Table XIX. Approximate Experimental and Calculated π-Electron Densities at Para Carbon in p-XC_6H_5

	Exptl q_{best}^a	CNDO/2 q_{calcd}
NMe_2	1.080	1.047
OH	1.059	1.043
F	1.045	1.027
Me	1.020	1.015
H	(1.000)	(1.000)
CF_3	0.982	0.976
CN	0.978	0.992
NO_2	0.974	0.964
CHO	0.961	0.979
BF_2	0.952	0.945

[a] Reference 31.

stituents are appreciably less than the "experimental" values in every case.

The second feature regarding Figure 7 is that the slopes of the plots are of different orders of magnitude (0.0006 and 0.0002 electron/ppm for the upper "π"-electron effect plot and 0.0016 electron/ppm for the lower "σ"-electron effect plot). This result indicates (as seems intuitively reasonable) that the F nmr shifts are more highly dependent upon charge density in the fluorine $2p_z$ (π) than in the $2p_y$ (σ) orbital. Dewar has recently reached a similar conclusion based upon correlations of F nmr shifts for aryl polyfluorides with his calculated $\Delta q_{(\pi)}^F$ values.[25] A consequence of this different dependence is that the F nmr shifts for p-XC_6H_4F compounds are not correlated by the substituent effect on the total charge density of fluorine, $\Delta q_{(tot)}^F = \Delta q_{(\pi)}^F + \Delta q_{(\sigma)}^F$. The ^{13}C nmr shifts for substituted benzenes, pyridine, and quinolines are reported[32] to be best correlated by $\Delta q_{(tot)}^C$. For the F nmr shifts, the inadequacy of the correlation with $\Delta q_{(tot)}^F$ values is readily seen by comparison of these values with corresponding para shifts, $\int_H^{p-X}$ (listed in Table XX).

Table XX. Comparison of $10^4\Delta q_{tot}^F$ and $\int_H^{p-X}$ Values for p-XC_6H_4F

Substituent, X	Δq_π^F	Δq_σ^F	Δq_{tot}^F	$-\int_H^{p-X}$, ppm
BF_2	65	12	77	10.04
CHO	30	14	44	9.15
NO_2	51	72	123	9.20
CN	18	25	43	8.95
CF_3	33	44	77	5.05
H	0	0	0	0
Me	−10	−3	−13	−5.40
F	−18	39	21	−6.80
OH	−34	17	−17	−11.60
NMe_2	−37	2	−35	−15.90

Finally, with respect to fluorine shifts in the 4-substituted [2.2.2]bicyclooctyl 1-fluorides, it is of interest that the few available substituent effects are in a qualitative σ_I order, but the direction of the shift is opposite to that of the fluorobenzene system.[33] However, Stock has presented evidence that geometrical considerations probably are the dominant factor influencing these experimental F nmr shifts.[28]

Acknowledgment. The helpful comments and suggestions of Dr. Stanton Ehrenson are gratefully acknowledged. We are also indebted to Professors R. D. Topsom, L. M. Stock, and C. Eaborn for valuable comments in the preparation of this manuscript.

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[32] J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

[33] G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **90**, 212 (1968).

Self-Consistent-Field Wave Functions for $1,2\text{-}B_4C_2H_6$ and $1,6\text{-}B_4C_2H_6$

Irving R. Epstein,[1] Thomas F. Koetzle, Richard M. Stevens, and William N. Lipscomb[2]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.

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Abstract: SCF molecular orbital wave functions for the two isomers of $B_4C_2H_6$ have been obtained from a minimum basis set of Slater-type atomic orbitals. Ionization potentials of 9.90 and 9.25 eV are predicted, respectively, for the 1,2 and the 1,6 isomers. The 1,6 isomer is computed to be more stable than the 1,2 isomer by about 15 kcal/mol. Charge densities are presented in certain sections of these isomers. In $1,2\text{-}B_4C_2H_6$, atom B_3 (attached to two C atoms) is expected to be sightly less reactive toward electrophiles than atom B_4 (attached to one C atom). The calculated dipole moment of 2.95 D makes the carbon side of the 1,2 isomer positive, but the value is expected to be too large by about a factor of 2, because of the minimum basis set.

The polyhedral carboranes are a series of extremely stable compounds, for which a quite extensive chemistry has grown up in recent years.[3–6] They have been the subject of much theoretical investigation by molecular orbital (MO) techniques which has provided insight into their interesting properties. Both the

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[1] National Science Foundation Predoctoral Fellow.

[2] Address correspondence to this author.

[3] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

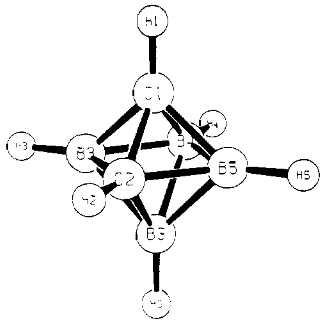

Figure 1. 1,2-$B_4C_2H_6$.

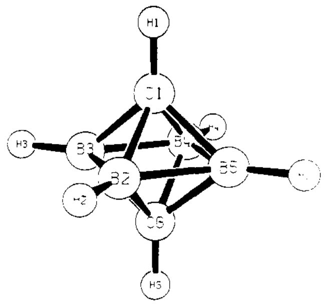

Figure 2. 1,6-$B_4C_2H_6$.

extended Hückel method[7] and the nonempirical molecular orbital (NEMO) method[8] have been used previously to calculate approximate wave functions for molecules in the series.[9] In this paper we report self-consistent-field (SCF) wave functions for the two isomers of $B_4C_2H_6$.

