the bridge hydrogen nucleus, but partitioning of this distribution to compute atomic populations requires that H_b surrender charge to both boron atoms, resulting in an H_b population lower than that of H_t. Although partitioning of the electron density has taken more charge from H_b, the total density near H_b is greater because of its proximity to both boron atoms.

Discussion of Results

A thorough comparison of extended and optimized minimum STO basis sets for B_2H_6 has suggested the following conclusions. Boron hydride energies, ionization potentials, diamagnetic susceptibility and shielding constants, and total electron densities may be reliably computed from minimum basis set wave functions. Minimum basis set difference densities and quadrupole coupling constants are only qualitatively correct. The "prescription"[14c] for computing atomization energies appears more accurate when a small, rather than large, basis set is used.

From the results of this work and other studies,[22] we are inclined to feel that Mulliken overlap and atomic populations provide an easily misinterpreted characterization of electron density. Mulliken overlap populations neglect the effect of one-center charge distributions on molecular binding, while Mulliken charges reveal little about total electron density. Thus a comparison of B–B overlap populations from wave functions A and B (see Table III) suggests that direct B–B bonding is reduced in the latter wave function, when in fact just the opposite is true (see Figure 1). Similarly, the Mulliken charges on H_b and H_t seem to imply greater electron density near H_t, but our diamagnetic shielding calculations and electron density maps belie this implication. An alternative method of partitioning electron density has recently been suggested by Bader, Beddall, and Cade (BBC).[42] Although BBC feel their scheme allows a "natural partitioning" of the charge distribution, the technique is clearly more cumbersome than Mulliken's and the applicability to general polyatomics is not yet tested. In lieu of a better partitioning scheme, we are inclined to feel that electron density contour maps are the most reliable and practical means of characterizing charge distributions.

The accuracy of our minimum basis diamagnetic shielding constants suggests that wave functions previously obtained for larger boron hydrides may be used to compute reliable diamagnetic chemical shifts and thus provide a useful comparison with numbers obtained by more approximate ring current calculations.[12] Since the absolute proton chemical shifts in B_2H_6 are known,[40] a determination of both diamagnetic and paramagnetic proton shielding constants in other boron hydrides should be possible when the chemical shifts relative to B_2H_6 protons are known.[11,31b] A report of such calculations is planned for future publication.

Acknowledgment. We thank the Office of Naval Research and the Harvard Computation Center for their support of this work. E. A. L. thanks the National Science Foundation for a predoctoral fellowship. We gratefully acknowledge several helpful discussions with Dr. E. Switkes.

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A Self-Consistent Field Study of Decarborane(14)

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Abstract: A self-consistent field wave function for decaborane(14), $B_{10}H_{14}$, has been obtained from a minimum basis set of Slater-type orbitals. Electron density and difference density maps are used to discuss molecular bonding properties and possible valence structures. Static reactivity indices are found to correlate well with the experimental order of electrophilic and nucleophilic substitutions. The atomization energy and ionization potential are found in good agreement with experimental numbers, but the dipole moment is too large by roughly 40%. Theoretical values for the diamagnetic susceptibility and shielding constants are reported and the implications of these numbers discussed.

The chemical and physical properties of decaborane(14), $B_{10}H_{14}$, have been more extensively studied than those of any other boron hydride. The geometry is accurately known from the neutron diffraction study of Tippe and Hamilton,[1] and the nuclear magnetic resonance (nmr) spectra of both ^{11}B and ^1H have been completely analyzed.[2,3] The ionization potential,[4] heat of formation,[5] dipole moment,[6] and magnetic susceptibility[6] have all been determined, and voluminous literature exists on the molecule's reactivity, particularly in regard to addition and substitution reactions.[7]

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[1] A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8**, 464 (1969).

[2] (a) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **79**, 4606 (1957); **80**, 2760 (1958); (b) T. Shapiro, M. Lustig, and R. E. Williams, *ibid.*, **81**, 838 (1959); (c) J. A. Dupont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962); (d) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *ibid.*, **86**, 402 (1964); (e) P. C. Keller, D. MacLean, and R. Schaeffer, *Chem. Commun.*, **204** (1964).

[3] T. Onak and D. Marynick, *Trans. Faraday Soc.*, **66**, 1843 (1970).

[4] (a) J. L. Margrave, *J. Chem. Phys.*, **32**, 1889 (1960); (b) R. M. Reese, quoted by V. H. Dibeler, quoted by J. L. Margrave in ref 4a; (c) J. J. Kaufman, *et al.*, Office of Naval Research Report No. 2, RIAS, March 19, 1962.

[5] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

[6] R. S. Bottei and A. W. Laubengayer, *ibid.*, **66**, 1449 (1962).

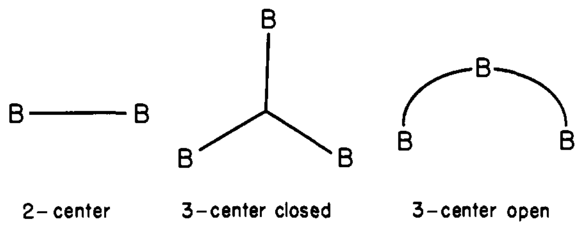

Figure 1. Types of boron framework bonds.

