
2-center	1.0	1.0	...	1.0	...	...
3-center open	0.5	1.0	0.5	...	0.5	...
3-center central	0.667	0.667	0.667	0.667	0.667	0.667

IV. Results

The method of analysis described above was applied to a number of boron hydride molecules and ions, both known and hypothetical. Some of the results obtained are shown in Tables II and III, with the numbering conventions used given by Figures 2 and 3.

The species in Figure 2 have all been characterized

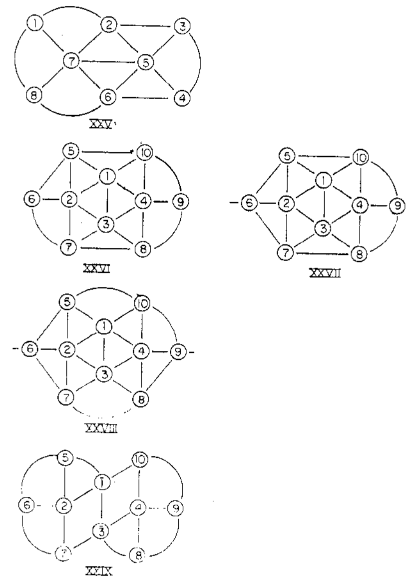

Figure 3.—Possible boron hydride topologies. Symbols are the same as those in Figure 2.

Table II
Boron Hydride Valence Structures

Molecule	Topology[a]	No. of symmetry-equiv structures	B–B bonds[b]
B_2H_6	I		
1		1	. . .
		1	
B_3H_8	II		
1		1	2–3
		1	
B_4H_{10}	III		
1		1	2–4
		1	
B_5H_9	IV		
1		4	1–2, 2–3
		4	
B_5H_{11}	V		
1		1	. . .
		1	
B_6H_{10}	VI		
1		1	1–4, 2–6
2		2	1–3, 2–6
		3	
$B_8H_{13}^-$	VII		
1		2	1–7, 2–3
2		2	1–3, 5–7
3		1	3–8, 5–7
4		2	1–7, 3–4
5		2	3–4, 5–7
6		1	1–7, 2–5
		10	
B_9H_{15}	VIII		
1		1	2–3, 4–7
2		2	2–3, 5–7
3		2	3–6, 5–7
4		2	2–5, 7–8
5		1	2–5, 3–6
6		2	2–3, 7–8
		10	
$B_9H_{14}^-$	IXA		
1		2	1–6
		2	
$B_9H_{14}^-$	IXB		
1		2	2–6
2		2	6–8
		4	
$B_{10}H_{14}$	X		
1		1	. . .
		1	
$B_{10}H_{14}^{2-}$	X		
1		4	1–2, 3–8, 6–7
2		4	1–2, 6–7, 8–9
3		2	1–3, 5–6, 8–9
4		2	1–3, 5–6, 9–10
5		4	1–5, 3–7, 8–9
6		4	1–5, 6–7, 8–9
7		4	1–5, 6–7, 9–10
		24	
$B_{10}H_{14}$	XI		
1		2	2–5, 4–10
2		2	2–7, 4–10
3		4	4–9, 5–10
4		4	2–5, 4–9
5		4	1–2, 4–10
6		4	2–3, 4–10
7		4	1–4, 7–8
		24	
$B_{10}H_{14}^{2-}$	XI		
1		1	1–3, 2–6, 4–9, 5–10, 7–8
		1	
$B_6H_8^{2-}$ ($B_4C_2H_8$)	XII	0	. . .
$B_{10}H_{16}$	XIII		
1		16	1–2, 1–3, 1–6, 6–7, 6–8
		16	
$B_6H_6^{2-}$ ($B_4C_2H_6$)	XIV		
1		8	1–2, 1–3, 2–3
2		24	1–2, 1–3, 2–4
		32	
$B_{10}H_{10}^{2-}$ ($B_8C_2H_{10}$)	XV		
1		16	1–3, 1–4, 7–8
2		8	1–3, 1–4, 2–9
3		16	1–3, 1–4, 5–9
4		16	1–3, 1–4, 8–9
5		8	1–3, 2–9, 4–10
6		8	1–3, 6–9, 4–10
		72	
B_4H_4	XVI		
1		1	. . .
		1	
$B_5H_5^{2-}$ ($B_3C_2H_5$)	XVII		
1		2	1–2, 1–3, 1–4
		2	
$B_7H_7^{2-}$ ($B_5C_2H_7$)			
1		20	1–2, 2–3, 4–5
		20	
$B_8H_8^{2-}$ ($B_6C_2H_8$)	XIX		
1		8	1–2, 2–5,5–8
		8	
$B_9H_9^{2-}$($B_7C_2H_9$)	XX		
1		12	1–7, 3–7, 2–8
2		4	1–7, 2–8, 3–9
		16	
$B_{11}H_{11}^{2-}$ ($B_9C_2H_{11}$)	XXI		
1		4	2–3, 2–8, 4–5
2		4	2–3, 4–5, 8–9
3		4	2–3, 2–8, 4–11
4		4	2–3, 4–11, 8–9
		16	
B_6H_{12}	XXII		
1		2	3–4
2		1	3–6
		3	
B_8H_{14}	XXIII		
1		2	4–5
2		1	5–7
		3	
B_8H_{14}	XXIV		
1		2	2–5
2		2	3–5
3		1	4–7
		5	
B_8H_{12}	XXV		
1		2	2–7, 4–6
2		1	2–3, 4–6
3		2	2–3, 1–7
		5	
$B_{10}H_{13}^-$	XXVI		
1		1	2–3, 4–8, 5–6
2		1	2–3, 4–10, 5–6
3		1	2–3, 5–6, 5–10
4		1	1–4, 2–5, 5–6
5		1	1–5, 3–4, 5–10
6		1	2–5, 3–4, 5–6
7		1	3–4, 5–6, 5–10
8		1	1–5, 4–9, 5–10
9		1	2–5, 4–8, 5–6
10		1	2–5, 4–9, 5–6
11		1	2–5, 4–10, 5–6
12		1	2–6, 4–8, 5–6
13		1	2–6, 5–6, 7–8
14		1	2–6, 4–10, 5–6
15		1	2–6, 5–6, 5–10
16		1	4–9, 5–6, 5–10
		16	

