Physical and Inorganic Chemistry

Studies of Polyatomic Molecules Using Self-Consistent-Field Wave Functions. B_4H_{10}, B_5H_9, and B_5H_{11}

Eugene Switkes, Irving R. Epstein, John A. Tossell, Richard M. Stevens, and William N. Lipscomb

Contribution from the Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138. Received January 9, 1970

Abstract: SCF wave functions for B_4H_{10}, B_5H_9, and B_5H_{11} show (1) all atomic (Mulliken) charges are less than ± 0.1 e, (2) apex borons are more negative than other borons, (3) borons in BH_2 groups are more positive than borons in BH groups, (4) no simple correlation exists between one-center diagonal F-matrix elements and charge, (5) all terminal hydrogens are negative and all bridge hydrogens are positive, (6) most properties of the unique hydrogen in the symmetry plane of B_5H_{11} are intermediate between bridge and terminal hydrogens, (7) bridge hydrogens between BH and BH_2 groups are more strongly bonded toward the BH group, and (8) very low electron density directly between two B atoms exists if these borons are joined by a bridge hydrogen.

For some 40 years the ideas underlying the chemistry of electron-deficient molecules have been a challenge to theoretical and experimental chemists.[1-5] The boron hydrides, based upon polyhedra or their fragments, display an extensive chemistry. Both the geometrical and valence structures have correlated[2] much of the chemistry, and have provided impetus for discoveries of new species and reactions.

Wave functions based upon the extended Hückel (EH) method, which was developed, formalized, and programmed first[6] for the boron hydrides, have been given a logical foundation and improvement by parametrization from self-consistent-field (SCF) model calculations.[7] A next more sophisticated step is the evaluation of accurate SCF wave functions for these boron hydrides. Owing to our desire for transferable parameters among atoms in molecules, as well as for extension of the SCF method to complex molecules, we employ Slater-type orbitals within a minimum basis set.

An accurate SCF wave function and localized valence structure have been reported recently[8] for B_2H_6. Strong support for a localized bridge three-center BHB bond was obtained, and boron hybrids of $sp^{2.5}$ were obtained from the optimized minimum basis set. In the present study we extend these SCF calculations and analysis of the wave functions to B_4H_{10}, B_5H_9, and B_5H_{11}.

In undertaking these SCF computations we have hoped to provide a quantitative basis for correlating some of the fascinating experimental observations on boron hydrides. Although our *ab initio* LCAO SCF calculations are among the most accurate which have been performed on larger molecules, we have tried to restrict our discussions only to those molecular properties where we can hope to obtain relatively unambiguous and physically relevant interpretations despite the limitations of the SCF approximations. The wave functions we present in this paper are the basis for

(1) K. Freudenberg, "Intramolekulare Umlagerung Optischaktiver Systeme," from the Sitzungberichte der Heidelberger Akademie der Wissenschaften, Walter de Gruyter and Co., Berlin and Leipzig, 1927.

(2) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y. 1963.

(3) (a) J. O. Hirschfelder, H. Eyring, and N. Rosen, *J. Chem. Phys.*, 4, 130 (1936); (b) J. O. Hirschfelder, *ibid.*, 6, 795 (1938).

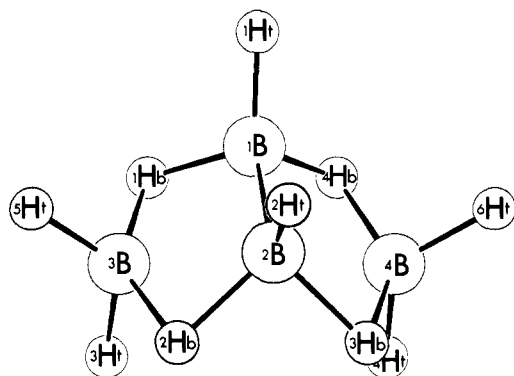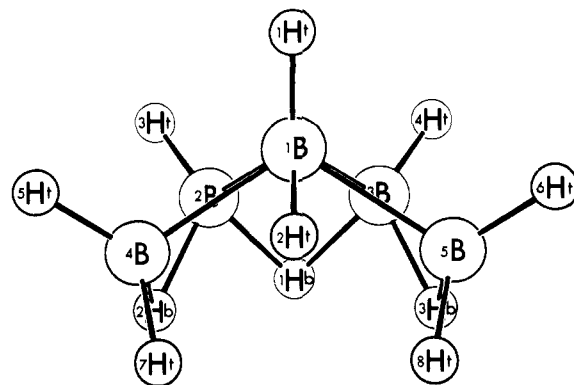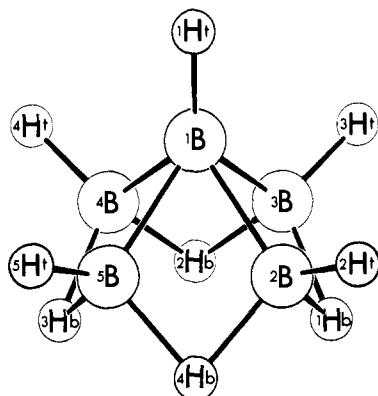(4) H. C. Longuet-Higgins, *J. Chim. Phys.*, 46, 269 (1949).

(5) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 60, 836 (1938).

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

(7) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 2361 (1966).

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

Figure 1. B_4H_{10}.

Figure 2. B_5H_9.

Figure 3. B_5H_{11}.

studies of three such properties which may be analyzed in terms of the one-electron charge distribution.

A primary aim of our calculations has been to provide an *ab initio* analysis of bonding in the polyhedral boron hydrides. In this paper we discuss the interpretation of previously proposed bonding schemes in terms of the calculated electron densities, net atomic charges, and overlap populations. In the following paper[9] we include a detailed analysis of bonding, preferred valence structures, and equivalent resonance structures in terms of localized orbital transformations on the SCF wave functions for B_4H_{10}, B_5H_9, and B_5H_{11}. Another aim of these calculations has been to relate wave functions to magnetic properties and chemical reactivities of boron hydrides. We discuss below possible relations of the calculated ground-state charge densities to these properties. Presently one of the authors (J. A. T.) is applying the SCF wave functions to somewhat more detailed calculations of the ^1H and ^{11}B chemical shifts in these molecules. By utilizing the available wave functions for this series of four related molecules (B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}), we may obtain interpretations of the trends in boron-11 chemical shifts among nuclei in different molecules as well as look at the relative shifts of boron nuclei in different geometric positions of the same molecule. This forthcoming analysis will be especially interesting because of the paramagnetic susceptibility predicted by a very complete coupled Hartree–Fock calculation[10] for

the closed-shell $^1\Sigma$ state of diatomic BH. We also present a very qualitative discussion of reactivities in these boron hydrides. More quantitative calculations, now in progress, will be the topic of a subsequent publication. The level of reliability of these SCF wave functions for a series of related molecules may permit correlation of the relative reactivities for borons in different hydrides as well as explain the differences in reactivity for borons at nonequivalent sites in the same molecule, in those reactions in which the transition state retains some features of the initial charge distribution.

As large polyatomic calculations using Slater-type orbitals become feasible one may compare the results with those of other *ab initio* and empirical methods and reevaluate the strengths and limitations of the SCF approximation. For this purpose we report the SCF energies, dipole moments, Koopmans ionization potentials, atomic populations, and atomization energies calculated from our wave functions. Using an approximate, but nonempirical, method, Boer, Newton, and Lipscomb[7,11] have studied these boron hydrides. We discuss their predictions on the transferability of diagonal SCF one-electron Hamiltonian elements and their other approximations. We compare our results with those obtained by their method as well as with those from semiempirical calculations.