Both 1,2- and 1,6-$B_4C_2H_6$ are distorted octahedra assumed to possess C_{2v} and D_{4h} symmetry, respectively. Coordinates for the unique atoms are given in Table I and the molecules are drawn in Figures 1 and 2. The geometry of the 1,2 isomer was taken from a recent microwave spectroscopic study.[10] Average B–B and B–C bond lengths from this structure were then used to construct approximate coordinates for the 1,6 isomer. The H atoms were positioned to give B–H and C–H bond lengths of 1.196 and 1.102 Å, respectively.

Table I. Unique Coordinates for $B_4C_2H_6$ (au)

	Atom	*x*	*y*	*z*
1,2 isomer[a]	C_1	1.455	−1.436	0.0
	B_3	0.0	0.0	2.301
	B_4	1.655	1.595	0.0
	H_1	2.938	−2.898	0.0
	H_3	0.0	0.0	4.561
	H_4	3.283	3.163	0.0
1,6 isomer[b]	C_1	0.0	0.0	1.990
	B_2	2.320	0.0	0.0
	H_1	0.0	0.0	4.073
	H_2	4.581	0.0	0.0

[a] Twofold axis along *y*. [b] Fourfold axis along *z*.

The SCF calculations utilized a modified form of Stevens' program[11] for the IBM 7094 computer. Computations, in which each unique integral was calculated to five decimal places, required about 200 min for the 1,2 isomer and 150 min for the more symmetrical 1,6 isomer. The minimum basis set of Slater orbitals had optimized exponents (Table II) taken from B_2H_6[12] for B and from C_2H_6[11] for C. In Tables III and IV we show the wave functions and SCF energies. Agreement with the virial theorem is quite good for both molecules and only slightly worse than that obtained in the optimized calculation for B_2H_6.[12]

Table II. Optimized Exponents

From B_2H_6		From C_2H_6	
Orbital	Exponent	Orbital	Exponent
B_{1s}	4.680	C_{1s}	5.680
B_{2s}	1.443	C_{2s}	1.730
B_{2p}	1.477	C_{2p}	1.760
H_{1s}	1.147	H_{1s}	1.160

Molecular Energies and Ionization Potentials

First ionization potentials, from the energies of the least stable filled orbitals, are 9.90 eV for 1,2-$B_4C_2H_6$ and 9.25 eV for 1,6-$B_4C_2H_6$. No experimental results are available for comparison, but in a series of SCF calculations on boron hydrides,[13] calculated ionization potentials differed from the observed values by as much as 15%.

Atomization energies, using Clementi's best single-ζ atomic energies[14] as a reference, are calculated to be −1.363 and −1.387 au for the 1,2 and 1,6 isomers, respectively. We have noted in our discussion of the boron hydrides[13] that a fortuitous, but consistent cancellation of the energy errors involved in computing atomization energies may result from using optimized molecular exponents in calculating the atomic energies. Using this procedure, we find the atomization energies to be 2.706 and 2.730 au for the respective isomers. Most of the difference between the two sets of atomization energies comes from the large increase in the carbon atom energy in going from Clementi's best-atom exponents to the highly contracted carbon basis set employed here. From the difference in total energies, we predict the symmetric 1,6 isomer to be the more stable of the two by 15 kcal/mol, in agreement with qualitative observations.[15]

Population Analysis

The Mulliken charges and bonded overlap populations[16] for the two isomers are presented in Tables V and VI, respectively. The charge distribution confirms our expectations that carbon is more electronegative than

(4) T. Onak, *Advan. Organometal. Chem.*, 3, 263 (1965).

(5) M. F. Hawthorne in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 223.

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

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

(8) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966).

(9) For a review of some of these calculations, see J. A. Potenza, Ph.D. Thesis, Harvard University, 1966.

(10) R. A. Beaudet, *J. Chem. Phys.*, **53**, 1899 (1970).

(11) R. M. Stevens, *ibid.*, **52**, 1397 (1970).

(12) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *ibid.*, **51**, 2085 (1969).

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

(14) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(15) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *J. Amer. Chem. Soc.*, **85**, 3167 (1963).

(16) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

Table III. 1,2-$B_4C_2H_6$ Occupied and Three Lowest Unoccupied Molecular Orbitals and Energies (in au)