TABLE II (*Continued*)

Molecule	Topology[a]	No. of symmetry-equiv struc-tures	B–B bonds[b]
$B_{10}H_{13}^-$	XXVII		
1		2	4–8, 5–6
2		2	5–6, 7–8
3		2	4–10, 5–6
4		2	5–6, 5–10
		8	
$B_{10}H_{15}^-$ ($B_{10}H_{12}L_2L'$)	XXVIII		
1		1	1–3, 5–6
2		1	1–3, 6–7
3		1	1–5, 3–4
4		1	3–4, 5–6
5		1	2–3, 5–6
6		1	3–8, 6–7
7		1	3–8, 5–6
8		1	1–5, 3–7
9		1	3–7, 5–6
10		1	1–5, 6–7
		10	
$B_{10}H_{14}$	XXIX		
1		1	1–2, 2–7, 3–4, 4–10
2		2	1–2, 2–5, 3–4, 4–10
3		1	1–2, 2–5, 3–4, 4–8
4		2	2–6, 3–4, 3–7, 4–10
5		2	2–6, 2–7, 3–4, 4–10
6		2	2–6, 3–4, 3–7, 4–8
7		2	2–5, 2–6, 3–4, 4–10
8		2	2–6, 2–7, 3–4, 4–8
9		2	2–5, 2–6, 3–4, 4–8
10		2	1–10, 2–6, 2–7, 4–9
11		2	1–10, 2–5, 2–6, 4–9
12		1	2–6, 2–7, 4–9, 4–10
13		2	2–5, 2–6, 4–9, 4–10
14		1	2–5, 2–6, 4–8, 4–9
		24	

[a] See Figures 2 and 3. [b] Only the two-center bonds are given, since for the molecules listed here, the B–B–B bonds are then uniquely determined (however, see Appendix I).

experimentally and have been the subject of several theoretical studies.[5,15,17] All of them, with the exception of $B_6H_8^{2-}$, topology XII, possess one or more allowable valence structures. We have previously argued[5d] that $B_6H_8^{2-}$ (*i.e.*, $CB_5H_8^-$ or $C_2B_4H_8$) valence structures will be of the multiply bonded π-donation type. Many other topological arrangements were investigated, some of which are shown in Figure 3. In general, hypothetical topologies give rise to no allowed structures or to far fewer structures than the topologies for known hydrides with the same number of borons. Some quite plausible (but experimentally unknown) arrangements give rise to no structures at all. These include cubic B_8H_8 and $B_8H_8^{2-}$ and the icosahedral (minus one apex) $B_{11}H_{11}^{2-}$ and several other structures considered by Kettle and Tomlinson.[18]

