All spectra were obtained on a superconducting spectrometer built by Professor F. A. L. Anet of this department (59 kG) with 251 MHz ^1H, 63.1 MHz ^{13}C, and 80.5 MHz ^{11}B. The ^1H and ^{11}B spectra were obtained using continous wave techniques, while the ^{13}C spectra were obtained using Fourier transform techniques, normally with the accumulation of 10,000 transients.

The use of eq 1 implies that the magnetic properties vary linearly with temperature. The normal method used to evaluate A_n is from linear plots of $(\Delta\nu/\nu_0)$ vs. $1/T$. In the majority of the paramagnetic metallocarboranes, such a method of evaluation has proved impossible. The minimal temperature range imposed by the solubility of the complexes in appropriate solvents (ca. -30 to $+30°$), coupled with the large uncertainty in accurate chemical shift measurements on very broad peaks, precluded any meaningful temperature dependence data to be obtained. However, within the experimental limitations, the plots of $(\Delta\nu/\nu_0)$ vs. $1/T$ were approximately linear. Rather the magnetic behavior of the ground state and excited state was estimated from the available esr and magnetic susceptbility data.

Self-Consistent Field Wave Functions of Boron Hydrides and Ions: B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$

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Abstract: A minimum basis set of Slater orbitals has been used for *ab initio* self-consistent field wave functions for B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$. From these wave functions we give bond midpoint densities, overlap populations, atomic charges, molecular dipole moments, diamagnetic susceptibilities, and diamagnetic shielding constants. Some analysis is also given relating probable sites of nucleophilic and electrophilic attack to the charge distributions, and some discussion is included relating to the few positive (unbound) occupied eigenvalues of the negative ions. A comparison is also made of these accurately computed SCF results with approximate SCF wave functions obtained by the method of partial retention of diatomic differential overlap (PRDDO). Excellent charge distributions and eigenvalues are obtained by the PRDDO method in computing times less than those of the SCF method by about a factor of 50.

B oron hydrides, carboranes, and their derivatives have been studied extensively by theoretical and experimental methods in recent years. Synthetic methods have yielded a large number of new interesting compounds. Closely related theoretical studies have indicated new features of electronic structures, rearrangements, and reactivities of electron deficient species. Recent theoretical studies have included *ab initio* self-consistent field (SCF) studies,[1] from which localized molecular orbitals (LMO) have been obtained[2,3] supporting three-center bond theory.[4] New insight has also been obtained in terms of percentages of delocalization of bonds and, most notably, a new theory in which transferable fractional bonds occur.[5] Simplification of the topological theory[4,6] of localized

bonds in electron-deficient molecules has also occurred, allowing a conceptually simple but powerful method for understanding of valence structures and chemical reactivities and providing a systematization of boron chemistry.

Partly as a result of substantial progress in computer capabilities and effective programs, *ab initio* SCF wave functions have recently become available for a number of small boron hydrides and their ions, including BH_3,[7] BH_4^-,[8] B_2H_6,[3a] $B_2H_7^-$,[9] $B_3H_8^-$,[10] B_4H_4,[11] B_4H_{10},[12] B_5H_9,[12] and B_6H_{10}.[3c] Among the larger boranes, only $B_{10}H_{14}$[13] has previously been studied by SCF methods. Here, we extend these theoretical methods to B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$. Some of the ground-state properties studied are charge distributions, overlap populations, midpoint densities in bonds, ionization potentials, atomization energies, diamagnetic susceptibilities, and diamagnetic contributions to chemical shifts.

In a separate section we compare *ab initio* SCF results

(1) For a review, see W. N. Lipscomb, "The Chemistry of Boron Hydrides," E. L. Muetterties, Ed., in press.

(2) (a) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963); (b) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949); (c) G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1960); (d) J. E. Lennard-Jones and J. A. Pople, *ibid.*, **202**, 166 (1950); (e) J. E. Lennard-Jones and J. A. Pople, *ibid.*, **210**, 190 (1951).

(3) (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).

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

(5) (a) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 8692 (1972); (b) D. S. Marynick and W. N. Lipscomb, *ibid.*, **94**, 8699 (1972); (c) I. R. Epstein, D. S. Marynick, and W. N. Lipscomb, *ibid.*, **95**, 1760 (1973).

(6) (a) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971); (b) I. R. Epstein, *Inorg. Chem.*, **12**, 709 (1973).

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

(8) R. A. Hegstrom, W. E. Palke, and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 920 (1967).

(9) J. H. Hall, Jr., D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*, **11**, 3126 (1972).

(10) I. M. Pepperberg and D. A. Dixon, private communication.

(11) J. H. Hall, Jr., I. R. Epstein, and W. N. Lipscomb, *Inorg. Chem.*, **12**, 915 (1973).

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

(13) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4467 (1972).
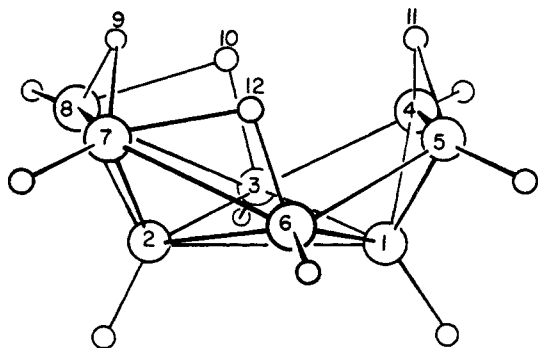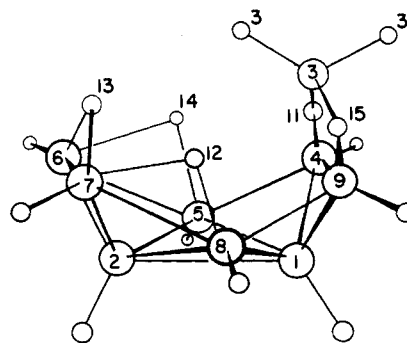
Figure 1. B_8H_{12}, symmetry C_s.

Figure 2. B_9H_{15}, symmetry C_s.

with those obtained from a very efficient method for approximating these SCF results, the PRDDO method (partial retention of diatomic differential overlap[14]). This approximate method is an especially good compromise between accuracy and speed of computation for obtaining wave functions for molecular systems which are currently too large for direct *ab initio* investigations.

Methods

All *ab initio* SCF calculations, performed with Stevens' program,[15] were made using a minimum basis set of Slater atomic orbitals (AO's). Exponents were taken from the optimized set for diborane (Table I). All one- and two-electron integrals were evaluated to an accuracy of 0.0001 au or better. In Table II we

Table I. Exponents

B	1s	4.680	H_t	1.147
	2s	1.443	H_b	1.209
	2p	1.477		

Table II. SCF Computation Times[a]

Molecule	AO integral evaluation	Symmetry orbital integral transformation	Solution of the HF eq	Symmetry[b]
$B_6H_6{}^{2-}$	2	1	0.08	D_4
B_8H_{12}	30	4	9	C_s
B_9H_{15}	35	6	23	C_s
$B_{10}H_{10}{}^{2-}$	53	8	19	C_2
$B_{10}H_{14}{}^{2-}$	60	20	7	C_{2v}

[a] All times are in minutes for the IBM 360/195 computer and do not include elapsed time. [b] These are the point groups used in the calculation and were chosen for computational convenience. They do not necessarily reflect the complete symmetries of the molecules.

summarize computing times for (a) evaluation of integrals over AO's, (b) transformation of integrals over AO's to integrals over symmetry orbitals, and (c) solution of the SCF equations.[16] Coordinates are given in Table III for B_8H_{12} (Figure 1), B_9H_{15} (Figure 2), $B_6H_6{}^{2-}$ (Figure 3), $B_{10}H_{10}{}^{2-}$ (Figure 4), and $B_{10}H_{14}{}^{2-}$ (Figure 5). Except for $B_6H_6{}^{2-}$, the coordinates for the boron atoms were taken from the crystal structures for B_8H_{12},[17] B_9H_{15},[18a] $B_{10}H_{10}{}^{2-}$,[19] and

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(16) (a) C. C. F. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); (b) G. G. Hall, *Proc. Roy. Soc., Ser. A*, **205**, 541 (1951).

