Localized Bonds in Self-Consistent-Field Wave Functions for Polyatomic Molecules. II. Boron Hydrides

Eugene Switkes,[1a] **William N. Lipscomb,**[1b] **and Marshall D. Newton**[1c]

Contribution from the Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138, and the Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received January 9, 1970*

Abstract: The minimum basis set self-consistent-field wave functions for B_4H_{10}, B_5H_9, and B_5H_{11} have been localized by an objective procedure in which the orbital self-energy $D = \Sigma_i(ii|ii)$ is maximized. The uniqueness of this procedure is discussed in terms of the second-order self-repulsion energy and initialization with a unitary transformation generated from random numbers. The B–H(terminal) bonds are quite localized and reasonably transferable. Likewise the B–H(bridge)–B orbitals are well localized and tend to give increased bonding toward a BH group rather than a BH_2 group when both are involved in the bond. The unique H atom attached to the apex of B_5H_{11} shows bonding properties intermediate between those of a bridge H and a terminal H. In B_4H_{10} there is a reasonably well-localized B–B single bond. Neither B_5H_9 nor B_5H_{11} shows open B–B–B bonds involving nonadjacent basal B atoms. Ambiguities in the B_5H_9 localization arise from the weak coupling of the boron framework orbitals to the self-repulsion energy, but B_5H_{11} shows two nicely localized central three-center B–B–B bonds in which the bonding density is somewhat displaced toward the direction between the apical and BH boron atoms.

The inability of the two-center two-electron bond picture to provide an adequate description of the bonding and structures of electron-deficient boron hydrides prompted the formulation of a semiquantitative theory of multicenter bonding.[2] This theory has successfully correlated many of the interesting structural and electronic properties of electron-deficient molecules while preserving the useful concept of transferability inherent in the two-center two-electron bond picture. In paper I of this series[3] we discussed the localized bond picture of diborane which featured two localized three-center bridge hydrogen bonds. The agreement of these quantitatively and objectively determined local orbitals with those predicted by three-center theory[2] has encouraged us to extend our discussions to the larger boron hydrides.

In the preceding paper[4] we presented the results of SCF calculations on B_4H_{10}, B_5H_9, and B_5H_{11} and discuss various molecular properties in terms of the canonical molecular orbitals and the total determinantal wave function. In the present paper we use these canonical orbitals and their associated two-electron integrals to partition the full wave function into localized molecular orbitals which maximize the orbital self-repulsion energy, $D = \Sigma_i(ii|ii)$. The advantages of this technique developed by Lennard-Jones, Hall, Pople,[5] Edmiston, and Ruedenberg[6] over methods based on other localization criteria are discussed in detail elsewhere.[3,7] However, we emphasize that an *ab initio* self-energy method requires no prior assumptions about the form of the localized orbitals, and thus the resulting picture of bonding will hopefully be independent of preconceived ideas and prejudices.

The three molecules B_4H_{10}, B_5H_9, and B_5H_{11} provide excellent examples of the various types of bonds predicted by three-center theory. In the context of this theory B_4H_{10} is expected to exhibit a two-center boron–boron (1B–2B) bond. In B_5H_9 the possibility of equivalent resonance structures[8] and nonequivalent valence structures[9] involving three-center boron bonds arises. In B_5H_{11} three-center bond theory is unable to select a preferred valence structure from two chemically reasonable nonequivalent structures differing in the type of boron–boron bonding invoked. The bridge hydrogen bond between the BH and BH_2 groups and the unique 1B–2H_t bond in B_5H_{11} offer two more examples of the interesting bonding found in these boron hydrides.

In the discussion which follows we analyze the predictions of the semiquantitative theory in terms of our localized orbitals and use our results to determine the preferred (by the self-energy criterion) valence structures in cases where the three-center theory fails to make such distinctions. Comparisons of bonds in the three molecules indicate a degree of transferability of the localized bonds. An analysis of the hybridization of boron in the various bonding orbitals provides a link between the SCF LCAO wave function and the early concepts of bonding in polyatomic molecules.[10] The angles which these hybrids make with the internuclear

---

(1) (a) Harvard University; (b) address correspondence to this author at Harvard University; (c) Carnegie-Mellon University.

(2) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Inc., New York, N. Y., 1963; (b) W. H. Eberhardt, B. L. Crawford, and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954); (c) H. C. Longuet-Higgins, *J. Chim. Phys.*, **46**, 275 (1949); (d) H. C. Longuet-Higgins, *J. Roy. Inst. Chem.*, 77, 197 (1953).

(3) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).

(4) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 3837 (1970).

(5) (a) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949); (b) G. G. Hall and J. E. Lennard-Jones, *ibid., Ser. A*, **202**, 155 (1950); (c) J. E. Lennard-Jones and J. A. Pople, *ibid., Ser. A*, **202**, 166 (1950); *Ser. A*, **210**, 190 (1951).