Calculations

Our LCAO SCF calculations were performed on an IBM 7094, Model I, computer using a modified version of the program described by Stevens.[12] The geometries of the boron frameworks have been taken from X-ray diffraction studies[13–15] and the hydrogen coordinates have been idealized using suggested angles and distances.[2] The assumed symmetries were C_{2v}, C_{4v}, and C_s for B_4H_{10}, B_5H_9, and B_5H_{11}, respectively. The coordinates of the unique atoms are given in Table I. Our labeling of the atoms is shown in Figures 1–3.

Our basis consisted of a minimum set of Slater-type orbitals with exponents taken from an optimized calculation for diborane.[8] These exponents are 1.147

(9) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(10) (a) R. M. Stevens and W. N. Lipscomb, *J. Chem. Phys.*, **42**, 3666 (1965); (b) R. A. Hegstrom and W. N. Lipscomb, *ibid.*, **45**, 2378 (1966).

(11) F. P. Boer, "Molecular and Valence Structures of Boron Compounds," Ph.D. Thesis, Harvard University, 1965.

(12) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(13) C. E. Nordman and W. N. Lipscomb, *ibid.*, **21**, 1856 (1953), B_4H_{10} structure.

(14) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, **5**, 260 (1952), B_5H_9 structure.

(15) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954), B_5H_{11} structure.

Table I. Unique Coordinates for Boron Hydrides (au)

		x	y	z
B4H10[a]	1Ht	2.71313	0.0	-1.98557
	3Ht	0.0	2.67363	3.82733
	5Ht	0.0	4.42724	0.22396
	1Hb	2.57295	1.81222	1.47906
	1B	1.65354	0.0	0.0
	3B	0.0	2.63244	1.57889
B5H9[b]	1Ht	0.0	0.0	4.30542
	2Ht	4.42977	0.0	0.91555
	1Hb	1.84496	1.84496	-1.68509
	1B	0.0	0.0	2.05662
	2B	2.36580	0.0	0.0
B5H11[c]	1Ht	0.0	1.99750	3.99470
	2Ht	0.0	4.19050	0.77060
	3Ht	2.78980	-1.64580	1.04810
	5Ht	4.70746	3.28840	1.3345
	7Ht	2.48090	4.68300	-1.50250
	1Hb	0.0	-0.30120	-1.87730
	2Hb	2.72120	1.35970	-1.86100
	1B	0.0	2.16740	1.75240
	2B	1.67240	0.0	0.0
	4B	2.91140	3.0063	0.0

[a] xz and yz are symmetry planes. [b] z is a symmetry axis. [c] yz is the symmetry plane.

Energetics

The total energies and virial ratios from our wave functions are given in Tables II, III, and IV. Deviations of the virial ratio from unity are small and comparable in magnitude to that for B_2H_6.[8] Slightly larger deviations in the higher hydrides are expected because of the greater uncertainties in the molecular geometry and lack of reoptimization of exponents.

In Table V we compare the atomization energies calculated from our wave functions with values from more approximate calculations and from experiment. The accurate estimation of reaction energies from Hartree–Fock wave functions requires either a consistent cancellation of correlation energies or an appropriate estimate of these quantities. We suggest that minimum basis set calculations such as ours do not treat molecules with an accuracy comparable to an optimized single-ζ atomic calculation,[17] and thus we present both the usual atomization energies utilizing Clementi's atomic energies[17] and atomization energies utilizing SCF calculations for boron and hydrogen,

Table II. B_4H_{10} Occupied (and Lowest Unoccupied) Molecular Orbitals and Energies

		-7.6174	-7.6174	-7.5979	-7.5976	-0.9455	-0.7727	-0.7441	-0.6291	-0.5579	-0.5534	-0.5141	-0.5033	-0.4898	-0.4544	-0.4312	0.2435
1H7	1S	0.000	0.000	0.003	0.003	0.054	0.000	-0.121	0.225	0.000	-0.111	0.000	0.281	0.421	0.000	0.081	0.000
2H7	1S	0.000	0.000	0.003	-0.003	0.054	0.000	0.121	0.225	0.000	-0.111	0.000	0.281	-0.421	0.000	0.081	0.000
3H7	1S	0.004	0.004	0.000	0.000	0.058	0.139	0.000	-0.252	0.000	-0.027	0.374	0.215	0.000	-0.136	0.267	0.257
4H7	1S	-0.004	0.004	0.000	0.000	0.058	-0.139	0.000	-0.252	0.000	-0.027	-0.374	0.215	0.000	0.136	0.267	-0.257
5H7	1S	0.003	0.004	0.000	0.000	0.048	0.145	0.000	-0.067	0.000	-0.363	-0.216	-0.157	0.000	-0.353	-0.042	0.021
6H7	1S	-0.003	0.004	0.000	0.000	0.048	-0.145	0.000	-0.067	0.000	-0.363	0.216	-0.157	0.000	0.353	-0.042	-0.021
1H8	1S	0.002	0.002	0.003	0.003	0.124	0.157	-0.226	-0.039	-0.306	0.040	-0.013	0.073	-0.135	0.188	-0.256	-0.548
2H8	1S	0.002	0.002	0.003	-0.003	0.124	0.157	0.226	-0.039	0.306	0.040	-0.013	0.073	0.135	0.188	-0.256	-0.548
3H8	1S	-0.002	0.002	0.003	-0.003	0.124	-0.157	0.226	-0.039	-0.306	0.040	0.013	0.073	0.135	-0.188	-0.256	0.548
4H8	1S	-0.002	0.002	0.003	0.003	0.124	-0.157	-0.226	-0.039	0.306	0.040	0.013	0.073	-0.135	-0.188	-0.256	0.548
1B	1S	0.000	-0.005	-0.703	-0.703	-0.122	0.000	0.116	-0.090	0.000	-0.023	0.000	-0.012	-0.050	0.000	-0.015	0.000
	2S	0.000	0.003	-0.018	-0.023	0.257	0.000	-0.307	0.260	0.000	0.073	0.000	0.035	0.046	0.000	0.046	0.000
	2P2	0.000	0.001	-0.002	-0.001	0.077	0.000	-0.076	-0.151	0.000	0.165	0.300	-0.151	-0.302	0.000	-0.195	0.000
	2PX	0.000	-0.002	-0.001	0.003	-0.077	0.000	-0.091	-0.037	0.000	-0.091	0.000	0.287	0.104	0.000	-0.334	0.000
	2PY	0.303	0.000	0.000	0.000	0.000	0.152	0.000	0.000	-0.238	0.000	-0.097	0.000	0.000	0.231	0.000	0.221
2B	1S	0.000	-0.005	-0.703	0.703	-0.122	0.000	-0.116	-0.090	0.000	-0.023	0.000	-0.012	0.050	0.000	-0.015	0.000
	2S	0.000	0.003	-0.018	0.023	0.257	0.000	0.307	0.260	0.000	0.073	0.000	0.035	-0.140	0.000	0.046	0.000
	2P2	0.000	0.001	-0.002	0.001	0.077	0.000	0.077	-0.151	0.000	0.165	0.000	-0.151	0.302	0.000	-0.155	0.000
	2PX	0.000	0.002	0.001	0.003	0.077	0.000	-0.091	0.037	0.000	0.091	0.000	-0.287	0.104	0.000	0.334	0.000
	2PY	0.003	0.000	0.000	0.000	0.000	0.152	0.000	0.000	0.238	0.000	-0.097	0.000	0.000	0.231	0.000	0.221
3B	1S	-0.703	-0.703	0.005	0.000	-0.100	-0.139	0.000	0.073	0.000	0.058	-0.097	0.000	0.000	0.000	0.000	0.221
	2S	-0.020	-0.020	0.004	0.000	0.207	0.350	0.000	-0.205	0.000	-0.172	-0.016	0.021	0.003	0.029	-0.032	-0.058
	2P2	0.001	0.001	-0.002	0.000	-0.027	-0.017	0.000	-0.167	0.000	0.114	0.047	-0.062	0.000	-0.081	0.102	0.262
	2PX	0.000	0.000	0.000	0.001	0.000	0.000	-0.146	0.000	-0.256	0.000	0.352	0.239	0.000	-0.028	0.136	-0.221
	2PY	0.002	0.002	-0.003	0.000	-0.078	-0.022	0.000	-0.042	0.000	-0.268	-0.072	0.000	-0.121	0.000	0.000	0.000
4B	1S	0.703	-0.703	0.005	0.000	-0.100	0.139	0.000	0.073	0.000	0.058	-0.072	0.010	0.000	-0.317	-0.048	-0.361
	2S	0.020	-0.020	0.004	0.000	0.207	-0.350	0.000	-0.205	0.000	-0.172	-0.047	-0.062	0.000	0.081	-0.032	0.058
	2P2	-0.001	0.001	-0.002	0.000	-0.027	0.017	0.000	-0.167	0.000	0.114	-0.352	0.239	0.000	0.028	0.102	-0.262
	2PX	0.000	0.000	0.000	0.001	0.000	0.000	-0.146	0.000	0.256	0.000	0.000	0.000	-0.121	0.000	0.136	0.221
	2PY	0.002	-0.002	0.003	0.000	0.078	-0.022	0.000	0.042	0.000	0.268	-0.072	-0.010	0.000	-0.317	0.048	-0.361

