

debted to Drs. A. H. Filbey and W. E. Burt for helpful suggestions throughout the course of our work. The

microanalytical work by Mrs. Patricia Wilson and Mr. Paul Kemp is gratefully appreciated.

[CONTRIBUTION FROM BOEING SCIENTIFIC RESEARCH LABORATORIES, SEATTLE, WASHINGTON]

## Molecular Orbitals in $B_5H_9$ and $B_{10}H_{16}$ <sup>1</sup>

BY EMMETT B. MOORE, JR.

RECEIVED SEPTEMBER 26, 1962

A linear combination of atomic orbitals study of the seven boron framework atomic orbitals and the six boron framework electrons of  $B_5H_9$  yields three bonding molecular orbitals. The energy of the highest filled molecular orbital (M.O.) is  $-11.0$  e.v., which compares favorably with the observed ionization energy of  $10.8$  e.v. The population matrix yields a formal charge of  $-0.87e$  on the apex boron atom and of  $+0.22e$  on each basal boron, the order of which agrees with the experimental order. These charges yield a dipole moment of  $4.6 D$ . When account is taken of the hydridic nature of the bridge hydrogens and the apex terminal hydrogen, the dipole moment becomes  $1.8 D$ , compared with the experimental value of  $2.13 D$ . A similar study of the 16 boron framework atomic orbitals and 14 framework electrons of  $B_{10}H_{16}$  yields seven bonding M.O.'s, an energy of  $-10.2$  e.v. for the highest filled M.O., a charge of  $-0.86e$  on each apex boron and a charge of  $+0.22e$  on each basal boron. Comparison of the electron population matrices of the two molecules shows that only single bond character may be attached to the boron-boron bond between the two halves of  $B_{10}H_{16}$  even though enough properly oriented atomic orbitals are available for the formation of a triple bond.

### Introduction

The recent discovery and elucidation<sup>2</sup> of the molecular structure of  $B_{10}H_{16}$  disclosed a previously unknown boron hydride structural feature: two adjacent boron atoms without any hydrogen atoms attached to either boron. In all the other known boron hydride molecules and ions at least one hydrogen atom is attached to each boron atom. Since this boron-boron bond is unique, it is of interest to investigate its character, particularly since in  $B_{10}H_{16}$  the boron atomic orbitals may be arranged in such a fashion as to suggest the possibility of a triple bond, even though the molecule as a whole is electron deficient.

When the structure of  $B_{10}H_{16}$  was announced, we had already completed our investigation of the electronic structure of  $B_5H_9$ , which we carried out in order to confirm the general usefulness, with respect to the boron hydrides, of the method which we used to study<sup>3,4</sup> the electronic structure of  $B_{10}H_{14}$ . Since the structures of  $B_5H_9$  and  $B_{10}H_{16}$  are closely related it was not difficult to examine the electronic structure of  $B_{10}H_{16}$  by the same means. For other theoretical treatments of  $B_5H_9$  see references 5 and 6.

The purpose of this paper, then, is to report the results of our studies of the electronic structures of  $B_5H_9$  and  $B_{10}H_{16}$  and to examine the character of the unique boron-boron bond in  $B_{10}H_{16}$ .

**General Method.**—We used the same linear combination of atomic orbitals method that we used for  $B_{10}H_{14}$  in which the molecular orbital

$$\Psi_j = \sum_r c_{rj} \Phi_r$$

leads to the set of equations

$$(\alpha_{rr} - E)c_r + \sum_s' (\beta_{rs} - S_{rs} E)c_s = 0$$

where

$$\alpha_{rr} = \int \Phi_r H \Phi_r d\tau, \beta_{rs} = \int \Phi_r H \Phi_s d\tau \text{ and } S_{rs} = \int \Phi_r \Phi_s d\tau$$

With the assumption that the resonance integrals are proportional to the overlap integrals,  $\beta_{rs} = K S_{rs}$ , the equations become

$$(\alpha_{rr} - E)c_r + \sum_s' (K - E) S_{rs} c_s = 0 \quad (1)$$

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

(2) R. Grimes, F. E. Wang, R. Lewin and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 996 (1961).