(17) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

(18) (a) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957); (b) R. Schaeffer, private communication.

Table III. Coordinates[a]

		x	y	z
$B_6H_6{}^{2-}$ [b]	B_1	0.0	0.0	2.2685
	H_1	0.0	0.0	4.5295
B_8H_{12} [b]	B_1	2.8192	0.0	0.0
	B_2	4.3926	0.0	-3.0799
	B_3	2.5430	2.6831	-2.0461
	B_4	0.0	1.5819	0.0
	B_7	2.6294	-1.6089	-5.2875
	H_1	4.2406	0.0	1.7426
	H_2	6.6408	0.0	-3.1316
	H_3	3.3531	4.7582	-1.7384
	H_4	-1.6520	3.0856	1.2997
	H_7	3.1886	-2.9678	-6.9897
	H_9	0.8813	0.0	-6.0557
	H_{10}	0.6466	2.6107	-3.7584
	H_{11}	-1.5737	0.0	-1.1478
B_9H_{15} [c]	B_1	-3.0935	0.0	0.0
	B_2	0.0003	0.0	-2.9054
	B_3	-6.8895	0.0	0.0
	B_4	-5.6043	1.6955	-2.7951
	B_5	-2.0644	2.7195	-2.6007
	B_6	0.0	1.6809	0.0
	H_1	-2.7509	0.0	-6.3941
	H_2	1.5114	0.0	-4.5708
	H_3	-9.1326	0.0	-0.1593
	$H_3{}'$	-5.6473	0.0	1.8745
	H_4	-6.8829	2.8822	-4.2153
	H_5	-1.4450	4.6735	-3.5254
	H_6	1.3346	3.1795	1.0018
	H_{11}	-6.4062	-2.3433	-0.5569
	H_{12}	-2.0598	-3.0236	-0.1518
	H_{13}	-1.0771	0.0	1.4551
$B_{10}H_{10}{}^{2-}$ [b]	B_1	0.0	0.0	3.4846
	B_2	2.5122	0.0	1.4221
	H_1	0.0	0.0	5.7334
	H_2	4.6379	0.0	2.1558
$B_{10}H_{14}{}^{2-}$ [d]	B_1	0.0	1.7007	1.1025
	B_2	2.6817	0.0	0.0
	B_5	1.7830	2.7721	-1.5538
	B_6	3.2088	0.0	-3.2611
	H_1	0.0	2.8095	3.0681
	H_2	4.5626	0.0	1.1789
	H_5	2.6852	4.7973	-1.4574
	H_6	5.4043	0.0	-3.6633
	$H_6{}'$	2.0323	0.0	-5.1579
	H_{13}	0.0	3.3088	-3.3097

[a] Atomic units. [b] The molecule is centered at (0, 0, 0). [c] The symmetry plane is xz. [d] The symmetry planes are xz and yz.

$B_{10}H_{14}{}^{2-}$[20] and subsequently idealized to the symmetry expected for the molecule or ion when isolated from the crystalline environment. The B–B bond length in $B_6H_6{}^{2-}$ was optimized and is in excellent

(19) C. H. Schwalbe and W. N. Lipscomb, *Inorg. Chem.*, **10**, 160 (1971).

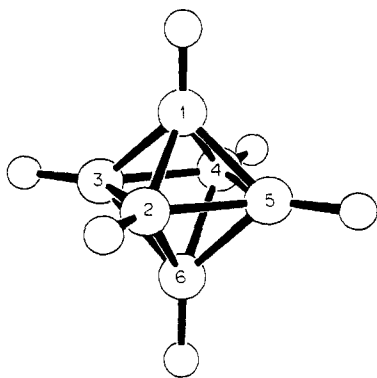(20) D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, **12**, 546 (1973).

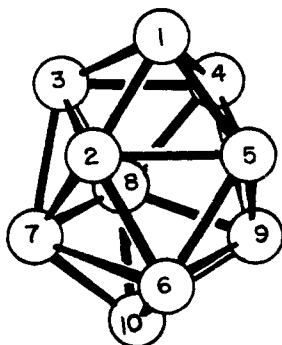**Figure 3.** $B_6H_6^{2-}$, symmetry O_h.

Figure 4. $B_{10}H_{10}^{2-}$, symmetry D_{4d}. H atoms have been omitted for clarity.

agreement with the boron–boron distance from the X-ray diffraction study.[21] The B–H$_t$ distances were taken as 1.19 Å, except in $B_{10}H_{14}^{2-}$ where a value of 1.20 Å was assumed. Inasmuch as the accuracy of the X-ray diffraction study did not permit determination of the asymmetry of bridge hydrogen atoms in B_9H_{15}, although the bonding topology was established with certainty, we assumed that all hydrogen bridges were symmetrical in this molecule.

SCF Results

B_8H_{12}. The eight-boron framework found in topological studies of boron hydrides has been a challenge to chemical synthesis. Structures for B_8H_{12} (and B_8H_{14}) have been proposed,[22] and the synthesis and crystal structure have subsequently been reported.[17] Topological theory in its present form for boron hydrides (excluding carboranes) requires only central three-center bonds in the boron framework,[6a] and leads to only five topologically allowed valence structures (Table IV). A localized valence structure which is a

Table IV. Topologically Allowed Structures for B_8H_{12}[a]

B–B bonds		
3–2	5–6	(2)
3–4	5–6	(1)
3–4	2–8	(2)

[a] Only B–B bonds are given because the three-center bonds are then uniquely determined aside from satisfying the molecular symmetry (C_s). The number in parentheses gives the number of symmetrically equivalent structures with the indicated topology.

(21) R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965).
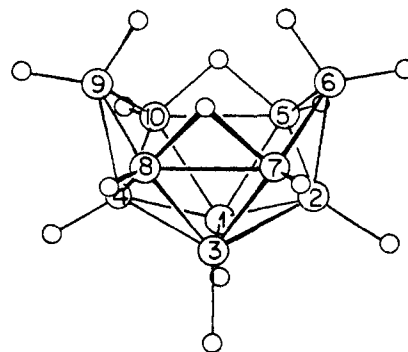
(22) Reference 4, p 29.

Figure 5. $B_{10}H_{14}^{2-}$, symmetry C_{2v}.

combination of the originally proposed structure[22] and other topologically allowed structures (Table IV) is presented in the PRDDO section.

