

# Self-Consistent Field Wave Function and Localized Orbitals for 2,4-Dicarbaheptaborane(7). The Fractional Three-Center Bond

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**Abstract:** A minimum basis set self-consistent field wave function for 2,4-dicarbaheptaborane(7) has been calculated. Molecular properties such as charge distributions, bond strengths, dipole moments, diamagnetic chemical shifts, ionization potentials, and atomization energy are examined and the reactivity of the molecule is discussed in terms of the ground-state charge distribution. Localized orbitals obtained by maximizing the self-repulsion energy yield one boron atom ( $B_3$ ) which appears to be participating in five bonds to other atoms; however only fractions of atomic orbitals are used for some or all of these bonds. These fractional bonds are discussed in terms of their directional character, hybridization, and per cent delocalization, and the relationships among fractional bonding, molecular symmetry, and the topological theory of the boron hydrides are explored.

The carborane 2,4-dicarbaheptaborane(7) is well characterized chemically<sup>1,2</sup> and structurally.<sup>3</sup> This carborane and several others have been the subject of considerable theoretical investigation by molecular orbital techniques, which have already proved useful in understanding the interesting properties of the structurally similar boron hydrides. Results at the extended Hückel,<sup>4</sup> CNDO,<sup>5</sup> and NEMO<sup>6</sup> levels of approximation are already available for many of these compounds, but only two, 1,2- $C_2B_4H_6$  and 1,6- $C_2B_4H_6$ , have been the subject of *ab initio* self-consistent field (SCF) calculations.<sup>7</sup> In this paper we present the minimum basis set Slater orbital SCF wave function for 2,4- $C_2B_5H_7$ , and we examine such properties as ground-state charge distribution, overlap populations, bond midpoint densities, ionization potentials, diamagnetic chemical shifts, atomization energies, and molecular, bond, and atomic dipole moments.

The use of localized molecular orbitals<sup>8-13</sup> (LMO's) in the boron hydrides<sup>14-16</sup> has provided new insight into the valence structure and hybridization of these compounds. Localized orbitals have also recently provided the impetus for a new and simpler topological theory<sup>17</sup> of the boron hydrides. We now initiate the study of localized orbitals in the carboranes by presenting the LMO's for 2,4- $C_2H_5B_7$ , obtained directly from the SCF wave function.

- (1) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *Inorg. Chem.*, **9**, 2285 (1970).
- (2) R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 5072 (1970).
- (3) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **41**, 2166 (1965).
- (4) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3489 (1962).
- (5) C. S. Cheung, R. A. Beaudet, and G. A. Segal, *J. Amer. Chem. Soc.*, **92**, 4158 (1970).
- (6) T. F. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, **9**, 2743 (1970).
- (7) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *ibid.*, **9**, 7019 (1970).
- (8) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963).
- (9) J. C. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949).
- (10) G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1950).
- (11) J. E. Lennard-Jones and J. A. Pople, *ibid.*, **202**, 166 (1950).
- (12) J. E. Lennard-Jones and J. A. Pople, *ibid.*, **210**, 190 (1951).
- (13) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, 597 (1965).
- (14) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *ibid.*, **51**, 2085 (1969).
- (15) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).
- (16) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971).
- (17) I. R. Epstein and W. N. Lipscomb, *ibid.*, **10**, 1921 (1971).

The concept of fractional three-center bonding<sup>18</sup> has recently been introduced to describe the valence structures of 2,4- $C_2B_5H_7$ , 4,5- $C_2B_4H_8$ , 1,6- $C_2B_4H_8$ , and  $B_3H_9$ . We present here a detailed discussion of fractional bonding in  $C_2B_5H_7$ , and we explore the relationships among fractional bonding, molecular structure and symmetry, and the topological theory<sup>17,19</sup> of the boron hydrides.

## Procedure

The geometry of  $C_2B_5H_7$  (Figure 1) was taken from the microwave study,<sup>3</sup> with B-H and C-H bond distances idealized to 1.19 and 1.09 Å, respectively. Coordinates in atomic units are listed in Table I. The

Table I. Coordinates of Unique Atoms<sup>a,b</sup>

	x	y	z
$B_1$	0.0	0.0	2.201
$C_2$	0.758	2.235	0.0
$B_3$	2.637	0.0	0.0
$B_5$	-2.117	-1.560	0.0
$H_1$	0.0	0.0	4.450
$H_2$	1.376	4.200	0.0
$H_3$	4.886	0.0	0.0
$H_5$	-3.877	-2.950	0.0

<sup>a</sup> Coordinates in atomic units. <sup>b</sup> The symmetry planes are  $xy$  and  $xz$ .

SCF calculation was performed with Stevens' program<sup>20</sup> for the IBM 360/65 computer. A minimum basis set of Slater orbitals was employed, with optimized exponents (Table II) taken from diborane<sup>14</sup> and ethane.<sup>20</sup> Each unique integral was accurately computed to at

Table II. Exponents

B	1s	4.68	C	1s	5.680	<sup>H</sup> B	1s	1.147
	2s	1.443		2s	1.730	<sup>H</sup> C	1s	1.160
	2p	1.477		2p	1.760			