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

(4) E. B. Moore, Jr., *ibid.*, **37**, 675 (1962).

(5) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *ibid.*, **22**, 989 (1954).

(6) W. N. Lipscomb, *ibid.*, **25**, 38 (1956).

The orbital  $\Phi_r$  may be an atomic orbital on center  $r$  but more often it is a symmetry orbital, which is a linear combination of atomic orbitals on different centers. With the aid of group theory, the symmetry orbitals may be determined and the equations simplified according to the point group of the molecule. For our purposes hybrid orbitals on the boron atoms, as suggested by the atomic arrangements, are more suitable starting orbitals than pure 2s and 2p atomic orbitals. Thus the symmetry orbitals become linear combinations of hybrid orbitals which are in turn linear combinations of the boron 2s and 2p atomic orbitals.

In both  $B_5H_9$  and  $B_{10}H_{16}$  we neglected the boron 1s atomic orbitals and electrons and assumed that the 2s and 2p atomic orbitals are hybridized according to the arrangement of atoms around the boron in question. We assumed that each terminal hydrogen atom is bonded to a single boron atom by a two-electron, two-center bond and that each bridge hydrogen atom is bonded to two boron atoms by a two-electron, three-center bond.<sup>5</sup> This uses two electrons and two atomic orbitals for each terminal hydrogen and two electrons and three atomic orbitals for each bridge hydrogen. These orbitals and electrons were not considered further in the calculations except at the end where they were brought into the  $B_5H_9$  dipole moment discussion.

We determined the symmetry orbitals, evaluated all the hybrid orbital overlap integrals using Slater orbitals, and then calculated the symmetry orbital normalization factors  $N_{rr}$  and the symmetry orbital overlap integrals  $S_{rs}$ . We evaluated the symmetry orbital coulomb integrals by writing them out in terms of atomic orbitals and by assuming the boron 2s and 2p coulomb integrals to be equal to the valence state ionization energies,<sup>7</sup> that is

$$\int \Phi_{2s} H \Phi_{2s} d\tau = -15.36 \text{ e.v. and } \int \Phi_{2p} H \Phi_{2p} d\tau = -8.63 \text{ e.v.}$$

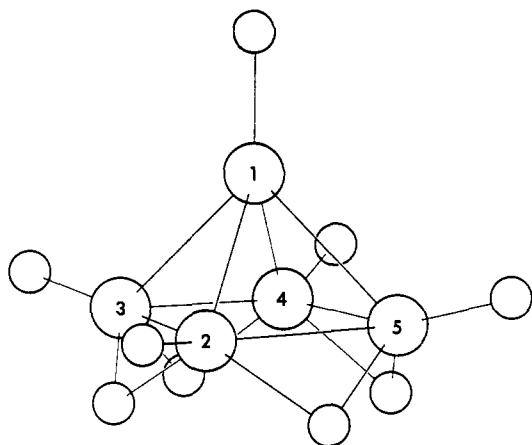
We then solved eq. 1 several times on the IBM 7090 computer using a different value of  $K$  each time. We chose values of  $K$  between  $-10$  and  $-25$  e.v.

It should be remarked that the evaluation of overlap integrals between hybrid orbitals pointing in arbitrary directions is not as straightforward as the evaluation of overlap integrals for a diatomic molecule, for which tables<sup>8,9</sup> and computer programs<sup>10</sup> are readily available.

(7) R. S. Mulliken, *ibid.*, **2**, 782 (1934).

(8) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *ibid.*, **17**, 1248 (1949).

(9) M. Kotani, E. Ishiguro, K. Hijakata, T. Nakamura and A. Amemiya, *J. Phys. Soc. Japan*, **8**, 463 (1953).

Fig. 1.—Molecular structure of  $B_5H_9$ .

