

Boron Hydrides: LCAO-MO and Resonance Studies

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The results of an LCAO-MO calculation for the boron hydrides and hydride ions B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{11} , B_6H_{10} , B_7H_{13} , $B_{10}H_{14}$, $B_{10}H_{16}$, BH_4^- , $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{10}^{-2}$, $B_{10}H_{14}^{-2}$, $B_{12}H_{12}^{-2}$ are reported. Charge distributions and overlap populations are calculated from the wavefunctions for real distances and for idealized molecules with all distances equal. The three-center bond theory is extended to incorporate unsymmetric equivalent structures with concomitant improvement in charge distributions. These are compared with the presumably better LCAO-MO charges. The valence structure of a new boron hydride, $B_{18}H_{22}$, is discussed.

WE present in this paper the results of an LCAO-MO calculation on those boron hydrides and boron hydride ions whose structures or analogues have been definitely established by x-ray diffraction, electron diffraction or spectroscopic methods. Fourteen molecular species qualify: B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{11} , B_6H_{10} , B_7H_{13} , $B_{10}H_{14}$, $B_{10}H_{16}$, BH_4^- , $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{10}^{-2}$, $B_{10}H_{14}^{-2}$, $B_{12}H_{12}^{-2}$. Energy levels and wavefunctions have been computed and, from the latter, charge distributions and overlap populations have also been calculated. Before embarking on a discussion of computational details and results, we wish to make some remarks concerning the three-center bond theory for the boron hydrides.¹

EQUIVALENT AND RESONANCE STRUCTURES FOR THE BORON HYDRIDES

The three-center bond formalism for describing the valence structures of the boron hydrides is only eight years old.² Its youth has not precluded the development of misleading ideas and bad habits regarding the capabilities of the theory, primarily based on over-literal interpretations of the little graphs which we, in our present state of less than blissful ignorance, draw to give an inkling of the filled orbital nature and the electron distribution in these molecules. The prime example is the case of decaborane. The original structure presented (structure 1 of Table VI) has single

bonds linking positions 2 and 6, and 4 and 9, three-center bonds connecting other borons. Is the 2-6 or 4-9 bond weaker or stronger than any other connection in the molecule? The original structure also gave a charge distribution whose primary disturbing feature was that borons 6 and 9 came out nonpositive, in contradiction to the considerable evidence for the predominance of nucleophilic attack at these positions. How is this to be explained?

We would like here to answer these rhetorical questions and couple them with some warnings. Our contention is that a more realistic charge distribution and perhaps bond-order gradation may be brought about by consideration of *all* of the equivalent and resonance structures of a boron hydride, not only the most symmetric ones. An unstated procedure of the original three-center bond theory was that only structures satisfying the molecular symmetry should be considered. The analogy may be drawn to the singling out of Kekulé structures in the simplified valence-bond approach to aromatics. In principle there is no objection to structures of lower symmetry, which when coupled as several resonance forms, yield the full molecular symmetry in the population analysis. This problem was already clear from the failure to write a three-center structure of C_{4v} symmetry for B_5H_9 ; one instead had to compromise on a pair of C_{2v} resonance hybrids.

We would like, at this point, to delineate the distinction between resonance and equivalent structures. The former, as for B_3H_9 , are a set of symmetry equivalent structures which when considered as a group, have the molecular symmetry. The latter, as the two usual

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¹ W. N. Lipscomb, in *Advances in Inorg. Chem. Radiochem.* 1, 117 (1959) and references therein.² W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.* 22, 989 (1954).

structures drawn for B_nH_m , are distinct ways of relative arrangements of single bonds and three-center bonds in the boron framework. While symmetry demands that all the resonance structures of a given equivalent form enter the wavefunction or the population analysis with equal coefficients, there are no such symmetry requirements on different equivalent forms. The fact that we will weigh them equally in the subsequent discussion only indicates the symmetry of our ignorance.

The problem, then, is to find *all* the equivalent and resonance structures of a molecule. Our experience in this matter has shown that the human mind is both a fallible and extremely efficient mechanism. The latter point has become clear recently as we have attempted to program that most efficient and most unimaginative of man's tools, the digital computer, to find all the structures for us. The problem is one of combinatorics and of logic, and we have been surprised to find that human logic has so far been very efficient. Unfortunately the program has not yet yielded results. On the other hand, we are continuing with its development, since the computer does well in combinatorial problems, in exhausting all the possibilities. We have often thought that we had all the equivalent structures, only to find a week, or a year, later that we had missed some very obvious ones. The listing of boron hydride structures which we present is to the best of our present knowledge complete. This does not mean that it is absolutely complete. The saving grace here is that once we have written down most of the structures, the discovery of the few we had omitted does not affect greatly the ordering in the population analysis. The latter stabilizes very quickly.^{2a}