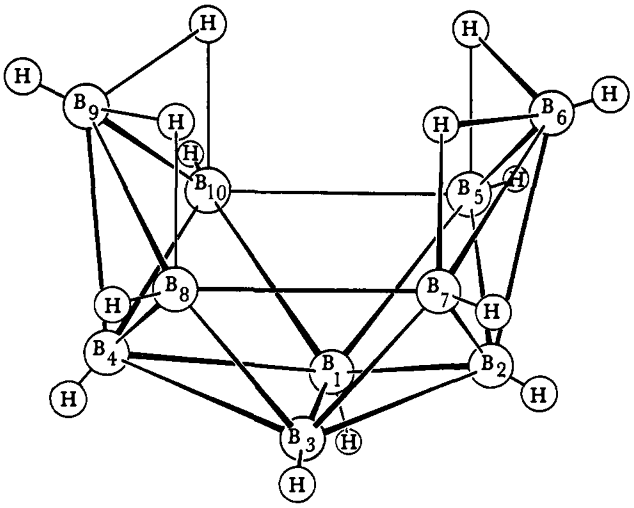

Figure 2. Nuclear geometry of $B_{10}H_{14}$.

Thus $B_{10}H_{14}$ provides a rich source of experimental data with which to compare the results of a self-consistent field (SCF) calculation. Motivation for such a study is further enhanced by curiosity regarding the nature of electron-deficient bonding in $B_{10}H_{14}$. If one allows only for the possibility of boron–hydrogen terminal and bridge bonds, for boron–boron (B–B) two-center bonds, and for B–B–B open and closed three-center bonds (see Figure 1), the number of possible valence structures for $B_{10}H_{14}$ (consistent with the known geometry) is at least 111.[7] Localization of the SCF molecular orbitals (MO's) obtained from calculations on smaller boron hydrides has provided a revealing characterization of boron framework bonding,[8] and we are hopeful that localization of the canonical MO's computed from this study will prove equally illuminating.[9]

Computer Programs

Computer programs used to perform the SCF calculation were written by Stevens and have been discussed in a previous paper.[10] The complete SCF calculation was performed on an IBM 360-65 computer and required a total time of 15.5 hr, of which 12 hr were spent in the evaluation of approximately 560,000 atomic orbital two-electron integrals. Transformation of these integrals to a symmetry orbital basis involved an additional 2.67 hr of computer time. One-electron properties were computed with a program written by Laws and described elsewhere.[11] The atomic SCF program required for the calculation of difference density maps was written by Laws and programmers at the Massachusetts Department of Corrections, Walpole, Mass.[12]

Calculations

The wave function is composed of a minimal basis set of Slater-type orbitals (STO's). Orbital exponents were obtained from the optimal diborane wave function reported earlier[8a] and are identical with the exponents used in several previous boron hydride calculations[8] (4.68 for B 1s, 1.4426 for B 2s, 1.4772 for B 2p, 1.2095 for H_b and 1.1473 for H_t). The molecular geometry is taken from the neutron diffraction study of ref 1. The molecule was assumed to have C_{2v} symmetry. Hence some averaging of the coordinates reported by Tippe and Hamilton was required. In Table I we have listed the unique nuclear coordinates used in the SCF calculation. The numbering system corresponds to that employed in Figure 2.

Table I. Coordinates of Unique Nuclei in $B_{10}H_{14}$[a]

Atom	x	y	z
H(1)	0.0	3.03507	−2.50524
H(2)	4.51156	0.0	−1.43904
H(5)	2.86787	4.64677	1.84590
H(6)	5.26744	0.0	4.38951
H(56)	1.89784	1.83944	4.15480
B(1)	0.0	1.67214	−0.71035
B(2)	2.82142	0.0	0.0
B(5)	1.86419	2.66754	1.84590
B(6)	3.37745	0.0	3.20218

[a] All coordinates are given in atomic units. H(56) is the bridge hydrogen between B(5) and B(6) (see Figure 2).

Energies

In Table II we list various energy-related quantities computed from our SCF wave function. Deviation of the virial ratio from unity is small and comparable to that found in other boron hydride calculations.[8] Reoptimization of the orbital exponents would presumably improve this ratio. The "prescription" for computing boron hydride atomization energies[13] is found

Table II. $B_{10}H_{14}$ Energy Analysis[a]

	This calcn	Exptl
Total energy	−254.4791	
Nuclear repulsion	414.5026	
Kinetic energy	254.8821	
Nuclear attraction	−1413.3525	
$-E/T$	0.9984	1.0
Atomization energy	−3.303	−3.312[b]
Ionization potential	0.389	0.404, 0.393, 0.377[c]

[a] All numbers are reported in atomic units. 1 au of energy = 10,9678 cm^{-1}. [b] This number is equal to the experimental heat of atomization at 25° reported in ref 5. [c] Reference 4.

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(7) For a compendium of research prior to 1962, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(8) (a) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969); (b) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970); (c) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971).

(9) Such a study is planned by Dr. M. D. Newton.

(10) R. M. Stevens, *J. Chem. Phys.*, **55**, 1725 (1971).

(11) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *ibid.*, **56**, 2029 (1972).

(12) Inquiries concerning the availability of the source or object decks for this program should be made to W. N. L.

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

once again to give remarkable agreement with experiment. However, our calculated atomization energy corresponds to a motionless molecule at 0°K and is not rigorously comparable to the heat of atomization at 298°K reported by Gunn and Green.[5] Proper thermodynamic corrections[14] would require knowledge of the molecule's 66 normal vibrational frequencies, the determination of which would be a rather formidable experimental task. The Koopmans' ionization potential,[15] as in previous boron hydride calculations, is found to agree well with the experimental result.

Population Analysis and Bonding

The degree of correlation between B–B internuclear distances and Mulliken overlap populations[15a] is shown in Table III. An explanation for the anomalously low B(5)–B(6) overlap lies in the fact that B(5) and B(6) are joined primarily by a hydrogen bridge rather than by a direct B–B bond (see Figure 2). Unfortunately, Mulliken atomic and overlap populations can sometimes be misleading in their characterization of more subtle features of the charge distribution, since they depend on an arbitrary scheme for partitioning the electron density.[16] However, the total density function is independent of any such partitioning and hence should allow a more refined analysis of electron bonding.