Under certain conditions, static reactivity indices such as Mulliken charges[23] and inner shell eigenvalues have been surprisingly successful in predicting electrophilic and nucleophilic attack in boron hydrides and especially in carboranes.[3c,4,5,12,13] These indices are valid only if the course of the reaction is determined by the initial ground-state charge distribution and therefore must be restricted to relatively simple reactions, especially those not involving extensive rearrangements. In B_8H_{12}, both Mulliken charges and inner shell eigenvalues (Tables V and VI) suggest that B_2 and B_3 (B_6) are the most susceptible to electrophilic substitution and that order is $B_2 > B_3 > B_1 > B_7$ and B_4. Nucleophilic substitution presumably would occur preferentially in the reverse order. Perhaps more to the point, the cumulative charges in the highest filled molecular orbitals (Table VII) are in qualitative agreement with this order. The atoms with the most negative charges in the highest filled molecular orbitals are assumed to be most susceptible to electrophilic attack and least susceptible to nucleophilic attack. Examination of Table VII indicates that, for the larger boron hydrides, the summation of the atomic populations for the frontier orbitals must include more orbitals than were necessary for the smaller boranes[12] (e.g., B_4H_{10}, B_5H_{11}, and B_6H_{10}) before the relative orders of nucleophilic and electrophilic substitutions stabilize. For example, in B_8H_{12} the order of electrophilic substitution remains constant and agrees qualitatively with the order predicted by the eigenvalues and charges only after the populations of the first five frontier orbitals are summed. This trend is also adhered to in B_9H_{15}, $B_{10}H_{10}^{2-}$, $B_{10}H_{14}^{2-}$, and, as previously noted,[12] in $B_{10}H_{14}$. Accurate SCF calculations on smaller boranes[12] previously indicated that only two or three of the highest occupied orbitals need be summed before qualitative predictions about reactivity were possible. Dobson and Schaeffer[24] indicate that Lewis base attack in B_8H_{12} is most probable at B_4, and least probable at B_3, consistent with the theoretical results here. With respect to electrophilic substitution, expected theoretically at B_2 preferentially, we add the qualification that, as in $C_2B_4H_8$,[5b] there may be an additional problem in achieving effective orbital overlap in an electrophilic

(23) (a) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955); (b) J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970).

(24) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 406 (1968).

Table V. Midpoint Densities and SCF and PRDDO Overlap Populations

Bond		Bond length[a]	Midpoint density	Overlap populations	
				Ab initio	PRDDO
$B_6H_6^{2-}$	B_1–B_2	1.70	0.120	0.530	0.532
	B_1–H_1	1.196	0.161	0.750	0.752
B_8H_{12}	B_1–B_2	1.83	0.125	0.380	0.390
	B_1–B_3	1.79	0.106	0.396	0.394
	B_1–B_4	1.71	0.124	0.486	0.468
	B_2–B_3	1.81	0.109	0.402	0.402
	B_2–B_7	1.72	0.124	0.474	0.472
	B_3–B_4	1.82	0.124	0.500	0.504
	B_3–B_8	1.81	0.123	0.358	0.362
	B_4–B_5	1.67	0.128	0.498	0.492
	B_7–B_8	1.70	0.129	0.422	0.422
	B_1–H_1	1.19	0.175	0.826	0.824
	B_2–H_2	1.19	0.177	0.830	0.828
	B_3–H_3	1.19	0.177	0.830	0.826
	B_3–H_{10}	1.33	0.114	0.388	0.392
	B_4–H_4	1.19	0.177	0.824	0.820
	B_4–H_{11}	1.33	0.111	8.376	0.380
	B_7–H_7	1.19	0.174	0.832	0.824
	B_7–H_9	1.30	0.177	0.376	0.380
	B_8–H_{10}	1.43	0.099	0.336	0.340
B_9H_{15}	B_1–B_2	1.77	0.110	0.370	0.382
	B_1–B_4	1.79	0.104	0.402	0.410
	B_1–B_5	1.75	0.113	0.476	0.472
	B_2–B_5	1.81	0.108	0.394	0.394
	B_2–B_6	1.78	0.115	0.466	0.466
	B_3–B_4	1.86	0.093	0.281	0.284
	B_4–B_5	1.95	0.093	0.406	0.416
	B_4–B_9	1.76	0.097	0.470	0.460
	B_5–B_6	1.84	0.096	0.310	0.314
	B_6–B_7	1.78	0.103	0.388	0.374
	B_1–H_1	1.19	0.179	0.828	0.834
	B_2–H_2	1.19	0.176	0.833	0.830
	B_3–H_3	1.19	0.179	0.824	0.816
	B_3–H_3'	1.19	0.173	0.814	0.812
	B_3–H_{15}	1.30	0.107	0.340	0.346
	B_4–H_4	1.19	0.176	0.826	0.820
	B_4–H_{15}	1.30	0.114	0.440	0.444
	B_5–H_5	1.19	0.177	0.832	0.826
	B_5–H_{14}	1.31	0.106	0.384	0.384
	B_6–H_6	1.19	0.178	0.832	0.824
	B_6–H_{13}	1.30	0.111	0.381	0.388
	B_6–H_{14}	1.31	0.115	0.402	0.412
$B_{10}H_{10}^{2-}$	B_1–B_2	1.72	0.127	0.436	0.538
	B_2–B_3	1.88	0.096	0.388	0.336
	B_2–B_6	1.82	0.108	0.453	0.458
	B_1–H_1	1.19	0.161	0.786	0.782
	B_2–H_2	1.19	0.163	0.780	0.776
$B_{10}H_{14}^{2-}$	B_1–B_2	1.78	0.112	0.418	0.424
	B_1–B_3	1.81	0.109	0.400	0.402
	B_1–B_5	1.78	0.116	0.451	0.450
	B_2–B_5	1.75	0.113	0.466	0.468
	B_2–B_6	1.75	0.107	0.421	0.426
	B_5–B_6	1.88	0.110	0.468	0.470
	B_5–B_{10}	1.89	0.089	0.265	0.274
	B_1–H_1	1.19	0.165	0.796	0.792
	B_2–H_2	1.17	0.172	0.812	0.806
	B_5–H_5	1.17	0.169	0.794	0.788
	B_5–H_{13}	1.35	0.105	0.400	0.404
	B_6–H_6	1.18	0.166	0.780	0.770
	B_6–H_6'	1.18	0.167	0.787	0.786
$B_{12}H_{12}^{2-}$	B_2–B_2				0.440
	B_1–H_1				0.794

[a] Ångstrom units.

Table VI. *Ab Initio* SCF and PRDDO Inner Shell Eigenvalues and Mulliken Charges

	Atom	Ab Initio SCF		PRDDO	
		Eigenvalue[a]	Charge	Eigenvalue[a]	Charge
$B_6H_6^{2-}$	B_1	−7.021	−0.25	−7.020	−0.22
	H_1		−0.08		−0.08
B_8H_{12}	B_2	−7.567	−0.01	−7.567	−0.04
	B_3	−7.590	0.00	−7.595	0.00
	B_1	−7.597	+0.05	−7.598	+0.03
	B_4	−7.603	+0.08	−7.612	+0.68
	B_7	−7.644	+0.07	−7.656	+0.08
	H_1		−0.06		−0.05
	H_2		−0.07		−0.06
	H_3		−0.06		−0.06
	H_4		−0.06		−0.05
	H_7		−0.04		−0.04
	H_9		+0.03		+0.03
	H_{10}		+0.04		+0.05
	H_{11}		−0.02		−0.03
B_9H_{15}	B_2	−7.568	−0.02	−7.568	−0.05
	B_4	−7.590	+0.01	−7.594	+0.00
	B_1	−7.607	+0.05	−7.608	+0.03
	B_5	−7.611	+0.05	−7.620	+0.06
	B_3	−7.616	+0.02	−7.631	+0.03
	B_6	−7.672	+0.10	−7.672	+0.10
	H_1		−0.04		−0.03
	H_2		−0.07		−0.06
	H_3		−0.05		−0.07
	H_3'		−0.09		−0.10
	H_4		−0.06		−0.06
	H_5		−0.06		−0.06
	H_6		−0.03		−0.03
	H_{11}		+0.06		+0.07
	H_{12}		+0.02		+0.03
	H_{13}		+0.02		+0.02
$B_{10}H_{10}^{2-}$	B_1	−7.215	−0.06	−7.131	−0.06
	B_2	−7.162	0.00	−7.167	−0.01
	H_1		−0.20		−0.19
	H_2		−0.19		−0.18
$B_{10}H_{14}^{2-}$	B_6	−7.146	−0.02	−7.156	−0.02
	B_1	−7.178	−0.03	−7.185	−0.03
	B_5	−7.198	+0.01	−7.208	0.00
	B_2	−7.216	+0.03	−7.220	+0.01
	H_1		−0.17		−0.16
	H_2		−0.15		−0.14
	H_5		−0.17		−0.17
	H_6		−0.20		−0.21
	H_6'		−0.14		−0.14
	H_{13}		+0.11		+0.02
$B_{12}H_{12}^{2-}$	B_1			−7.210	−0.01
	H_1				−0.16

[a] Atomic units.

