gested by the rearrangements and by the great simplicity of molecular spectra found in these complex polyhedral molecular species.

Acknowledgment.—We wish to thank the Office of Naval Research, the U. S. Army Research Office (Durham), and the Advanced Research Projects Agency for support of this research. Also, we thank G. S. Pawley for discussions and for use of the rigid body least-squares refinement program which reduces thermal parameters to 15 per molecule, and which is a special case of a theory by V. Schomaker which includes, in addition, the six additional screw-rotational tensor components omitted in these refinements.

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Geometrical Theory of Boron Hydrides

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Received August 3, 1964

Based upon the assumptions that in some probable new boron hydrides the geometrical and bonding environments of B atoms will be similar to those in known hydrides, that all stable boron hydride molecules encounter external H···H contacts only upon collision with other molecules of the same or similar type, and finally that all intramolecular H···H contacts are reasonable ($\geqslant$ about 2 Å.) it is shown here that only a very limited number of predicted new boron hydrides based upon a single icosahedral fragment can be expected. Geometrical structural predictions are given for these possible new boron hydrides.

The three-center resonance and molecular orbital theories[1] of boron hydrides take the steric properties of boron hydride structures into account in only a general and not very restrictive way. Accordingly, it seems appropriate to give specific attention to the problems of intramolecular and intermolecular steric requirements, within the framework of these valence theories, in the hope that only a limited number of predictions would result. This paper represents a first theory of this type and is restricted to neutral single icosahedral fragments for the boron arrangements. We have therefore specifically excluded boron hydride ions, fragments, or polyhedra joined by BBB or BB[2] bonds (*e.g.*, $B_{10}H_{16}$), by single or double hydrogen bridges[3] (*e.g.*, $B_{20}H_{19}^-$), by the sharing of two B atoms[1] (*e.g.*, $B_{18}H_{22}$ and *i*-$B_{18}H_{22}$) or of four B atoms (*e.g.*, $B_{20}H_{16}$), or fragments obtained from possible degradation of structures in such a way that these joinings are preserved. Equivalent theories of these additional kinds of molecules and ions can easily be derived by similar methods.

Accordingly, the assumptions and procedures are as follows. (1) Construct models of the known boranes, ions, and ligand derivatives from balls precisely drilled according to the internuclear straight lines between all nearest neighboring atoms. These angles have been listed[1,4] for all of the known compounds, including[5] B_8H_{12}. (2) Choose from these models all different types of balls (Table I), but, for the single icosahedral frameworks considered here, limit the choices to B atoms having at least one terminal H atom (H_t). (3) Construct all possible models with the use of B–B distances of about 1.8 Å., B–H_t distances of 1.2 Å., and B–H_b (bridge) distances of about 1.4 Å., on a scale of 1 Å. = 10 cm. (4) Reject all models which have intramolecular H···H contacts of less than about 2.0 Å. where these H atoms

TABLE I

NEAREST COORDINATION ENVIRONMENTS OF
B ATOMS OF ALL TYPES

B	H_t[a]	H_b[a]	Example
2	2	1	$B_3H_8^-$, the symmetry related B atoms
2	2	2	$B_3H_8^-$, the unique B
3	1	1	B_6H_{10}, nonapical atoms joined with the short bond
3	1	2	B_4H_{10}, the inner pair
3	2	0	$C_2H_5NH_2B_8H_{12}NHC_2H_5$, B joined to C_2H_5-NH_2
3	2	1	$B_9H_{13}NCCH_3$, the BH_2 groups
4	1	0	$B_9H_{13}NCCH_3$, the BH on the symmetry plane
4	1	1	B_9H_{15}, adjacent to the BH_2 group
4	2	0	B_5H_{11}, apex
5	1	0	B_6H_{10}, apex
(5	0	0)[b]	$B_{10}H_{16}$, atoms joining the B_5H_8 units
(5	0	2)[b]	*i*-$B_{18}H_{22}$, on the molecular twofold axis
(6	0	0)[b]	B (elementary), not yet found in the hydrides
(6	0	1)[b]	$B_{18}H_{22}$, nearest molecular center of symmetry
(7	0	0)[b]	*i*-$B_{18}H_{22}$, on the molecular twofold axis