Table III. Comparison of Overlap Populations and Internuclear Distances[a]

Overlap population	Nuclei	Nuclei	Internuclear distance
0.505	B(2)–B(6)	B(2)–B(6)	3.2501
0.457	B(1)–B(5)	B(1)–B(5)	3.3167
0.425	B(1)–B(3)	B(1)–B(3)	3.3443
0.405	B(1)–B(2)	B(5)–B(6)	3.3534
0.400	B(2)–B(5)	B(1)–B(2)	3.3558
0.365	B(5)–B(10)	B(2)–B(5)	3.3822
0.358	B(5)–B(6)	B(5)–B(10)	3.7284
−0.060	B(5)–B(7)	B(5)–B(7)	5.3351
0.365	B(6)–H(56)	B(6)–H(56)	2.5456
0.406	B(5)–H(56)	B(5)–H(56)	2.4531

[a] Distances are given in atomic units.

Previous work[16d] has suggested that minimum basis set total electron density maps are in good quantitative agreement with similar maps obtained from large basis set wave functions. Difference densities (molecular density minus the sum of spherical atom densities) also provide useful information for the study of bonding effects. We have previously discovered that the agreement between minimum and expanded basis set difference densities is unfortunately only qualitative.[16d] The minimum basis set tends to underestimate significantly the accumulation of charge in the bonding regions between nuclei. However, minimum basis set difference densities do emphasize characteristics (particularly asymmetries) of the charge distribution which may be only faintly discernible from examination of the total density maps, and they do allow comparisons among similar bonding situations. For these reasons we have included difference density contour maps in the discussion below.[17]

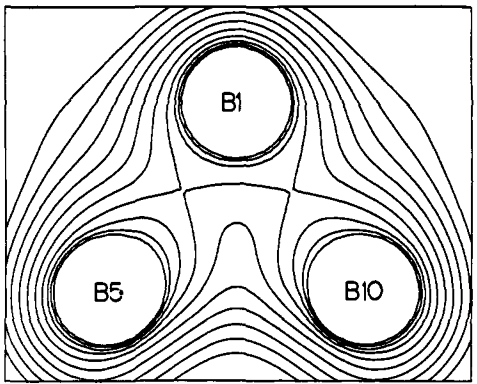

fig. 3a

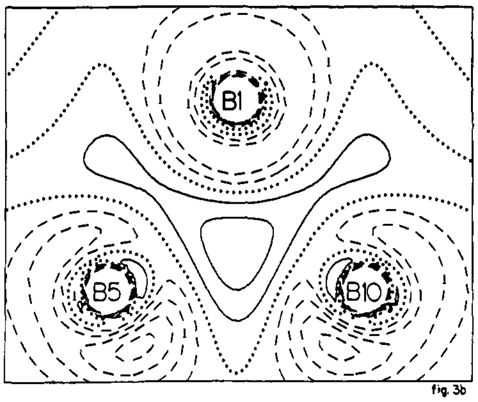

fig. 3b

Figure 3. Total density and difference density in the B(5)–B(10)–B(1) plane. Total density contours begin at 0.05 e/au^3 and increase by 0.01 e/au^3 per contour interval. Difference density contour intervals are 0.05 e/Å^3. Solid lines represent positive contours, dotted lines correspond to zero electron density, and dashed lines represent negative contours.

Figure 3 shows electron densities in the B(5)–B(10)–B(1) triangle. The bonding is obviously stronger between B(5) (B(10)) and B(1) than between B(5) and B(10). The ridge of maximum electron density lies almost on a straight line from B(5) (B(10)) to B(1). However, our difference density map shows that the greatest positive increase in charge has occurred near the midpoint of the B(5)–B(10) axis. The appearance of the total density map is not surprising in view of the geometry of this boron triangle (see Table IV). The

Table IV. Mulliken Charges

Atom	Charge
B(1)	0.0294
B(2)	−0.0101
B(5)	0.0439
B(6)	0.0920
H(1)	−0.0518
H(2)	−0.0607
H(5)	−0.0477
H(6)	−0.0336
H(56)	−0.0213

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(14) (a) L. C. Snyder, *J. Chem. Phys.*, **46**, 3602 (1967); (b) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2189 (1969).

(15) (a) T. Koopmans, *Physica (Utrecht)*, **1**, 105 (1933); (b) M. D. Newton, *J. Chem. Phys.*, **48**, 2825 (1968).

(16) (a) R. S. Mulliken, *ibid.*, **23**, 1833 (1955); (b) R. S. Mulliken, *ibid.*, **36**, 3428 (1962); (c) C. W. Kern and M. Karplus, *ibid.*, **40**, 1374 (1964); (d) L. Paoloni, *ibid.*, 30, 1045 (1955); (d) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4461 (1972).

(17) The difference densities reported here were obtained using atomic wave functions composed of the optimized minimum basis functions for B_2H_6. The ground state wave function for boron and hydrogen was subtracted out. This approach has been used in previous boron hydride calculations (see ref 8).