(6) (a) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963); (b) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965); (c) C. Edmiston and K. Ruedenberg in "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 63; (d) K. Ruedenberg in "Istanbul Lectures on Quantum Chemistry," O. Sinanoğlu, Ed., Academic Press, New York, N. Y., 1966, p 263.

(7) (a) C. Trindle and O. Şinanoğlu, *J. Chem. Phys.*, **49**, 65 (1968); (b) C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

(8) Equivalent resonance structures are structures related by molecular symmetry transformations and therefore having the same self-repulsion energies.

(9) Nonequivalent valence structures are structures not interconvertible by symmetry transformations and thus in general having different self-repulsion energies.

(10) C. A. Coulson, "Valence," Oxford University Press, London, 1961, p 203.

directions are used to distinguish between central and open three-center boron bonds in B_5H_9 and B_5H_{11}.

Calculations

The unitary localization transformation was determined by maximizing the self-repulsion energy according to the procedure suggested by Edmiston and Ruedenberg.[6] Following their suggestions[6b] we performed successive two-orbital transformations in a predetermined order rather than searching for the particular two-orbital transformation which would have the greatest localizing effect. The only input necessary for such a calculation is the two-electron integrals over occupied molecular orbitals, as determined from the orbital coefficients and basis orbital integrals discussed in the preceding paper.[4] The iterations were continued until a convergence of at least 2×10^{-5} was reached in each of the transformation elements. The calculations were performed on an IBM 7094, Model I, computer. Computer times for the localizations and analyses (as described in the following sections) were 20, 75, and 140 min for B_4H_{10}, B_5H_9, and B_5H_{11}, respectively. A description of the molecular geometries, basis set, and labeling of the atoms is found in the preceding paper.[4]

Convergence and Second-Order Energy Test

In calculations such as ours where one utilizes an iterative procedure to maximize a function of many variables, the problem of convergence to a true maximum requires attention. Our program contains two features which provide information about the point of convergence of the Edmiston–Ruedenberg procedure (a point where the first-order change in the self-repulsion is zero and the diagonal elements of the second-order self-repulsion energy given in eq 1 are negative). It was discovered[11] that a special ordering of the two-orbital transformations on the canonical orbitals of planar ammonia leads to convergence to a lower self-repulsion energy than is obtained from other orderings.[12] With this in mind, we find it useful to begin each localization by subjecting the canonical orbitals to a unitary transformation generated from random numbers. In some cases the uniqueness of the localization may be checked by repeating the calculation with several random starting guesses. The random transformations also serve as starting points in searches for multiple maxima and equivalent resonance forms.

A second check on the nature of convergence is based on Taylor's expression for the second-order change in self-repulsion energy.[13] Rewritten in a form convenient for computation, this change in second-order energy due to an infinitesimal transformation becomes

$$\begin{aligned} D_2 = \sum_{\substack{(ij) \geq (mn) \\ \text{pairs}}} \{[(ii|in) + (in|nn) - 2(in|jj) - \\ 4(ij|jn)]\delta_{jm}[(jj|jn) + (jn|nn) - 2(ii|jn) - \\ 4(ij|in)]\delta_{im} - [(ii|im) + (im|mm) - \\ 2(im|jj) - 4(ij|mj)]\delta_{jn}\} A_{ij}A_{mn} \quad (1) \end{aligned}$$

where the A_{kl}'s ($k > l$) are the $N(N-1)/2$ independent off-diagonal elements of the infinitesimal unitary transformation and the δ_{kl}'s are Kronecker δ's. Since this expression is a quadratic form in the elements of the infinitesimal transformation matrix, there exists a linear transformation of these elements which will render the second-order energy in diagonal form

$$D = \sum_{(ij)} \nu_{ij} A_{ij}' A_{ij}' \quad (2)$$

where the ν_{ij}'s are the eigenvalues of the coefficient matrix displayed in (1) and the A_{ij}''s are linear combinations of the original A_{kl}'s as determined by the eigenvectors of (1). The nature of the self-repulsion energy in the vicinity of a point where the change in first-order energy is zero (one of the conditions for Edmiston–Ruedenberg convergence) may be ascertained from this diagonal form. If all of the eigenvalues ν_{ij} are negative, any infinitesimal unitary transformation will lower the self-repulsion energy; thus convergence has occurred to a relative maximum. By a similar argument the appearance of both positive and negative eigenvalues implies convergence to a saddle point on the self-repulsion energy surface. A zero eigenvalue indicates that an infinite number of equivalent resonance forms, interrelated by the eigenvector associated with this eigenvalue, may be found along a ridge of the energy surface (to second order).