[a] The subscripts t and b refer to terminal and bridge H atoms, respectively. [b] Atoms of types listed in parentheses are required for structure types not considered in this paper, *e.g.*, structures based upon polyhedra or fragments joined by boron–boron bonds, by one or more bridge H atoms, or by common B atoms.

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(1) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, p. 227 ff.

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

(4) R. D. Dobrott, L. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964); see footnote 3.

(5) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964); *Inorg. Chem.*, **3**, 1659 (1964).

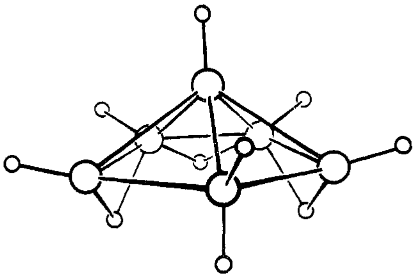

Fig. 1.—A proposed B_6H_{10} structure based upon an icosahedral cap of B atoms. This structure may be an intermediate in H atom rearrangement of known B_6H_{10}.

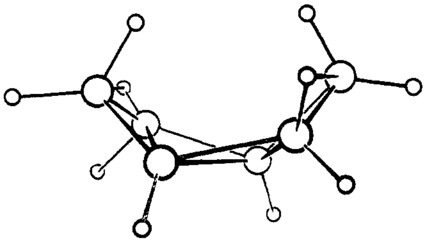

Fig. 2.—A very open B_6H_{10} structure, which may be subject to H atom attack at exposed B atoms.

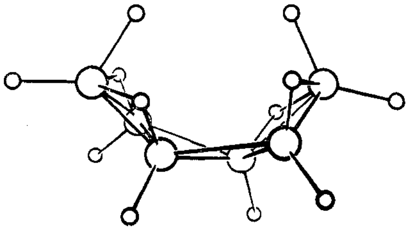

Fig. 3.—A proposed structure for B_6H_{12} in which outer parts of the molecule resemble arrangements in B_4H_{10} and B_9H_{15}.

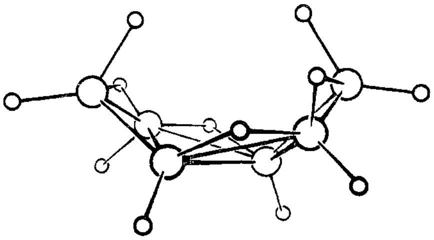

Fig. 4.—A proposed structure for B_6H_{12}.

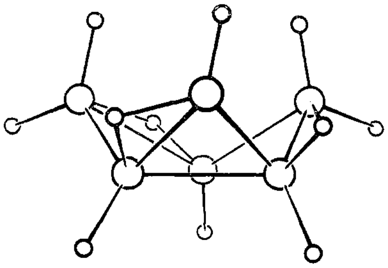

Fig. 5.—A B_6H_{12} possibility, but less preferred than the structures of Fig. 3 and 4.

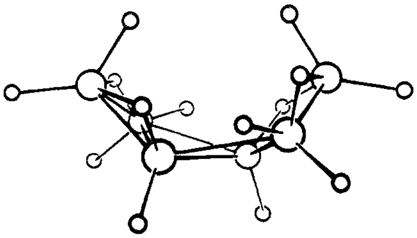

Fig. 6.—A proposed B_6H_{14} structure, which may have some crowding of H atoms.