TABLE III

THREE-CENTER POPULATION ANALYSES[a] FOR SOME BORON HYDRIDES

Molecule	Top-ology	Atom[b]	Charge	Bond[b]	Dis-tance[c]	Over-lap Popula-tion
$B_3H_8^-$	II	1	0.00	1–2	1.77	0.50
		2	−0.50	2–3	1.80	1.00
B_4H_{10}	III	1	0.00	1–2	1.84	0.50
		2	0.00	2–4	1.71	1.00
B_5H_9	IV	1	−0.67	1–2	1.69	0.83
		2	0.17	2–3	1.80	0.67
B_5H_{11}	V	1	−0.17	1–2	1.76	1.17
		2	0.33	1–3	1.87	0.67
		3	−0.33	2–3	1.72	0.67
				2,4	1.77	0.50
B_6H_{10}	VI	1	−0.33	1–2	1.80	0.78
		2	−0.28	1–3	1.75	0.67
		3	0.33	1–4	1.74	0.78
		4	0.22	2–3	1.74	0.94
				2–6	1.60	1.00
				3–4	1.79	0.72
$B_8H_{13}^-$ ($LB_8H_{11}NH_2$)[d]	VII	1	0.00	1–3	1.79	0.73
		3	−0.30	1–6	1.86	0.70
		4	0.27	1–7	1.92	0.77
		5	−0.60	1–8	1.74	0.80
		8	−0.03	3–4	1.82	0.73
				3–8	1.79	0.77
				4–6	2.00	0.83
				5–7	1.92	0.83
				5–8	1.73	0.80
B_9H_{15}	VIII	1	0.00	1–2	1.85	0.50
		2	−0.10	2–3	1.80	0.83
		4	−0.03	2–4	1.77	0.80
		5	0.00	2–5	1.96	0.77
		7	−0.30	4–5	1.77	0.80
		8	0.27	4–7	1.76	0.77
				5–7	1.83	0.73
				5–8	1.79	0.70
				7–8	1.75	0.73
				8–9	1.82	0.83
$B_9H_{14}^-$ ($B_9H_{13}L$)[e]	IXA	1	−0.67	1–2	1.74	0.67
		2	0.00	1–6	1.87	0.83
		3	0.00	2–4	1.76	0.67
		4	0.00	2–6	1.75	1.00
		6	0.00	3–4	1.76	1.33
		8	−0.17	3–8	1.87	0.67
				4–5	1.83	0.67
				4–6	1.78	0.67
				4–8	1.72	0.67
				6–8	1.85	0.50
$B_{10}H_{14}^{2-}$ ($B_{10}H_{12}L_2$)[f]	X	1	−0.25	1–2	1.76	0.78
		2	−0.06	1–3	1.84	0.72
		5	−0.04	1–5	1.78	0.74
		6	−0.61			
				2–5	1.75	0.81
				2–6	1.74	0.78
				5–6	1.86	0.81
				5–10	1.88	0.61
$B_{10}H_{14}$	XI	1	−0.08	1–2	1.79	0.76
		2	−0.28	1–3	1.71	0.78
		5	0.04	1–5	1.78	0.81
		6	0.28	2–5	1.78	0.74
				2–6	1.72	0.72
				5–6	1.77	0.78
				5–10	2.01	0.72
$B_{10}H_{10}^{2-}$	XV	1	−0.33	1–3	1.73	0.92
		3	−0.17	3–4	1.86	0.72
				3–8	1.81	0.74

[a] Averaged over all allowable structures with unit weights. [b] Only one of a set of symmetry-equivalent atoms or bonds is given. [c] Symmetry-average experimental distances (Å) taken from ref 11. [d] L attached at B7; NH_2 replaces bridge hydrogen H46. [e] L attached at B1. [f] L attached at B6 and B9.