The hybrid orbitals make it necessary to choose proper linear combinations of s and p orbitals and the arbitrary directions in space of these hybrids make it necessary to resolve the overlap integrals into suitable combinations of pi and sigma type overlap integrals. For this purpose we used the method of resolution which we used<sup>11</sup> for  $B_{10}H_{14}$ . Hoffmann and Lipscomb<sup>12</sup> have more recently discussed a similar problem. The values of the hybrid orbital overlap integrals are given in the Appendix.

We then carried out a population analysis<sup>13</sup> of the bonding molecular orbitals of each molecule. If the molecular orbitals are written out completely as linear combinations of atomic orbitals  $\Phi_i$  on centers r

$$\Psi_j = \sum_r c_{rj} \Phi_r$$

the population matrix may be written as

$$Q = [q_{rs}] = 2S_{rs} \sum_j c_{rj} c_{sj}$$

The 2 arises in this case because each molecular orbital is doubly filled. The sum of a row or column of this matrix is the gross atomic population

$$(gap)_s = \sum_r q_{rs}$$

which is a measure of the negative charge associated with center s. The formal charge on each atom is this gross atomic population subtracted from the positive charge on the atom.

**Molecular Structures.**—The molecular structures of  $B_5H_9$  and  $B_{10}H_{16}$  as determined by X-ray diffraction studies<sup>2,14</sup> are shown in Fig. 1 and 3. The structure of  $B_5H_9$  has also been investigated with the use of microwave techniques.<sup>15</sup>

The five boron atoms in  $B_5H_9$  form a square pyramid, with one terminal hydrogen atom attached to each boron atom. A bridge hydrogen atom joins each pair of nearest neighbor basal boron atoms.

$B_{10}H_{16}$  is simply two  $B_5H_9$  molecules joined at the apex borons, with the apex terminal hydrogen atoms removed. The basal borons of the top  $B_5H_9$  unit eclipse the basal borons of the bottom  $B_5H_9$  unit in projection along the fourfold axis.

The atomic parameters used in calculating the overlap integrals are the microwave parameters of Hrostowski and Myers<sup>15</sup> for  $B_5H_9$  and the X-ray parameters of Grimes, Wang, Lewin and Lipscomb<sup>2</sup> for  $B_{10}H_{16}$ . It would have been more appropriate, perhaps, to use

(10) A. C. Switendick and F. J. Corbato, Quarterly Progress Report, Solid State and Molecular Theory Group, Mass. Inst. Tech., Oct. 15, 1959, p. 70.

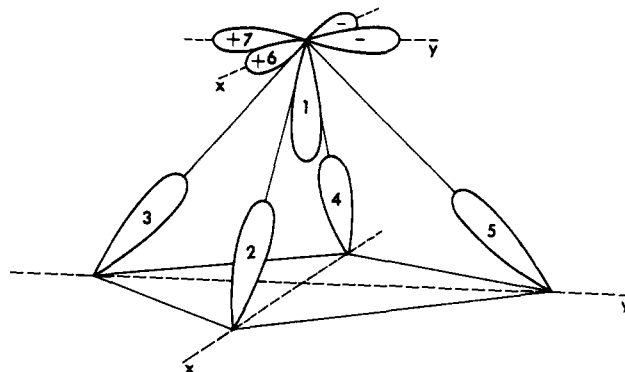
(11) E. B. Moore, Jr., Boeing Scientific Research Laboratories Document DL-82-0067, September, 1960.

(12) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(13) W. C. Hamilton, *Proc. Roy. Soc. (London)*, **A253**, 395 (1956).

(14) W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, **5**, 260 (1952).

(15) H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, **23**, 262 (1954).

Fig. 2.— $B_5H_9$  boron framework orbitals.

the X-ray diffraction parameters in each case; however the  $B_5H_9$  study was completed before the discovery of  $B_{10}H_{16}$  was announced, so the more reliable<sup>5</sup> microwave parameters were used for  $B_5H_9$ . The  $B_5H_9$  microwave interatomic distances and the  $B_{10}H_{16}$  X-ray diffraction interatomic distances are listed in the Appendix.