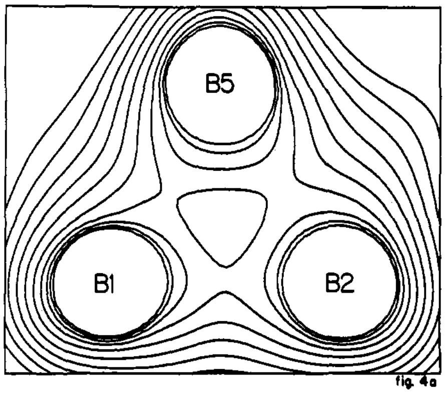

fig. 4a

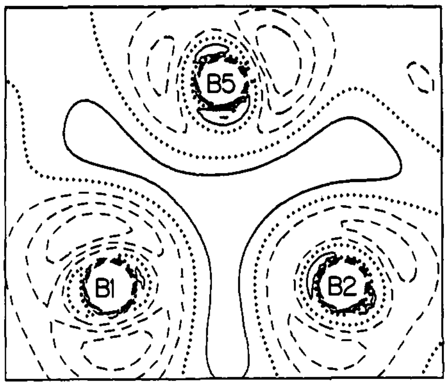

fig. 4b

Figure 4. Total density and difference density in the B(1)–B(2)–B(5) plane. Same contours as those of Figure 3.

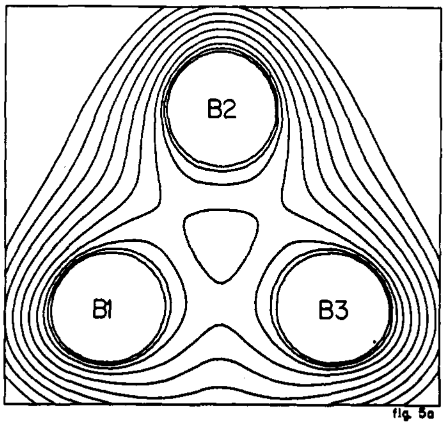

fig. 5a

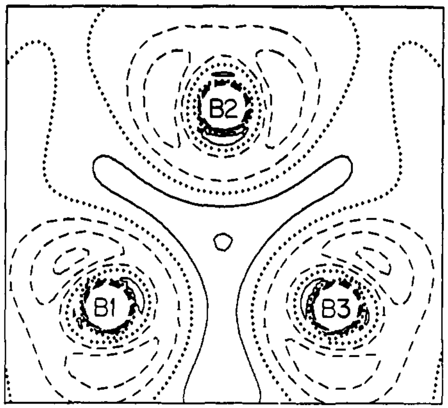

fig. 5b

Figure 5. Total density and difference density in the B(1)–B(3)–B(2) plane. Same contours as those of Figure 3.

difference density indicates that the electron distribution has tended to compensate for the long B(5)–B(10) internuclear distance.

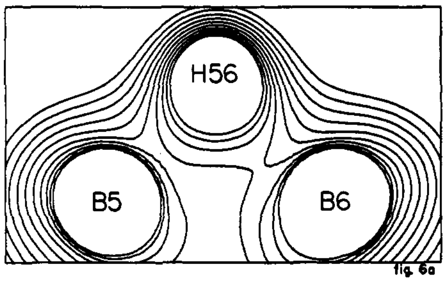

fig. 6a

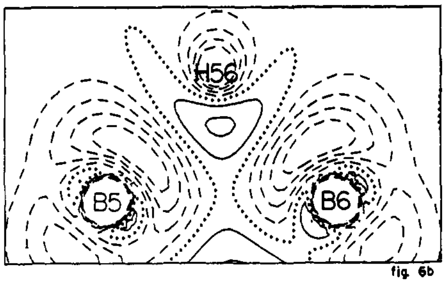

fig. 6b

Figure 6. Total density and difference density in the B(5)–B(6)–H(56) plane. Same contours as those of Figure 3.

Figure 4 shows the electron distribution in the B(1)–B(2)–B(5) plane. The order of strongest bonding would appear to be (strongest) B(2)–B(5), B(1)–B(2), and B(1)–B(5) (weakest). Curiously this order is just the opposite from that implied by the atomic overlap populations (see Table III). We have previously discussed the shortcomings of Mulliken overlap populations as a guide to chemical bonding, particularly their neglect of anisotropies in orbital shape and of polarization in one-center charge distributions.[16d] In fact the electron density in Figure 4 is so close to possessing threefold symmetry as to imply almost equal bonding between all three borons (a closed three-center bond). The large overlap population between B(1) and B(5) would appear to be a consequence of the borons' proximity to each other rather than a reflection of greater electron binding.

In Figure 5 we show electron density contours in the B(1)–B(3)–B(2) plane. Both the density and difference density maps indicate that the bonding is strongest between B(1) and B(3) (in accord with our overlap populations in Table III). As in Figure 4, there is a local depression in electron density near the center of the boron triangle, but the concentration of charge is somewhat greater in Figure 5 than in Figure 4. (This is particularly evident in the difference density maps.) The nearly threefold symmetry of the total electron density is also apparent in Figure 5 although the difference density map is somewhat less symmetric than that of Figure 4.

Density contours in the plane of the bridge hydrogen (B(5)–B(6)–H(56)) are shown in Figure 6. The bonding of B(5) and B(6) *via* the bridge hydrogen and the paucity of electron density along the B–B axis are clearly evident here (thus accounting for the anomalously low B(5)–B(6) overlap population). The contours clearly show greater electron density between B(6) and H(56), despite the fact that H(56) is closer to B(5) (see Table III). This behavior may be an artifact of the minimum basis set, particularly since there are no polarization functions on hydrogen. Thus the density on H(56) is unable to discriminate between B(5) and B(6), while the