Table VII. Sum of the Atomic Populations in Several Highest Occupied Orbitals[a]

Molecule	Atom	Cumulative population					
		1	2	3	4	5	6
B_8H_{12}	B_1	0.04	0.06	0.44	0.78	1.03	1.13
	B_2	0.12	0.54	0.98	1.06	1.42	1.46
	B_3	0.22	0.52	0.62	0.96	1.05	1.26
	B_4	0.46	0.60	0.74	0.86	0.96	1.01
	B_7	0.16	0.32	0.38	0.40	0.52	0.65
B_9H_{15}	B_1	0.18	0.10	0.46	0.74	0.94	0.96
	B_2	0.00	0.60	0.82	1.07	1.23	1.50
	B_3	0.08	0.06	0.08	0.28	0.30	0.62
	B_4	0.15	0.58	0.86	0.94	1.09	1.23
	B_5	0.24	0.53	0.60	0.62	0.89	0.89
	B_6	0.43	0.24	0.30	0.35	0.40	0.50
$B_{10}H_{10}^{2-}$	B_1	0.38	0.78	0.78	0.78	0.96	1.14
	B_2	0.24	0.30	0.42	0.75	0.94	1.05
$B_{10}H_{14}^{2-}$	B_1	0.14	0.22	0.65	0.89	0.89	1.00
	B_2	0.30	0.08	0.11	0.38	0.40	0.63
	B_5	0.24	0.52	0.68	0.73	0.84	1.02
	B_6	0.34	0.60	0.65	0.81	0.99	1.02

[a] Cumulative number of electrons in the highest occupied MO's on the given B atom, starting with the highest occupied MO for column 1, the highest two MO's for column 2, etc.

transition state involving B_2, which lies on the molecular plane of symmetry.

The energy analysis for B_8H_{12} is given in Table VIII. The calculated molecular dipole moment (Table IX) is possibly too large by a factor of about 2, if our previous results on minimum basis set SCF results[3c,12,13] apply also to B_8H_{12}.

Table VIII. Energetics[a]

	$B_6H_6^{2-}$	B_8H_{12}	B_9H_{15}	$B_{10}H_{10}^{2-}$	$B_{10}H_{14}^{2-}$
Nuclear attraction energy	−676.515	−1036.372	−1243.481	−1360.920	−1432.480
Nuclear repulsion energy	153.615	283.783	357.539	376.673	410.386
Kinetic energy	153.304	204.284	230.578	253.813	256.195
−E/T	0.9854	0.9985	0.9988	0.9935	0.9929
Total energy	−151.078	−203.985	−230.319	−252.173	−254.378
Atomization energy[b]	1.152	2.172	2.551	2.297	2.567
Ionization potential[c]		0.338	0.353		

[a] Atomic units. [b] Using molecular exponents for the reference atomic SCF energies. [c] Ionization potential of highest occupied molecular orbital.

Table IX. Dipole Moments[a]

	Components			Resultant
	x	y	z	
B_8H_{12}	−1.995	0.0	−0.858	1.475 au
	−3.045	0.0	−2.180	3.745 D
B_9H_{15}	0.244	0.0	1.438	1.458 au
	0.618	0.0	3.651	3.703 D

[a] The dipole moment of a negative ion such as $B_{10}H_{14}^{2-}$ is origin dependent and hence is not given here.

B_9H_{15}. Most Lewis bases are expected[25] to cleave BH_3 from the exposed doubly bridged BH_2 group in B_9H_{15}, at B_8 in Figure 2, with addition of the base (L) to B_4 (or B_9) of B_9H_{15} to yield $B_8H_{12}L$. This process has been shown to occur by Schaeffer and Snedden.[26] On the other hand, for substitution reactions the Mulliken charges, inner shell eigenvalues (Table VI), and outermost orbital populations (Table VII) suggest electrophilic attack in the order $B_2 > B_4 > B_1 > B_5 > B_3$, B_6, while nucleophilic attack would be expected in approximately the reverse order. We base our reactivity predictions largely on inner shell eigenvalues and cumulative outermost orbital populations and not on the possibly less reliable Mulliken charges.

The probable directions of the asymmetries of the bridge hydrogens in B_9H_{15} can be deduced from the overlap populations. Although the bridge hydrogens in the calculation were placed symmetrically with respect to the two bonded borons, the overlap populations of B_4–H_{15}, B_3–H_{15}, B_6–H_{14}, and B_5–H_{14} suggested that H_{15} is more closely bonded to B_4 than to B_3, and that H_{14} is closer to B_6 than to B_5. These asymmetries are in agreement with the early, less precise, X-ray diffraction study[18a] of B_9H_{15} and with a recent unpublished X-ray diffraction study[18b] which determined the bridge hydrogen positions more precisely. Finally, the bridge hydrogen asymmetry in B_9H_{15} agrees with that found in B_4H_{10},[4] in the regions where these molecules have a common topology.

$B_6H_6^{2-}$. No previous ab initio SCF studies have been made on $B_nH_n^{2-}$ species, which are generally closed polyhedra with n boron vertices, each with an external B–H bond. The predicted[27] $B_6H_6^{2-}$ ion has been discovered[19] and is isoelectronic with the two isomers of $C_2B_4H_6$.

We have optimized the B–B distance to a value of 1.70 Å, assuming a B–H distance of 1.19 Å. While the

agreement with the experimental value[21] of 1.69 ± 0.01 Å is excellent, we feel certain from the virial ratio of 0.985 (Table VIII) that the orbital exponents are not optimal but probably are too large if the behavior in other negative ions is a good indication.[3a,8] We have, nevertheless, retained the diborane exponents primarily for consistency but also in order not to use excessive computing time.

The wave function (Table X) shows that 12 of the 26 valence electrons of $B_6H_6^{2-}$ are associated with positive SCF eigenvalues. We discuss this behavior below. The energy gap to the lowest unoccupied molecular orbital (0.664 au) is large, and the inner shell eigenvalues of about −7.02 au show the destabilizing effect of additional electron repulsions as compared with the inner shell eigenvalues of −7.55 to −7.65 au in neutral boron hydrides. Also the valence shell eigenvalues are generally higher in energy in the negative ions as compared with those in the neutral species, for the same reason. These effects are quite general for the known species of molecules and ions.

$B_{10}H_{10}^{2-}$. This anion, a cage bicapped Archimedian antiprism (Figure 4), has an extensive known derivative chemistry, as does $B_{12}H_{12}^{2-}$.[28] Electrophilic and nucleophilic substitution have been studied, but the detailed mechanisms have not always been elucidated in enough detail to establish the relation between the initial steps and the position of substitution. Probably, most electrophilic attack occurs at the apical position and most nucleophilic attack occurs at the equatorial position, unless a cooperative transition state occurs in a complex. Mulliken charges, inner shell eigenvalues, and outermost orbitals are consistent with this assignment, but further studies are required, both experimental and theoretical, on mechanisms and especially on possible transition states. Qualitative agreement of the relative charges on the apex and equatorial atoms was obtained by Armstrong, Perkins, and Stewart,[29] but their quantitative disagreement with our SCF results is several times the charges that we report here (Table VI).

No preferred valence structure can be assigned for $B_{10}H_{10}^{2-}$, especially in the absence of a study of localized molecular orbitals. The 72 topologically allowed valence structures[6] argue for considerable resonance stabilization and for a reasonably even distribution of charge in this anion. The closed polyhedral structure also makes preferential removal of a boron difficult, as compared with the more open species of the form B_nH_{n+4} or especially B_nH_{n+6}, where $n > 2$.