		-11.272	-11.272	-7.572	-7.572	-7.554	-7.553	-1.206	-0.853	-0.797	-0.733	-0.654	-0.603	-0.553	-0.503	-0.497	-0.495	-0.411	-0.408	-0.364	0.266	0.280	0.298
H1	1S	-C.C03	0.0C3	C.00C	0.000	C.000	0.000	0.046	0.200	0.210	0.000	0.240	0.296	0.096	0.113	0.0C0	-0.168	-0.116	0.000	0.000	0.000	-0.058	-0.009
H2	1S	-0.003	-0.0C3	0.000	0.000	0.000	-0.000	0.046	-0.200	0.210	0.0C0	0.240	-0.296	0.096	0.113	0.0C0	0.168	-0.116	0.000	0.000	0.000	0.058	-0.009
H3	1S	-C.000	0.0C0	-0.003	0.003	-0.000	0.000	0.022	0.000	-0.016	-0.146	0.081	0.000	-0.387	0.C43	-0.368	0.000	0.024	0.000	-0.115	0.000	0.000	-0.033
H4	1S	C.000	0.0C0	0.000	-0.000	0.003	0.003	0.017	0.039	-0.061	0.000	0.160	-0.202	0.046	-0.341	0.000	-0.369	0.148	0.000	0.000	0.000	-0.026	0.039
H5	1S	-0.C00	0.000	0.003	0.0C3	-0.000	0.000	0.022	0.000	-0.016	0.146	0.081	0.000	-0.387	0.043	0.368	0.000	0.024	0.000	0.115	0.000	0.000	-C.033
H6	1S	0.000	-0.000	0.000	-0.000	0.003	-0.003	0.017	-0.039	-0.061	0.000	0.160	0.202	0.046	-0.341	0.0C0	0.369	0.148	C.C00	0.000	0.000	0.026	0.039
C1	1S	0.704	-0.7C3	0.000	-0.000	C.000	0.000	-0.136	-0.141	-0.083	0.000	-0.002	-0.018	-0.016	0.004	0.0C0	-0.029	-0.022	0.000	C.000	C.000	-0.009	0.006
	2S	C.016	-0.019	0.000	0.005	0.002	0.002	0.349	0.464	0.299	0.000	-0.003	0.045	0.042	-0.042	0.0C0	0.125	0.1C5	0.000	0.000	0.000	0.045	-0.047
	2PZ	C.C00	0.0C0	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	-0.289	0.000	0.000	0.000	C.000	0.247	0.000	0.0C0	-0.415	-0.213	-0.570	0.000	0.000
	2PX	C.000	0.0C3	0.000	-0.001	0.001	0.001	-0.124	0.122	-0.001	0.000	0.339	0.108	0.113	C.294	0.000	-0.057	0.132	0.000	0.000	0.000	-0.325	0.248
	2PY	0.002	-0.0C1	0.000	0.001	0.001	0.002	0.086	0.049	-0.234	0.000	-0.095	-0.303	0.027	0.136	0.CC0	0.244	0.323	C.000	0.000	0.000	-0.314	0.226
C2	1S	0.704	0.7C3	0.000	-0.000	0.000	-0.000	-0.136	0.141	-0.083	0.000	-0.002	0.018	-0.016	0.004	0.0C0	0.029	-0.022	0.000	0.000	0.00C	0.009	0.006
	2S	C.016	0.019	0.00C	0.0C5	0.002	-0.002	0.349	-0.464	0.299	0.000	-0.003	-0.045	0.042	-0.042	0.0C0	-C.125	0.105	0.000	0.000	C.000	-0.045	-0.047
	2PZ	C.000	0.000	-0.003	0.0C0	0.000	0.000	0.000	0.000	0.000	-0.289	0.000	0.000	0.000	0.000	0.247	0.000	0.000	0.415	-0.213	0.570	0.000	0.000
	2PX	-C.000	0.0C3	0.000	0.001	-0.001	0.001	0.124	0.122	0.001	0.000	-0.339	0.108	-0.113	-C.294	0.0C0	-0.057	-0.132	0.C00	0.000	0.000	-0.325	-0.248
	2PY	0.002	0.0C1	0.000	0.001	0.001	-0.002	0.086	-0.049	-0.234	0.000	-0.095	0.303	0.027	0.136	0.0C0	-0.244	0.323	C.000	0.000	0.000	0.314	0.226
B3	1S	C.0C0	0.000	0.7C3	-0.703	0.014	0.000	-0.082	0.000	0.042	0.147	-0.019	0.000	0.095	-0.021	0.027	0.000	0.C08	0.000	-0.027	0.000	0.000	-0.009