Figure 1 shows some of the boron hydride frameworks. The various structures we have derived for the neutral boron hydrides are listed in Table I. Column three of Table I contains the number of resonance forms belonging to the particular equivalent structure. Only one of the resonance forms is described; the others may be generated by applying the symmetry opera-

^{2a} Note added in proof: The computer program mentioned has been induced to produce results. The structures listed in Table I now represent all possible reasonable three-center bond patterns. We have excluded those in which the same two borons are bonded by both a central three-center bond and either an open three-center or normal single bond. We have also excluded those patterns in which borons are bonded by either a single bond or open three-center bond and either another open three-center bond or hydrogen bridge. The initial human effort produced 26 out of 30 structures for B_9H_{15} , 109 out of 111 structures for $B_{10}H_{14}$. For $B_9H_{14}^-$ there are altogether three structures with the following charge distribution:

1,3	0.00	5,9	-0.17
2	-0.11	6,8	+0.11
4	0.00	7	-0.78.

For $B_{10}H_{14}^{-2}$ there are altogether 87 structures with the charge distribution

1,2	-0.27	5,7,8,10	-0.01
3,4	-0.10	6,9	-0.62.

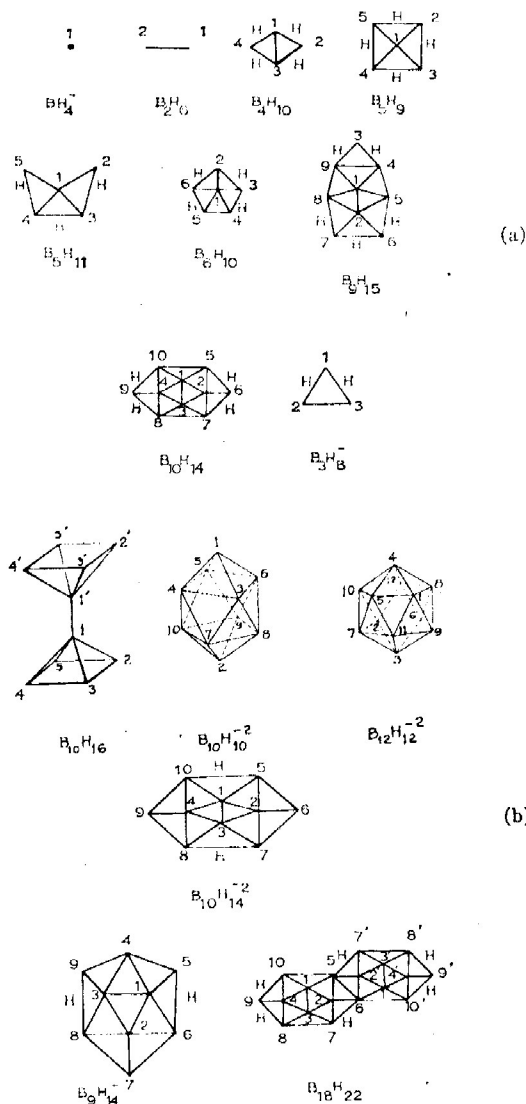


FIG. 1. Numbering convention for the boron hydrides.

tions of Column 2 to the listed form. In order to simplify the compilation we give only the position of single bonds and open three-center bonds. This procedure is sufficient since the central three-center bonds can be filled in uniquely in order to complete the particular valence pattern of the molecule. B_2H_6 and B_4H_{10} allow only one structure each, and are therefore absent from the listing.

These structures contain some in which two open three-center bonds cross and a single bond originates at the crossing. Such structures, though not explicitly barred, were not considered in the first three-center bond treatments, because the necessary hybridization at the central boron seemed difficult to achieve. Although less favorable, these structures are not impos-

distributions obtained with all three-center bond structures, we now turn to the LCAO-MO calculations.

COMPUTATION

A computer program described previously^{3,6} has been extended to calculate the energy levels and wavefunctions of the known boron hydrides and borohydride ions. The input parameters consist of the Cartesian coordinates of N arbitrarily situated boron atoms and M hydrogens ($4N+M \leq 68$, but this limitation is an artificial one imposed by the size of the computer memory, and may be easily removed), boron $2s$ and $2p$ and hydrogen $1s$ Coulomb integrals, and the proportionality constant K , in the relation $\beta_{rs} = K S_{rs}$, where S is the overlap between Slater orbitals and K is taken equal for all interactions. The set of equations $\sum_s (H_{rs} - ES_{rs}) C_s = 0$ is solved with all interactions or overlaps included. The program also performs a Mulliken population analysis on the resulting molecular orbitals, calculating overlap populations and gross atomic populations (charges). The boron Coulomb integrals were rather arbitrarily set equal to the corresponding valence state ionization potentials: $\alpha(2s) =$

-15.36 eV, $\alpha(2p) = -8.63$ eV. The value of K was set equal to -21 eV throughout, primarily to compare with calculations carried out with the same value by Moore *et al.*⁷