Electronic energy = -208.1403 au Two-electron energy = 134.0889 au
Nuclear repulsion = 103.8844 au Kinetic energy = 104.2516 au
Total energy = -104.2559 au -E/T = 1.00004

for terminal hydrogens, 1.209 for bridge hydrogens, 4.680 for boron 1s, 1.443 for boron 2s, and 1.477 for boron 2p. Each unique integral over atomic orbitals was calculated to at least five decimal place accuracy, and full advantage was taken of molecular symmetry. Approximate computation times were 116, 140, and 320 min for B_4H_{10}, B_5H_9, and B_5H_{11}, respectively.

The wave functions and SCF energies are listed in Tables II, III, and IV. Although our calculations employ minimum basis sets, their quality is enhanced by the favorable ratio of basis functions to electron pairs in minimum basis sets for neutral boron hydride molecules. This 2:1 ratio provides a freedom not available in minimum basis set calculations involving heavier atoms of the first row in the periodic table, and is shown in B_2H_6 by the relatively small energy improvement found by extending the basis set.[8,16] However, extension of the basis set may allow for adequate polarization at the H atom positions.

(16) R. T. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *J. Chem. Phys.*, **45**, 2835 (1966).

which use our optimized molecular exponents from diborane. The surprising degree of cancellation of energy errors arising from correlation, atomic orbital contraction,[18] and our limited basis sets, evidenced in the latter method for calculating the atomization energies of boron hydrides, is also found in calculations on hydrocarbons.[19] Here atomic energies calculated using optimized molecular exponents were subtracted from the molecular energies. We emphasize the fortuitous, if consistent, nature of such an approximation or "prescription" for atomization energies and refer to more complete discussions which make the correct alterations on experimental enthalpies before comparison with calculated electronic energies.[20] Table V also contains the ratios of these atomization energies to the corresponding energies of B_2H_6. As may be

(17) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).
(18) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).
(19) E. Switkes and J. Tosell, unpublished results.
(20) (a) L. C. Snyder, *J. Chem. Phys.*, **46**, 3602 (1967); (b) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2189 (1969).

Table III. B_5H_9 Occupied (and Lowest Unoccupied) Molecular Orbitals and Energies

(Large matrix of molecular orbital coefficients with column energies: −7.6112, −7.6110, −7.6110, −7.6106, −7.5018, −1.0219, −0.7761, −0.7761, −0.6801, −0.5804, −0.5707, −0.5590, −0.5104, −0.5104, −0.4611, −0.3794, −0.3794, 0.1905)

Electronic energy = −265.8357 au   Two-electron energy = 175.5347 au
Nuclear repulsion = 137.5292 au   Kinetic energy = 128.6543 au
Total energy = −128.3065 au   −E/T = 0.99730

Table IV. B_5H_{11} Occupied (and Lowest Unoccupied) Molecular Orbitals and Energies

(Large matrix of molecular orbital coefficients with column energies: −7.6385, −7.6383, −7.6012, −7.6012, −7.5445, −1.0016, −0.8365, −0.7697, −0.6864, −0.6118, −0.5903, −0.5502, −0.5430, −0.5040, −0.4738, −0.4736, −0.4364, −0.4013, 0.1770)

Electronic energy = −275.5640 au   Two-electron energy = 183.7597 au
Nuclear repulsion = 146.1359 au   Kinetic energy = 129.7291 au
Total energy = −129.4281 au   −E/T = 0.99768

Table V. Atomization Energies (au)

	A				$A/A_{B_2H_6}$			
	SCF[a]	SCF[b]	Exptl[c]	NEMO[a]	SCF[a]	SCF[b]	Exptl[c]	NEMO[a]
B_2H_6	−0.721	−0.917	−0.917	−1.022	1.0	1.0	1.0	1.0
B_4H_{10}	−1.262	−1.659	−1.670	−1.758[d]	1.748	1.782	1.821	1.719
B_5H_9	−1.315	−1.762	−1.800	−1.896[d]	1.827	1.893	1.963	1.852
B_5H_{11}	−1.436	−1.894	−1.954	−1.910[e]	1.989	2.034	2.131	1.868

[a] The reference atoms employ Clementi's best single-ζ exponents: $E(B)$, −24.4984; $E(H)$, −0.500.[17] [b] The reference atoms employ optimized diborane exponents: $E(B_t)$, −24.4372; $E(H_t)$, −0.4892; $E(H_{Br})$, −0.4781. [c] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961). [d] Reference 7 (Slater exponents with H 1s = 1.20). [e] Reference 11 (partially optimized BH_3 exponents).

Tabel VI. Ionization Potentials

	SCF	Exptl[a]	NEMO
B_4H_{10}	0.431	0.382	0.415[b]
B_5H_9	0.379	0.386	0.387[b]
B_5H_{11}	0.401	0.379	0.403[c]

[a] T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 581 (1964). [b] Reference 7 (Slater exponents, H 1s = 1.2). [c] Reference 11 (partially optimized BH_3 exponents).

expected, this ratio is always smaller than the experimental ratio, because of lack of exponent optimization in the calculations for the larger boron

hydrides. First ionization potentials calculated from the orbital eigenvalues are compared in Table VI with those from NEMO calculations and with the experimental values.