- (18) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 1748 (1972).
- (19) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 1212 (1957).
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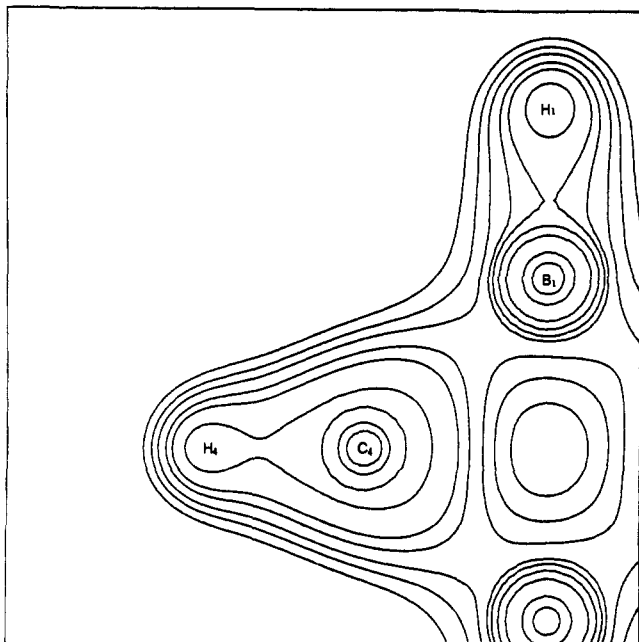


Figure 2. Electron density map of the  $H_4C_4B_1$  plane. The contours in this map and all of the maps in this paper are 10.0, 3.0, 0.50, 0.25, 0.17, 0.14, 0.11, 0.09, and 0.07 e/au<sup>3</sup>.

Table V. Overlap Populations and Electron Densities

Bond	Distance <sup>a</sup>	Overlap population	Midpoint density <sup>b</sup>
B <sub>1</sub> B <sub>3</sub>	1.818	0.28	0.077
B <sub>1</sub> B <sub>5</sub>	1.815	0.36	0.082
B <sub>3</sub> B <sub>6</sub>	1.651	0.64	0.147
C <sub>2</sub> B <sub>1</sub>	1.708	0.41	0.085
C <sub>2</sub> B <sub>6</sub>	1.563	0.62	0.186
C <sub>2</sub> B <sub>3</sub>	1.545	0.66	0.193
B <sub>1</sub> H <sub>1</sub>	1.19	0.81	0.173
B <sub>3</sub> H <sub>5</sub>	1.19	0.81	0.173
B <sub>3</sub> H <sub>3</sub>	1.19	0.81	0.171
C <sub>2</sub> H <sub>2</sub>	1.09	0.77	0.270

<sup>a</sup> Ångstroms. <sup>b</sup> Electron/au<sup>3</sup>.

all adjacent B-B and B-C interactions. We may draw the following conclusions from the bond midpoint densities. (1) The bonding interactions in the equatorial plane of this molecule are uniformly stronger than those involving an apex atom. This effect is to be expected because there are no bridge hydrogens in the molecule (compare, for example, the bond strengths in this molecule to those in 4,5-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> given in the following paper). (2) The B<sub>1</sub>-C<sub>2</sub>, B<sub>1</sub>-B<sub>3</sub>, and B<sub>1</sub>-B<sub>5</sub> densities are quite similar, although as expected the B-C interaction is the strongest. (3) The C<sub>2</sub>-B<sub>3</sub> and C<sub>2</sub>-B<sub>5</sub> interactions are also very similar, both with respect to bond midpoint densities and overlap populations.

In Figures 2 and 3 we show electron density maps for the  $H_4C_4H_1$  and  $H_1B_1H_3$  planes. The B-H and C-H bond are especially evident and they localize (see below) to B-H and C-H orbitals (LMO's). Note also that the asymmetry of the B<sub>1</sub>-H<sub>1</sub> bond is away from B<sub>3</sub> (Figure 3) and that the center of the molecule is a minimum in electron density.

Electron density maps for the three remaining planes of interest are shown in Figures 4, 5, and 6. These planes include all of the unique faces of the pentagonal

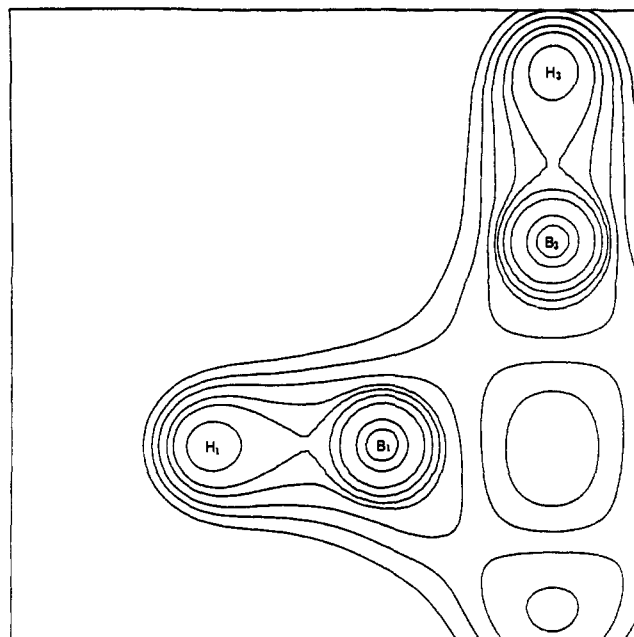


Figure 3. Electron density map of the  $H_1B_1B_3$  plane.

bipyramid, and it is again apparent that the equatorial interactions B<sub>3</sub>-B<sub>6</sub>, B<sub>3</sub>-C<sub>4</sub>, and B<sub>3</sub>-C<sub>1</sub> are considerably stronger than the apical interactions B<sub>1</sub>-B<sub>3</sub>, B<sub>1</sub>-C<sub>4</sub>, and B<sub>1</sub>-B<sub>5</sub>.