$B_5H_9$ .—As suggested by the molecular structure, we assumed that the 2s and the  $2p_z$  orbital on boron 1 are digonally hybridized with the two hybrids pointing in opposite directions along the fourfold axis. One of the two remaining 2p orbitals is parallel to the line joining borons 2 and 4 and the other is parallel to the line joining borons 3 and 5. We assumed that the positive lobes of the 2p orbitals are in the direction of borons 2 and 3, respectively. We also assumed that the 2s and 2p orbitals on boron atoms 2, 3, 4, and 5 are tetrahedrally hybridized with one hybrid pointing toward the terminal hydrogen atom, with two pointing toward bridge hydrogens and with the remaining hybrid orbital pointing toward boron 1. Of the 24 electrons and 29 atomic orbitals available for bonding, 18 electrons and 22 orbitals are used in bonding the five terminal hydrogens and four bridge hydrogens to their nearest neighbor boron atoms, leaving six electrons and seven orbitals for boron framework bonding. The boron atom notation is shown in Fig. 1 and the framework hybrid orbital notation is shown in Fig. 2.

Group theory for the point group  $C_{4v}$  shows that the secular determinant factors into a  $2 \times 2$  determinant of symmetry  $A_1$ , a  $1 \times 1$  of symmetry  $B_1$ , and a  $2 \times 2$  of symmetry E. The resulting symmetry orbitals are listed in Table I together with the appropriate normal-

TABLE I

 $B_5H_9$  SYMMETRY ORBITALS AND NORMALIZATION FACTORS

	$\Phi_1 = 1.000$ (1) <sup>a</sup>
$a_1$	$\Phi_2 = 0.334$ (2 + 4 + 3 + 5)
$b_1$	$\Phi_3 = 0.852$ (2 + 4 - 3 - 5)
e	$\Phi_4 = 0.842$ (2 - 4)
	$\Phi_4' = 0.842$ (3 - 5)
	$\Phi_5 = 1.000$ (6)
	$\Phi_5' = 1.000$ (7)

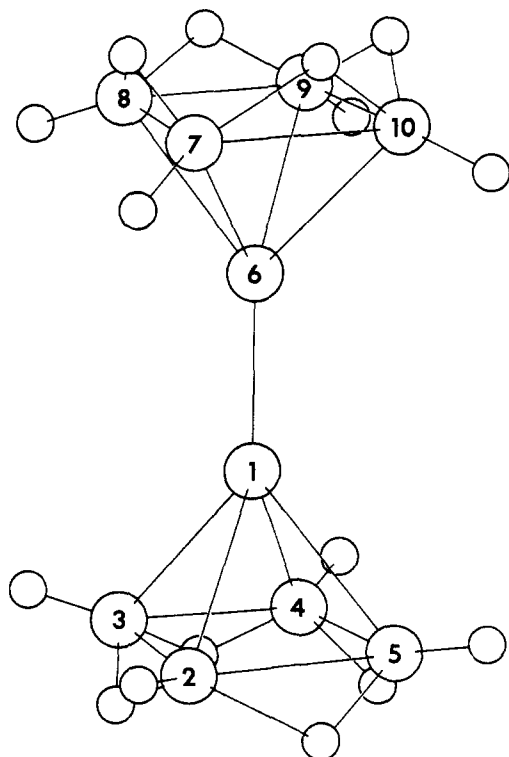
<sup>a</sup> Numbers in parentheses refer to the hybrid atomic orbitals of Fig. 2.