Examples representative of the information provided by these eigenvalues and their eigenvectors include the following. (1) When the planar ammonia wave function is localized by applying the Edmiston–Ruedenberg procedure to the canonical orbitals ordered by their canonical one-electron energies (ϵ_i), the localization converges to orbitals which exhibit one positive second-order energy eigenvalue (ν_{ij}) indicative of convergence to a saddle point energy. If the calculation is repeated with a random starting guess, a localized structure with a higher self-repulsion energy and all negative ν_{ij}'s (relative maximum on the self-repulsion energy surface) is obtained. (2) The small eigenvalues ($\pm 10^{-5}$) occurring in the B_5H_9 localized orbital analyses indicate the presence of resonance structures of nearly equal self-repulsion energy. In a future publication[14] examples of the information available from this multidimensional "second-derivative test" will be discussed in more detail.

Energy Results

Table I compares the various energy components from the canonical and local orbital pictures. As has been previously discussed,[3] maximization of the self-repulsion energy is accompanied by a simultaneous minimization of the magnitudes of the interorbital coulomb energy, $4\Sigma_{i>j}(ii|jj)$, and interorbital exchange energy, $2\Sigma_{i>j}(ij|ij)$. The minimization of this nonclassical exchange or "Pauli interference" energy is an especially interesting feature in view of our contention that the local orbital transformation serves to connect the Hartree–Fock wave function with the traditional concepts of electron pair bonding. As can be seen in Table I, the exchange energies corresponding to these localized boron hydride wave functions are reduced to less than 10% of the analogous canonical values.

The second-order energy analysis of our localized wave functions provides several interesting results. Localizations of the B_4H_{10} wave function initiated with

---

[11] R. M. Pitzer and W. A. Palke, private communication.

[12] U. Kaldor, *J. Chem. Phys.*, **46**, 1981 (1967).

[13] W. J. Taylor, *ibid.*, **48**, 2385 (1968).

[14] M. D. Newton and E. Switkes, manuscript in preparation.

Table I. Energy Analysis

	Two electron	Self-repulsion[a]	Coulomb[b]	Exchange[c]	Interorbital coulomb[d]
B_4H_{10}					
Canonical	134.0889	9.8042	143.3702	−9.2813	133.5660
Local	134.0889	18.39[illegible]	134.7777	−0.6889	116.3811
B_5H_9					
Canonical	175.5347	11.9255	186.3872	−10.8524	174.4617
Local	175.5347	21.7915	176.5211	−0.9864	154.7296
B_5H_{11}					
Canonical	183.7597	8.6657	198.5174	−14.7577	189.8517
Local	183.7597	22.4877	184.6955	−0.9357	162.2078

[a] $\Sigma_i(ii|ii)$. [b] $\Sigma_{i>j}4(ii|jj) + \Sigma_i(ii|ii)$. [c] $-\Sigma_{i>j}2(ij|ij)$. [d] $\Sigma_{i>j}4(ii|jj)$.

two independent starting guesses converged to identical orbitals. The eigenvalue of smallest magnitude obtained from the second-order energy analysis was −0.51, indicating convergence to a stable relative maximum. We began the B_5H_{11} localization with a random starting guess and again found that the second-order self-repulsion energy eigenvalue of smallest magnitude, −0.24, indicated convergence to a relative maximum. For B_5H_9 two nonequivalent resonance structures (and their symmetry-equivalent forms) were obtained from several independent random starting guesses. Although to the precision of the calculation each of these nonequivalent structures had the same self-repulsion energy, 29.7915 au, they are not related by a symmetry operation of the C_{4v} point group. Second-order energy eigenvalues of 3×10^{-5} and -1×10^{-5} for structures A and B (see Table V), respectively, are on the order of the precision of the calculation and show that the self-repulsion energy surface is very flat in the neighborhood of these structures. The significance of the eigenvectors obtained from the second-order energy analysis is discussed in the next section.

Bonding

Even though the Edmiston–Ruedenberg procedure requires no prior assumptions about the nature of the bonding, we find that the localization calculations for B_4H_{10}, B_5H_9, and B_5H_{11} produce orbitals which are consistent with the traditional concepts of bonding in electron-deficient molecules. The B_4H_{10} localization gives four inner-shell boron orbitals, six B–H_t bond orbitals, four asymmetric three-center B–H_b–B orbitals, and one framework boron orbital. Our second-order energy analysis shows that a transformation among the B–H_b–B and boron framework orbitals is the one least coupled to the self-repulsion criterion. In B_5H_9 we find five inner-shell orbitals, five B–H_t orbitals, four B–H_b–B orbitals, and three framework boron orbitals. In this molecule the eigenvector corresponding to the 10^{-5} second-order energy eigenvalue shows that a particular linear combination of boron framework and, to a lesser extent, B–H_b–B, orbitals is very weakly coupled to the self-repulsion energy. It is important to remember that any deviation from C_{4v} symmetry which occurs in the localized boron framework orbitals for a particular resonance structure of B_5H_9 must be accompanied by asymmetries in other local orbitals (*e.g.*, B–H_b–B). The determinant of doubly occupied local orbitals must display the total symmetry of the molecule (as must the determinant of canonical orbitals). The localized orbitals for B_5H_{11} may be interpreted as five inner-shell boron orbitals, eight B–H_t bond orbitals (to a first approximation), one symmetric B–H_b–B bridge hydrogen bond, two equivalent asymmetric B–H_b–B bond orbitals, and two *equivalent* boron framework bonds. The eigenvector with second-order energy eigenvalue of smallest magnitude connects the boron framework, B–H_b–B, and 1B–2H_t bond orbitals to the self-energy.