We do not wish to suggest that the existence of many valence structures for a given topology implies the existence of a molecule with that topology or that failure to give rise to allowed structures makes a topological arrangement forbidden. Nonetheless, our three-center calculations do show a strong correlation with chemical experience and with chemical and geometrical intuition. For example, the $B_{10}H_{10}^{2-}$ ion has a strong "aromatic-like" character[17] as shown by its remarkably high diamagnetic susceptibility.[19] Since this species possesses more allowable valence structures than any other that we have investigated, we might characterize its behavior in the same resonance-structure language often applied to aromatic organic molecules. The $B_9H_{14}^-$ ion was first predicted[17] to have topology IXA, like the B_9H_{13} (CH_3CN) molecule.[20] However, a recent

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(17) See W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, for a review.

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

(19) R. Hoffmann, unpublished results, 1962.

(20) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961), especially Figure 3.

determination[21] shows that the $B_9H_{14}^-$ structure is of topology IXB, a possibility noted by Wang, Simpson, and Lipscomb[20] and suggested by the relative numbers of allowed valence structures, 2 for IXA and 4 for IXB.

Another illustration is given by the $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ structures (X and XI). The neutral molecule has been shown[22] to possess topology XI. A structure determination on $B_{10}H_{14}^{2-}$ is now in progress, but the best current guess of its structure is similar to that found in the $B_{10}H_{12}(NCCH_3)_2$ X-ray study,[23] *i.e.*, topology X. In both cases, Table II shows a 24:1 ratio of allowed structures in favor of the experimental topologies.

Hydrides with topologies XXII, XXIII, and XXIV were proposed by Lipscomb[24] from purely geometrical considerations. On the basis of the number of allowed valence structures, these molecules appear to be the most likely of those predicted by the geometrical theory. The eight-boron framework in topologies XXIII, XXIV, and XXV seems to offer an especially promising direction for synthetic chemists.[25]

Another example is $B_{10}H_{13}^-$, for which structures XXVI and XXVII have been assigned previously.[17] Another structure based upon this B_{10} unit has hydrogen atoms bridging the 5–6, the 7–8, and the 9–10 pairs of boron atoms. This structure has 8 valence forms, but has a more nearly uniform charge distribution (either +0.17 or −0.17 at each boron atom) than do the other structures. If the 16 resonance forms of XXVI are not to be weighted equally, the choice of the most stable structure is difficult for $B_{10}H_{13}^-$.

It would be extremely desirable if the topological theory could be used to generate, or at least to test, proposed intermediates in boron hydride reactions. Topology XXVIII is that proposed by Lipscomb[17] for the initial attack of C_2H_5OH on $B_{10}H_{12}L_2$ to begin the formation of $B(OC_2H_5)_3$ and $B_9H_{13}L$. The large number of valence structures suggests that XXVIII is indeed a plausible intermediate. However, no allowed structures result from a second step (attack on the B8–B9 bond) analogous to the first. We suggest, therefore, that intermediate XXVIII breaks down by a more complicated mechanism, possibly involving topological rearrangement of the boron framework. The transformation of $B_{10}H_{16}$ to $B_{10}H_{14}$ has been suggested[17] to occur by a least-motion path involving an intermediate with topology XXIX. While this intermediate does appear to be strongly resonance stabilized, the other proposed steps in the reaction pathway do not have allowed valence structures. Recent work by Hoffmann[26] has shown that non-least-motion paths are probably far more common than had previously been thought. We suggest that this reaction may occur by such a non-least-motion pathway, though the attractive intermediate XXIX may still play a role.

In Table III, we give population analyses for a number of experimentally characterized boron hydrides. The charge distributions agree rather well with those inferred experimentally or obtained from molecular orbital calculations. The calculated overlap populations correlate considerably less well with the observed bond distances. One source of error in these calculations is our use of equal weights for the different nonequivalent valence structures. This practice has been justified picturesquely, if overcautiously, by reference to "the symmetry of our ignorance."[3b] In fact, as recognized by Simpson,[16] our ignorance is not totally symmetric. We know at least that structures which require a large amount of charge separation will be less favorable than those in which no atom deviates greatly from neutrality.

An attempt by Simpson, *et al.*,[16c] to introduce weighting factors dependent upon total charge separation gave rise to no significant changes in the population analyses. We show here, in a preliminary study, that weighting factors can be found which will make reasonable changes in the populations. However, since there are no firm theoretical grounds for any *particular* choice of weights and since the results obtained are not, at this point, demonstrably superior to the unweighted results, we present only a brief discussion and a single example.