TABLE II

 $B_5H_9$  MOLECULAR ORBITALS AND ORBITAL ENERGIES

$E$ (e.v.)	
-13.663	$\Psi_{a_1}(1) = 0.423\Phi_1 + 0.612\Phi_2$
-11.016	$\Psi_e(1) = 0.539\Phi_4 + 0.568\Phi_5$
-1.375	$\Psi_{b_1}(1) = \Phi_3$
2.680	$\Psi_e(2) = 1.173\Phi_4 - 1.158\Phi_5$
3.805	$\Psi_{a_1}(2) = 1.934\Phi_1 - 1.883\Phi_2$

ization factors. After calculating the symmetry orbital overlap integrals and the symmetry orbital coulomb

Fig. 3.—Molecular structure of B<sub>10</sub>H<sub>16</sub>.

integrals, we solved eq. 1 using several values of  $K$  and found that  $K = -15$  e.v. gave theoretical values of the charge distribution, dipole moment and ionization energy which best agreed with the experimental values. The molecular orbital energies and wave functions are listed in Table II.

The population analysis of the three wave functions of lowest energy yields the following formal charge on each boron atom

1	2, 3, 4, 5
-0.870e	+0.217e

Here  $\Psi_{a_1}(1)$  contains two electrons, but  $\Psi_e(1)$  is doubly degenerate and therefore contains four electrons. This order of charges agrees with the experimental order as inferred from nuclear magnetic resonance data<sup>16,17</sup> and from the chemical reactions<sup>18</sup> of B<sub>5</sub>H<sub>9</sub>. The charge order also agrees with the charge order found theoretically by Eberhardt, Crawford and Lipscomb.<sup>5</sup>

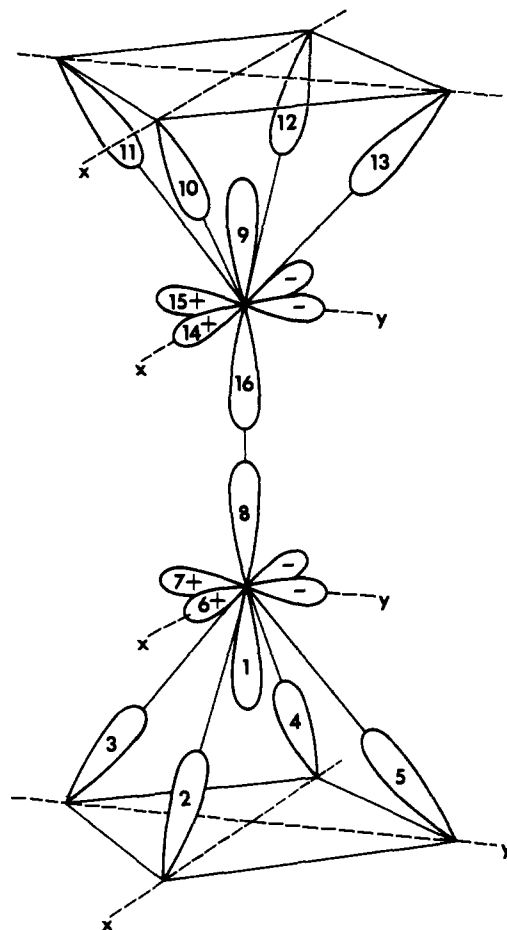
The dipole moment based on these charges and the parameters of Hrostowski and Myers is 4.6  $D$ . Lipscomb<sup>17</sup> interprets the proton nuclear magnetic resonance spectrum<sup>19</sup> of B<sub>5</sub>H<sub>9</sub> as showing that the apex hydrogen atom is slightly negatively charged and that the bridge hydrogen atoms are even more negatively charged. The assumption of 0.1e negative charge on the apex hydrogen and 0.2e negative charge on each bridge hydrogen does not seem to be unreasonable in view of the self-consistent field study of B<sub>2</sub>H<sub>6</sub> by Hamilton<sup>13</sup> in which the bridge hydrogen atoms were found to be 0.2e negatively charged. The hydrogen atom positions are not well defined, but the X-ray diffraction data<sup>14</sup> indicate a distance of 1.21 Å. between the apex boron and the apex hydrogen, a distance of 1.35 Å. between a basal boron and its nearest neighbor bridge hydrogen (H<sub>b</sub>), and an angle of 119° between the B<sub>2</sub>-B<sub>3</sub>-B<sub>4</sub> plane and the B<sub>2</sub>-H<sub>b</sub>-B<sub>3</sub> plane. With these

(16) R. Schaeffer, J. N. Shoolery and R. Jones, *J. Am. Chem. Soc.*, **79**, 4606 (1957).