In the following discussion we compare the various inner-shell, B–H_t, B–H_b–B, and boron framework bonds in B_4H_{10}, B_5H_9, and B_5H_{11}. We use a Mulliken population analysis[15] to partition the total orbital populations (two electrons per orbital) into contributions from each atom. These atomic populations provide both an indication of bond polarities and a measure of the degree of delocalization forced by the required orthogonality of the orbitals. A second measure of delocalization may be ascertained from the root-mean-square per cent deviation of a truncated orbital from the full localized orbital. In eq 3 the ϕ_i^L's are the localized

$$d_i^{\mathrm{RMS}} = \left[\frac{1}{2}\int(\phi_i^L - \phi_i^T)^2 d\tau\right]^{1/2} 100\% \qquad (3)$$

orbitals and the ϕ_i^T's are truncated orbitals obtained by removing the nonlocal contributions to ϕ_i^L (*e.g.*, contributions from orbitals centered on atoms other than the bridge hydrogen and the two relevant borons in a B–H_b–B localized molecular orbital) and renormalizing. This measure of delocalization is zero if ϕ_i^L is completely localized on the atoms forming the bond, and becomes 100% if ϕ_i^L and ϕ_i^T are orthogonal.

In paper I of the series[3] we indicated how the traditional concept of hybridization could be analyzed using the local orbitals from our *ab initio* calculations. Explicit wave functions for the calculated boron hybrid orbitals used for bridge and terminal boron–hydrogen bonds were displayed. In the following discussion we extend this analysis to the larger boron hydrides. The degree of hybridization, sp^x, is calculated as the ratio of the sums of the squares of p-orbital coefficients to the square of the s-orbital coefficient. The s orbitals are linear combinations of 2s and 1s Slater functions as determined by the localization and are similar to hydrogen-like 2s orbitals in that they have a radial node. To complete the analysis of hybridization we calculate the angle which the hybrid orbitals make with the relevant internuclear directions (the B–H_t, B–H_b, or B–B directions in terminal hydrogen, bridge hydrogen, and boron framework bonding, respectively).

[15] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

Table II. Inner Shells

		Population	% delocalization
B_4H_{10}	1B (2)[a]	2.003	3.6
	3B (2)	2.003	3.4
B_5H_9	1B (1)	2.005	3.9
	2B (4)	2.004	3.6
B_5H_{11}	1B (1)	2.004	3.8
	2B (2)	2.003	3.6
	4B (2)	2.003	3.5

[a] Number of equivalent orbitals indicated in parentheses.

Table III. Boron–Terminal Hydrogen Bonds[a]

		Population		Hybridization,		
		B	H_t	sp^x	Angle,[b] deg	Delocalization,[c] %
B_4H_{10}	$1B–1H_t$ (2)[d]	0.94	1.07	1.5	1.0	7.0
	$3B–3H_t$ (2)	0.92	1.09	1.8	0.9	8.3
	$3B–5H_t$ (2)	0.94	1.09	1.8	1.4	7.1
B_5H_9[e]	$1B–1H_t$ (1)	0.91	1.10	1.3	0.0	6.1
	$2B–2H_t$ (4)	0.95	1.05	1.5	3.4	6.4
B_5H_{11}	$1B–1H_t$ (1)	0.93	1.09	1.7	0.2	6.4
	$1B–2H_t$ (2)	0.76	0.98	3.4	5.1	14.5
	$2B–3H_t$ (2)	0.97	1.05	1.4	6.8	6.3
	$5B–5H_t$ (2)	0.94	1.08	1.6	5.6	6.1
	$5B–7H_t$ (2)	0.89	1.10	2.1	1.6	9.7

[a] All $B–H_t$ bond distances are 1.19 Å. [b] Angle with internuclear direction. [c] See eq 3. [d] Number of equivalent bonds. [e] $B–H_t$ bonds are essentially identical in the various resonance structures obtained for B_5H_9.

Inner Shells

Table II gives the populations and root-mean-square delocalization of the inner-shell orbitals. The number of equivalent inner-shell orbitals of a particular type is indicated in parentheses. All the calculations produce well-localized boron inner-shell orbitals consistent with traditional concepts of electronic structure. The eigenvalues of the second-order energy matrix indicate a strong coupling of these local inner shells to the self-repulsion energy.