(25) (a) R. W. Parry and L. J. Edwards, J. Amer. Chem. Soc., 81, 3554 (1959); (b) W. N. Lipscomb, J. Inorg. Nucl. Chem., 11, 1 (1959).

(26) R. Schaeffer and L. G. Sneddon, Inorg. Chem., 11, 3102 (1972).

(27) (a) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954); (b) H. C. Longuet-Higgins and M. deV. Roberts, Proc. Roy. Soc., Ser. A, 224, 336 (1954).

(28) E. L. Muetterties and W. H. Noth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(29) D. R. Armstrong, P. G. Perkins, and J. P. Stewart, J. Chem. Soc. A, 627 (1973).

Table X. Eigenvalues[a]

B₆H₆²⁻ (Oₕ)	B₈H₁₂ (Cₛ)	B₉H₁₅ (Cₛ)	B₁₀H₁₀²⁻ (D₄d)	B₁₀H₁₄²⁻ (C₂ᵥ)
(3t_ag +0.808)	(10a'' +0.096)	(11a'' +0.101)	(5e₁ +0.604)	(10b₁ +0.567)
3t₁ᵤ 0.144	17a' −0.338	20a' −0.353	4e₁ 0.056	4a₂ 0.090
2t₂g 0.024	9a'' −0.428	10a'' −0.420	3e₂ 0.007	7b₂ −0.018
2e_g −0.108	16a' −0.454	19a' −0.456	3e₃ −0.041	13a₁ −0.023
3a₁g −0.134	8a'' −0.462	18a' −0.456	5a₁ −0.054	9b₁ −0.044
2t₁ᵤ −0.208	15a' −0.474	9a' −0.463	3e₁ −0.105	12a₁ −0.074
2a₁g −0.498	14a' −0.490	17a' −0.493	5b₂ −0.144	3a₂ −0.083
1s levels:	13a' −0.510	16a' −0.502	4b₂ −0.165	8b₁ −0.085
−7.021	7a'' −0.527	8a'' −0.503	2e₂ −0.218	11a₁ −0.094
	12a' −0.554	15a' −0.527	2e₃ −0.225	6b₂ −0.117
	6a'' −0.556	7a'' −0.540	5a₁ −0.238	10a₁ −0.146
	11a' −0.607	14a' −0.561	4a₁ −0.254	5b₂ −0.158
	5a'' −0.636	13a' −0.595	2e₁ −0.388	7b₁ −0.164
	10a' −0.643	12a' −0.620	3b₂ −0.442	6b₁ −0.202
	9a' −0.669	6a'' −0.621	3a₁ −0.619	9a₁ −0.228
	8a' −0.773	11a' −0.690	1s levels:	8a₁ −0.261
	4a'' −0.827	10a' −0.700	−7.125 (apex)	4b₂ −0.263
	7a' −0.903	5a'' −0.721	−7.162	5b₁ −0.277
	6a' −1.033	9a' −0.831		2a₂ −0.282
	1s levels:	4a'' −0.857		7a₁ −0.339
	−7.567 to	8a' −0.927		6a₁ −0.407
	−7.644	7a' −1.031		4b₁ −0.468
		1s levels:		3b₂ −0.484
		−7.568 to		5a₁ −0.624
		−7.672		1s levels:
				−7.146 to
				−7.216

[a] The numbers in parentheses are the eigenvalues of the lowest unoccupied molecular orbitals.

B₁₀H₁₄²⁻. Reduction of B₁₀H₁₄ to the dianion and the structure of B₁₀H₁₄²⁻ were predicted from valence theory.[4] This dianion can be prepared from B₁₀H₁₄ by reduction using sodium in liquid ammonia (or ether) or by reaction of BH₄⁻ with B₁₀H₁₃⁻. A recent X-ray diffraction study confirms the presence of two bridging hydrogens and two BH₂ groups in B₁₀H₁₄²⁻ (2632 topology[4]). Thus in the reduction of B₁₀H₁₄, which has four bridge hydrogens in 4620 topology, there is a hydrogen rearrangement, although the boron positions change about 0.1 Å or less. Three-center bond theory gives 24 resonance structures for B₁₀H₁₄ (4620) but only one valence structure for B₁₀H₁₄ rearranged to have two bridge hydrogens and two BH₂ groups (2802 topology). Similarly B₁₀H₁₄²⁻ (2632) has 24 resonance structures but only one valence structure if it is rearranged to have four bridge hydrogens. Thus an argument based upon resonance stabilization favors the observed structures of B₁₀H₁₄ and B₁₀H₁₄²⁻.

This conclusion was confirmed in a study[30] by the PRDDO method[14] in which B₁₀H₁₄²⁻ in the 2632 topology was found to be about 150 kcal/mol more stable than B₁₀H₁₄²⁻ in the four-bridge (4450) topology having the geometry of B₁₀H₁₄. Also, for B₁₀H₁₄ the 4620 topology is favored over the 2802 topology (B₁₀H₁₄²⁻ geometry) by about 50 kcal/mol. Less certain, because of the unknown detailed distances, is the indication from PRDDO theory that for B₁₀H₁₄⁻ the B₁₀H₁₄²⁻ geometry is more stable than the B₁₀H₁₄ geometry by about 50 kcal/mol.[30]

If the substitution chemistry of B₁₀H₁₄²⁻ exists one might conclude that electrophilic attack on boron occurs in the order B₁ ≈ B₆ ≈ B₅ > B₂ (Tables VI and VII), although the outermost charges suggest that atoms B₁, B₆, and B₅ are comparable and that B₂ should be last in this order. However, electron loss dominates the

chemistry of B₁₀H₁₄²⁻. Iodination yields B₁₀H₁₄ and I⁻, and anhydrous HCl also yields B₁₀H₁₄.[31]

Localization of the molecular orbitals has, so far, been performed[32] on an INDO wave function which yields the fractional three-center bond description deduced[21] on the basis of similar bonding situations in simpler molecules.[3d,5] Further studies of localized orbitals, derived from PRDDO wave functions, for B₁₀H₁₄ and B₁₀H₁₄²⁻ are in progress here.

Orbital energies which are apparently unstable with respect to loss of an electron (positive eigenvalues) occur for various numbers of orbitals in the negative ions: six in B₆H₆²⁻ (SCF), four in B₁₀H₁₀²⁻ (SCF), one for B₁₀H₁₄²⁻ (SCF) and none for B₁₂H₁₂²⁻ (PRDDO, below). In the closed polyhedral species, these numbers correspond to the relative reactivities (B₆H₆²⁻ > B₁₀H₁₀²⁻ > B₁₂H₁₂²⁻), although other factors such as change of coordination number of boron from five to six, and change of valence electron–orbital ratios from 0.87 to 0.84 to 0.83, may be related. Using a modified CNDO method, Armstrong, Perkins, and Stewart[29] find three occupied orbitals having positive eigenvalues in B₆H₆²⁻, seven in B₁₀H₁₀²⁻, and four in B₁₂H₁₂²⁻. However, their ordering of one-electron energies, particularly in the occupied outer valence levels, is not in good agreement with our results.

These outermost occupied orbitals having positive eigenvalues imply that the binding potential is too weak in the SCF approximation used here. These occupied orbitals may in some future study be stabilized by (a) optimization of exponents in the SCF wave functions, (b) extension of the basis set to the Hartree–Fock limit, (c) inclusion of electron correlation, and (or) (d) solvation of the ion.

(30) D. A. Kleier, private communication.

(31) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, Chapter 5.

(32) M. D. Newton, private communication.