These maps also provide a good example of the danger of attempting to guess the localized orbitals from the electron density. Both the B<sub>1</sub>B<sub>3</sub>C<sub>4</sub> and B<sub>1</sub>B<sub>3</sub>C<sub>1</sub> planes appear to be ideal candidates for central (but unsymmetrical) three-center bonding, but only in the B<sub>1</sub>B<sub>3</sub>C<sub>4</sub> plane does such bonding occur (see below). Similarly, a B<sub>3</sub>-B<sub>6</sub> single bond is suggested by Figure 6; however, the corresponding LMO is a central B<sub>1</sub>-B<sub>3</sub>-B<sub>6</sub> (and B<sub>7</sub>-B<sub>3</sub>-B<sub>6</sub>) three-center bond. The relationship between the LMO's and the total density will be explored in more detail in the section on localized orbitals.

The Mulliken charges (Table VI) indicate that the

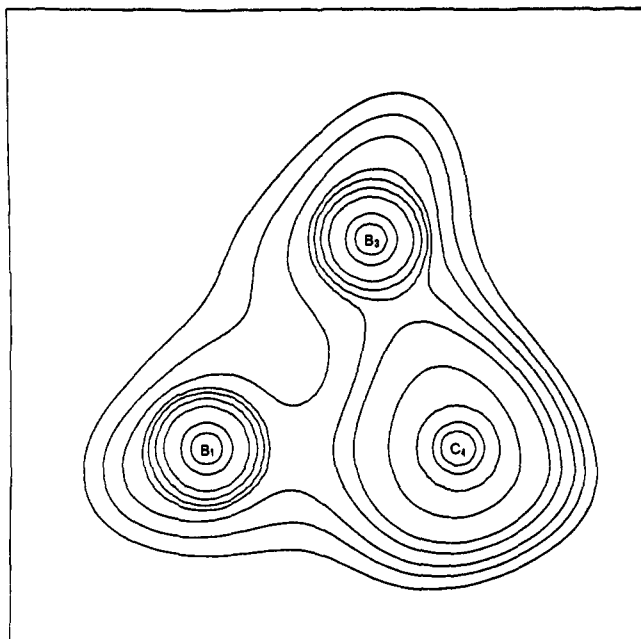
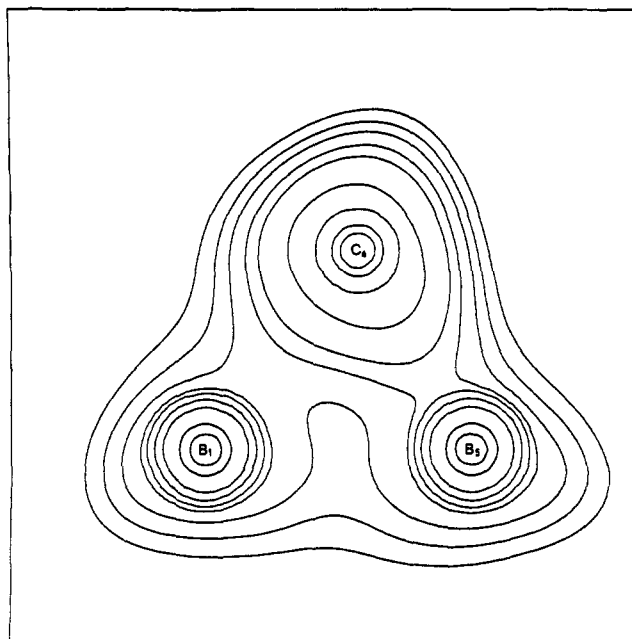
Table VI. Mulliken Charges and Inner-Shell Eigenvalues

Atom	Charge	ε <sup>a</sup>
B <sub>1</sub>	+0.118	-7.6086
C <sub>2</sub>	-0.126	-11.2495
B <sub>3</sub>	+0.122	-7.5982
B <sub>5</sub>	+0.064	-7.5514
H <sub>1</sub>	-0.069	
H <sub>2</sub>	+0.071	
H <sub>3</sub>	-0.071	
H <sub>5</sub>	-0.083	

<sup>a</sup> Atomic units.

most negative boron is B<sub>5</sub>, followed by B<sub>1</sub> and B<sub>3</sub>. Buenker and Peyerimhoff<sup>27</sup> have suggested that inner-shell orbital energies for various atoms give information about charge distribution. By this criterion the inner shell with the lowest (most negative) eigenvalue corresponds to the most positive atom. Analysis of pre-

(27) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **3**, 37 (1969).

Figure 4. Electron density map of the  $C_4B_3B_1$  plane.Figure 5. Electron density map of the  $C_4B_3B_1$  plane.

viously calculated<sup>7,14,16,21,28</sup> SCF wave functions for boron hydrides and carboranes (Table VII) shows that

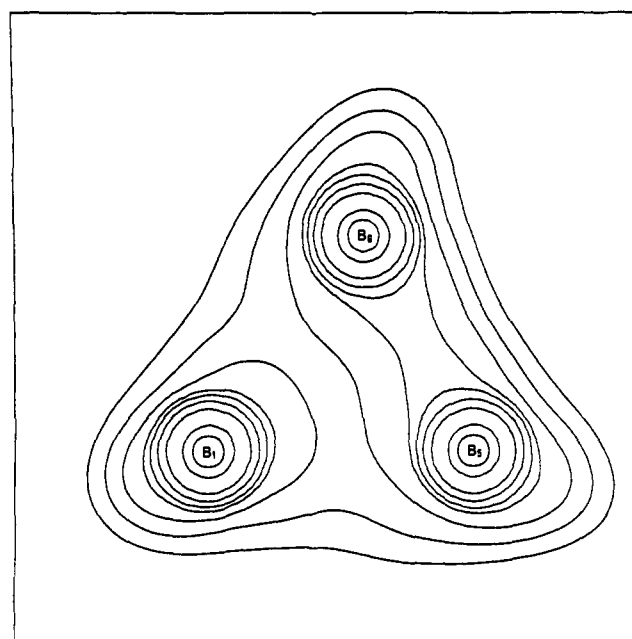
**Table VII.** Inner-Shell Eigenvalues and Mulliken Charges for Other Boron Hydrides and Carboranes