(17) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(18) N. J. Blay, I. Dunstan and R. L. Williams, *J. Chem. Soc.*, 430 (1960).

(19) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

Fig. 4.—B<sub>10</sub>H<sub>16</sub> boron framework orbitals.

assumptions the dipole moment becomes 1.8  $D$ , which is in reasonable agreement with the experimental value<sup>15</sup> of 2.13  $D$ .

Finally the orbital energy of the highest filled M.O., -11.0 e.v., is to be compared<sup>20</sup> with the experimental ionization energy of 10.8 e.v. observed by Margrave<sup>21</sup> and 10.3 e.v. observed by Kaufman.<sup>22</sup>

B<sub>10</sub>H<sub>16</sub>.—Again as suggested by the molecular structure we assumed that the 2s and 2p<sub>z</sub> orbitals on boron atoms 1 and 6 are digonally hybridized along the four-fold axis leaving a 2p<sub>x</sub> and a 2p<sub>y</sub> orbital on each boron, pointing, respectively, in a direction parallel to the line joining borons 2 and 4 and parallel to the line joining borons 3 and 5. We also assumed that the 2s and 2p orbitals on borons 2, 3, 4, 5, 7, 8, 9, and 10 are tetrahedrally hybridized with one hybrid pointing toward the nearest terminal hydrogen atom, with two pointing toward the nearest bridge hydrogens and with the remaining orbital pointing toward boron 1 in the case of borons 2, 3, 4 and 5 and pointing toward boron 6 in the case of borons 7, 8, 9 and 10. Of the 46 electrons and 56 atomic orbitals available for bonding, 32 electrons and 40 orbitals are used in bonding the eight terminal hydrogens and eight bridge hydrogens to their nearest neighbor boron atoms, leaving 14 electrons and 16 orbitals for boron framework bonding. The boron atom notation is shown in Fig. 3 and the framework hybrid orbital notation is shown in Fig. 4.

Group theory for the point group D<sub>4h</sub> shows that the secular determinant factors into a 3 × 3 determinant of symmetry A<sub>1g</sub>, a 3 × 3 of symmetry A<sub>2u</sub>, a 2 × 2 of

(20) R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 179.

(21) J. L. Margrave, *J. Chem. Phys.*, **32**, 1889 (1960).

(22) J. J. Kaufman, private communication.

symmetry  $E_g$ , a  $2 \times 2$  of symmetry  $E_u$ , a  $1 \times 1$  of symmetry  $B_{1g}$  and a  $1 \times 1$  of symmetry  $B_{2u}$ . The resulting symmetry orbitals are listed in Table III together with the appropriate normalization factors. After calculating the symmetry orbital overlap integrals and the symmetry orbital coulomb integrals, we solved eq. 1 this time using only  $K = -15$  e.v. The molecular orbital energies and wave functions are listed in Table IV.

TABLE III

$B_{10}H_{16}$  SYMMETRY ORBITALS AND NORMALIZATION FACTORS

	$\Phi_1 = 0.724(1 + 9)^a$
$a_{1g}$	$\Phi_2 = .230(2 + 3 + 4 + 5 + 10 + 11 + 12 + 13)$
	$\Phi_3 = .529(8 + 16)$
$b_{1g}$	$\Phi_4 = .610(2 + 4 - 3 - 5 + 10 + 12 - 11 - 13)$
$e_g$	$\Phi_5 = .609(2 - 4 - 10 + 12)$
	$\Phi_5' = .609(3 - 5 - 11 + 13)$
	$\Phi_6 = .815(6 - 14)$
	$\Phi_6' = .815(7 - 15)$
$a_{2u}$	$\Phi_7 = .692(1 - 9)$
	$\Phi_8 = .237(2 + 3 + 4 + 5 - 10 - 11 - 12 - 13)$
	$\Phi_9 = 1.530(8 - 16)$
$b_{2u}$	$\Phi_{10} = 0.614(2 + 4 - 3 - 5 - 10 - 12 + 11 + 13)$
$e_u$	$\Phi_{11} = .598(2 - 4 + 10 - 12)$
	$\Phi_{11}' = .598(3 - 5 + 11 - 13)$
	$\Phi_{12} = .633(6 + 14)$
	$\Phi_{12}' = .633(7 + 15)$