Table XI. Diamagnetic Susceptibility and Tensor Components[a]

	χ_{xx}^{d}	χ_{yy}^{d}	χ_{zz}^{d}	χ^{d}	χ^{p}	χ_{expt}
B_8H_{12}	−766.979	−608.964	−467.968	−614.637		
B_9H_{15}	−626.844	−896.873	−955.929	−826.552		
$B_6H_6^{2-}$	−314.791	−314.791	−314.791	−104.928		
$B_{10}H_{10}^{2-}$	−773.651	−773.651	−655.803	−734.430	+602.430	−132.0[b]
$B_{10}H_{14}^{2-}$	−1458.547	−1540.628	−993.366	−1330.847		

[a] All quantities are in ppm (cm³/mol). [b] A. Kaczmarczyk and G. Kolski, *J. Phys. Chem.*, **68**, 1227 (1964).

Table XII. ¹¹B Chemical Shifts (experimental)[a]

		δ, ppm
B_8H_{12}	B(4,5,7,8)	−7.50
	B(3,6)	+19.4
	B(1,2)	+22.0
B_9H_{15}	B(1)	−17.2
	B(5,8 or 6,7)	−7.1
	B(6,7 or 5,8)	−3.3
	B(3)	−3.5
	B(4,9)	+32.9
	B(2)	+47.5
$B_6H_6^{2-}$	B(1)	+13.0
$B_{10}H_{10}^{2-}$	B(1)	4.9
	B(2)	+28.2 ± 1

[a] All ¹¹B chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$.

Table XIII. ¹H Chemical Shifts (experimental)[a]

		δ, ppm
B_8H_{12}	H_t(4,5,7,8)	−3.93
	H_t(1,2 or 3,6)	−1.18
	H_t(3,6 or 1,2)	−0.83
	H_B	+2.33
	H_B	+3.17
$B_{10}H_{10}^{2-}$	H(1)	−0.9
	H(2)	−4.3

[a] All ¹H shifts are relative to tetramethylsilane.

Table XIV. ¹¹B Diamagnetic Chemical Shifts

	Atom	σ^{d}
B_8H_{12}	B_1	411.132
	B_2	411.356
	B_3	402.132
	B_4	389.427
	B_7	391.365
B_9H_{15}	B_1	432.116
	B_2	424.058
	B_3	391.309
	B_4	414.632
	B_5	418.201
	B_6	402.651
$B_6H_6^{2-}$	B_1	367.282
$B_{10}H_{10}^{2-}$	B_1	431.291
	B_2	440.182
$B_{10}H_{14}^{2-}$	B_1	377.614
	B_3	381.052
	B_5	370.049
	B_9	358.658

Table XV. ¹H Chemical Shifts

	Atom	σ^{d}	σ^{abs}	σ^{p}
B_8H_{12}	1	203.687	26.23 or 25.78	−177.46 or −177.90
	2	203.338	26.23 or 25.78	−177.11 or −177.56
	3	197.307	25.78 or 26.23	−171.53 or −171.08
	4	186.168	28.91	−157.26
	7	187.557	28.91	−158.65
	9	222.208	35.1 or 35.9	−187.11 or −186.31
	10	230.338	35.1 or 35.9	−195.24 or −194.44
	11	221.711	35.1 or 35.9	−186.61 or −185.81
B_9H_{15}	1	218.144		
	2	216.031		
	3	196.950		
	3′	219.226		
	4	210.262		
	5	211.825		
	6	198.246		
	11	236.088		
	12	248.016		
	13	242.265		
$B_6H_6^{2-}$	H_1	164.907		
$B_{10}H_{10}^{2-}$	H_1	216.340	32.05	−184.29
	H_2	225.395	32.05	−193.34
$B_{10}H_{14}^{2-}$	1	198.696		
	3	200.923		
	5	193.434		
	9	187.289		
	9′	207.935		
	H_B	223.572		

Magnetic Properties. A minimum-basis set of Slater orbitals is known to yield values of diamagnetic susceptibilities and diamagnetic contributions to the chemical shift which are accurate to a few per cent.[13,33,34] These quantities are averages over the ground-state molecular wave function. The diamagnetic susceptibility χ^{d} is proportional to $\Sigma_i \langle r_i^2 \rangle$ for all electrons, i, where the origin can be taken at the molecular center of mass. Similarly, the diamagnetic shift σ^{d} is proportional to the average $\Sigma_i \langle r_i^{-1} \rangle$ for all electrons, where the origin is usually taken at the nucleus for which the shift is computed. Total susceptibilities and shielding are obtainable only upon additional calculation of the paramagnetic parts χ^{p} and σ^{p}, respectively, which require an optimized basis set at least three times the size of those used in the present study. We shall exhibit values of χ^{p} and σ^{p} from our calculated values of χ^{d} and χ^{d}, from the relations $\chi^{p} = \chi - \chi^{d}$ and $\sigma^{p} = \sigma - \sigma^{d}$, when the values of χ and σ are known. The results for magnetic susceptibility are summarized in Table XI.

Experimental ¹¹B and ¹H chemical shifts[35] are given in Tables XII and XIII. These total chemical shifts do not parallel the calculated diamagnetic shifts (Tables XIV and XV) because of the large paramagnetic contributions. Absolute ¹H chemical shifts are known,

(33) (a) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **56**, 2029 (1972); (b) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **84**, 4661 (1972).

(34) (a) W. N. Lipscomb, "MTP International Review of Science, Theoretical Chemistry," W. Myers Brown, Ed., Medical and Technical Publishing Co., Oxford, England, 1972, pp 167–196; (b) W. N. Lipscomb, "Advances in Nuclear Magnetic Resonance," Vol. 2, J. T. Waugh, Ed., Academic Press, New York, N. Y., 1966, p 137.

(35) (a) B_8H_{12}, R. Rietz, R. Schaeffer, and L. Sneddon, *Inorg. Chem.*, **11**, 1242 (1972); (b) B_9H_{15}, A. Allerhand, A. Clouse, R. Rietz, T. Rosenberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **94**, 2445 (1972); (c) $B_6H_6^{2-}$ and $B_{10}H_{10}^{2-}$, G. Eaton and W. N. Lipscomb, "Nuclear Magnetic Resonance of Boron Compounds," W. A. Benjamin, New York, N. Y., 1969.

Table XVI. PRDDO Energy Analysis[a]

	$B_6H_6^{2-}$	B_8H_{12}	B_9H_{13}	$B_{10}H_{10}^{2-}$	$B_{10}H_{14}^{2-}$	$B_{12}H_{12}^{2-}$
Nuclear attraction energy	-686.454	-1036.027	-1234.004	-1360.556	-1431.954	-1784.920
Nuclear repulsion energy	153.615	283.782	357.539	376.672	410.386	529.880
Kinetic energy	153.454	204.139	230.395	253.023	256.023	304.140
$-E/T$	0.9859	1.0004	1.0007	0.9954	0.9954	0.9972
Total energy	-151.291	-204.212	-230.561	-252.558	-254.736	-303.295
Ionization potential[b]		0.364	0.376			0.067

[a] Atomic units. [b] Ionization potential of highest occupied molecular orbital.

among these species, only for B_8H_{12} and $B_{10}H_{10}^{2-}$ (Table XV) from the ^1H absolute shifts for B_2H_6 (H_t, 29.0; H_b, 33.3) and the ^1H shifts in B_8H_{12} and $B_{10}H_{10}^{2-}$ relative to B_2H_6. Some ambiguities[35a] in the ^1H shifts B_8H_{12} give rise to the different possible values of σ^p for hydrogens in B_8H_{12} as indicated in Table XV. Probably owing to internal tautomerism the chemical shifts relating to positions 4, 5, 7, and 8 appear to be equivalent (C_{2v}) in the nmr spectra. However, our calculated values were obtained using the C_s symmetry of the X-ray diffraction study[17] of B_8H_{12} (Figure 1). In B_9H_{15} and in $B_{10}H_{14}$[13] the ^{11}B diamagnetic shifts for different boron atoms within the molecule do not follow the order of the total chemical shift.