Compound	Atom <sup>a</sup>	Charge	$\epsilon^b$
$B_4H_{10}$	$B_1$	-0.02	-7.598
	$B_3$	+0.08	-7.617
$B_5H_9$	$B_1$	0.00	-7.508
	$B_2$	+0.06	-7.611
$B_5H_{11}$	$B_1$	-0.08	-7.544
	$B_2$	+0.05	-7.638
	$B_4$	+0.09	-7.601
$B_6H_{10}$	$B_1$	-0.02	-7.554
	$B_2$	+0.07	-7.645
	$B_3$	+0.06	-7.630
	$B_4$	+0.04	-7.552
1,2- $C_2B_4H_6$	$B_3$	+0.09	-7.572
	$B_4$	+0.08	-7.554
4,5- $C_2B_4H_6$	$B_1$	+0.02	-7.560
	$B_2$	+0.07	-7.618
$B_{10}H_{14}$	$B_3$	+0.06	-7.562
	$B_1$	+0.03	-7.590
	$B_2$	-0.01	-7.573
	$B_5$	+0.04	-7.624
	$B_6$	+0.09	-7.663

<sup>a</sup> The numbering systems used are found in ref 14, 16, 21, and 28.  
<sup>b</sup> Atomic units.

inner-shell eigenvalues and Mulliken charges predict the same relative charges for  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_{10}H_{14}$ , 1,2- $C_2B_4H_6$ , and 4,5- $C_2B_4H_6$  but disagree for  $B_5H_{11}$ ,  $B_6H_{10}$ , and 2,4- $C_2B_5H_7$  (Table VI). For  $C_2B_5H_7$  this discrepancy is not serious, because both criteria predict  $B_3$  to be the most negative and  $B_1$  and  $B_2$  to have very similar charges. In order of decreasing negative charge our best estimate of the relative charges on boron for this compound is therefore (negative)  $B_3 < B_1 \approx B_2$  (positive). The implications of this result

(28) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4467 (1972).

Figure 6. Electron density map of the  $B_3B_5B_1$  plane.

will be discussed in more detail in the section on reactivity.

### Dipole Moment

The atomic, bond, and total dipole moments were calculated by the origin invariant method of Ruedenberg<sup>29</sup> and are listed in Table VIII. All bond moments are consistent with those calculated for other boron hydrides and carboranes. The magnitude of the total moment is within 30% of the experimental value.<sup>3</sup> This theoretical moment is remarkably accurate for a minimum basis set wave function. The direction of the dipole moment makes the carbon end of the molecule positive.

(29) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

Table VIII. Dipole Moments<sup>a</sup>

	$x$	Total
B <sub>1</sub>	0.147	0.251
C <sub>2</sub>	0.119	0.163
B <sub>3</sub>	-0.269	0.269
B <sub>5</sub>	0.295	0.295
B <sub>1</sub> -H <sub>1</sub>	-0.058	1.267
C <sub>2</sub> -H <sub>2</sub>	-0.335	1.046
B <sub>3</sub> -H <sub>3</sub>	-1.244	1.244
B <sub>5</sub> -H <sub>5</sub>	0.947	1.252
B <sub>1</sub> -C <sub>2</sub>	-0.107	0.467
B <sub>1</sub> -B <sub>3</sub>	-0.279	0.449
B <sub>1</sub> -B <sub>5</sub>	0.302	0.467
C <sub>2</sub> -B <sub>3</sub>	-0.013	0.439
C <sub>2</sub> -B <sub>5</sub>	-0.023	0.114
B <sub>3</sub> -B <sub>5</sub>	0.427	0.427
Total atomic moment	0.850	0.850
Total bond moment	0.023	0.023
Total ionic moment	0.897	0.897
Total dipole moment	1.770	1.770 <sup>b</sup>

<sup>a</sup> Debyes. <sup>b</sup> The experimental value<sup>2</sup> is 1.32 D.

### Chemical Shifts

Diamagnetic contributions to the chemical shift are directly proportional to the expectation value of  $1/r$  and are given with remarkable accuracy<sup>26</sup> by a minimum basis set of Slater orbitals. In Table IX we list the

Table IX. <sup>1</sup>H Chemical Shifts<sup>a</sup>

Atom	$\sigma_{\text{abs}}^b$	$\sigma_d$	$\sigma_p$
H <sub>1</sub>	32.8	182.6	-149.8
H <sub>2</sub>	27.4	192.7	-165.3
H <sub>3</sub>	28.2	178.6	-150.4
H <sub>5</sub>	28.9	177.7	-148.7

<sup>a</sup> In ppm. <sup>b</sup> Assuming an absolute chemical shift for the terminal hydrogens of diborane of 29.0 ppm and relative chemical shifts for C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> and B<sub>2</sub>H<sub>6</sub> from: G. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

absolute chemical shifts of the B-H<sub>t</sub> hydrogens of C<sub>2</sub>B<sub>3</sub>H<sub>7</sub>, the calculated diamagnetic contributions  $\sigma_d$ , and the paramagnetic contributions  $\sigma_p$  calculated from the equation

$$\sigma_p = \sigma_{\text{exp}} - \sigma_d$$

The calculations of  $\sigma_d$  place the gauge origin at the nucleus, but we emphasize that both  $\sigma_d$  and  $\sigma_p$  are strongly origin dependent. Their sum, however, is independent of origin in the limit of a complete basis set. At this choice of origin the apex hydrogen is correctly predicted from the diamagnetic part only to resonate at higher field than any of the equatorial B-H<sub>t</sub> hydrogens; however the equatorial hydrogen H<sub>3</sub> is predicted to be more shielded than H<sub>5</sub>, opposite to the order found experimentally. This disagreement reflects the importance of the paramagnetic contribution.