	2S	-C.004	0.0C0	0.020	-0.020	0.006	0.000	0.114	0.000	-0.080	-0.398	0.062	0.000	-0.276	0.044	-0.052	0.000	-0.017	0.000	0.094	0.000	0.000	0.056
	2PZ	C.002	0.0C0	-0.004	0.004	-0.002	0.000	-0.102	0.000	0.063	0.079	0.084	0.000	-0.240	0.001	-0.338	0.000	0.034	0.000	-0.144	0.000	0.000	-0.018
	2PX	C.000	0.0C2	0.000	0.0C0	0.000	0.003	0.000	0.108	0.000	0.000	0.000	-0.108	0.000	C.000	0.0C0	0.101	0.0C0	-0.369	0.000	0.123	0.609	0.000
	2PY	C.002	0.0C0	-0.000	0.000	0.002	0.000	-0.018	0.000	-0.109	0.046	0.090	0.000	0.048	0.057	-0.050	0.000	-0.150	0.000	0.385	0.000	0.000	-0.630
B4	1S	0.000	-0.0C0	C.000	-0.015	-0.703	-0.703	-0.067	-0.064	0.101	0.000	-0.084	0.107	-0.035	0.035	0.0C0	0.038	0.022	0.000	0.000	0.000	-0.704	0.003
	2S	-C.002	0.0C2	C.000	0.005	-0.018	-0.023	0.085	0.156	-0.231	0.000	0.246	-0.301	0.090	-0.097	0.000	-0.090	-0.070	0.000	0.000	0.000	-0.002	-0.010
	2PZ	C.C00	0.0C0	-0.004	0.000	0.000	0.000	0.000	0.000	0.000	-0.127	0.000	0.000	0.000	0.000	0.023	0.000	0.000	-0.218	0.346	0.592	0.000	0.000
	2PX	-C.000	-0.0C0	0.000	-0.001	0.001	0.004	-0.050	0.012	0.112	0.000	0.026	-0.082	-0.006	-0.151	0.0C0	-0.166	0.388	0.000	0.000	0.000	-0.246	-0.318
	2PY	C.002	-0.002	0.000	-0.002	0.003	0.002	-0.067	-0.099	0.038	0.000	0.052	0.043	-0.024	-C.250	0.000	-0.263	-0.149	C.000	0.000	0.000	0.258	0.319
B5	1S	0.000	0.000	-0.703	-0.703	0.014	0.000	-0.082	0.000	0.042	-0.147	-0.019	0.000	0.095	-0.021	-0.027	0.000	0.0C8	0.000	0.027	0.000	0.000	-0.009
	2S	-0.004	0.0C0	-0.020	-0.020	0.006	0.000	0.114	0.000	-0.080	0.398	0.062	0.000	-0.276	C.C44	0.052	C.0C0	-0.017	C.000	-0.094	0.000	0.000	0.056
	2PZ	-C.002	0.000	-0.004	-0.004	C.002	0.000	0.102	0.000	-0.063	0.079	-0.084	0.000	0.240	-0.C01	-0.338	C.CC0	-0.034	0.000	-0.144	0.000	0.000	0.018
	2PX	0.000	0.0C2	0.000	0.0C0	0.000	0.003	0.000	0.108	0.000	0.000	0.000	-0.108	0.000	C.000	0.0C0	0.101	0.000	0.369	0.000	-0.123	0.609	0.000
	2PY	0.002	0.0C0	0.000	0.0C0	0.002	0.000	-0.018	0.000	-0.109	-0.046	0.090	0.000	0.048	0.057	0.050	0.000	-0.150	0.000	-0.385	0.000	0.000	-0.630
B6	1S	0.000	0.0C0	0.00C	-0.015	-0.703	0.703	-0.067	0.064	0.101	0.000	-0.084	-0.107	-0.035	0.035	0.CC0	-0.038	0.022	0.000	0.000	0.000	0.004	0.003
	2S	-C.C02	-0.0C2	C.000	0.005	-0.018	0.023	C.085	-0.156	-0.231	0.000	0.246	0.301	0.090	-0.097	0.0C0	0.090	-0.070	0.000	0.000	0.000	0.002	-0.010
	2PZ	C.C00	0.0C0	-0.004	0.000	0.000	0.000	0.000	0.000	0.000	-C.127	0.000	0.000	0.000	C.000	0.023	0.000	0.000	0.218	0.346	-0.592	0.000	0.000
	2PX	0.000	-0.000	0.000	0.001	-0.001	0.004	0.050	0.012	-0.112	0.000	-0.026	-0.082	0.006	0.151	0.0C0	-0.166	-0.388	C.000	0.000	0.000	-0.246	0.318
	2PY	0.002	0.002	0.00C	-0.002	0.003	-0.002	-0.067	0.099	0.038	0.000	0.052	-0.043	-0.024	-C.250	0.0C0	0.263	-0.149	0.000	0.000	0.000	-0.250	0.319