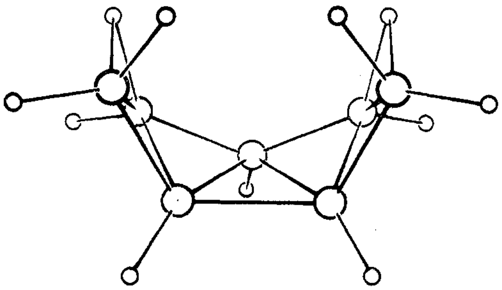

Fig. 7.—A B_7H_{11} proposal, which has somewhat exposed B atoms.

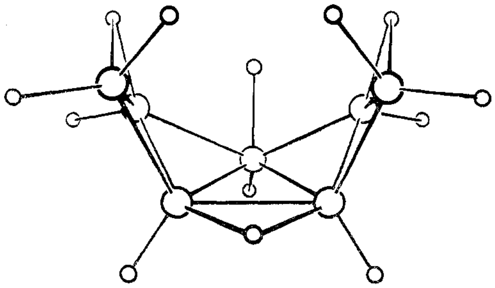

Fig. 8.—Predicted B_7H_{13} structure.

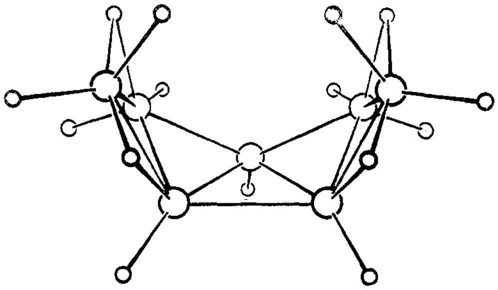

Fig. 9.—Predicted B_7H_{15} structure.

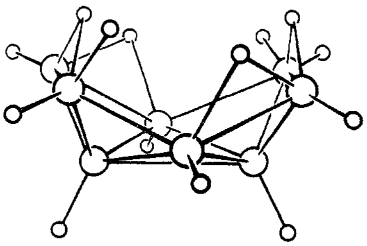

Fig. 10.—A proposed B_8H_{14} structure, which shows slight crowding of H atoms.

are on different B atoms. (5) Reject all models which expose a B atom to H atoms of a different molecule upon collision: all intermolecular contacts are therefore to be H · · · H upon collision, as they are in all of the crystalline solids. (6) Finally, reject all molecular structures not satisfying the three-center resonance bond theory,[1] which has been exhaustively searched for compact icosahedral fragments B_n for $n \leqslant 7$[6] with the aid of a program for the IBM 7094 written by R. Hoffmann.

(6) When the computing budgets allowed in chemistry research grants become comparable with the problems that can now be solved, we shall be able to remove this limitation.

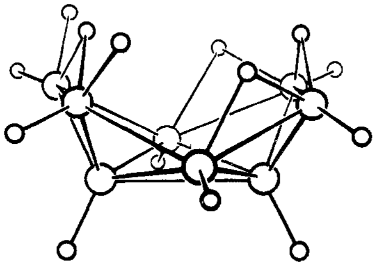

Fig. 11.—A less probable B_8H_{14} structure, which does indicate some H atom crowding.

The results are summarized in Table II. Only those possible hydrides based upon a single icosahedral fragment have been considered, and the hydrides of known structure have been omitted. The existence of B_8H_{12} was strongly indicated by this theory before this compound had been found, but the question of predicting its symmetry as C_s, C_2, or C_{2v} had not previously been settled by molecular orbital calculations,[5] which favor the observed C_s symmetry.