The experimental <sup>11</sup>B chemical shifts and the calculated  $\sigma_d$  values (Table X) may not be directly compared, because the absolute chemical shifts of the borons are not known. Again, with the gauge origin at the nucleus, the apex boron B<sub>1</sub> is correctly predicted to resonate at higher field than B<sub>3</sub> or B<sub>5</sub>, but the difference in shielding between apical and equatorial borons

Table X. <sup>11</sup>B Chemical Shifts

Atom	$\sigma_{\text{exp}}^a$	$\sigma_d^b$
B <sub>1</sub>	23.5	393.6
B <sub>3</sub>	-5.0	390.3
B <sub>5</sub>	-2.0	382.1

<sup>a</sup> In ppm relative to boron trifluoride ethyl etherate. Footnote b, Table IX. <sup>b</sup> These values may not be directly compared to  $\sigma_{\text{exp}}$  because the absolute <sup>11</sup>B chemical shifts are not known.

is underestimated. This effect is almost certainly due to the large paramagnetic contribution  $\sigma_p$ .

### Reactivity

Reactivity indices computed from a ground-state wave function are useful and valid only when the course of a reaction (usually nucleophilic or electrophilic) is determined principally by the ground-state charge distribution. These static indices have worked remarkably well for hydrocarbons and a number of boron hydrides,<sup>21,28</sup> but we emphasize that there is no *a priori* reason to expect them to work for all, or even for most, molecules. A case in which they fail seriously will be discussed in the following paper.

Let us assume that the boron atom with the most negative charge will be most susceptible to electrophilic attack. If total charges are comparable, we look at populations of the highest filled molecular orbitals. Both Mulliken charges and inner-shell eigenvalues indicate that B<sub>3</sub> is the most negative boron, and in fact chlorination and bromination<sup>2</sup> of C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> under electrophilic conditions yield exclusively the 5-halo derivative. Our calculated charge distribution suggests no preference for electrophilic attack at B<sub>1</sub> or B<sub>3</sub>.

Nucleophilic substitution should occur at the boron with the largest positive charge or greatest population in the first few virtual orbitals. The charges on B<sub>1</sub> and B<sub>3</sub> are about equal, but the populations of the first few virtual orbitals strongly suggest preference for nucleophilic attack at B<sub>3</sub>, followed by B<sub>1</sub>, and finally the more negative B<sub>5</sub>. The experimental order is not yet known, although C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> does readily undergo nucleophilic base degradation.<sup>2</sup>

### Localized Orbitals

The Edmiston-Ruedenberg<sup>8</sup> procedure for obtaining localized molecular orbitals has been used successfully for a number of boron hydrides.<sup>7,15-16</sup> This method maximizes the self-repulsion energy

$$J = \sum_i (\phi_i | \phi_i | \phi_i | \phi_i) = \sum_i \int \phi_i(1) \phi_i(1) \frac{1}{r_{12}} \phi_i(2) \phi_i(2) dv_1 dv_2$$

and is therefore a completely objective and *ab initio* procedure. Application of this procedure to the boron hydrides has yielded highly localized inner-shell orbitals, B-H<sub>t</sub> and B-H<sub>b</sub>-B, and central B-B-B three-center bonds. Although no open three-center B-B-B bonds have yet been found, open B-C-B bonds do occur<sup>20</sup> in 1,2-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. Localization calculations on systems with a high degree of symmetry tend to be somewhat ambiguous.<sup>15,30-32</sup>

(30) I. R. Epstein, D. S. Marynick, and W. N. Lipscomb, submitted for publication.

(31) J. H. Hall, I. Epstein, and W. N. Lipscomb, unpublished results.

(32) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43** 397 (1965).

Localized orbitals are found from the canonical SCF orbital by calculating successive  $2 \times 2$  unitary matrices<sup>8</sup> which maximize  $J$  for each orbital pair and then iterating until numerical convergence of the LMO expansion coefficients is obtained. The LMO's are thus constrained in two important ways: first, the *total* wave function is invariant (to within a phase factor) and second, the LMO's are mutually orthogonal. The first constraint is clearly physically meaningful, while the second is merely a by-product of the method used. We hasten to point out, however, that the orthogonality constraint does not generally prevent one from obtaining highly localized orbitals and is therefore not a serious constraint.

Starting from a randomly generated unitary matrix the ER procedure converged to the localized orbitals given in Table XI and illustrated in Figure 7. For

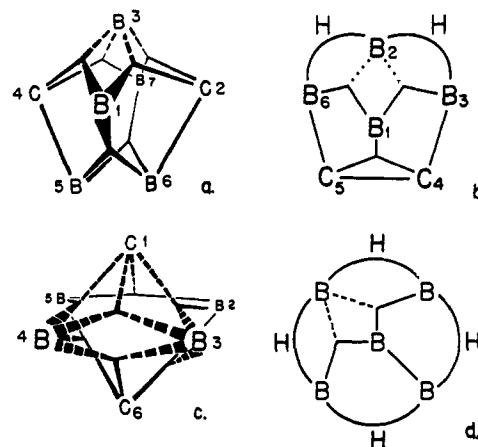


Figure 7. Localized valence structures for (a) 2,4- $C_2B_5H_7$ , (b) 4,5- $C_2B_4H_8$ , (c) 1,6- $C_2B_4H_8$ , and (d)  $B_5H_9$ .