The inconsistent agreement of these energy-related quantities with experiment emphasizes the care which must be exercised when using minimum basis set SCF wave functions in interpretations of energetics. However, schemes which allow some estimation of the correlation energy[20–23] have been used to obtain

(21) E. Clementi, *J. Chem. Phys.*, **38**, 2248 (1963).
(22) C. Hollister and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **88**, 13 (1966).

reaction energies of chemical accuracy from Hartree-Fock SCF wave functions. The Koopmans ionization potentials seem especially sensitive to changes in orbital exponents. NEMO calculations[11] using partially optimized BH_3 orbital exponents (B 1s = 4.68, B 2s = 1.38, B 2p = 1.35, H 1s = 1.20) give ionization potentials similar to those obtained from our SCF calculations, while Table VI indicates that the use of Slater exponents in NEMO calculations[7] yields markedly different ionization potentials. This sensitivity is also evident in B_2H_6, where both Slater[24] and optimized[8] basis sets have been used in SCF computations.

The accurate SCF wave functions also enable us to check some of the approximations of the NEMO theory. In Table VII we list the relevant SCF Hamil-

Table VII. Comparison of Diagonal SCF Hamiltonian Matrix Elements and NEMO α's (au)

	$F_{B\,2s}$	$F_{B\,2p}{}^{av}$		$F_{H\,1s}$
B_2H_6	−1.133	−0.318	H_t	−0.473
			H_b	−0.566
B_4H_{10} 1B	−1.177	−0.275	$1H_t$	−0.465
2B	−1.156	−0.247	$3H_t$	−0.491
			$5H_t$	−0.477
			$1H_b$	−0.527
B_5H_9 1B	−1.175	−0.277	$1H_t$	−0.418
2B	−1.201	−0.297	$2H_t$	−0.464
			$1H_b$	−0.576
B_5H_{11} 1B	−1.192	−0.295	$1H_t$	−0.439
2B	−1.225	−0.319	$2H_t$	−0.605
4B	−1.153	−0.242	$3H_t$	−0.483
			$5H_t$	−0.461
			$7H_t$	−0.478
			$1H_b$	−0.619
			$2H_b$	−0.599
NEMO[a]	−1.081	−0.337	H_t	−0.464
			H_b	−0.593

[a] Reference 7.

tonian matrix elements and the diagonal Hamiltonian elements (α' s) used by Boer, Newton, and Lipscomb.[7,11] These comparisons show that the use of single values of α for all terminal or bridge hydrogens or for all borons produces serious errors in charge distributions and eigenvalues. We observe in Table VII that the BH_2 borons (B_4H_{10}, 2B; B_5H_{11}, 2B) have α's which are higher than those for any of the other borons. We also find that apical terminal hydrogens (B_5H_9, $1H_t$; B_5H_{11}, $1H_t$; α_{av} = 0.428) may be distinguished from other terminal hydrogen (α_{av} = −0.473) by their higher values of α. Bridge hydrogen α's are always more negative than terminal hydrogen α's except for $2H_t$ in B_5H_{11}. This unique hydrogen assumes a value for α characteristic of a bridge hydrogen. Although this atom is designated as a normal terminal hydrogen in formal valence structures, its geometric position and participation in multicenter localized bonding[9] make such distinctions ambiguous. Unfortunately, even within the groups of chemically similar atoms noted above there are still significant variations in α. The applicability of such a grouping is further reduced by its failure to take into account the anisotropy of the boron 2p α's. Newton, Boer, and

(23) (a) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 614 (1967); (b) *ibid.*, **47**, 649 (1967).
(24) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).

Lipscomb suggested that unreasonable charge distributions in their NEMO calculations might be due to overestimation of the boron 2s, 2p zero-overlap Hamiltonian matrix elements. The B 2s, B $2p_z$ matrix element for 1B in B_5H_9 in our calculation is 0.2137, somewhat smaller than the NEMO value (0.250). Also, B 2s, B 2p elements for boron atoms bonded to two terminal hydrogens are approximately 0.06 to 0.08, slightly smaller than the 0.10 for the B 2s, B $2p_z$ element in the B_2H_6 calculation which Newton, Boer, and Lipscomb used for calibration of their zero-overlap approximation factor.

Population Analysis

The Mulliken charges and significant overlap populations[25] for B_4H_{10}, B_5H_9, and B_5H_{11} are given in Tables VIII and IX. We omit an atom-by-atom

Table VIII. Charge Distributions

B₄H₁₀		B₅H₉		B₅H₁₁	
Atom	Charge	Atom	Charge	Atom	Charge
1B	−0.02	1B	0.00	1B	−0.08
3B	+0.08	2B	+0.06	2B	+0.05
$1H_t$	−0.05	$1H_t$	−0.09	4B	+0.09
$3H_t$	−0.07	$2H_t$	−0.04	$1H_t$	−0.07
$5H_t$	−0.07	$1H_b$	+0.01	$2H_t$	+0.06
$1H_b$	+0.06			$3H_t$	−0.03
				$5H_t$	−0.06
				$7H_t$	−0.07
				$1H_b$	+0.03
				$2H_b$	+0.06

Table IX. Bond Overlap Populations

	Bond	Distance, Å	Overlap populations
B_4H_{10}	1B–2B	1.75	0.534
	1B–3B	1.84	0.299
	1B–$1H_t$	1.19	0.825
	3B–$3H_t$	1.19	0.819
	3B–$5H_t$	1.19	0.830
	1B–$1H_b$	1.33	0.479
	3B–$1H_b$	1.43	0.285
B_5H_9	1B–2B	1.66	0.531
	2B–3B	1.77	0.347
	1B–$1H_t$	1.19	0.832
	2B–$2H_t$	1.19	0.821
	2B–$1H_b$	1.35	0.388
B_5H_{11}	1B–2B	1.72	0.476
	1B–4B	1.85	0.324
	2B–3B	1.77	0.337
	2B–4B	1.72	0.414
	1B–$1H_t$	1.19	0.833
	1B–$2H_t$	1.19	0.613
	2B–$3H_t$	1.19	0.840
	4B–$5H_t$	1.19	0.821
	4B–$7H_t$	1.19	0.801
	2B–$1H_b$	1.34	0.381
	2B–$2H_b$	1.34	0.418
	4B–$2H_b$	1.32	0.330
	4B–$2H_t$	1.71	0.093

comparison of these results with those obtained from nonempirical molecular orbital (NEMO)[7,11] and extended Hückel (EH)[26] calculations on these molecules because of the difference in basis sets employed, since

(25) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(26) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

some wave functions which give nearly identical total electron densities give quite different Mulliken populations when decomposed in terms of different basis sets.[8,27] However, some of the more interesting trends are noted below.

Our atomic charges, as expected, are all smaller in magnitude than those calculated by the non-self-consistent methods.[7,11,26] We find that for all three molecules terminal hydrogens are slightly (<0.1 e) negative, while bridge hydrogens are slightly positive. These charges agree with those calculated[8] with the same exponents in B_2H_6, where the terminal hydrogen had a charge of -0.07 e while the charge on bridge hydrogen was $+0.01$ e. The only exception found to the above rule was the unique terminal hydrogen $2H_t$ in B_5H_{11}. This atom is the only known example of a second terminal hydrogen bonded to a boron which is connected to more than two other boron atoms. Lipscomb[2] has suggested that the lack of splitting of the 1B peak by this hydrogen in the ^{11}B nmr[28,29] implies that $2H_t$ is similar in character to a bridge hydrogen, as noted above. Our calculation of the charge on $2H_t$ of B_5H_{11} confirms this hypothesis.

The boron charges are quite small (<0.1 e), even smaller than the 0.13 e calculated for B_2H_6.[8] The apical positions in the two pentaboranes are markedly more negative than the basal positions, and borons bonded to two terminal hydrogens are found to be somewhat more positive than borons bonded to only one. It is interesting to note that Lipscomb[30] as early as 1956 predicted that the pentaboranes would have small charge separations and that the apical borons would be most negatively charged, by considering simplified LCAO molecular models. However, comparison of these atomic charges with the diagonal F-matrix elements (Table VII) indicates that the ω technique is not valid in its usual single linear form.