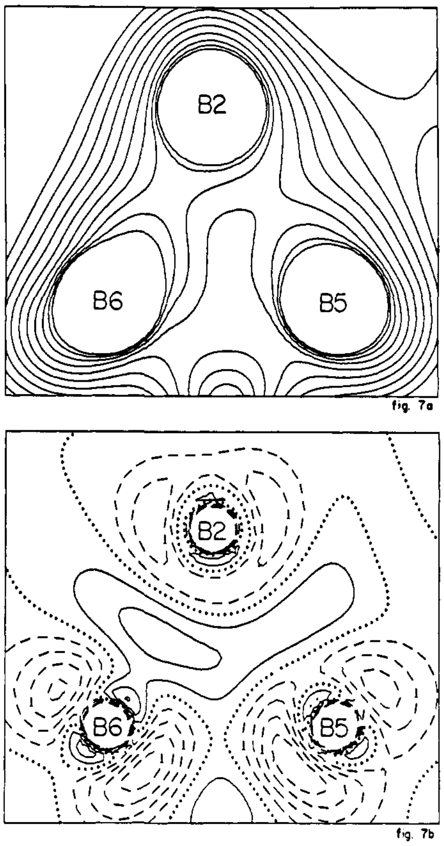

Figure 7. Total density and difference density in the B(6)–B(5)–B(2) plane. Same contours as those of Figure 3.

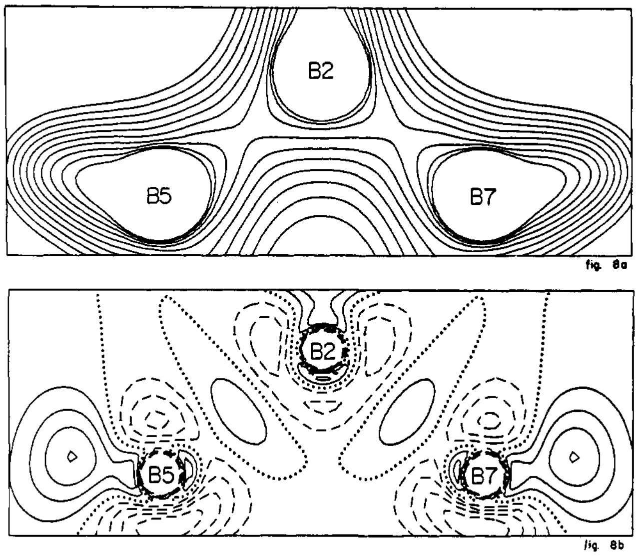

Figure 8. Total density and difference density in the B(5)–B(7)–B(2) plane. Same contours as those of Figure 3.

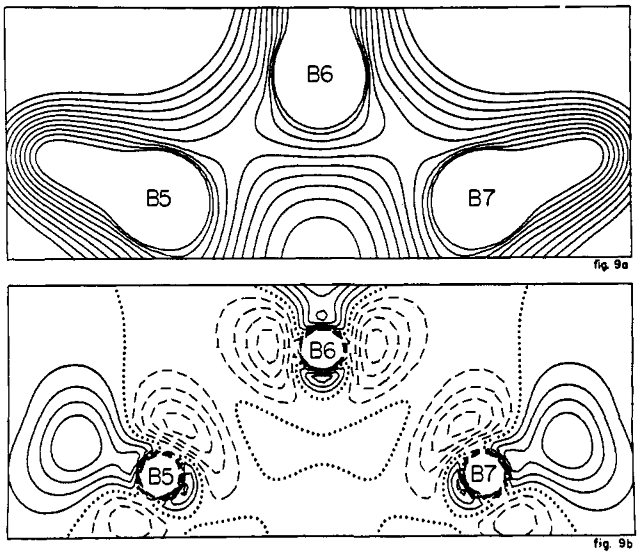

Figure 9. Total density and difference density in the B(5)–B(7)–B(6) plane. Same contours as those of Figure 3.

shape and polarization of valence shell orbitals on B(5) and B(6) are determined largely by bonding to other boron atoms. It would be interesting to investigate this question further with an extended basis set wave function at a time when such calculations are economically feasible.

In Figure 7 we show density contours in the B(6)–B(5)–B(2) plane. The presence of a strong B(2)–B(6) bond is clearly evident. As in Figure 6, we see little indication of a direct B(5)–B(6) bond, though the presence of the hydrogen bridge is apparent in the bottom of the figure. The concentration of electron density between B(5) and B(2) is sufficient to produce a fairly respectable B(2)–B(5) bond.

In Figure 8 we show electron density contours in the B(5)–B(7)–B(2) plane. The long B(5)–B(7) internuclear distance precludes the existence of any significant bonding between these nuclei. As in Figure 7, there is evidence of bonding between B(5) (B(7)) and B(2). The charge distribution in Figure 8 corresponds closely to that expected for an open three-center bond (see Figure 1).

Figure 9 shows density contours in the B(5)–B(7)–B(6) plane. There is little evidence for bonding between any of the nuclei in this figure. In particular, the difference density map is almost entirely negative along the B–B axes.

Unfortunately, it is rather difficult to unambiguously characterize the $B_{10}H_{14}$ valence structure on the basis of these electron density maps. Certainly a strong case can be made for a direct two-center bond between B(2) and B(6) (Figure 7) and a hydrogen bridge joining B(5) and B(6) (Figure 6). The most likely boron framework three-center bond would seem to be one of the closed variety involving B(1), B(2), and B(3) (Figure 5). The remaining bonds would appear to be an open three-center bond involving B(5), B(2), and B(7) (Figure 8) and an open or closed three-center bond involving B(5), B(10), and B(1) (Figure 3). This valence structure is indicated in Figure 10, where the B(5)–B(10)–B(1) three-center bond is depicted as being closed, in accord with an earlier prediction of Lipscomb.[7] The characterization of the B(5)–B(10)–B(1) bonding as open or closed is, however, a matter of some controversy. We return to this point later. Also, the open three-center bond B(5)–B(2)–B(7) may eventually be described as hybrids of equivalent structures involving only closed (*i.e.*, central) three-center bonds (Figure 11).