We investigated weighting factors of the form $v_i = \exp(-Q_i/a)$ and $w_i = (b + Q_i)^{-1}$ where $Q_i = \Sigma_{j=1}{}^{p}(q_i{}^{j})^2$ and $q_i{}^j$ denotes the net charge (in fractions of an electron) on boron atom j in the ith valence structure. For example, the weighted charge, $\bar{q}^j$, is then given, using exponential weights, by $\bar{q}^j = \Sigma_i v_i q_i{}^j / \Sigma v_i$. The parameters a and b were varied to see how drastic a weighting scheme was necessary to reorder charges and overlap populations. Ultimately a and b should be expressible as functions of the number of borons and the total charges. For the exponential case, the limit $a = \infty$ gives equal weights, while a approaching zero picks out the structure(s) with least charge separation. For the reciprocal weights, large values of b tend toward equal weights, while $b = 0$ gives a Q_i-dependent weighting scheme in which structures with all atoms neutral are selected, if such exist.

We find that the order of atomic charges is almost totally insensitive to the weighting scheme or lack of one. However, the order of overlap populations can be changed significantly by weights with low values of a or b. Surprisingly, the reciprocal weights w_i appear to be somewhat more useful than the exponential weights. Table IV shows for $B_{10}H_{14}$ (XI) the charges and overlap populations obtained from equal weights, from the

TABLE IV

WEIGHTED POPULATION ANALYSIS FOR $B_{10}H_{14}$

		Weights		
		Equal	v_i ($a \rightarrow 0$)	w_i ($b = 0.01$)
Atom		Weighted charges		
1		−0.08	0.00	−0.07
2		−0.28	−0.17	−0.27
5		0.04	0.00	0.04
6		0.28	0.17	0.28
Bond	Distance,[a] Å	Weighted overlap populations		
1–2	1.78	0.764	0.833	0.768
1–3	1.77	0.778	0.833	0.768
1–5	1.76	0.806	0.833	0.814
2–5	1.79	0.736	0.667	0.729
2–6	1.72	0.722	0.833	0.740
5–6	1.78	0.778	0.667	0.760
5–10	1.97	0.722	0.833	0.734

[a] A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8,** 464 (1969).

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(21) N. N. Greenwood, H. J. Gysling, and J. A. McGinnety, *Chem. Commun.*, 505 (1970).

(22) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, **3**, 436 (1950).

(23) J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

(24) W. N. Lipscomb, *Inorg. Chem.*, **3**, 1683 (1964).

(25) See, *e.g.*, J. Dobson and R. Schaeffer, *ibid.*, **7**, 402 (1968).

(26) R. Hoffmann, to be submitted for publication.

minimum Q_i structures (v_i with $a \rightarrow 0$), and from w_i weights with $b = 0.1$.

V. Discussion

The methods described here are not by any means limited to boron hydrides. The computer-assisted design of complex organic syntheses investigated by Corey and Wipke[27] draws heavily on topological techniques. When combined with geometrical considerations[24] and chemical insights, topological methods can be extremely powerful in the prediction of new molecules and of stable intermediates. Extension of the theory to the more general class of electron-deficient compounds should be straightforward. The interesting case in which more than three centers participate in a single semilocalized orbital, for example, in certain intermetallic compounds, will be more difficult to handle computationally. Nonetheless, the principles remain the same: conservation of electrons and orbitals and the requirement that all pairs of neighbors participate in at least one common bond.

We have limited our calculations here to molecules with fewer than 12 borons, but we believe that no new principles would be illustrated by the inclusion of calculations on larger structures. Calculations on larger structures are still a strain on current research budgets, even at this level of approximation. We estimate that a topological study of $B_{20}H_{16}$[28] would require about 70 min on the IBM 360/65 with the present program, though we hope to lower this considerably by further programming modifications. Much information about larger boron hydrides may be gleaned from symmetry considerations applied to combinations of smaller ones, as in the characterization[3b] of $B_{18}H_{22}$ as two symmetry-related decaborane units. It is well known[17] that most, but not all,[16b,28] known stable boron hydrides possess at least a mirror plane and often considerably higher symmetry. A more general topological approach to the study of the boron hydrides would include a systematic, preferably computerized method for generating trial topologies. This question, which becomes crucial for the study of large molecules, is under investigation. One must always bear in mind, however, that purely topological arguments which disregard steric and other important factors are likely to lead to erroneous conclusions.