A comparison of the boron charges with those predicted by the three-center valence theory[2,26] shows agreement in the order of the charges for B_5H_9, and distinguishes between apical and basal boron in B_5H_{11}. These two calculations disagree in the charges predicted for the basal boron atoms of B_5H_{11}, for which the three-center charges are $q_{2B} = +0.39$, $q_{4B} = -0.06$, while $q_{2B} = +0.05$ and $q_{4B} = +0.09$ in the SCF calculations. Three-center theory predicts all boron atoms in B_4H_{10} to be neutral.

Comparison of our charge distributions with those calculated by other more approximate methods[11,24,26,31,32] indicates good agreement with hydrogen charges (where given), but considerable disagreement in boron charges.

This disagreement among the various methods is not at all surprising in view of the fact that SCF calculations, even on B_2H_6, show large disagreement in charge distributions between optimized Slater,[8] unoptimized Slater,[24] and gaussian[33] basis sets. A recent investigation[27] has shown that even the small changes in electron density produced by going from isotropic to anisotropic 2p orbitals in HCN produce rather large changes in the atomic charges because of modifications in the partitioning of the density. We would suggest that such small charge differences as we have found here should not be taken as an infallible guide to chemical behavior, but that they be used with caution in drawing inferences about molecular properties which may be evaluated by comparison with experiment.

Although the overlap populations are also dependent on the choice of basis set and the partitioning used, we find better agreement here with other calculations than for charges because the overlap populations are determined to a very great extent by the molecular geometry. The B–H_t values appear to be nearly independent of molecular environment, the average B–H_t overlap for the three molecules being B_4H_{10}, 0.825; B_5H_9, 0.823; and B_5H_{11} (omitting 1B–2H_t), 0.822. All bonds of this type have overlap populations within 0.02 of the average. The fluctuation in B–H_b overlap populations is somewhat greater, but the average for a molecule seems to be fairly constant. The values for the average B–H_b overlap populations are 0.382 for B_4H_{10}, 0.388 for B_5H_9, and 0.376 for B_5H_{11}. As expected, the asymmetric B–H–B bridges in B_4H_{10} and the unique hydrogen $2H_t$ in B_5H_{11} showed markedly asymmetric overlap populations.

The overlap populations for the 2B–2H_b–4B bond in B_5H_{11} are quite significant. No experimental determination has yet been made of whether this bridge hydrogen lies closer to 2B or to 4B. In our calculation we had 2H_b very slightly (0.02 Å) closer to 4B. However, the overlap populations are 0.418 for 2B–2H_b and 0.330 for 4B–2H_b, an asymmetry opposite in direction to the small difference in the assumed geometry. Therefore, we predict that further structural studies will show that the asymmetric bridge hydrogen in B_5H_{11} is closer to the BH group than to the BH_2 group. In B_4H_{10}, for which the B–H–B geometry is known,[13] the bridge hydrogen is 0.2 Å closer to the B–H group, and the overlap populations calculated with the asymmetric bridge agree with this displacement (1B–1H_b = 0.479, 3B–1H_b = 0.285).

Boron–boron overlap populations vary over a wide range, but generally tend to confirm the valence structures shown in Figures 1–3. Borons bonded directly to each other show overlap populations higher than do borons bonded through hydrogen bridges; the difference in overlap population is generally about half of the B–H_b population.

The unique hydrogen $2H_t$ in B_5H_{11} shows an abnormally small overlap population (0.613) with its bonding boron 1B. However, the difference between this value and the normal B–H_t overlap population is compensated for by the unusually large nonbonded positive overlap population (0.093) between $2H_t$ and the two borons 4B and 5B. Thus we have further evidence for the remarkable role which this atom plays in the structural chemistry of boron hydrides.

If the bonds are listed in order of overlap populations, our results agree quite well with the orders calculated by NEMO, EH, and three-center theory, although the magnitudes differ considerably. There is a discrepancy in B_5H_{11}, where Boer[11] and Hoffmann

(27) E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, 51, 5229 (1969).

(28) R. E. Williams, S. G. Gibbins, and I. Shapiro, *ibid.*, 30, 320 (1959).

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

(30) W. N. Lipscomb, *J. Chem. Phys.*, 25, 38 (1956).

(31) E. B. Moore, Jr., *J. Amer. Chem. Soc.*, 85, 676 (1963).

(32) J. E. Larcher and J. W. Linnett, *Theor. Chim. Acta*, 12, 127 (1968).

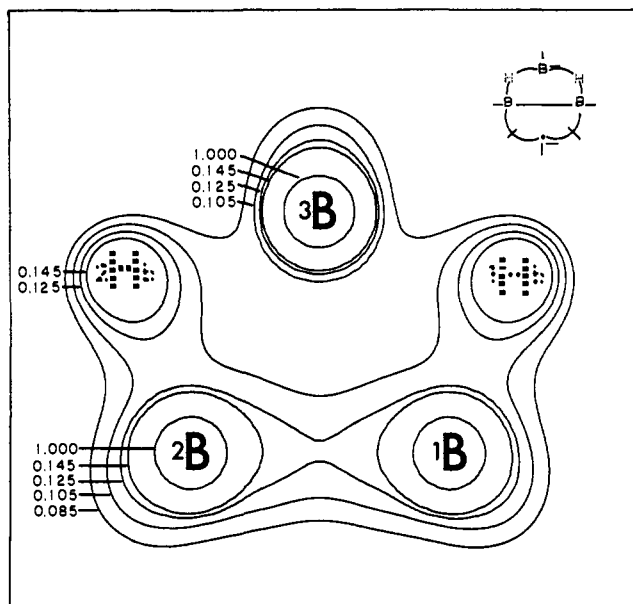(33) L. Burnelle and J. J. Kaufman, *J. Chem. Phys.*, 43, 3510 (1965).

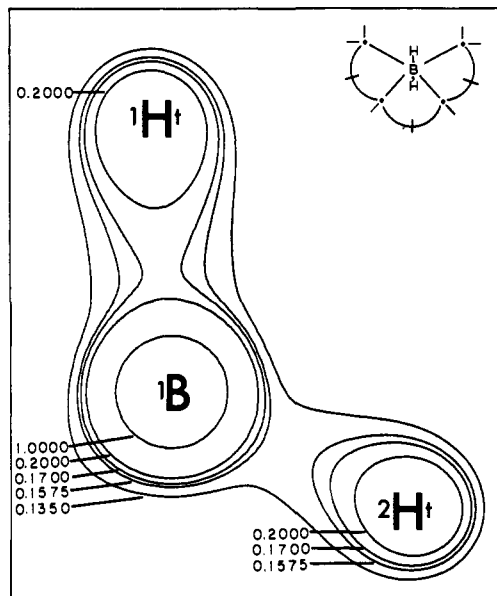Figure 4. Total electron density (electrons/au³) in the 1B-2B-3B plane of B_4H_{10}.