If one relaxes the restriction that the valence bonding reflects the total molecular symmetry, the number of possible structures greatly increases. In previous boron hydride studies[8] the canonical SCF–MO's have been

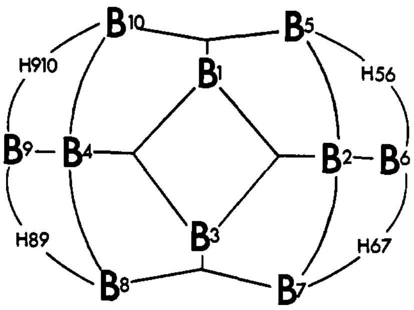

Figure 10. Possible boron framework structure in $B_{10}H_{14}$. View down C_2 axis. The terminal hydrogens have been omitted from the figure. Open three-center bonds are $B_5B_2B_7$ and $B_8B_4B_{10}$.

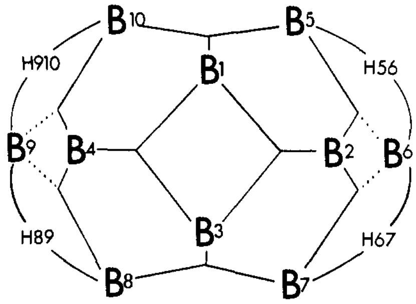

Figure 11. A suggested probable alternative valence structure based upon fractional three-center bonds, $B_5B_2B_6$, $B_7B_2B_6$, $B_8B_4B_9$, and $B_{10}B_4B_9$. One terminal hydrogen has been omitted from each B atom. Hence, B_6 (or B_9) has five bonds which require only four valance orbitals from B_6 (or B_9). Fractional central three-center bonds have been found in simpler boranes and carboranes: D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 1748 (1972).

localized by applying a succession of unitary transformations to the molecular orbitals so as to minimize the nonclassical, off-diagonal exchange or "Pauli interference" energy.[18] Though the total electron density necessarily retains the symmetry of the molecule, the valence structures to which the localized molecular orbitals most nearly correspond frequently do not. In such cases the total density is regarded as a resonance hybrid of certain valence structures. In none of these previous localizations has any one of the boron framework localized molecular orbitals been found to correspond to an open three-center bond. In view of our total density maps (especially Figures 3 and 8) we are particularly curious to see the results of a localization for $B_{10}H_{14}$.[9]

Comparison with Experiment

Brill, Dietrich, and Dierks[19] have published experimental difference density contour maps of the B–H–B bridge hydrogen plane and the B(2)–H(2) terminal bond. Their data were obtained from a low-temperature (−160°) neutron and X-ray diffraction study. Our Figure 6b is in qualitative agreement with the corresponding map (Figure 3 of ref 19) obtained by Brill, *et al.* The region of positive density covers roughly the same area, though the maximum positive density in our map is only about half that found in ref 19. We expect that extension of our basis set would remove much of this discrepancy. Brill, *et al.*, conclude from their hydrogen bridge difference density that "the B–H–B bonds are not characteristic open three-center bonds."[19] We believe that they are, but that the characteristics of difference density arise because the B–H–B bonds are bent. In our Figure 6, the lack of charge between B(5) and B(6) is not at all typical of a closed three-center bond (compare to Figure 5). Therefore, if one must choose between an open and closed description of the hydrogen bridge three-center bonding, we feel the former characterization is the more appropriate.

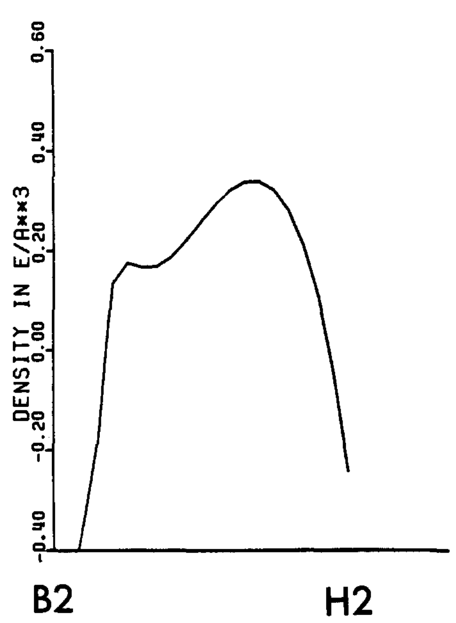

Figure 12. Difference density along B(2)–H(2) axis. The negative density near B(2) is off the scale of the plot.

In Figure 12 we have plotted a one-dimensional difference density along the B(2)–H(2) axis. This plot compares well with the corresponding map (Figure 2 of ref 19) obtained by Brill, *et al.* The maximum positive density in Figure 12 is 0.34 e/Å^3, compared to a peak density between 0.4 and 0.5 e/Å^3 in Figure 2 of ref 19. The effects of series termination and least-squares refinements undoubtedly produce some uncertainty in the experimental results, and we have previously noted the tendency of our minimum basis set difference densities to underestimate the concentration of charge in the bonding regions.[16d] Consequently we feel the agreement between our theoretical maps and the experimental results of ref 19 is probably about as good as can be expected, and somewhat fortuitous.