<sup>a</sup> Numbers in parentheses refer to the hybrid atomic orbitals of Fig. 4.

TABLE IV

$B_{10}H_{16}$  MOLECULAR ORBITALS AND ORBITAL ENERGIES

E (e.v.)	
-13.8049	$\Psi_{a_{1g}}(1) = 0.2957\Phi_1 + 0.5609\Phi_2 + 0.4197\Phi_3$
-13.7015	$\Psi_{a_{2u}}(1) = .4317\Phi_7 + .6009\Phi_8 - .0064\Phi_9$
-13.1177	$\Psi_{a_{1g}}(2) = .3291\Phi_1 + .2968\Phi_2 - .9014\Phi_3$
-11.3423	$\Psi_{e_u}(1) = .4581\Phi_{11} + .6641\Phi_{12}$
-10.2148	$\Psi_{e_g}(1) = .6332\Phi_6 + .4858\Phi_6$
-1.1098	$\Psi_{a_{2u}}(2) = .3719\Phi_7 - .4325\Phi_8 - .9649\Phi_9$
-1.0519	$\Psi_{e_u}(2) = 1.1320\Phi_{11} - 1.0248\Phi_{12}$
-1.0461	$\Psi_{b_{1g}}(1) = \Phi_4$
-0.8517	$\Psi_{b_{2u}}(1) = \Phi_{10}$
3.8747	$\Psi_{e_g}(2) = 1.0647\Phi_5 - 1.1395\Phi_5$
4.8244	$\Psi_{a_{2u}}(3) = 1.9634\Phi_7 - 1.8999\Phi_8 + 0.2824\Phi_9$
5.5414	$\Psi_{a_{1g}}(3) = 1.9596\Phi_1 - 1.9990\Phi_2 + 0.5634\Phi_3$

The population analysis of the seven molecular orbitals of lowest energy yields the following formal charge on each boron atom

$$\begin{array}{cc} 1, 6 & 2, 3, 4, 5, 7, 8, 9, 10 \\ -0.863e & +0.216e \end{array}$$

The dipole moment is of course zero on account of the symmetry of the molecule.

The orbital energy of the highest filled M.O. is -10.2 e.v., which suggests that the ionization energy of  $B_{10}H_{16}$  ought to be close to this value, perhaps a few tenths of an e.v. lower.

It is of interest to inquire whether or not the boron-boron bond ( $B_1-B_6$ ) between the two halves of the  $B_{10}H_{16}$  molecule has some double or triple bond character. Each of these apex boron atoms has a digonal hybrid and two p orbitals properly oriented for the possible formation of a triple bond. While there is no perfectly satisfactory way of estimating this bond order, as good a method as any is the inspection of the off-diagonal elements of the population matrix. These elements are sums of terms of the form  $c_r c_s S_{rs}$  where  $c_r$  and  $c_s$  are atomic orbital coefficients and  $S_{rs}$  is the overlap integral between the two atomic orbitals. It seems reasonable that the bond order between two adjacent atoms should be related to the sum over all molecular orbitals of products of this form.