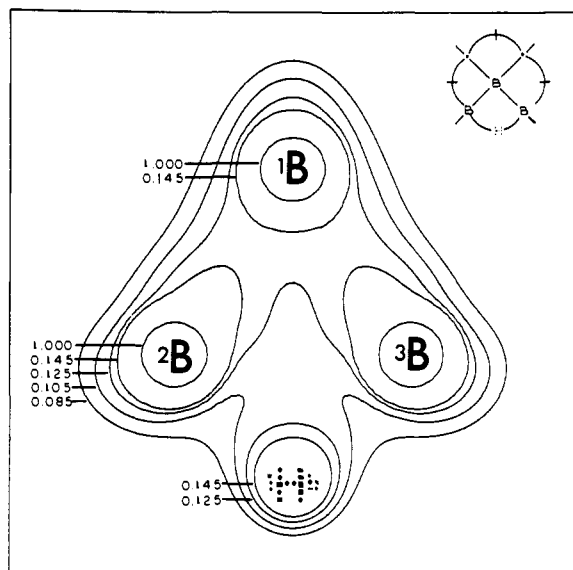Figure 6. Total electron density (electrons/au³) in $1H_t$-1B-$2H_t$ plane of B_5H_{11}.

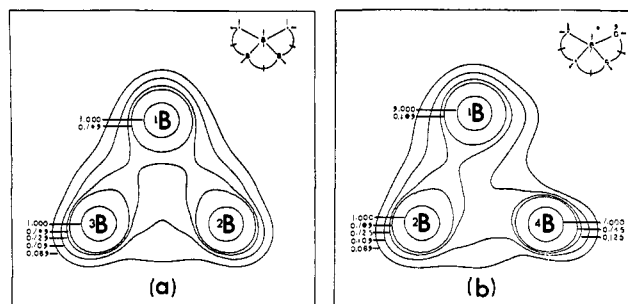Figure 5. Total electron density (electrons/au³) in the 1B-2B-3B plane of B_5H_9.

Figure 7. Total electron densities (electrons/au³) of the boron-boron bonds in B_5H_{11}: (a) 1B-2B-3B plane, (b) 1B-2B-4B plane.
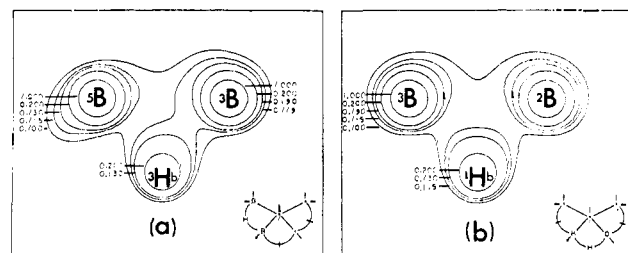

Figure 8. Total electron densities (electrons/au³) of the bridge hydrogen bonds in B_5H_{11}: (a) 3B-$3H_b$-5B plane, (b) 2B-$1H_b$-3B plane.

and Lipscomb[26] find the 1B-4B overlap population to be nearly as great as that for 1B-2B, while we find the former to be the lowest B-B population in the molecule.

Finally, we find no evidence for the large negative (−0.62) 1B-2B overlap populations in B_5H_9 calculated by Larcher and Linnett.[32] Thus the necessity for invoking ionic bonding between essentially neutral boron atoms in order to explain the molecular stability[32] does not arise in our calculation.

Perhaps a more accurate picture of bonding in these boron hydrides is provided by the total density maps in Figures 4-8. These maps tend to confirm the conclusions drawn from the population analysis, but unlike the total charges and overlap populations, the point density is invariant to a transformation within the basis set. In Figure 4 we show the density in the plane determined by the atoms 1B, 2B, and 3B in B_4H_{10}. The strong bonding between 1B and 2B is in striking contrast

to the much lower densities in the 1B-3B internuclear region. Although the bridge hydrogens $1H_b$ and $2H_b$ are not directly in the 1B-2B-3B plane, the shadows[34] of the hydrogen bridge bonds can be seen in Figure 4. In Figure 5 the total electron density in the 1B-2B-3B plane of B_5H_9 is shown along with the shadow of the three-center bridge bond involving $1H_b$. This map clearly shows bonds between apical and basal-plane borons, and B-H_b-B bonding involving borons in the

(34) When a substantial electron density is present from a bond involving an atom not quite in the plane selected for the section, we refer to this density as the shadow of that bond.
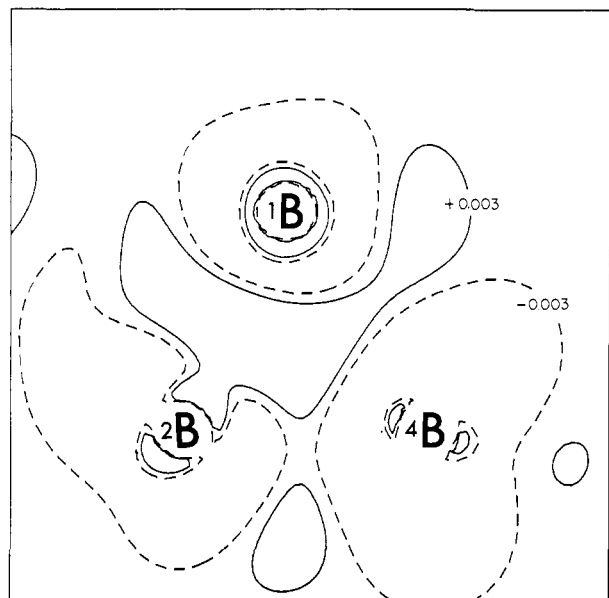
Figure 9. Difference density (molecular — spherical atoms; electrons/au^3) in the three-center 1B-2B-4B bond in B$_5$H$_{11}$: positive contours (—) +0.003 electron/au^3, negative contours (- - -) —0.003 electron/au^3.

fourfold positions. The electron density in the 2B-3B internuclear region is considerably lower. Some insight into the rather unique properties of 2H$_t$ in B$_5$H$_{11}$ may be gained from Figure 6, which shows the total density in the 1H$_t$-1B-2H$_t$ plane of B$_5$H$_{11}$. Although equal bond distances were assumed for the 1B-1H$_t$ and 1B-2H$_t$ bonds, and these two hydrogens were assigned the same orbital exponent, the difference in the bonding densities is striking. Comparison with Figure 8 indicates that the density in the 1B-2H$_t$ bond is intermediate between that in the 1B-1H$_t$ terminal bond and those in the 2B-1H$_b$-3B and 2B-2H$_b$-4B bridge hydrogen bonds. In Figure 7 we show the total densities in the two nonequivalent three-boron planes in B$_5$H$_{11}$. The bonding between the apical and basal borons in the symmetric 1B-2B-3B plane of B$_5$H$_{11}$, as shown in Figure 7a, is similar to that found in B$_5$H$_9$. Electron density in the asymmetric 1B-2B-4B bonding plane is shown in Figure 7b. In this plane the bonding density originating at atom 4B is not directed exactly toward any other atom. The relevance of this observation to three-center boron bonding is discussed more fully in the following paper.[9] In Figure 8a we exhibit the asymmetric nature of the 3B-3H-5B bridge hydrogen bond. As was noted in the overlap population analysis, bonding of a bridge hydrogen to a B-H$_t$ boron appears to be stronger than that of a bridge hydrogen to B(H$_t$)$_2$. Figure 8b shows symmetric three-center hydrogen bridge bonding in the 2B-1H$_b$-3B plane.

Further insight into the nature of bonding may be obtained by considering difference electron densities. In Figure 9 we display a difference density map for the asymmetric three-boron plane in B$_5$H$_{11}$. This map was constructed using SCF atomic wave functions from a calculation which employed the same basis orbitals as used for the boron and hydrogen atoms in our molecular calculations.[19] We have chosen to subtract these spherical atomic densities rather than valence-state atomic densities[35] from our molecular density.