Table II

Predicted Hydrides

Figure	Molecule	Symmetry	Remarks
1	B_6H_{10}	C_s	Rearrange[3] to known B_6H_{10}?
2	B_6H_{10}	C_2	B atoms exposed to H atom attack
3	B_6H_{12}	C_2	Predicted. Outer parts like B_4H_{10}
4	B_6H_{12}	C_2	Predicted
5	B_6H_{12}	C_3	B atoms somewhat exposed
6	B_6H_{14}	C_2	H atoms somewhat crowded
7	B_7H_{11}	C_s	B atoms exposed
8	B_7H_{13}	C_s	Predicted
9	B_7H_{15}	C_s	Predicted
10	B_8H_{14}	C_2	Predicted? Slight H atom crowding
11	B_8H_{14}	C_s	More H atom crowding than in C_2 model
12	B_9H_{13}	C_s	Predicted in absence of ligand donors

The H atom arrangement in the B_6H_{10} structure (Fig. 1) is distinct, but not greatly different from that in the known B_6H_{10} structure; hence this hypothetical structure may merely be a low energy intermediate in an intramolecular rearrangement,[1] possibly solvent promoted, which may be required to yield the observed apparent equivalence[1] of the nonapical B atoms in the ^{11}B nuclear magnetic resonance spectrum. No separate existence is therefore expected for this B_6H_{10} structure. A second B_6H_{10} structure (Fig. 2) seems far too open to attack by H atoms of BH_3 at exposed B atoms, but this hydride, and similarly open hydrides further down the list, may be more stable if purified in low-temperature fractionating systems.

All three of the B_6H_{12} structures (Fig. 3, 4, and 5) have been mentioned earlier.[4] The structure shown in Fig. 3 is that most closely related to the arrangements in known hydrides in general, and in B_4H_{10} in particular where there are also BH_2 groups joined to the rest of the molecule by two bridge H atoms. B_6H_{12} is a known compound,[7] but its structure has not yet been determined.

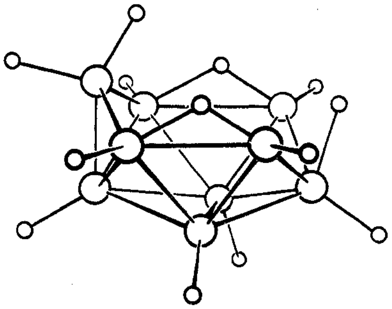

Fig. 12.—Predicted B_9H_{13} structure.

Of the B_7 hydrides, the B_7H_{11} structure (Fig. 7) seems too open to attack by H atoms of BH_3 at exposed B atoms. Both B_7H_{13} (Fig. 8) and B_7H_{15} (Fig. 9) satisfy the steric and hydrogen-covering properties, and hence are predicted. The boron arrangements for these B_7 hydrides are not as compact as the B_7 geometry obtained by adding a B atom across a B–B contact of the known B_6H_{10} structure, but no satisfactory boron hydrides can yet be predicted for this B arrangement. Two mass spectroscopic studies[8,9] suggest the existence of B_7 hydrides.

The B_8H_{14} of C_2 symmetry (Fig. 10) seems more plausible than that of C_s symmetry (Fig. 11), but both can be constructed from known bonding arrangements about B.

Finally, B_9H_{13} (Fig. 12) based upon the boron arrangement of $B_9H_{13}NCCH_3$[1] is a very satisfactory structure, and surely this molecule should be sought. The thermal stability of $B_9H_{13}NCCH_3$ suggests, however, that ligand addition and accompanying H atom rearrangement may occur readily, and therefore the existence of B_9H_{13} may require an environment quite free of electron-donating ligands.

In summary, then, we predict two different structures for B_6H_{12} of which the one having BH_2 groups linked to the remainder of the molecule by two bridge H atoms is preferred. The barrier for transformation between these two structures may be small enough to render the second structure unstable. Also we predict B_9H_{13}, B_7H_{13}, B_7H_{15}, and probably B_6H_{14} and B_8H_{14}. This theory, which is primarily geometrical and based upon the presently known compounds, yields a smaller number of predictions than do the theories based exclusively upon either resonating three-center bonds or molecular orbitals.

Acknowledgment.—It is a pleasure to acknowledge discussions of the three-center bond resonance theory with Roald Hoffmann, and to record support of this research by the Office of Naval Research and the U. S. Army Research Office (Durham).

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