Electronic energy	-353.919	Two-electron energy	232.177
Nuclear repulsion	176.318	Kinetic energy	178.005
Total energy	-177.601	-E/T	0.99773

Table IV. 1,6-$B_4C_2H_6$ Occupied and Three Lowest Unoccupied Molecular Orbitals and Energies (in au)

		-11.244	-11.244	-7.576	-7.576	-7.576	-7.575	-1.184	-0.886	-0.727	-0.727	-0.696	-0.581	-0.544	-0.509	-0.492	-0.492	-0.442	-0.442	-0.340	0.271	0.271	0.302
H1	1S	C.003	-0.0C3	-0.000	0.000	0.000	0.000	0.039	0.179	0.000	0.000	0.349	-0.079	0.000	C.383	0.0C0	0.C0C	0.000	0.000	0.000	C.000	0.000	0.000
H2	1S	C.000	0.000	-C.002	-0.0C3	0.000	-0.002	0.024	0.000	0.155	0.000	0.017	0.262	-0.297	C.000	0.358	0.000	0.000	0.000	0.000	0.092	0.0C0	0.000
H3	1S	C.C00	0.0C0	-0.C02	0.0C0	0.003	0.002	0.024	0.000	0.000	-0.155	0.017	0.262	0.297	C.000	0.000	-0.398	0.000	0.000	0.000	0.000	-0.092	0.000
H4	1S	C.000	0.0CC	-0.002	0.003	0.000	-0.002	0.024	0.000	-0.155	0.000	0.017	0.262	-0.297	C.C00	-0.398	0.00C	0.000	0.000	0.000	-0.092	0.000	0.000
H5	1S	C.000	0.0C0	-0.002	0.0C0	-0.003	0.002	0.024	0.000	0.000	0.155	0.017	0.262	0.297	C.000	0.0C0	0.398	0.000	0.000	0.000	0.000	0.092	0.000
H6	1S	0.C03	0.0C3	-0.000	0.000	0.000	0.000	0.039	-0.179	0.000	0.000	0.349	-0.079	0.000	-0.383	0.0C0	0.000	0.00C	0.000	0.000	0.000	0.000	0.000
C1	1S	-C.703	0.7C3	-0.0C0	0.0C0	0.000	0.000	-0.123	-0.160	0.000	0.000	-0.071	0.037	0.000	C.C34	0.0C0	0.C00	0.000	0.000	0.000	0.000	0.0C0	0.000
	2S	-C.018	0.017	-0.006	0.0C0	0.000	0.0C0	0.307	0.516	0.000	0.000	0.248	-0.114	0.000	-0.164	0.0CC	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PZ	C.C02	-0.0C1	0.002	0.000	C.000	0.000	-0.135	0.005	0.000	0.000	0.336	-0.004	0.000	0.437	0.0C0	0.000	C.0C0	0.000	0.000	0.000	0.000	0.000
	2PX	C.000	0.0C0	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	0.000	0.000	-0.157	0.000	0.000	0.471	0.000	0.518	0.000	0.000
	2PY	C.000	0.0C0	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	C.000	0.0C0	-0.197	0.471	0.000	0.000	0.000	0.518	0.000
B2	1S	-C.000	0.000	0.497	0.703	0.000	0.497	-0.086	0.000	-0.151	0.000	0.019	-0.066	0.077	C.000	-0.016	0.000	0.00C	0.000	0.000	0.006	0.000	0.000
	2S	0.004	0.0C0	0.010	0.02C	C.000	0.018	0.124	0.000	0.408	0.000	-0.028	0.198	-C.215	C.000	0.018	0.000	0.0C0	0.000	0.000	0.004	0.000	0.000
	2PZ	C.000	-0.0C3	0.000	0.000	0.000	C.000	0.000	0.112	0.000	C.000	0.000	0.000	0.000	-0.162	0.0C0	0.000	0.000	0.362	0.000	0.000	0.000	0.601
	2PX	-C.003	0.0C0	-C.001	-0.0C4	0.000	-0.004	-0.111	0.000	-0.078	0.000	0.077	0.180	-0.168	0.000	0.367	0.C00	0.0C0	0.000	0.000	-0.027	0.000	0.000
	2PY	0.000	0.0C0	0.000	0.000	-0.004	0.000	0.000	0.000	0.000	0.154	0.000	0.000	0.000	C.000	0.000	-C.100	0.0C0	0.000	-0.415	0.000	-0.653	0.000
B3	1S	-C.000	C.0C0	0.497	0.0C0	-0.703	-0.497	-0.086	0.000	0.000	0.151	C.019	-0.066	-0.077	C.000	0.0C0	0.016	0.000	0.000	0.000	0.000	-0.006	0.000
	2S	C.004	0.0C0	0.01C	0.000	-0.020	-0.018	0.124	0.000	0.000	-0.408	-0.028	0.198	0.215	C.000	0.0C0	-0.018	0.0C0	0.000	0.000	0.000	-0.004	0.000
	2PZ	C.000	-0.0C3	0.060	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	-C.162	0.0C0	0.000	-0.362	0.000	0.000	0.000	0.000	-0.601
	2PX	0.000	0.000	0.000	-0.004	0.000	C.000	0.000	0.000	0.154	0.C00	0.000	0.000	0.000	0.000	-0.1C0	C.00C	C.0C0	0.000	0.415	-0.653	0.000	0.000
	2PY	C.003	0.0C0	0.001	0.000	-0.004	-0.004	0.111	0.000	0.000	-0.078	-0.077	-0.180	-0.168	0.000	0.0C0	0.367	0.000	0.000	0.000	0.000	-0.027	0.000
B4	1S	-C.000	0.0C0	0.497	-0.703	0.000	0.497	-0.086	0.000	0.151	0.000	0.019	-0.066	0.077	C.00C	0.016	0.000	0.000	0.000	0.000	-0.006	0.000	0.000
	2S	0.004	0.0CC	0.01C	-0.020	0.000	0.018	0.124	0.000	-0.408	0.000	-0.028	0.198	-0.215	C.000	-0.018	0.000	0.000	0.000	0.000	-0.004	0.000	0.000
	2PZ	C.000	-0.0C3	0.000	0.000	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	-C.162	0.0C0	0.000	0.000	-0.362	0.000	0.000	0.000	0.601
	2PX	C.003	0.000	0.001	-0.0C4	0.000	0.004	0.111	0.000	-0.078	0.000	-0.077	-0.180	0.168	C.000	0.367	0.C00	0.000	0.000	0.000	-0.027	0.000	0.000
	2PY	C.000	0.0C0	0.000	0.0C0	-0.004	0.000	0.000	0.000	0.000	0.154	0.000	0.000	0.000	C.000	0.0C0	-0.100	0.000	0.000	0.415	0.000	-0.653	0.000
B5	1S	-0.000	0.0C0	0.497	0.0C0	0.703	-0.497	-0.086	0.000	0.000	-C.151	0.019	-0.066	-0.077	0.000	0.000	-0.016	0.000	C.000	0.000	0.000	0.006	0.000
	2S	0.004	0.0C0	0.01C	0.000	0.020	-0.018	0.124	0.000	0.000	0.408	-0.028	0.198	0.215	C.000	0.0C0	0.018	0.000	0.000	0.000	C.000	0.004	0.000
	2PZ	C.000	-0.0C3	0.C00	0.0C0	0.000	0.000	0.000	0.112	0.000	0.000	0.000	0.000	0.000	-0.162	0.00C	0.000	0.362	0.000	0.000	0.000	0.000	-0.601
	2PX	C.000	0.000	0.000	-0.004	0.000	0.000	0.000	0.000	0.154	0.000	0.000	0.000	0.000	C.000	-0.1C0	0.000	0.000	0.000	-0.415	-0.653	0.000	0.000
	2PY	-0.003	0.0C0	-0.001	0.000	-0.004	0.004	-0.111	0.000	0.000	-0.078	0.077	0.180	0.168	C.000	0.000	0.367	0.000	0.000	0.000	0.000	-0.027	0.000
C6	1S	-0.703	-0.7C3	-0.000	0.000	0.000	0.000	-0.123	0.160	0.000	0.000	-0.071	0.037	0.000	-0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2S	-C.018	-0.017	-0.006	0.000	0.000	0.000	0.307	-0.516	0.000	0.000	0.248	-0.114	0.000	C.164	0.0C0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PZ	-C.002	-0.0C1	-0.002	0.000	0.000	0.000	0.135	0.005	0.000	0.000	-0.336	0.004	0.000	C.437	0.0C0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2PX	0.000	0.0C0	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	0.000	0.000	0.000	0.000	0.000	-0.197	0.000	0.000	-0.471	0.000	0.518	0.000	0.000
	2PY	C.000	0.0C0	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.254	C.000	0.000	0.000	C.000	0.0C0	-0.197	-0.471	0.000	0.000	0.000	0.518	0.000