Finally, we wish to take note of the peculiar cyclic path which the theoretical study of boron hydride structures has taken. The first qualitative topological calculations[2,7] inspired semiempirical quantitative studies,[3b] which in turn gave rise to more exact, nonempirical[4] and finally SCF[5] calculations. The localized orbitals from the SCF wave functions have now suggested a refinement on the topological approach. Perhaps the cycle is starting again and a new set of more accurate and more revealing studies of the boron hydrides will spring from these modest beginnings.

Acknowledgments.—We thank Dr. P. G. Simpson for providing a listing of his topological program for comparison. This work was supported in part by the Office of Naval Research.

Appendix I

Hoffmann and Lipscomb[3b] have stated that specifying the two-center bonds (and open three-center bonds if allowed) in a molecule uniquely determines the position of the central three-center bonds and hence is sufficient to specify the valence structure of the molecule. This conjecture has never, to our knowledge, been challenged. We present here a simple, though hypothetical, counterexample.

Consider the ion $B_5H_{10}^+$, derived by protonation of the apex boron of the well-known species B_5H_9. Such an ion is by no means unlikely, since calculations[5b] show the apex boron to be considerably more negative than the basal borons. The topological diagram and numbering convention are given in Figure 4a. After forming the required B–H and B–H–B bonds, we are left with four electrons and six orbitals for the boron framework. Both simple observation and our computer program show that the acceptable structures are those shown in Figure 4b and c, thus disproving the Hoffmann–Lipscomb conjecture.

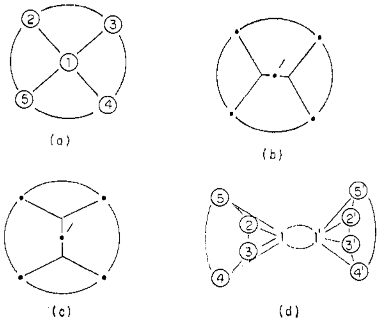

Figure 4.—$B_5H_{10}^+$ valence structures and a dimer.

We note that none of the other species studied gave such nonunique arrangements of three-center bonds. However, one can generate any number of such species by appropriately linking together $B_5H_{10}^+$ units. For example, Figure 4 shows a $B_{10}H_{20}^{2+}$ ion formed by linking two $B_5H_{16}^+$ units by a double hydrogen bridge. We note the similarity to the diborane structure and suggest the possibility of obtaining such an adduct from a B_2H_6–B_5H_9 mixture in a highly acid medium at low temperatures. An analogous B_4H_{10} type adduct may be envisioned by inserting two BH groups with a single bond between then in place of the hydrogens bridging borons 1 and 1′ in Figure 4d.

Appendix II

The closed polyhedral boranes, $B_nH_n^l$, have long been of great theoretical and experimental interest. In particular there has been much speculation about the source of the stability of the doubly negative ions of this series. We present in this section a simple topological argument as to the possible stable charge states for species.

The neutral molecules B_nH_n ($n > 4$) consisting of only B–H subunits have $2n$ electrons and $3n$ orbitals available for boron framework bonding. Thus their three-center valence structures must have n three-center and no two-center bonds. If we add two electrons to form $B_nH_n^{2-}$, we find that valence structures must have $n - 2$ three-center and 3 two-center bonds. If two electrons are removed to form $B_nH_n^{2+}$, we have $n - 1$ electron pairs and $3n$ orbitals. Thus, no suitable valence structures can be written for $B_nH_n^{2+}$ or for any

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(27) E. J. Corey and W. T. Wipke, *Science*, **166**, 178 (1969).

(28) L. B. Friedman, R. E. Cook, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 6862 (1968).

other B_nH_n cations employing only two- and three-center bonding. Since $3(n - 1) < 3n$, there are not enough electrons. Four- and higher-center bonds are required in order to use all available orbitals.