In this manner we can see the effects of valence-state promotion and quantum mechanical interference on the bonding density. Figure 9 illustrates the accumulation of promotion and interference density in the central 1B-2B-4B bond in B$_5$H$_{11}$. It is to be remembered, however, that mechanisms other than valence-state promotion and interference (e.g., electrostatic interactions, orbital contractions)[18] can be responsible for bonding. Interpretation of these difference densities must also include the realization that in polyatomic molecules several bonds may compete for the available electron density on an atom, and thus a negative difference density can exist along a bonding direction where the total density exhibits a relative maximum.

Dipole Moments

Although the molecular dipole moment is not a unique measure of the electron density, dipole moments (Table X) provide a reliable test of the adequacy of our

Table X. Dipole Moments (D)

		$\mu_{classical}$	μ_{atom}	μ_{bond}	μ_{total}	μ_{exptl}
B$_4$H$_{10}$	SCF^a	0.76	0.38	—0.14	1.00	0.56^d
	NEMO^b	1.54	0.73	0.42	2.69	
B$_5$H$_9$	SCF^a	—1.54	—2.44	0.32	—3.66	—2.13^e
	NEMO^b	—5.16	—1.86	—1.46	—8.48	
B$_5$H$_{11}$	SCF^a	1.97	1.47	0.37	3.17	
	NEMO^c	1.61			3.98	

^{a} Present work. ^{b} Reference 7. ^{c} Reference 11. ^{d} Reference 36. ^{e} Reference 37.

wave functions, since the total moments are independent of basis-set partitioning and can be directly measured experimentally. Atomic, bond, and classical (Mulliken point charge) contributions to the dipole moments were calculated using the origin-invariant partitioning method of Ruedenberg.[18] The results are shown in Table XI. Our values for the two molecules, B$_4$H$_{10}$ and B$_5$H$_9$, whose dipole moments have been measured[36,37] are somewhat better than those calculated by NEMO,[7] but are still nearly twice the experimental value. This discrepancy can be attributed to our use of a partially optimized minimum basis set[38] and will probably also occur in B$_5$H$_{11}$, the dipole moment of which has not yet been measured.

The NEMO values for the various contributions to the dipole moment are also included in Table X, although this partitioning is somewhat dependent on the basis set. Extended Hückel values for dipole moments are probably unreliable, as evidenced by a number of recent studies[39] of this method and the fact that the two different sets of empirical parameters used by Hoffmann and Lipscomb[26] gave values for B$_5$H$_9$ which differed by a factor of 5.5.

The dipoles predicted by consideration of all three-center valence structures[26] are 0, 4.07, and 2.36 D for

(35) (a) R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys., 46, 3341 (1967); (b) R. F. W. Bader, I. Keaveny, and P. E. Cade, ibid., 47, 3381 (1967).
(36) J. R. Weaver, C. W. Hertsch, and R. W. Parry, ibid., 30, 1075 (1959).
(37) H. J. Hrostowski, R. J. Meyers, and G. C. Pimentel, ibid., 20, 518 (1952).
(38) B. J. Ransil, Rev. Mod. Phys., 32, 239 (1960).
(39) See, e.g., A. Pullman, Int. J. Quantum Chem., 25, 187 (1968).

Table XI. Atomic and Bond Moments (D)

	B4H10			B5H9			B5H11		
	z	Total		z	Total		y	z	Total
1B	0.38	0.38	1B	−0.42	0.42	1B	−0.01	−0.34	0.34
2B	−0.20	0.50	2B	−0.50	0.55	2B	0.20	−0.43	0.52
1B–2B	0.20	0.20	1B–2B	−0.29	0.44	4B	−0.34	0.12	0.41
1B–3B	0.02	0.03	2B–3B	−0.05	0.16	1B–2B	0.04	−0.16	0.23
3B–3H$_t$	−1.32	1.32	1B–1H$_t$	−1.23	1.23	1B–4B	0.06	−0.10	0.16
3B–5H$_t$	0.74	1.34	2B–2H$_t$	−0.35	1.28	2B–3B	0.03	0.00	0.03
1B–1H$_b$	−0.49	0.86	2B–1H$_b$	0.55	0.71	2B–4B	−0.02	−0.13	0.18
3B–1H$_b$	0.07	0.52				1B–1H$_t$	0.10	−1.31	1.31
						1B–2H$_t$	−1.04	0.38	1.11
						2B–3H$_t$	1.00	−0.51	1.28
						4B–5H$_t$	−0.07	−0.75	1.32
						4B–7H$_t$	−0.97	0.85	1.32
						2B–1H$_b$	0.21	0.54	0.72
						2B–2H$_b$	−0.29	0.59	0.78
						4B–2H$_b$	0.45	0.47	0.65
						4B–2H$_t$	−0.05	−0.11	0.20

B_4H_{10}, B_5H_9, and B_5H_{11}, respectively. Agreement with our results is fair. Our values for the pentaboranes also fall well below the three-center single valence structure upper limits of 5.23 D for B_5H_9 and 4.75 D for B_5H_{11} calculated by Eberhardt, Crawford, and Lipscomb.[40] The prediction by these authors that such negligible dipole moment as exists in B_4H_{10} will be due to B–H bond contribution rather than formal charge separation is not borne out by our results. In fact, though the individual B–H bond moments are quite large (0.50–1.25 D vs. 1.00 D for the dipole moment), they tend to cancel each other, and the net bond moment actually opposes the total dipole moment.

Values for atomic and bond moments in the three molecules are given in Table XI. These components are generally smaller than in the NEMO calculations[7] on B_4H_{10} and B_5H_9, which are the only other calculations for which such an analysis was available. Boron atomic moments all lie between 0.35 and 0.55 D, while B–B bond moments are much smaller—less than 0.25 D, except for the anomalously large value of 0.43 D for 1B–2B in B_5H_9. Like overlap populations, B–H$_t$ bond moments are remarkably independent of molecular environment and are all about 1.3 D. Bridge B–H moments are somewhat smaller and much more variable. The 1B–2H$_t$ "pseudobridge" in B_5H_{11} is again exceptional with a moment about 0.2 D too low for a B–H$_t$ bond being compensated for by a 4B–2H$_t$ moment of approximately the same magnitude, far too large for a normal nonbonded B–H interaction. We note that both our SCF atomic and bond moments show far more constancy from molecule to molecule and from position to position within a molecule than do their NEMO counterparts.

In all three molecules the net bond moment is small and opposite in direction to the total dipole moment. This effect is due completely to the fact, noted by Boer, Newton, and Lipscomb,[7] that bridge B–H bonds make large contributions in opposition to the net molecular moment. The (negative) bridge contributions to the three dipole moments are 1.7, 4.4, and 3.3 D for B_4H_{10}, B_5H_9, and B_5H_{11}, respectively.

Although our total dipole moments for B_4H_{10} and B_5H_9 are still nearly twice the experimental values, we feel that their order is probably correct and that one

may reliably predict that the dipole moment of B_5H_{11} will be found to be between those of B_4H_{10} and B_5H_9, probably somewhat closer to the latter.