The input coordinates for the known boron hydrides were taken from the best x-ray or electron-diffraction parameters⁸; in some cases ($B_{10}H_{14}$, B_9H_{16} , $B_{10}H_{12}^{2-}$, $B_{12}H_{12}^{2-}$) these were adjusted to yield the apparent symmetry planes; in the others the original parameters were retained and the symmetrization, when appropriate, applied to the results of the population analysis. For B_6H_9 , considerations of consistency led us to use the x-ray determined distances rather than the presumably more accurate microwave values. The ions $B_{10}H_{14}^{2-}$ and $B_9H_{14}^-$ were included even though the structure determinations have been performed only on their acetonitrile analogs, $B_{10}H_{12}(NCCH_3)_2$ and $B_9H_{13}NCCH_3$. The substituted hydrogens were replaced in these molecules at a distance of 1.21 Å from the substituted boron, in the direction of the acetonitrile N, the latter direction determined in the corresponding x-ray study. The framework projections and the labeling convention used in this paper are given in Fig. 1.

In the first calculation on B_2H_6 the Coulomb integral for all hydrogens was set equal to -13.61 eV. The resulting charge distribution was

B	+0.233,
H _t	-0.156,
H _b	+0.080.

These charges are in disagreement with the nonempirical *SCF* calculation of Yamazaki,⁹ who obtains

B	+0.22,
H _t	+0.01,
H _b	-0.24.

Molecule	All structures	"Good" structures*	Symmetric structures	Most symmetric
$B_{10}H_{14}$	111	81	9	1
1, 3	-0.03	-0.07	-0.11	0
2, 4	-0.46	-0.36	-0.30	-0.67
6, 9	+0.29	+0.29	+0.22	0
5, 7, 8, 10	+0.10	+0.07	+0.09	+0.33
B_9H_{16}	30	25	3	
1	-0.09	-0.09	-0.22	
2	-0.50	-0.45	-0.33	
3	0	0	0	
4, 9	-0.10	-0.09	-0.17	
5, 8	+0.09	+0.06	+0.11	
6, 7	+0.30	+0.31	+0.33	
B_6H_{10}	12	9	1	
1	-0.72	-0.63	-0.33	
2	+0.36	+0.37	0	
3, 6	+0.35	+0.30	+0.33	
4, 5	-0.17	-0.17	-0.17	
B_5H_{11}	3	2		
1	-0.67	-0.50		
2, 5	-0.06	-0.08		
3, 4	+0.39	+0.33		
B_4H_9	6			2
1	-0.78			-1.00
2, 3, 4, 5	+0.20			+0.25
$B_{10}H_{16}$	84			
1, 1'	-0.70			
2'-5, 2'-5'	+0.18			

* Structures with 2 three-center bonds crossing eliminated.

⁶ R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 3489 (1962).

⁷ E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **35**, 1329 (1961); **37**, 675 (1962).

⁸ B_2H_6 : K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.* **73**, 1482 (1951). B_4H_{10} , B_5H_{11} , $B_{10}H_{14}$: E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.* **27**, 209 (1957) and references therein. B_6H_{12} : W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.* **5**, 260 (1952). B_6H_{10} : F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **28**, 56 (1958). B_9H_{13} : Refined parameters were kindly communicated to us by P. G. Simpson. See P. G. Simpson and W. N. Lipscomb, *ibid.* **35**, 1340 (1961). $B_{10}H_{16}$: The distances given in R. Grimes, F. E. Wang, R. Lewin and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.* **47**, 996 (1961) are very rough and H atoms were not located. The molecule used in this calculation was simply constructed from two pyramids of B_5H_5 structure, 1.74 Å apart. BH_4^- : P. J. Ford and R. E. Richards, *Discussions Faraday Soc.* **19**, 230 (1955). $B_3H_8^-$: C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.* **82**, 5758 (1960). $B_3H_4^-$: B_9H_{13} (CH_3CN) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.* **35**, 1335 (1961). There are some errors in Table III of this reference. x, y, z for $H_{6,5',8,8'}$ should be replaced by $1-x, 1-y, 1-z$; indices 6 and 6' should be switched with 8 and 8' for hydrogens. Primed and unprimed atoms in Fig. 2 must also be interchanged. $B_{10}H_{12}^{2-}$: $B_{10}H_{12}(CH_3CN)_2$ J. v. d. M. Reddy and W. N. Lipscomb, *ibid.* **31**, 610 (1959). $B_{10}H_{14}^{2-}$: R. Dobrott and W. N. Lipscomb, *ibid.* **37**, 1779 (1962). $B_{12}H_{12}^{2-}$: J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.* **82**, 4427 (1960).

⁹ M. Yamazaki, *J. Chem. Phys.* **27**, 1401 (1957).