Boron–Terminal Hydrogen Bonds

The localized valence structure for diborane[3] exhibits four equivalent $B–H_t$ bonds which resemble localized C–H bonds in saturated hydrocarbons.[14] In B_4H_{10}, B_5H_9, and B_5H_{11} we find that each hydrogen with a single well-defined near-neighbor boron atom participates in a well-localized two-center two-electron bond. Even though this distribution of electron pairs is not ensured by any explicit assumption required for the self-repulsion energy localizations, the results confirm the predictions of the three-center bond theory developed to explain the structures of boron hydrides.[2a,b]

In Table III we compare the boron–terminal hydrogen bond orbitals in B_4H_{10}, B_5H_9, and B_5H_{11}. The atomic populations reflect the slight polarity, $B^{\delta+}–H^{\delta-}$, of all authentic $B–H_t$ bonds found in our calculations. Comparison of the orbital charges on these terminal hydrogens with the net charges calculated from the total wave function[4] indicates that the localized orbitals provide an accurate measure of the total charge (maximum deviation 0.03 electron). The root-mean-square delocalizations show that the nonlocal contributions required to maintain orthogonality are small.

Traditional discussions of hybridization[10,16] have required that the hybrid orbitals be related to the s and p atomic basis orbitals by a unitary transformation. Since the hybrids determined from the localized orbitals are not bound by this restriction, they reflect the relative s- and p-orbital energies as well as the directional nature of the bonds. The degree of hybridization (sp^x) is relatively consistent in the various boron–terminal hydrogen bonds although the hybridization for BH_t borons is slightly less than for borons participating in $B(H_t)_2$ boron–terminal hydrogen bonds. The deviation of the direction of the hybrid from the internuclear direction is most noticeable in B_5H_9 and B_5H_{11}. In these molecules distortions generally tend to be in a direction which reduces the repulsion of the $B–H_t$ bond electrons with adjacent bond pairs and the boron framework bonding.

The properties of the $1B–2H_t$ orbital in B_5H_{11} are in striking contrast to the regularities in "authentic" $B–H_t$ bonding noted above. The large delocalization, anomalous charge, and significant nonlocal populations (0.135 electron on 4B and 5B) reinforce the contention that this hydrogen exhibits properties intermediate between normal bridge and terminal hydrogens. The 5° deviation of the boron hybrid from the $B–H_t$ direction brings this hybrid closer to the 1B–4B–5B plane.

Boron–Bridge Hydrogen Bonds

The designation of a structure exhibiting two equivalent, well-localized $B–H_b–B$ bonds was a most interesting result of the diborane self-energy localization.[3] In Table IV we list the properties of three-center $B–H_b–B$ bond orbitals obtained in our localization of the larger boron hydrides. It is again encouraging to note that our calculated distribution of electron pairs gives a picture of three-center hydrogen bridge bonding consistent with existing qualitative theories. As discussed above, the self-energy localization for B_5H_9 represents a compromise, in that an attempt is made to describe an equivalent resonance structure not displaying the full fourfold molecular symmetry by a unitary transformation on a wave function having C_{4v} symmetry. Because of the coupling of bridge hydrogen bonds to the boron framework, the individual bridge hydrogen orbitals in a given resonance structure are not identical. The results on B_5H_9 given in Table IV represent averages over different $B–H_b–B$ bonds in a given resonance structure and over two of the resonance structures to which the localization can converge.

---

(16) P. Torkington, *J. Chem. Phys.*, 19, 528 (1951).

Table IV. Boron–Bridge Hydrogen Bonds

	Population			Hybridization, sp^x		Angle,[a] deg		Bond length, Å		Delocalization,[b] %
	B	H$_b$	B′	B	B′	B–H$_b$	H$_b$–B′	B–H$_b$	H$_b$–B′	
B_4H_{10}										
1B–1H$_b$–3B (4)[c]	0.63	0.95	0.43	3.5	4.3	3.7	19.2	1.33	1.43	9.5
B_5H_9[d]										
B–H–B′ (4)	0.50	1.01	0.50	3.4	3.4	3.3	3.3	1.35	1.85	9.9
B_5H_{11}										
2B–1H$_b$–3B (1)	0.53	0.97	0.53	3.4	3.4	12.0	12.0	1.34	1.34	9.9
2B–2H$_b$–4B (2)	0.59	0.96	0.44	4.2	4.8	9.0	15.1	1.34	1.32	10.0

[a] Angle with the internuclear direction. [b] See eq 3. [c] Number of equivalent bonds. [d] Averaged over two B_5H_9 structures obtained. Individual populations, for example, differ by no more than ±0.01 from average.