TABLE V  
POPULATION MATRICES

	$B_5H_9$			$B_{10}H_{16}$		
	$B_1$	$B_2$	$B_3$	$B_1$	$B_2$	$B_3$
$B_1$	1.650	0.305	...	$B_1$	2.271	0.291
$B_2$	.305	.495		$B_2$	.291	.531
$B_3$	.305	.040		$B_3$	.291	.041
$B_4$	.305	-.097		$B_4$	.291	-.114
$B_5$	.305	.040		$B_5$	.291	.041
	2.870	0.783		$B_6$	.444	-.004
				$B_7$	-.004	-.004
				$B_8$	-.004	.000
				$B_9$	-.004	.002
				$B_{10}$	-.004	.000
					3.863	0.784

Portions of the  $B_5H_9$  population matrix and the  $B_{10}H_{16}$  population matrix are given in Table V. It can be seen that the off-diagonal elements of the  $B_5H_9$  matrix are nearly the same as the off-diagonal elements of the  $B_{10}H_{16}$  population matrix in the  $B_1, B_2, B_3, B_4, B_5$  region where comparison is possible. The other off-diagonal elements, which relate the two halves of  $B_{10}H_{16}$ , are essentially zero, with the exception of the  $B_1-B_6$  element. In  $B_5H_9$  we assumed the apex-boron, apex-hydrogen bond to be a two-center, two-electron, single bond. Hence we conclude that the apex-boron, apex-boron bond ( $B_1-B_6$ ) in  $B_{10}H_{16}$  must be of the same character, otherwise substantial bond population would be drawn from the  $B_1-B_2, B_2-B_3, B_2-B_4$ , etc., elements of the  $B_{10}H_{16}$  population matrix and would be added to the  $B_1-B_6$  element. Furthermore, if one writes the  $B_{10}H_{16}$  population matrix in terms of the atomic orbitals of Fig. 4 rather than in terms of the boron atoms as in Table V, one finds that the total pi bond population between orbitals 6 and 14 and between orbitals 7 and 15 is only five per cent of the sigma bond population between orbitals 8 and 16. It is possible that this relatively small pi bond population is just sufficient to keep the molecule in the eclipsed form in the crystal but not sufficient to rule out internal rotation in other phases as already suggested by Lipscomb.<sup>2</sup> We conclude that the bond between the two halves of  $B_{10}H_{16}$  is essentially a single bond.<sup>23</sup>

**Acknowledgments.**—The author wishes to acknowledge the computing help of Mr. Dale Speakes and the use of the Boeing Company's IBM 7090 computer.

## Appendix

TABLE VI  
 $B_5H_9$  AND  $B_{10}H_{16}$  INTERATOMIC DISTANCES

$B_5H_9^a$	$B_{10}H_{16}^b$
$B_1-B_2 = 1.687 \text{ \AA.}$	$B_1-B_2 = 1.76 \text{ \AA.}$
$B_2-B_3 = 1.800 \text{ \AA.}$	$B_2-B_3 = 1.71 \text{ \AA.}$
	$B_1-B_6 = 1.74 \text{ \AA.}$

<sup>a</sup> Hrostowski and Myers. <sup>b</sup> Grimes, Wang, Lewin and Lipscomb.

TABLE VII  
BORON-BORON OVERLAP INTEGRALS. THE ORBITALS REFERRED TO ARE THOSE OF FIG. 2 AND 4

$B_5H_9$	$B_{10}H_{16}$	$B_{10}H_{16}$
$S_{1,2} = 0.646$	$S_{1,2} = 0.6468$	$S_{2,10} = 0.0251$
$S_{2,3} = .475$	$S_{1,9} = -.0454$	$S_{2,11} = .0176$
$S_{2,4} = .294$	$S_{1,10} = -.0167$	$S_{2,12} = .0124$
$S_{2,6} = .375$	$S_{1,16} = .0400$	$S_{2,14} = .0409$
	$S_{2,3} = .4897$	$S_{2,16} = .1561$
	$S_{2,4} = .3131$	$S_{8,14} = .2476$
	$S_{2,6} = .3382$	$S_{8,16} = .7864$
	$S_{2,8} = .1408$	

(23) The author has just received a preprint of a paper by R. Hoffmann and W. N. Lipscomb to be published in *J. Chem. Phys.* in which similar calculations have been carried out for most of the boron hydrides.