PRDDO Calculations. The new method of partial retention of diatomic differential overlap (PRDDO)[14] promises to provide an efficient procedure for studying the electronic structure of polyatomic molecules. This method aims for a compromise between maximum accuracy and sophistication in molecular computations while requiring a minimum in computer time. Basic to the PRDDO method is the requirement of only N^3 integrals over N atomic orbitals, instead of the N^4 integrals required by SCF theory. However, a small component of N^4 still remains because of the transformation to Löwdin orthogonalized atomic orbitals (OAO's). Halgren and Lipscomb[14] have shown that the "N^3 approximation" is indeed a good approximation. After the transformation to the OAO basis, all one-, two-, and three-center $1/r_{12}$ integrals are evaluated approximately. Rotational invariance is achieved by defining components of nonspherical atomic orbitals ($e.g.$, p_x, p_y, p_z) in terms of local principal axes, and, therefore, there is no need for single-center averaging processes. The version of PRDDO used in these calculations is parameterized by a least-squares fitting of the two-electron matrix elements calculated from the unparameterized PRDDO method with the two-electron matrix of a large number of ab $initio$ minimum-basis set calculations. The PRDDO procedure is objective in that it does not require experimental parameters ($e.g.$, valence-state ionization potentials) or assumptions regarding the bonding in molecules. In this sense, then, PRDDO is $strongly$ related to nonempirical or ab $initio$ methods, rather than to semiempirical methods ($e.g.$, CNDO and INDO).

We have used a Slater basis set having exponents as listed in Table I. The PRDDO charge distribution is in excellent agreement with the ab $initio$ calculations. The inner shell eigenvalues and Mulliken charges (Table VI) agree with the minimum-basis set results extremely well, and, in all cases, the predictions regarding electrophilic and nucleophilic substitution are the same as indicated by the ab $initio$ calculations. The overlap populations (Table V) are also in good agreement with the ab $initio$

results, and in every case (except for the B_1-B_2 bond in $B_{10}H_{10}^{2-}$) the relative values of the overlap populations are in the same directions as the ab $initio$ values. We also report overlap populations, inner shell eigenvalues, and Mulliken charges for $B_{12}H_{12}^{2-}$ [36] (Tables V and VI). Detailed comparison of these PRDDO results with those obtained by a different approximate method by Armstrong, Perkins, and Stewart[29] indicates that the PRDDO results are very much closer to the SCF results for these molecular properties.

Energetics from the PRDDO calculations are listed in Tables XVI and XVII. The eigenvalues agree well in magnitude and, in most cases, in ordering with the minimum-basis set eigenvalues (Table X). The only discrepancies in ordering occur in $B_6H_6^{2-}$ ($2e_g$ and $3a_{1g}$ reversed), $B_{10}H_{10}^{2-}$ ($4a_1$ and $2e_2$ reversed), and $B_{10}H_{14}^{2-}$ ($8b_1$ and $3a_2$ reversed). There are also only two positive eigenvalues for $B_{10}H_{10}^{2-}$, as opposed to four obtained in the ab $initio$ calculation; however, the ab $initio$ calculation yields only $+0.007$ au for two of the four positive eigenvalues.

We have recently localized PRDDO wave functions for B_8H_{12} using the Boys' method[37] of maximizing the sum of the squares of the distances between centroids of charge of the molecular orbitals. Earlier in this paper, we pointed out that for B_8H_{12}, as well as for the other molecules discussed here, PRDDO excellently reproduces the ab $initio$ SCF charge distribution. Work underway in this laboratory[38] indicates that LMO's for boranes obtained from PRDDO wave functions by Boys' procedure are nearly always in very good agreement with LMO's obtained from ab $initio$ SCF wave functions employing the Edmiston-Ruedenberg[2a] localization method.

The localized valence structure for B_8H_{12} is illustrated in Figure 6a and the topologically allowed structures in Figures 6b, 6c, and 6d. The interesting feature about the B_8H_{12} localization is the participation of B_1 in six bonds (some fractional) to other atoms. In boranes and carboranes previously studied, fractional bonds to any one boron atom have not exceeded five total bonds.[39] The localized valence structure is readily seen to be a simple combination of the topologically allowed[6a] valence structures, and the localized structure 6a is an especially good compromise between structure 6c which has a B_3-B_1-B_4 three-center bond and the originally proposed[22] structure for this molecule (6b),

(36) B-B distances are set equal to 1.77 Å and B-H distances are 1.2 Å. A regular icosahedron is assumed.

(37) S. F. Boys, $Rev.$ $Mod.$ $Phys.$, **32**, 300 (1960); J. M. Foster and S. F. Boys, $ibid.$, **32**, 300 (1960); S. F. Boys, "Quantum Theory of Atoms, Molecules and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 253.

(38) T. Halgren, D. Kleier, J. Hall, Jr., and W. Lipscomb, to be submitted for publication.

(39) W. N. Lipscomb, $Accounts$ $Chem.$ $Res.$, **6**, 257 (1973).

Table XVII. PRDDO Eigenvalues

B$_6$H$_6{}^{2-}$ (O$_h$)	B$_8$H$_{12}$ (C$_s$)	B$_9$H$_{15}$ (C$_s$)	B$_{10}$H$_{10}{}^{2-}$ (D$_{4d}$)	B$_{10}$H$_{14}{}^{2-}$ (C$_{2v}$)	B$_{12}$H$_{12}{}^{2-}$ (O$_h$)
(3t$_{2g}$ 0.794)	(10a'' +0.080)	(11a'' 0.084)	(5e$_1$ +0.585)	(10b$_1$ +0.546)	(1g$_g$ +0.609)
3t$_{1u}$ 0.122	17a' −0.365	20a' 0.376	4e$_1$ +0.025	4a$_2$ +0.063	1g$_u$ −0.067
2t$_{2g}$ 0.024	9a'' −0.447	10a'' −0.441	3e$_2$ −0.018	7b$_2$ −0.042	3h$_g$ −0.101
3a$_{1g}$ −0.132	16a' −0.469	19a' −0.466	3e$_3$ −0.064	13a$_1$ −0.047	3t$_{1u}$ −0.190
2e$_g$ −0.133	8a'' −0.476	18a' −0.472	5a$_1$ −0.073	9b$_1$ −0.066	2t$_{2u}$ −0.218
2t$_{1u}$ −0.232	15a' −0.486	9a' −0.477	3e$_1$ −0.115	12a$_1$ −0.088	3a$_g$ −0.282
2a$_{1g}$ −0.486	14a' −0.500	17a' −0.504	5b$_2$ −0.154	8b$_1$ −0.101	2h$_g$ −0.335
1s levels:	13a' −0.522	16a' −0.513	4b$_2$ −0.183	3a$_2$ −0.103	2t$_{1u}$ −0.535
−7.018 to	7a'' −0.534	8a'' −0.515	4a$_1$ −0.236	11a$_1$ −0.109	2a$_g$ −0.682
−7.027	12a' −0.556	15a' −0.536	2e$_2$ −0.244	6b$_2$ −0.133	1s levels:
	6a'' −0.575	7a'' −0.552	2e$_3$ −0.255	10a$_1$ −0.160	−7.209 to
	11a' −0.606	14a' −0.567	1b$_1$ −0.285	5b$_2$ −0.168	−7.219
	5a'' −0.661	13a' −0.612	2e$_1$ −0.417	7b$_1$ −0.173	
	10a' −0.663	12a' −0.621	3b$_2$ −0.474	6b$_1$ −0.228	
	9a' −0.690	6a'' −0.640	3a$_1$ −0.610	9a$_1$ −0.247	
	8a' −0.795	11a' −0.708	1s levels:	8a$_1$ −0.264	
	4a'' −0.855	10a' −0.726	−7.131 to	4b$_2$ −0.289	
	7a' −0.931	5a'' −0.739	−7.173	5b$_1$ −0.306	
	6a' −1.033	9a' −0.857		2a$_2$ −0.310	
	1s levels:	8a' −0.950		7a$_1$ −0.366	
	−7.567 to	7a' −1.036		6a$_1$ −0.433	
	−7.656	1s levels:		4b$_1$ −0.496	
		−7.568 to		3b$_2$ −0.512	
		−7.685		5a$_1$ −0.623	
				1s levels:	
				−7.156 to	
				−7.220	