Table XI. Localized Orbitals

	—Population—		Hybridization <sup>c</sup>			% delocalization <sup>a,b</sup>	
	B(C)	B(H)	B(C)	B	B		
Inner Shells							
$B_1$	2.002					4.8	
$C_2$	2.001					4.4	
$B_3$	2.004					5.0	
$B_5$	2.004					5.1	
B-H and C-H Orbitals							
$B_1-H_1$	0.93	1.08	1.34			8.1	
$C_2-H_2$	1.06	0.95	1.65			10.7	
$B_3-H_3$	0.93	1.08	1.26			7.0	
$B_5-H_5$	0.92	1.09	1.33			7.8	
Framework Orbitals							
$C_2-B_6$	1.12	0.68	2.51	3.23		17.9	
$B_1-B_5-B_6$	0.68	0.65	0.65	2.85	3.60	3.48	20.3
$B_7-B_5-B_6$	0.71	0.63	0.63	2.87	3.60	3.48	20.3
$C_2-B_1-B_3$	1.00	0.46	0.53	2.89	3.11	3.17	20.0
$C_2-B_7-B_3$	0.97	0.58	0.39	2.94	2.88	4.30	21.3
$C_4-B_1-B_3$	0.99	0.50	0.49	2.83	2.96	3.59	20.2
$C_4-B_7-B_3$	0.97	0.55	0.43	2.95	2.96	3.96	21.0

<sup>a</sup> Defined as  $[\frac{1}{2} \int (\phi_i^L - \phi_i^T)^2 dv]^{1/2} 100\%$  where  $\phi_i^L$  is the  $i$ th localized orbital and  $\phi_i^T$  is the  $i$ th localized orbital with all non-local contributions truncated and then renormalized. <sup>b</sup> The % delocalizations found in ref 14 and 16 are apparently incorrect. They should be multiplied by a factor of 1.41 before comparing them with the numbers in this table. <sup>c</sup> Reference 15.

completeness we also show the localized valence structures of 4,5- $C_2B_4H_8$ , 1,6- $C_2B_4H_8$ , and  $B_5H_9$  in Figure 7. The various components of the two-electron energy for the canonical and the localized orbitals of  $C_2B_5H_7$  are listed in Table XII. Applications of the second deriva-

Table XII. Components of the Two-Electron Energy<sup>a</sup>

Energy	Canonical	Localized
Total two-electron	290.8429	290.8429
Interorbital coulomb <sup>b</sup>	287.5965	261.5702
Exchange <sup>c</sup>	-14.6641	-1.6509
Self-repulsion <sup>d</sup>	17.9105	30.9237

<sup>a</sup> Atomic units. <sup>b</sup>  $\sum_{i>j} 4(ii|jj)$ . <sup>c</sup>  $-\sum_{i>j} 2(ij|ij)$ . <sup>d</sup>  $\sum_i (ii|ii)$ .

tive test<sup>15</sup> developed by Switkes, Lipscomb, and Newton showed that we are indeed at a relative maximum in the self-repulsion energy surface, with the largest second-order eigenvalue equal to  $-0.06$  au. Thus, any in-

finitesimal unitary transformation of these LMO's will result in a lowering of the self-repulsion energy. To search for possible multiple maxima in the self-repulsion energy we held the localized inner-shell orbitals constant, randomized the valence orbitals, and subjected the valence orbitals to several more ER cycles. The resultant LMO's were essentially identical with those of Table XI. Detailed examination of the effects of holding inner shells constant in  $B_5H_{10}$ <sup>16</sup> and 1,6- $C_2B_4H_8$ <sup>30</sup> strongly suggests that this procedure does not prejudice the localization toward a particular set of LMO's. Due to the large expenditure of computing time for these calculations no further localizations could be attempted. We note, however, that in every boron hydride and carborane localization which has converged to a true maximum ( $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_{11}$ ,  $B_6H_{10}$ ,  $B_4H_4$ , and 1,2- $C_2B_4H_6$ ), extensive searches for nonsymmetry equivalent multiple maxima have been unsuccessful, and we feel that it is highly unlikely that a similar extensive (and expensive) search will turn up multiple maxima here.

In marked contrast to most of the boron hydride localizations, the localized orbitals of Table XI and Figure 7 do *not* correspond to any of the topologically<sup>17,19</sup> allowed structures for  $C_2B_5H_7$ , because the atomic orbitals of  $B_3$  are participating in *five* bonding LMO's. In our preliminary note<sup>18</sup> we have shown that this situation is not unique to  $C_2B_5H_7$ , but also occurs in 4,5- $C_2B_4H_8$ , 1,6- $C_2B_4H_8$ , and  $B_5H_9$ , and we introduced the concept of fractional three-center bonds to describe these unusual bonding situations. We now address ourselves to three questions: what ways do these fractional bonds differ from more "normal" three-center bonds found in the boron hydrides, when does one expect to find fractional bonding, and what is the relationship of fractional bonding to the topological theory of the boron hydrides and carboranes?