Electronic energy	-354.126	Two-electron energy	232.423
Nuclear repulsion	176.501	Kinetic energy	178.006
Total energy	-177.625	-E/T	0.99786

boron, and that framework charges are small. Charges and overlap populations are in good agreement with those found in SCF calculations on boron hydrides[12,13] and hydrocarbons.[11]

The overlap populations do not correlate well with bond distances, particularly for B–B bonds. We find in the 1,6 isomer that the B–B overlap population is somewhat smaller and the B–C population somewhat larger than the average values in the 1,2 isomer. If an overlap population *vs.* bond distance correlation existed and were transferable between molecules, we should expect the actual B–B distance in 1,6-$B_4C_2H_6$ to be slightly longer than the value of 1 735 Å used in the present calculation, while the B–C distance should be shorter than our average value.[17] This optimistic assumption

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[17] While this paper was in preparation, results of a microwave

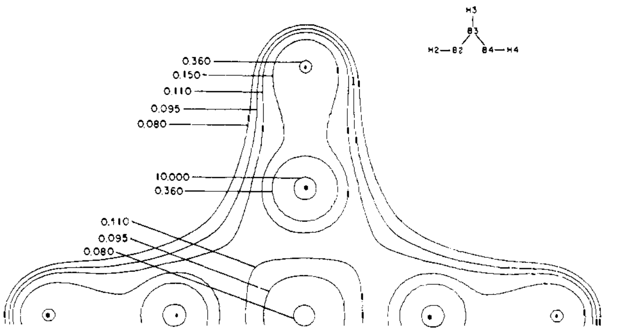

Figure 3. Total electron density (electrons/au^3) in the B_2–B_3–B_4–B_5 plane of 1,6-$B_4C_2H_6$. Atomic centers are indicated by x's.

about the value of overlap populations is probably unwarranted, however, especially for B–B bonds in the same polyhedron as B–C bonds (and C–C bonds if the C atoms are adjacent). An extreme example is the anomalously low overlap population calculated by the NEMO method for either normal or lengthened B–B bonds in 1,5-$B_3C_2H_5$.[17] Thus, the small difference between the B_2–B_3 population in 1,6-$B_4C_2H_6$ and the average B–B population in 1,2-$B_4C_2H_6$ could easily be due to this effect, rather than to an abnormally long B–B bond.

Table V. Net Mulliken Atomic Charges

	Atom	Charge
1,2 isomer	C_1	−0.08
	B_3	0.09
	B_4	0.08
	H_1	0.07
	H_3	−0.07
	H_4	−0.08
1,6 isomer	C_1	−0.10
	B_2	0.10
	H_1	0.05
	H_2	−0.07

Table VI. Bond Overlap Populations and Electron Densities

	Bond	Distance, Å	OP	Density[a]
1,2 isomer	C_1–C_2	1.54	0.52	0.207
	C_1–B_3	1.63	0.46	0.157
	C_1–B_4	1.61	0.52	0.170
	B_3–B_4	1.72	0.46	0.123
	B_4–B_6	1.75	0.50	0.122
	C_1–H_1	1.10	0.77	0.265
	B_3–H_3	1.20	0.81	0.170
	B_4–H_4	1.20	0.82	0.168
1,6 isomer	C_1–B_2	1.62	0.52	0.166
	B_2–B_3	1.74	0.40	0.115
	C_1–H_1	1.10	0.77	0.266
	B_2–H_2	1.20	0.81	0.170

[a] Evaluated at bond midpoint in electrons/au^3.

The fact that B–H bonds have greater overlap populations than C–H bonds is disturbing at first sight. However, one should not ordinarily compare overlap populations for pairs of atoms using different basis sets. The carbon atomic orbitals are far more contracted than their boron counterparts, giving lower overlap integrals even though the C–H distance is about 0.1 Å shorter than the B–H distance. The questionable significance of overlap or bond populations in view of ambiguities in partitioning the charge density has been discussed elsewhere.[13,18] Perhaps a more reliable comparison of B–H and C–H bonds is given by the electron densities at the midpoints of the bonds. This electron density is, of course, a property of the total wave function, and therefore invariant with respect to partitioning procedures. These midpoint values, shown in Table VI, clearly indicate that C–H bonds are, as expected, stronger than B–H bonds. Overlap populations *within* sets of B–B or B–C bonds generally follow the order of the midpoint densities, since within each set we use the same basis orbitals.