The orbital populations listed in Table IV agree well with the average populations (0.5, 1.0, 0.5) predicted by a simple molecular orbital treatment[2a,b] which does not take into account asymmetries in the B–H$_b$–B bond. Several interesting observations can be made about these asymmetries which appear naturally in local orbital calculations. In agreement with the measured geometric asymmetry[17] of the B–H$_b$–B bonds in B_4H_{10}, we find that 1B (with a single terminal hydrogen) has a larger population than 3B (with two terminal hydrogens). The exact position of the bridge hydrogens in B_5H_{11} is not known,[18] and, as was discussed in the preceding paper,[4] we placed 2H$_b$ in B_5H_{11} in a position approximately equidistant from 2B and 4B. In agreement with our conclusions from total density considerations,[4] we find the 2B–2H$_b$–4B localized bond populations (2B, 0.59 electron; 4B, 0.44 electron) to be asymmetrically displaced toward the boron with a single terminal hydrogen. This increased 2B–2H$_b$ bonding in the local orbital picture reinforces our prediction that more accurate structure determinations will show the asymmetric bridge hydrogens in B_5H_{11} to be closer to the BH basal borons than to the BH$_2$ basal borons.

The p-orbital contributions to the boron hybrids in B–H$_b$–B bonds are considerably larger than in the hybrids involved in B–H$_t$ bonding. This difference largely reflects the smaller H$_b$–B–H$_b$ angles and the larger B–H$_b$ distances. The deviation of the hybrids from the internuclear directions varies from molecule to molecule. In every case the deviation is in a direction which would enhance the direct overlap of the B–B hybrids, but the angles are not sufficient to give direct B–B bonding. Table IV also indicates that the B–H$_b$–B orbitals are well localized although, as expected, the per cent delocalization is higher for B–H$_b$–B orbitals than for B–H$_t$ orbitals.

Boron–Boron Bonding

The exact nature of bonding between framework boron atoms in boron hydrides cannot be completely resolved by structural considerations or qualitative bonding theory. Two distinct questions arise in the description of the valence structures for these larger boron hydrides. The first of these is to determine which atoms participate in a given polycentric two-electron bond. In Figures 1 and 2 we show the distinct bonding arrangements associated with the 4120 *styx* structure[2a,b,19] for B_5H_9 and the 3203 *styx* structure for B_5H_{11}. A second question concerns the directional nature of the three-center boron bonds. In the past it has been traditional, but by no means necessary, to

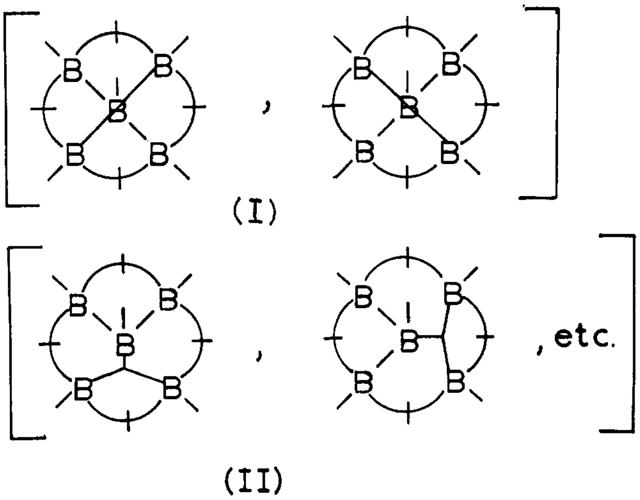


Figure 1. Resonance structures corresponding to 4120 *styx* bond arrangement in B_5H_9.

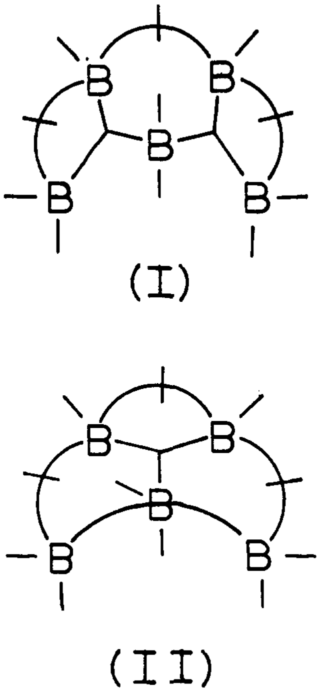


Figure 2. Resonance structures corresponding to 3203 *styx* bond arrangement in B_5H_{11}.

---

(17) C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 1856 (1953).

(18) L. R. Lavine and W. N. Lipscomb, *ibid.*, **22**, 614 (1954).

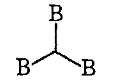
(19) *styx* structures refer to bond types possible in a given valence structure: *s* = number of hydrogen bridges, *t* = number of three-center boron bonds, *y* = number of boron–boron single bonds, *x* = number of BH$_2$ groups.