The only essential difference we find for fractional bonds is that one or more atoms are participating in five bonding LMO's. Since there are only four valence orbitals on each atom, only fractions of atomic orbitals are used for each LMO and the fractional three-center bonds will in general not have equal contributions from each atom. We have calculated (Table XI) the hybridization and per cent delocalization<sup>15</sup> for all of the LMO's of  $C_2B_5H_7$ , and we find these quantities to be

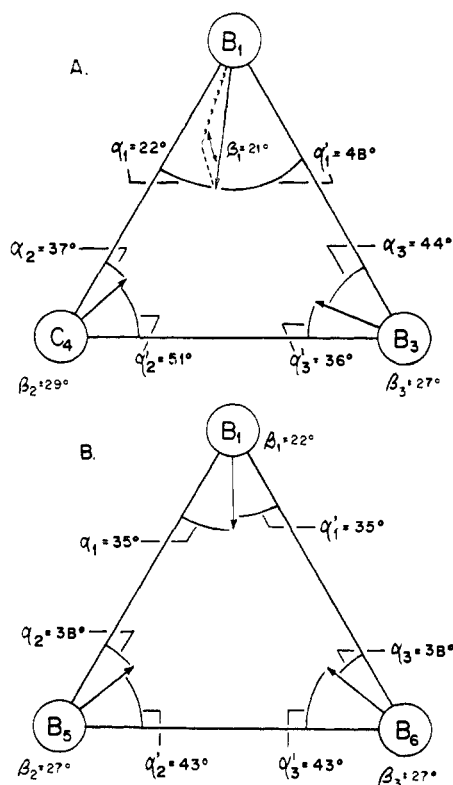


Figure 8. Directional character of the framework orbitals. The diagrams shown represent an average of the symmetry equivalent parts of the molecule: A,  $C_2B_3B_1$ ; B,  $B_5B_6B_1$ . The out-of-plane angle is  $\beta$ .

quite comparable to earlier results for the boron hydrides. Of course, the five hybrids on  $B_3$  are built up from only four linearly independent functions and cannot be orthogonal; however, hybrids derived from LMO's are not generally orthogonal even for simple bonding arrangements. A good discussion of this point may be found in ref 14. Finally, the directional character of the framework bonds (Figure 8) clearly indicates the central nature of these bonds.

The exact circumstances in which one expects to find fractional bonding are not yet clear and ultimately will become clear only when a large number of localizations are available for related compounds. The four molecules which to date have been found to exhibit this effect may, however, be naturally divided into two groups. The first group consists of those molecules for which the LMO's do not even approximately transform according to the point group of the molecule. This is the case for 1,6- $C_2B_4H_6$  and  $B_5H_9$ , which have fourfold symmetry axes but only seven and three framework orbitals, respectively. These molecules therefore tend to have rather delocalized LMO's, with multiple maxima on the self-repulsion energy surface corresponding to symmetry equivalent structures. Similar situations could possibly arise for  $B_6H_6^{2-}$ ,  $B_8H_8^{2-}$ ,  $B_{10}H_{10}^{2-}$ ,  $B_{12}H_{12}^{2-}$ , 1,12- $C_2B_{10}H_{12}$ , and any other molecule which contains an  $n$ -fold symmetry element ( $n > 2$ ) and does not have a number of framework orbitals which matches this symmetry in a simple way.

The second group consists of those molecules for which the LMO's do *approximately* transform according to the point group of the molecule. In this group are  $C_2B_5H_7$  and  $C_2B_4H_8$ , and the LMO's for these

molecules tend to be quite well localized and unique. A common geometrical feature of this group may be represented as



where the small circle represents an apex boron and the large circles are  $C_2-B_3-C_4$  for  $C_2B_5H_7$  and  $B_6-B_2-B_3$  for  $C_2B_4H_8$ . The relationship between this bonding scheme and topologically allowed bonding schemes such as



will be discussed in detail below for  $C_2B_5H_7$  and in the following paper for  $C_2B_4H_8$ . The necessary geometrical arrangement (shown above) for this type of fractional bonding is especially interesting because a number of boron hydrides and carboranes, including decaborane,<sup>28</sup> satisfy the general geometric requirement.

Finally, we wish to comment on the relationship between the topological theory of the boron hydrides and localization calculations. The topological approach assumes that the bonding in a molecule may be expressed as a linear combination of a number of valence structures which conform to a set of well defined rules. Localization calculations, on the other hand, attempt to find a *single* localized structure which best describes the bonding. In most of the earlier boron hydride localizations ( $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_{11}$ ,  $B_6H_{10}$ , and  $B_{10}H_{14}$ ), the LMO's closely corresponded to a topologically allowed structure, and thus we may infer that the correct topological description of any of the above molecules will have the valence structure corresponding to the LMO's weighted most heavily. For  $C_2B_5H_7$ ,  $C_2B_4H_8$ , 1,6- $C_2B_4H_6$ , and  $B_5H_9$  the LMO's do not closely correspond to a topologically allowed structure, but the topological approach in its present form is still useful and valid if it is possible to find some linear combination of allowed structures which correctly describes the bonding (relative overlap populations and charge distributions). We show below that this is indeed possible for  $C_2B_5H_7$ .