Magnetic Properties

A comparison of ^{11}B nmr shifts vs. net Mulliken charges[25] (Table XII) shows the expected correlation

Table XII. ^{11}B Nmr Shifts vs. Net Mulliken Charges

		σ,[a,b] ppm	q
B_4H_{10}	1B	40.0, 41.8	−0.02
	3B	6.5, 6.9	0.08
B_5H_9	1B	51.8	0.00
	2B	12.7	0.06
B_5H_{11}	1B	53.5	−0.08
	2B	31.7	0.05
	4B	2.3	0.09

[a] Relative to boron trifluoride etherate. [b] Reference 43.

between increasing negative charge and increasing magnetic shielding. The magnitude of the change, however, is too great to be explained by the variation in the Lamb[41] diamagnetic term alone, since the addition of one 2p electron to the boron atom gives a calculated increase in the diamagnetic term of only 13.1 ppm. Changes of the magnitude observed must be largely the result of changes in the paramagnetic or high-frequency terms. Optimization of the boron 2p exponents may be required for the accurate evaluation of these terms.[42] Three of the borons given are more shielded than is the borohydride ion ($\sigma_{NaBH_4} = 38.7$ ppm), for which the one-center paramagnetic term (in the minimum basis set approximation) is zero as a result of the equivalence of the p-orbital components. Thus the explanation of these high-field shifts must be contained in the two-center or "neighbor anisotropy" contributions to the paramagnetic term.

In all of our SCF calculations the bridge hydrogens are positive. It is therefore doubtful whether the experimental[43,44] high-field shift of the bridge hy-

(41) W. E. Lamb, Phys. Rev., 60, 817 (1941).
(42) M. Karplus and J. A. Pople, J. Chem. Phys., 38, 2803 (1963).
(43) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan and Co., New York, N. Y., 1964, p 417.
(44) G. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, Inc., New York, N. Y., 1969.

(40) W. H. Eberhardt, B. Crawford, and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954).

Switkes, Epstein, Tossell, Stevens, Lipscomb | *SCF Studies of B_4H_{10}, B_5H_9, B_5H_{11}*

drogens can be explained without considering two-center paramagnetic contributions to the chemical shift. The fact that hydrogens bonded to high-field borons (generally more negative) resonate at higher field *and* are more positively charged (less shielded diamagnetically) is another indication of the importance of paramagnetic terms. The paramagnetic contributions to the proton shielding may be approximated as a "neighbor anisotropy"[45] effect of the boron atoms if accurate values for susceptibility components can be calculated for these borons.

Reactivity

Efforts to correlate known boron hydride reactions with the results of our calculations are severely limited by a scarcity of experimental data and of clear-cut interpretations of reaction pathways. We shall, however, briefly discuss a few substitution reactions with reference to three of the more directly calculable indices of reactivity—atomic charges, frontier orbital populations, and free valences. Two of the authors (I. R. E. and J. A. T.) are now studying the application of more sophisticated methods to the calculation of boron hydride reactivities.

Two frequently applied criteria for predicting reactivity in ionic reactions are the atomic charges and the populations of the highest filled and lowest vacant molecular orbitals. In the first approximation one expects that nucleophilic substitution will take place most easily at the boron atom with the greatest positive (or lowest negative) charge or at the boron with the greatest population in the lowest vacant orbital. Similarly, electrophilic substitution is expected to occur at the site of greatest negative charge and greatest highest filled MO population. Our calculations of the atomic charge and frontier orbital criteria agree in predicting the order of ionic reactivities at the various atomic sites, with the exception of 2B and 4B in B_5H_{11}. The predicted order of reactivity for nucleophilic substitution is 3B > 1B in B_4H_{10}, 2B > 1B in B_5H_9, and 4B > 2B > 1B (charge) or 2B > 4B > 1B (lowest vacant MO) in B_5H_{11}. For electrophilic substitution one should find the reverse ordering of reactivity.

The only one of the three molecules for which electrophilic substitution has been definitely observed is B_5H_9. Gaines and Martens[46] found that substitution took place at 1B when B_5H_9 was chlorinated using $AlCl_3$ as the catalyst. Further evidence for electrophilic substitution at 1B is provided by the $AlCl_3$-catalyzed exchange of D with H in B_5H_9.[47] Also pentaborane(9) reacts with I_2 only at 1B,[48] and reactions with iodine by nonionic mechanisms are exceedingly rare. Finally, Friedel–Crafts ethylation of B_5H_9 occurs almost exclusively at the apical boron position.[49]

The concept of free valence[50] has been used to great advantage in the study of reactivities of conjugated systems. One predicts that the most reactive atom (i) in free-radical substitutions will be the one for which

$\sum_j p_{ij}$ is least (where the p_{ij} are the bond orders between atom i and its nearest neighbors j). A similar calculation using as our index

$$\sum_{\substack{j \neq i \\ P_{ij} > 0}} P_{ij}$$

where the P_{ij}'s are the Mulliken overlap populations, gives the following predicted order for free radical substitutions: 1B > 3B in B_4H_{10}, 2B > 1B in B_5H_9, and 4B > 2B > 1B in B_5H_{11}.

Dobson and Schaeffer[51] found that B_4H_{10} reacts with bromine (uncatalyzed) to give 3-B_4H_9Br. This result contradicts our prediction that 1B is more reactive, if the reaction does indeed proceed by a free-radical mechanism. However, the experiment is by no means unambiguous, and nucleophilic substitution remains a possibility. On the other hand, the displacement of bridge hydrogens toward the BH groups may leave the 3-boron sterically more available for formation of an activated complex. Gaines and Martens[46] also found, if they omitted the $AlCl_3$ when chlorinating B_5H_9, that the product was the 2-substituted pentaborane. This result suggests a free-radical pathway. Also, Burg[48] found mainly 2-substituted ClB_5H_8 and FB_5H_8 in uncatalyzed gas-phase flow reactions. The evidence, then, seems to indicate that B_5H_9 reacts by free-radical mechanisms at 2B as predicted.

Analysis of the product of the gas-phase reaction of B_5H_{11} with a mixture of mono- and dimethyl diboranes[52] indicates that a proton is replaced by a methyl group at 4B. Although the mechanism is by no means clear, a free-radical reaction seems fairly likely, in agreement with our prediction.

Thus simple reactivity indices do correlate fairly well the observed boron hydride reactivities. Great caution must be observed here, however, both because of the uncertainties in interpretation of the experiments and because of the crudeness of such measures of reactivity as atomic charges, which can depend on the choice of basis set. It is hoped that these and our forthcoming reactivity studies will inspire a more definitive experimental study of the reactions of the boron hydrides.

Finally, as noted above, other factors may dominate the reaction pathway. For examples we include steric factors in the formation of an activated complex; a succession of transformations such that the initial ground state of the molecule loses its effect in favor of an intermediate in the reaction pathway; differences in coordination number, when present; and solvent effects, especially when adducts of solvent molecules to electron-deficient species may be intermediates. Nevertheless, we hope that some simplified features of reactivity and of transition states can emerge at the SCF level, and we note that some success has already been obtained in reactivity studies[53,54] of the polyhedral carboranes at a lower level of approximation.

(45) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).
(46) D. F. Gaines and J. A. Martens, *Inorg. Chem.*, **7**, 704 (1968).
(47) T. P. Onak and R. E. Williams, *ibid.*, **1**, 106 (1962).
(48) A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 1407 (1968).
(49) N. J. Blay, I. Dunstan, and R. L. Williams, *J. Chem. Soc.*, 430 (1960).
(50) C. A. Coulson, *Discuss. Faraday Soc.*, **2**, 9 (1947).

(51) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **4**, 593 (1965).
(52) C. A. Lutz and D. M. Ritter, *Can. J. Chem.*, **41**, 1344 (1963).
(53) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1301 (1966).
(54) H. A. Beall and W. N. Lipscomb, *ibid.*, **6**, 874 (1967).