Table V. Boron–Boron Bonds

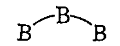
	B–B′–B″	Population B	Population B′	Population B″	Hybridization, sp^x B	Hybridization, sp^x B′	Hybridization, sp^x B″	Bond length, Å B–B′	Bond length, Å B′–B″	Bond length, Å B″–B	Delocalization,[a] %
	B_4H_{10}										
	1B–2B (1)[b]	0.81	0.81		3.0	3.0		1.75			13.8
	B_5H_9										
A[c]	1B–2B–3B (1)	0.71	0.63	0.65	5.2	3.2	3.2	1.66	1.77	1.66	14.6
	1B–5B–2B (1)	0.71	0.85	0.33	5.3	3.0	4.6				15.4
	1B–3B–4B (1)	0.71	0.31	0.86	5.3	4.8	3.0				15.5
B[c]	1B–5B–2B (1)	0.71	0.81	0.42	5.3	3.0	4.0				15.0
	1B–2B–3B (1)	0.71	0.55	0.72	5.2	3.5	3.1				14.7
	1B–3B–4B (1)	0.72	0.23	0.88	5.3	6.2	3.0				15.9
	B_5H_{11}										
	1B–2B–4B (2)	0.72	0.77	0.44	4.0	2.9	2.4	1.72	1.72	1.85	14.1

[a] See eq 3. [b] Number of equivalent bonds. [c] A and B are two of the equivalent resonance structures obtained.

designate three-center boron bonds between nearest neighbors as central or closed bonds



and to designate three-center bonds between non-nearest neighbors as open bonds



Using our local orbitals we can determine both the arrangement and directional character of the bonds in the valence structure of greatest self-repulsion energy. The use of an analysis based on the directions of the atomic hybrid orbitals allows for three-center boron bonding intermediate to pure open or symmetric central bonding.

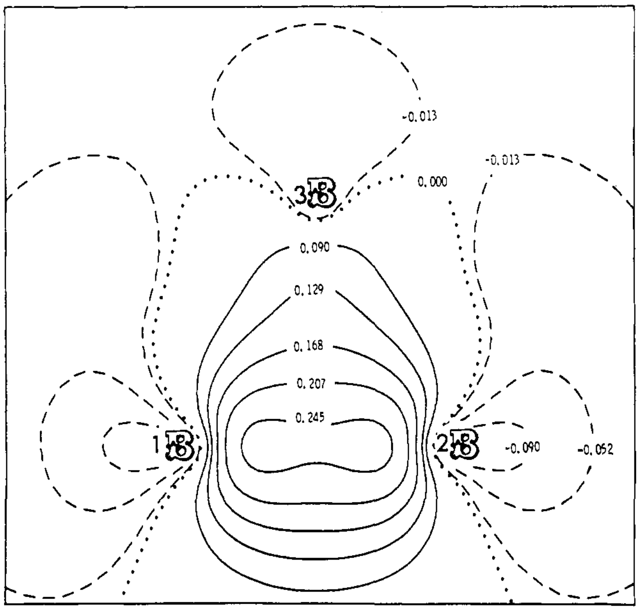


Figure 3. Local 1B–2B bond orbital in B_4H_{10} (electrons/au^3).

In B_4H_{10} we find a first example of a direct boron–boron single bond. The 14% delocalization is slightly less than that obtained in a very approximate treatment.[20] A hybridization of $sp^{3.0}$ is similar to that found in C–C single bonds.[14] Figure 3 is a plot of this B–B orbital in the 1B–2B–3B plane. The delocalization of this 1B–2B bond by contributions from the BH_2 borons (3B, 4B) can be seen in the contour map. Each of these BH_2 borons accounts for 0.19 electron in the total orbital population.

In Figure 1 we illustrate the two nonequivalent valence structures (I and II) associated with the most reasonable *styx* assignment for B_5H_9. Structure I features an open three-center bond formed by the apex and diagonally opposite basal borons. This assignment results in the two equivalent resonance forms shown. In structure II the three-center bond involves adjacent basal borons, and four equivalent resonance structures may be generated. Although, as previously discussed, the B_5H_9 localization is not unique, we may make certain observations based on properties common to all of the structures obtained at convergence. In Table V we list the properties of two such structures.

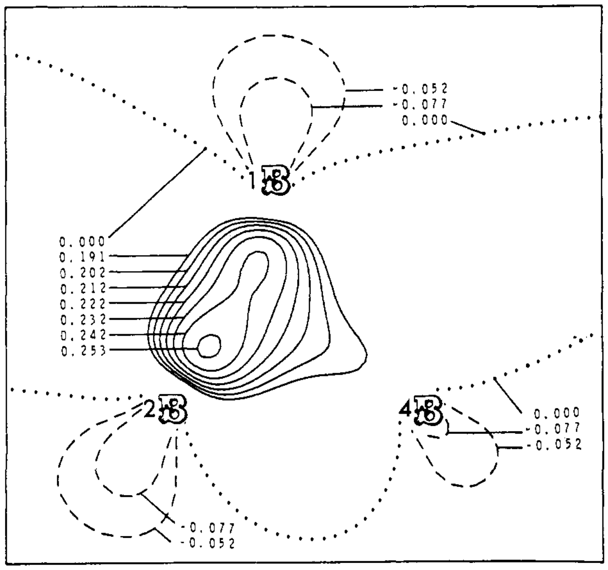


Figure 4. Local 1B–2B–4B bond orbital in B_5H_{11} (electrons/au^3).