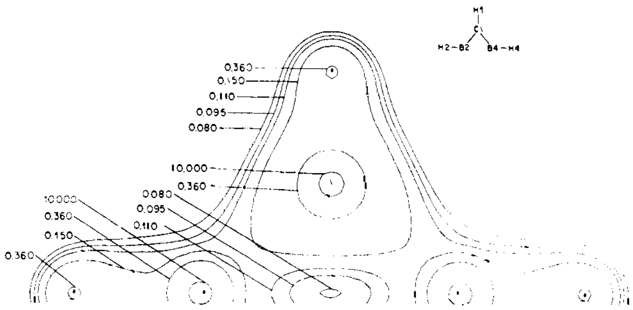

Figure 4. Total electron density (electrons/au^3) in the C_1–B_2–B_4–C_6 plane of 1,6-$B_4C_2H_6$.

The total electron density (square of the wave function) also enables us to study in more detail some of the other aspects of bonding in these molecules. In Figures 3–7 we present contour maps of the total density in several planes of interest. Figure 3 shows the four-boron plane of the 1,6 isomer. The B–H bonds are clearly visible, as is the "hole," or region of low electron density in the center of the molecule. Figure 4 shows the plane perpendicular to that of Figure 3, and includes the apical carbon. We see, first, that carbon has a far greater electron density than boron, as indicated by the greater extent of the C–H bond contour. Secondly, we note the nonspherical shape of the hole, which follows the geometry of the molecule, extending further across the longer B–B diagonal than across the shorter C–C distance. The total density in the B–C–B face of the 1,6 isomer (Figure 5) clearly indicates the effect of the carbon's greater electronegativity.

The total density in the B–B–C–C plane of 1,2-$B_4C_2H_6$ is drawn in Figure 6a. We again find higher electron density in C–H than in B–H bonds, and a central hole. In addition, there is a large overlap between the two C atoms. In order to determine whether this effect represents a true single bond in this electron-deficient molecule, we have calculated the difference density. This density, shown in Figure 6b, was derived by subtracting from our molecular density the contributions from noninteracting spherical B, C, and H atoms at the same positions and with the same Slater exponents used in the molecular calculation. The results

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structural study of 2-Cl-1,6-$B_4C_2H_5$ became available: R. A. Beaudet, private communication, Sept 22, 1969. Average bond lengths in this structure are B–B = 1.69 and B–C = 1.575 Å. A NEMO calculation (T. F. Koetzle and W. N. Lipscomb, submitted for publication) using these experimentally determined distances indicates that recalculation of SCF wave function with the revised geometry will probably result in only slight changes in the charge distribution.

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

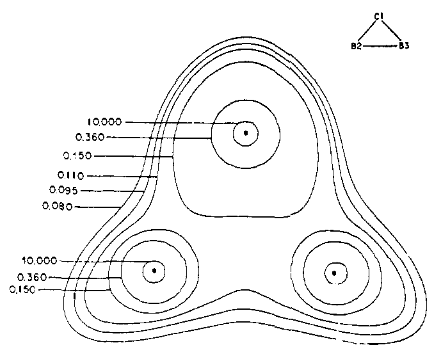

Figure 5. Total electron density (electrons/au^3) in the C_1–B_2–B_3 plane of 1,6-$B_4C_2H_6$.

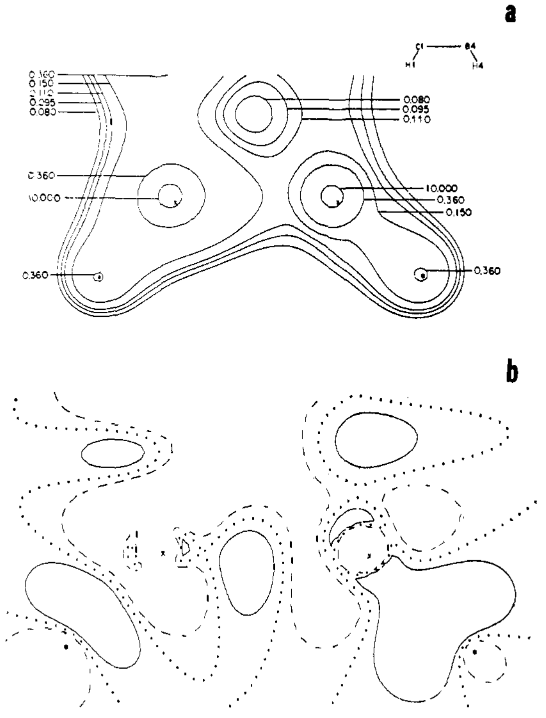

Figure 6. Electron density (electrons/au^3) in the C_1–C_2–B_4–B_6 plane of 1,2-$B_4C_2H_6$: (a) total density, (b) difference density. Contours are: —, 0.009; · · ·, 0.0; ---, −0.009.