Brill, *et al.*, also report that they find "slight evidence only for a 'central' three-center bond in the triangle B(5)–B(10–B(1)."[19] Our Figure 3a shows that the ridge of maximum electron density follows an almost straight line from B(5) to B(1) and from B(1) to B(10). This condition is imposed to a certain extent by the geometry of the molecule, since the distance between B(5) and B(10) is much greater than that between B(5) (B(10)) and B(1) (see Table III). As we earlier noted, the effect of bonding is to somewhat reduce this anisotropy in the electron charge distribution (Figure 3b). Certainly there is much more electron density between B(5) and B(10) in Figure 3a than between B(5) and B(6)

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[18] (a) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963); (b) *J. Chem. Phys.*, **43**, 597 (1965); (c) "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Lowdin, Ed., Academic Press, New York, N. Y., 1966, p 63.

[19] R. Brill, H. Dietrich, and H. Dierks, *Angew. Chem.*, **9**, 524 (1970).

Table V. Boron Populations in I Highest Filled and J Lowest Virtual Orbitals of $B_{10}H_{14}$[a,b]

I	1	2	3	4	5
Eigenvalue	−0.3889	−0.4283	−0.4368	−0.4551	−0.4695
Symmetry	$7b_2$	$9b_1$	$12a_1$	$4a_2$	$11a_1$
Atom B(1)	0.02316	0.2850	0.5347	0.6921	0.9963
B(2)	0.2185	0.5939	0.7039	0.9469	1.1023
B(5)	0.3109	0.3351	0.5124	0.7129	0.7434
B(6)	0.0737	0.3147	0.3407	0.3451	0.4250
J	1	2	3	4	5
Eigenvalue	0.0687	0.1789	0.2689	0.3026	0.3944
Symmetry	$13a_1$	$5a_2$	$10b_1$	$8b_2$	$14a_1$
Atom B(1)	0.1388	0.3634	0.3864	0.6300	0.7149
B(2)	0.0234	0.0271	0.1258	0.4412	0.5052
B(5)	0.2464	0.4597	0.7162	0.7787	0.9058
B(6)	0.3147	0.4859	0.8378	1.1478	1.5039

[a] Energies are given in atomic units. [b] Orbitals 27–11 are $8b_1$ −0.4762, $6b_2$ −0.4804, $3a_2$ −0.5130, $10a_1$ −0.5358, $5b_2$ −0.5368, $7b_1$ −0.5603, $6b_1$ −0.5778, $9a_1$ −0.5964, $8a_1$ −0.6303, $7a_1$ −0.6593, $4b_2$ −0.6665, $5b_1$ −0.7148, $2a_2$ −0.7437, $6a_1$ −0.8529, $3b_2$ −0.8643, $4b_1$ −0.9479, $5a_1$ −1.0601. Orbitals 1–10 range from −7.6628 to −7.5733 au. The LCAO coefficients are available from the Ph.D. Thesis of E. A. L., Harvard University, 1971.

in the hydrogen bridge bond (Figure 6). Our difference density map (Figure 3b) suggests that in cases such as this one, where the boron geometry seems to favor an open three-center bond, the electron density will adjust itself in favor of the closed three-center bond structure. The B(5)–B(10)–B(1) bonding is probably described most accurately as being intermediate between an open and closed three-center bond.

Reactivities

Reactivity indices computed from the ground state wave function necessarily ignore changes in the electronic structure and nuclear geometry produced by the attack of a reagent. Nevertheless, such measures of static charge distribution as overlap populations, Mulliken charges, and frontier orbital occupations have been notably successful in correlating and predicting reactivities in hydrocarbons.[20] Similar studies on B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10} have shown encouraging results,[8] but the lack of experimental work on these smaller boron hydrides has precluded an extensive comparison of theory and experiment.

Several means of estimating the likelihood of nucleophilic and electrophilic substitution have been employed in the past. As a first approximation, one assumes that a nucleophile will most likely attack the boron atom with the most positive charge or with the greatest population in the lowest excited molecular orbital (if the lowest excited molecular orbital were occupied). Similarly, electrophilic substitution is predicted to take place most readily at the boron atom with the most negative charge or with the greatest population in the highest filled molecular orbital. A wealth of experimental work[7] on $B_{10}H_{14}$ has shown that nucleophilic substitution reactions occur at boron atoms in the following order of preference: 6, 9 > 5, 7, 8, 10 > 1, 3 > 2, 4. The order of electrophilic substitution is just the reverse.

In Table IV we list the computed Mulliken charges and in Table V the sum of atomic populations in the I highest filled and J lowest virtual molecular orbitals for the unique boron atoms in $B_{10}H_{14}$. The Mulliken charges are found to lie in exactly the order suggested by the reactivity results, but the differences between these charges are too small to allow a conclusive statement as to their interpretive reliability. We have previously discussed the dependence of Mulliken charges on the choice of basis set partitioning scheme.[16d] The terminal hydrogen charges are found to lie in the same order as the charges of the borons to which they are attached.

The electron population in the highest filled MO (Table V) is not consistent with the observed order of electrophilic substitution, but the sum of atomic populations in the first several MO's shows a definite trend of boron populations in the order 2, 4 > 1, 3 > 5, 7, 8, 10 > 6, 9. This trend is exactly in accord with the observed order of electrophilic substitution. Since attack by any reagent will obviously produce some alteration and mixing of the molecular orbitals, it is perhaps more realistic (particularly in cases when the eigenvalues are closely spaced) to examine the atomic populations in the first several highest occupied (or lowest unoccupied) orbitals to see whether any trend is apparent, rather than to base one's conclusions on the atomic populations in only the highest occupied and lowest unoccupied orbitals. We admittedly make this observation with the benefit of hindsight. This science is known as retrospectroscopy.

The order of atomic populations in the lowest virtual MO is identical with the experimental order of nucleophilic substitution, and this trend is preserved throughout the next several MO's as well.