We may view the stability of the 2− ions as arising from a compromise between the destabilization caused by charge separation (which probably rules out 4− and 6− ions) and the added stabilization offered by the greater number of allowed valence structures. While the number of allowed valence structures mut be determined for each species by testing all possible structures for compliance with the topological rules, it seems likely that a greater number of *possible* structures will give rise to more *allowed* structures. For polyhedra in which each boron has three neighbors (*e.g.*, tetrahedron, trigonal bipyramid, octahedron) one can show that there are $3n - 6$ possible two-center and $3n - 8$ possible central three-center bonds. Thus B_nH_n will have $(3n - 8)!/[n!(2n - 8)!]$ possible structures arising from the different ways of choosing n objects from $3n - 8$. $B_nH_n^{2-}$ will have $[(3n - 8)!(3n - 6)!]/[(n - 2)!(2n - 6)!(3n - 9)!3!]$ where the additional terms arise from the possibility of choosing the two-center bonds in different ways. The ratio of the number of possible valence structures for $B_nH_n^{2-}$ to that for B_nH_n is thus $[(3n - 8)(3n - 7)(3n - 6)(n)\cdot(n - 1)]/[6(2n - 7)(2n - 6)]$, which increases from a minimum value of 120 at $n = 4$ and approaches $9n^3/8$ as n approaches infinity. Thus the 2− ions offer many more possible valence structures and, presumably, more allowable ones. Similar arguments may be given for polyhedra in which boron atoms have other numbers of nearest neighbors. Of course, the problem of symmetry degeneracy can spoil a resonance argument, and it does for tetrahedral B_4H_4, just as in organic chemistry it does for cyclobutadiene.

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The Crystal Structure and Molecular Geometry of a Bridged Bis-Dicarbollide Complex of Cobalt, $[(B_9C_2H_{10})_2S_2CH]Co^{III}$

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The novel substitution product $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ has previously been prepared by Francis and Hawthorne from the reaction of $K^+[(B_9C_2H_{11})_2Co^{III}]^-$ with carbon disulfide in the presence of $AlCl_3$; it crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4, no. 19) with $a = 10.923\ (10)$, $b = 13.173\ (10)$, and $c = 12.869\ (10)$ Å; $\rho_{obsd} = 1.421\ (6)$ and $\rho_{calcd} = 1.431$ g cm^{-3} for $Z = 4$. X-Ray diffraction data to $\sin\theta = 0.42$ (Mo Kα radiation) were collected by counter methods, the structure being solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogen) have been located, the final discrepancy index being $R_F = 7.88\%$ for the 1558 independent nonzero reflections. The crystal consists of molecular units of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$, separated by normal van der Waals distances. The cobalt atom is "sandwiched" between two mutually staggered 1,2-dicarbollide ligands and is linked symmetrically to the five atoms of each basal pentagonal face (Co–B = 2.017–2.128 Å, Co–C = 2.037–2.056 Å). The two icosahedra which share the cobalt(III) atom as a common apex are further linked *via* a S–CH–S bridge which spans B(8) and B(8′), the central boron atoms of the two metal-bonded B_3C_2 pentagonal faces.

Introduction

The substitution chemistry of bis-(1,2-dicarbollide) metal complexes is a newly developing field in which little structural work has been done.[3,4] Francis and Hawthorne[5] have prepared $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ by the reaction of $K^+[(B_9C_2H_{11})_2Co^{III}]^-$ with carbon disulfide in the presence of aluminum trichloride. Since this new product was believed to possess some unique structural features, it has been subjected to an X-ray diffraction study. Preliminary results have been reported previously;[6] complete details are given below.

Unit Cell and Space Group

Crystals of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ were supplied by Professor M. F. Hawthorne of the University of California, Los Angeles, Calif. They crystallize as bright orange parallelepipeds which are extended in the b direction. Optical examination and preliminary X-ray diffraction photographs indicated that the crystals were orthorhombic. A study of $hk0$, $h0l$ Weissenberg and $0\text{-}1kl$, $hk0\text{-}1$, $h0l$ precession photographs revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$; these are consistent only with the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4, no. 19).

Unit cell parameters, obtained from calibrated ($a_{NaCl} = 5.640$ Å) precession photographs taken with Mo Kα radiation (λ 0.7107 Å) at 24 ± 2°, are $a = 10.923\ (10)$, $b = 13.173\ (10)$, and $c = 12.869\ (10)$ Å. The unit cell volume is 1851.7 Å^3. The observed density of 1.421 (6) g cm^{-3}, by flotation in aqueous zinc iodide, is in excellent agreement with the value of 1.431 g cm^{-3} calculated for $M = 399.06$ and $Z = 4$.

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