In both calculations A and B we find that the major contributions to a given orbital come from the apex boron and two adjacent basal borons. This arrangement would indicate a preference for valence structure II of Figure 1. In a very loose sense the orbitals of calculation A resemble one of the equivalent resonance forms associated with this valence structure. These

---

(20) G. W. Adamson and J. W. Linnett, *J. Chem. Soc. A*, 1697 (1969).

orbitals might be taken to represent a symmetric three-center boron bond (1B–2B–3B) and two single apex-basal boron–boron bonds (1B–5B and 1B–4B). Assignment of such significance to one of the many possible sets of orbitals must be regarded with caution when it is remembered that the individual resonance forms in Figure 1 are of reduced symmetry, but the determinant of local orbitals must have the full C_{4v} symmetry. This multiplicity of results does not permit an analysis of the directional nature of three-center bonding in B_5H_9.

Two possible nonequivalent valence structures for the 3203 *styx* assignment for B_5H_{11} are shown in Figure 2. In contrast to B_5H_9, neither of these structures possesses equivalent resonance forms, and accordingly our calculation converged to a stable set of localized orbitals. The results given in Table V indicate the valence structure preferred by the self-energy criterion exhibits two equivalent three-center boron bonds between the apex and adjacent basal boron atoms. This assignment of bonds each involving three nonequivalent atoms corresponds to structure I shown in Figure 2. A plot of this three-center boron bond is given in Figure 4. Inspection of this map and the atomic populations (1B, 0.72; 2B, 0.77; 4B, 0.44) indicates the 1B–2B bonding to be stronger than bonding involving 4B. This result complements the total density picture in the preceding paper.

The well-defined B–B–B orbitals in B_5H_{11} provide an excellent opportunity to investigate the open or central nature of these bonds. In Figure 5 we present an illustration of the directions of hybrids participating in this bond. The angles β represent the angles between the hybrid direction and the 1B–2B–4B plane. Each of the hybrids is slightly bent in a direction outward from the boron framework. This deviation is greatest at the apex borons. The angles α give the angles between projection of the hybrids in the three-atom plane and the internuclear directions. These results and the contours of Figure 4 suggest that the 1B–2B–4B bond is a central three-center bond, asymmetric in a direction favoring 1B–2B bonding.

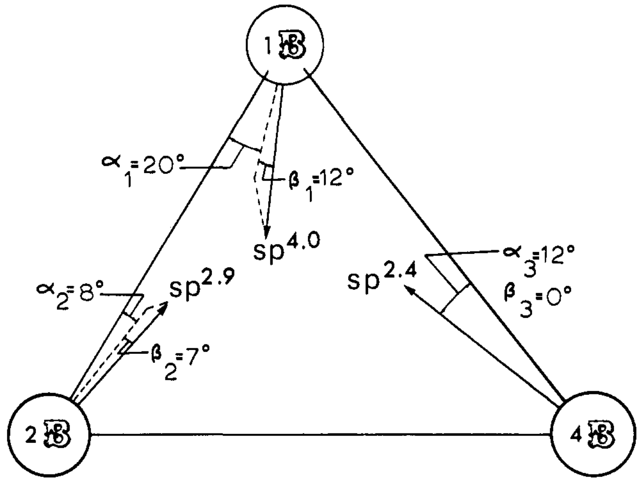


Figure 5. Direction of hybridization in the three-center 1B–2B–4B bond in B_5H_{11}.

The degree of hybridization for multicenter boron bonding indicates that a high degree of p character is required to satisfy the unusual angles of bonding in B_5H_9 and B_5H_{11}. As might be expected, the multicenter framework boron bonds show a higher degree of delocalization than bridge or terminal hydrogen bonds.[21]

Acknowledgments. We wish to thank Dr. R. M. Pitzer for an interesting discussion and the Office of Naval Research for support of this research. One of the authors (E. S.) is indebted to the National Science Foundation for a predoctoral fellowship.

(21) Note Added in Proof. A similar SCF calculation on B_6H_{10} (I. R. Epstein, J. A. Tossell, E. Switkes, R. A. Stevens, and W. N. Lipscomb, in preparation) yields a negative apex B atom (−0.02 electron), positive bridge H atoms (av, 0.025 electron) and negative terminal H atoms (av, −0.06 electron).