The reactivity indices used here measure only averaged radial features of the charge distribution and do not consider possible directions of reagent attack, steric factors, or solvent effects. It is encouraging to see that such crude indices of reactivity are apparently capable of giving fairly reliable answers.

Magnetic Properties

The nature of ^{11}B chemical shifts in boron hydrides has been a subject of much discussion.[3,21,22] In Table VI we list the experimental ^{11}B and ^{1}H chemical shifts (σ) for unique $B_{10}H_{14}$ nuclei, together with the diamagnetic (σ^d) and paramagnetic (σ^p) components.[23,24]

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(20) S. S. Sung, O. Chalvet, and R. Daudel, *J. Chem. Phys.*, 57, 30 (1960).

(21) (a) T. Onak, D. Marynick, P. Mattschei, and G. Dunks, *Inorg. Chem.*, 7, 1754 (1968); (b) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1797 (1969).

(22) G. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(23) N. F. Ramsey, *Phys. Rev.*, 28, 699 (1950).

(24) Calculated from the combined measurements of R. A. Ogg,

Table VI. Chemical Shifts (ppm) in $B_{10}H_{14}$

Nucleus	Rel exptl chemical shift[a]	Absolute chemical shift[b]	Diamagnetic shift[c]	Paramagnetic shift[d]
B(1)	−9.7		449.0	
B(2)	35.8		442.9	
B(5)	−0.7		443.3	
B(6)	−11.3		421.8	
H(1)	−3.63	29.2	232.7	−203.5
H(2)	−0.62	32.2	228.4	−196.2
H(5)	−3.13	29.7	222.7	−193.0
H(6)	−3.90	29.0	211.7	−182.7
H(56)	2.12	35.0	260.9	−225.9

[a] ^{11}B chemical shifts are given relative to the ^{11}B chemical shift in BF_3–Et_2O. ^1H chemical shifts are reported relative to the ^1H chemical shift in $Si(CH_3)_4$. [b] These values were computed from data in ref 22 and 24 plus relative chemical shifts in first column. [c] Computed using our SCF wave function with the gauge at the position of the shielded nucleus. [d] Difference between numbers in second and third columns.

Our previous work on B_2H_6[16d] has suggested that a large basis set calculation of the σ^d numbers would show agreement with our minimum basis set results to within a few hundredths of a per cent. The magnitude of the σ^p numbers indicates that relative proton chemical shifts in boron hydrides cannot be inferred from consideration of the diamagnetic contributions alone (at least when the gauge is taken at the shielded nucleus).

The H(56) diamagnetic chemical shift (Table VI) is much larger than any of the other proton σ^d constants, implying that the bridge hydrogen is surrounded by greater electron density. However, the H(56) Mulliken charge (Table IV) is the most positive of all hydrogen charges. An explanation for this discrepancy lies in the fact that partitioning of the total electron density according to Mulliken[16a] requires sharing of the bridge proton electron cloud with two boron atoms, while the terminal hydrogens must share with only one. Consequently the bridge proton is computed to have the least negative Mulliken charge, even though it is surrounded by greater electron density.[25] This observation is suggestive of the caution that must be used when interpreting such numbers.

Diamagnetic Susceptibility, Dipole Moment

Our previous work on B_2H_6 indicated that boron hydride diamagnetic susceptibilities computed from a minimum basis set wave function should lie within 1–2% of values obtained from a large basis set calculation.[16d] In Table VII we give the average diamagnetic susceptibility and tensor components computed from our SCF wave function. We have also computed the paramagnetic susceptibility χ^p from the total susceptibility reported by Bottei and Laubengayer[6] and our theoretical χ^d. An experimental check of this χ^p value would be possible from a knowledge of the $B_{10}H_{14}$ rotational magnetic moment,[26] but to our knowledge this quantity has not been measured.

Table VII. Decaborane(14) Magnetic Susceptibility and Dipole Moment[a]

	This calcn	Exptl
χ		−116 ± 1.5[b]
χ^d	−834.48	
χ^p	718[c]	
$\chi_{xx}{}^d$	−701.73	
$\chi_{yy}{}^d$	−843.05	
$\chi_{zz}{}^d$	−958.66	
μ	4.556	3.17, 3.62, 3.39[b]

[a] The gauge origin for χ^d and χ^p is the molecular center of mass; χ values are reported in parts per million; the dipole moment is given in Debyes. [b] Values are taken from ref 6. [c] Determined as the difference between χ (experimental) and χ^d (theoretical).

Our computed SCF dipole moment (Table VII) is apparently too large by somewhere between 30 and 50%. This agreement is somewhat better than that found in previous boron hydride minimum basis set calculations.[8]

Conclusions

Calculation of an SCF wave function for $B_{10}H_{14}$ has provided a set of canonical MO's from which localized orbitals may be obtained.[9] Examination of total electron density maps suggests a possible valence structure, but this bonding scheme must be considered highly tentative in the light of previous studies on other boron hydrides.[8]

Mulliken charges and frontier orbital populations are in good agreement with the experimental order of electrophilic and nucleophilic substitution reactions. As expected, the atomization energy and ionization potential are found to be in good agreement with experiment. The computed dipole moment is too large by roughly 40%. Our computed diamagnetic susceptibility and shielding constants are expected to be within a few per cent of experimental values, but at present there are no experimental results with which to test this hypothesis.

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Technical Report, Stanford University, 1955, and H. S. Gutowsky and C. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

(25) Matthew, XX, 16, "So the last will be first, and the first last."

(26) N. F. Ramsey, "Molecular Beams," Oxford University Press, New York, N. Y., 1956.