^{a} The numbers in parentheses are the eigenvalues of the lowest unoccupied molecular orbital.

a   b

(1)

(2)   (2)

c   d
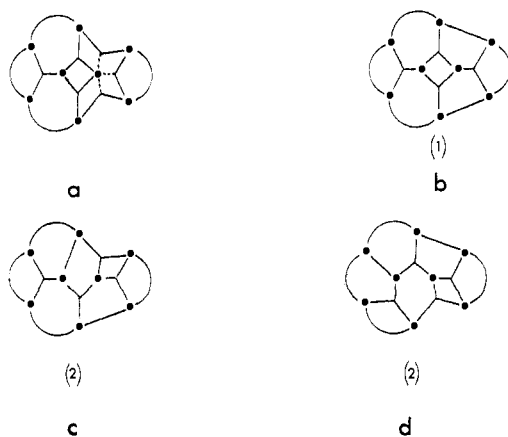
Figure 6. Localized valence structure and topologically allowed valence structures for B$_8$H$_{12}$. Structure 6a is the localized valence structure for B$_8$H$_{12}$. Structures 6b, 6c, and 6d are the topologically allowed structures for this molecule, and the numbers in parentheses give the number of structures with the illustrated topology. The structures equivalent to 6c and 6d are determined by the molecular symmetry (C$_s$). The localized valence structure for B$_9$H$_{15}$ is obtained by replacing the isolated BHB group (on the right of Figure 6a) by a BH(BH$_2$)HB group.

which has a rather long (1.82 Å) B$_3$–B$_4$ single bond interaction.

Localized orbitals have also been obtained for B$_9$H$_{15}$, again by maximizing the sum of the squares of the distances of the centroids of the MO's. The preferred simplied valence structure, as indicated by this localization, is very similar to the localized valence structure for B$_8$H$_{12}$, with B$_1$ participating in six bonds to borons B$_4$, B$_5$, B$_8$, and B$_9$. A paper on the localized valence structures for the boranes presented in this paper and other large boron hydrides is now in preparation,[40] and

(40) D. Dixon, J. Hall, Jr., T. Halgren, D. Kleier, L. Brown, and W. Lipscomb, to be submitted for publication.

therein the B$_8$H$_{12}$ and B$_9$H$_{15}$ localizations will be discussed in greater detail.

Finally, the computer time[41] required for a PRDDO calculation on B$_{10}$H$_{14}{}^{2-}$, for example, was only 4 min on the IBM 360/91 computer. We compare this to the 1.5 hr for the *ab initio* SCF calculation on the IBM 360/195. The 360/195 is faster by about a factor of 2 than the 360/91 for these types of calculations.

Conclusions

The *ab initio* SCF results agree well with experiment, where comparisons are possible for properties relating to electron density and one-electron operators. Theoretical studies of smaller boron hydrides have yielded much insight into the molecular structures of these molecules, and it is very encouraging that minimum-basis set SCF treatments appear to describe important features of the electronic structure of the larger boron hydrides. One next logical step in the study of the larger boranes would be a determination of the localized valence structures. This study is now under way in this laboratory using the approximate localization method of Boys.[38]

The PRDDO method clearly reproduces *ab initio* minimum-basis set results excellently. The method requires about the same computer time as do CNDO or INDO methods, which are considerably less accurate.

(41) The times referred to do not include elapsed times.

Cyclic Allenes. I. The Electronic Structure and Probable Deformation of the Allene Linkage When Included in a Ring. An INDO-MO Study

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Abstract: As a model for the medium and small cyclic allenes, INDO-MO calculations have been performed on a large number of distorted geometries of allene. Both the lowest singlet and triplet states were calculated, and the effect of geometrical distortion on total energy, charge distribution, and spin distribution were investigated. The calculations indicate that singlet 1,2-cyclooctadiene and 1,2-cycloheptadiene are probably bent at C-2 and also twisted somewhat from the orthogonal geometries. These distortions also bring about a moderate increase in charge separation, as compared with linear allenes. They further indicate that the singlet states of the smaller cyclic allenes are probably planar and bent. In these cases there is considerable charge delocalization and the allene moiety may best be considered as an allyl cation with an anion located at C-2 in the in-plane sp^2 orbital. For the triplet state the allene moiety is probably planar in all cases and is bent if the ring contains six or fewer atoms. These systems have little charge separation and may best be visualized as an allyl radical with a second unpaired electron in the in-plane p (or sp^2) orbital at C-2. Finally the calculations indicate that while 1,2-cycloheptadiene and larger cyclic allenes would have singlet ground states, 1,2-cyclohexadiene and smaller cyclic allenes may have triplet ground states.

The synthesis and isolation or trapping of highly strained molecules, such as polycyclic compounds with a number of small fused rings, small and medium ring acetylenes, and *trans*-olefins, has been an area of extensive research in organic chemistry during the past thirty years. The normal allene linkage requires a fixed geometrical arrangement of seven atoms, with open chain allenes having a linear structure and two orthogonal π bonds (I).

I
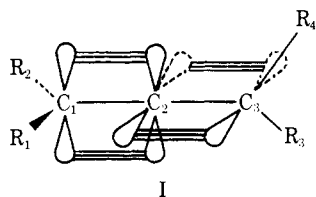
In I, the plane defined by R_1, R_2, C_1, and C_2 is perpendicular to that defined by R_3, R_4, C_3, and C_2. Molecular models suggest that the allene linkage can be included in only nine-membered or larger rings without distortion. If the ring size is decreased below this, it becomes necessary to deform the allene linkage in order to close the ring. Two deformations will facilitate ring closure. The first consists of bending the allene group at C_2, about an axis perpendicular to one of the methylene planes. This will introduce s character into the p orbital at C_2 which is perpendicular to the bending axis and which participates in one of the π bonds. This deformation will presumably weaken that π bond (II). The second deformation would retain the linear C_1–C_2–C_3 linkage, but would require one of the methylene

II
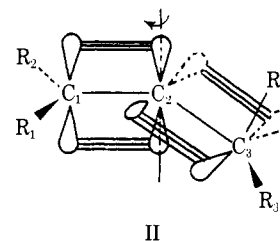
groups to be twisted to form a more nearly planar allene. This would tend to form a linear allyl arrangement of p orbitals with one nonbonding p orbital, perpendicular to the π system at C_2 (III).

III
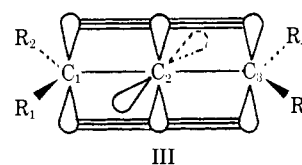
Of course, some mixture of both bending and twisting may occur and possibly is necessary in the seven- and eight-membered cyclic allenes. If both bending and twisting did occur simultaneously, it would most probably take the form of bending at C_2, resulting in the weakening of the π bond between C_2 and C_3 (say), coupled with twisting of the C_3 methylene around this weakened C_2–C_3 bond. This twisting of the weakened π bond while retaining the essentially normal double bond would be expected to lead to a more stable structure than would twisting of the C_1 methylene about C_1–C_2, which would destroy the normal π bond. In the ex-