If we do not consider structures with open three-center bonds there are 20 topologically allowed structures for 2,4- $C_2B_5H_7$  (Figure 9). The nearly symmetrical  $B_1-B_5-B_6$  and  $B_7-B_5-B_8$  central three-center bonds found in the localized orbitals strongly suggests that a good topological description of the molecule may be found by considering only structures which include these bonds. This reduces the number of structures to only eight (structures I and V plus their symmetry equivalent structures). In Table XIII we list the charges and bond orders calculated from these structures in the usual way<sup>17</sup> and we note that the relative charges and bond strengths for structure I nearly agree with those of Table V if we restrict our comparisons to atoms and bonds of the same type. Restriction of comparisons to atoms or bonds of the same types is equivalent to a new topological distinction between boron and carbon in the chemistry of carboranes. In fact, if we include small amounts of structure V in our topological description we can reproduce the relative orders of the SCF charges and bond orders exactly. Thus the present topological theory is quite capable of

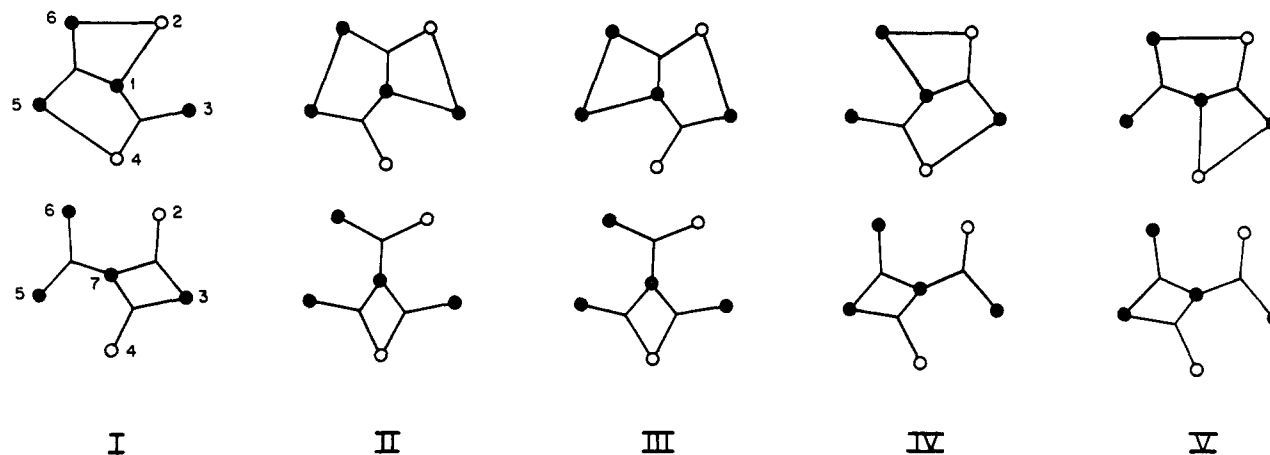


Figure 9. Topologically allowed structures for  $2,4\text{-C}_2\text{B}_5\text{H}_7$ . The dots are boron and the circles are carbon, and the two pentagonal pyramids are shown separately for clarity. Each of these structures has three other symmetry equivalent structures.

Table XIII. Population Analysis for Topologically Allowed Structures I and V

	I	V
Charges		
$\text{B}_1$	-0.167	-0.167
$\text{B}_3$	0.0	-0.333
$\text{B}_5$	-0.167	-0.167
Overlap Populations		
$\text{B}_1\text{-B}_3$	0.500	0.667
$\text{B}_1\text{-B}_5$	0.667	0.833
$\text{B}_3\text{-B}_5$	1.334	1.334
$\text{C}_2\text{-B}_6$	1.000	0.833
$\text{C}_2\text{-B}_3$	1.000	1.000

describing  $2,4\text{-C}_2\text{B}_5\text{H}_7$ , assuming, of course, that a proper weighting scheme can be developed which is independent of SCF and LMO calculations.

The use of fractional bonds in  $2,4\text{-C}_2\text{B}_5\text{H}_7$  and  $4,5\text{-C}_2\text{B}_4\text{H}_8$  allows us to write single valence structures which describe the bonding more accurately than any single topologically allowed structure. For the more symmetrical  $1,6\text{-C}_2\text{B}_4\text{H}_8$  and  $\text{B}_5\text{H}_9$ , the fractional bonding arrangements presented here allow us to write a set of symmetry equivalent structures which describe the bonding as well as or better than the corresponding, sometimes larger, set of topologically allowed structures.

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## A Self-Consistent Field and Localized Orbital Study of 4,5-Dicarbahexaborane(8)

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**Abstract:** A self-consistent field wave function has been calculated for 4,5-dicarbahexaborane(8) using the experimental geometry and a minimum basis set of Slater orbitals. The charge distribution, reactivity, diamagnetic chemical shifts, ionization potential, atomization energies, and dipole moments are discussed in terms of the ground-state charge distribution. Localized orbitals are found by the Edmiston-Ruedenberg method and a modified Taylor method, and the valence structure of the molecule is described in terms of fractional three-center bonds. A detailed discussion of the nature of the extremum in the self-repulsion energy surface is presented. The relationship between the topological theory of the boron hydrides and the valence structure of the molecule is discussed.

Dicarbahexaborane(8) ( $4,5\text{-C}_2\text{B}_4\text{H}_8$ ) is a member of the carborane series with the general formula  $\text{C}_n\text{B}_{6-n}\text{H}_{10-n}$  ( $n = 1, 2, 3, \text{ or } 4$ ) and may be considered to be derived from hexaborane(10) by replacement of two BH units ( $\text{B}_4\text{-H}_6$  and  $\text{B}_3\text{-H}_5$ ) with carbon. First discovered by Weiss and Shapiro,<sup>1</sup> this compound

(1) H. G. Weiss and I. Shapiro, U. S. Patent 3,086,996 (April 1963).

was characterized structurally by its  $^{11}\text{B}$  nmr spectrum<sup>2,3</sup> and by a single-crystal X-ray diffraction study<sup>4</sup>

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