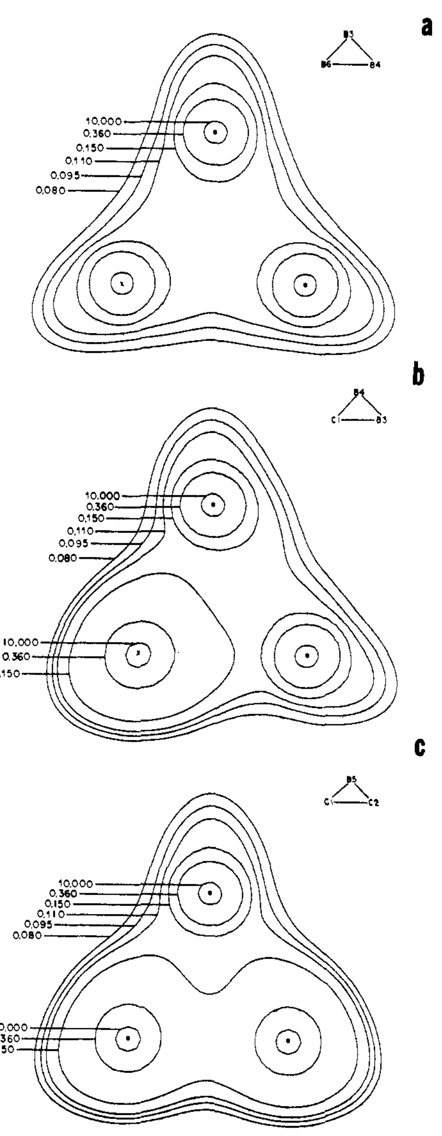

Figure 7. Total electron densities (electrons/au^3) in the face planes of 1,2-$B_4C_2H_6$: (a) B_3–B_4–B_6 plane, (b) C_1–B_3–B_4 plane, (c) C_1–C_2–B_5 plane.

indicate that the major contribution to the C–C overlap is from the overlap of spherical atomic electron densities rather than from any great molecular concentration of bond density. Difference density calculations also show that the holes are truly molecular phenomena. The difference densities at the centers of the holes are about −0.03 electron/au^3, while the positive difference densities at the midpoints of the bonds vary from 0.006 to 0.035 electron/au^3, depending on the type of bond. Even the difference density map does not distinguish among the many two-center and three-center resonance structures which may be drawn. Perhaps some slight preference for certain resonance structures may be made when localized orbitals for this molecule are determined.

In Figure 7 we show the densities on the faces of the distorted octahedron of 1,2-$B_4C_2H_6$. Again, no conclusions about two-center or three-center bonding can be drawn, although the greater overlap of C–C as compared to B–C and B–B bonds is clearly seen. Figure 7b is nearly identical with Figure 5 except for a very slight asymmetry between B_4 and B_5 in the 1,2 isomer. This strong resemblance illustrates the similarity of the bonding in the face planes of the two isomers. All maps of total electron density have been drawn using the same set of contours in order to facilitate comparisons between different planes.

Reactivity

The first molecular orbital calculations of carborane charge distributions and reactivities were undertaken by Hoffmann and Lipscomb[7] because the polyhedral carboranes afforded "an opportunity to overcome the *ex post facto* character usually present in reactivity predictions." At the time of writing, the $B_4C_2H_6$ isomers still provide such an opportunity.

While dynamic reactivity indices, which take into consideration the nature of the transition state, are generally more reliable than static indices, which are derived solely from calculations on the unperturbed molecule, the latter have been shown to be in good agreement with experimental reactivity data for boron hydrides and carboranes. Such indices as net atomic charges, frontier orbital populations, and free valences proved good indicators of boron hydride substitutions.[13] Net atomic charges calculated by the extended Hückel method correctly predict the position of attack for chlorine substitution[9,19] and for removal of boron by methoxide ion[20] in larger carboranes.

The net atomic charges suggest that in electrophilic substitution B_4 is expected to react in very slight preference to B_3 in 1,2-$B_4C_2H_6$. This order of boron reactivity is in keeping with the observations of Potenza and Lipscomb,[19] who found that Friedel–Crafts-type bromination of *o*-$B_{10}C_2H_{12}$ occurred first at those boron atoms furthest removed from the carbons; *i.e.*, electrophilic substitution takes place more easily at borons bonded to one carbon than at borons bonded to two carbons.

Except in comparing the two nonequivalent borons in the 1,2 isomer, consideration of frontier orbital populations gives little information about reactivity, since the different nuclear charges on the atoms make straightforward comparisons between boron and carbon impossible. Even in the less ambiguous case of B_3 *vs.* B_4 in 1,2-$B_4C_2H_6$, consideration of *only* the highest filled or lowest unfilled MO reverses the order of reactivity predicted by the net atomic charges. Inclusion of the highest three filled or lowest three virtual MO's, however, restores the order given by the charges. Consideration of three frontier orbitals rather than only one is justified by the relatively small energy differences (Tables III and IV) between the first three orbitals compared to the large gaps between the third and fourth orbitals (ϵ_1 0.452 au for 1,2-$B_4C_2H_6$, 0.445 au for 1,6-$B_4C_2H_6$) in both the occupied and virtual orbital sets.

Free valence calculations[13,21] indicate that in the 1,2 isomer, B_3 should be somewhat more reactive than B_1 toward free-radical substitutions. Comparison between the two molecules shows that B_2 in the symmetric isomer has a free valence identical with that of B_3 in the 1,2 isomer. Also, the C atoms of the more stable symmetric isomer should be less susceptible to free-radical attack than those of the 1,2 isomer.

Since experimental determinations of reactivities of these isomers in various types of reactions are nonexistent, our admittedly tentative reactivity predictions remain untested. Mechanisms involving several stages or rearrangements[22] will make interpretation of experiments difficult in the absence of a detailed pathway. In addition, steric considerations may also play a role in determining reactivity in these molecules. The slightly more contracted configuration near carbon in the 1,2 isomer should make B_1 somewhat more accessible than B_3 to attack by larger reagents. However, we hope that a projected study by one of the authors (I. R. E.) of boron hydride and carborane reactivities using more rigorous and dynamic theoretical methods will soon be complemented by definitive experimental investigations of these reactivities, and mechanistic studies.

Table VII. Atomic and Bond Moments (D)

	1,2 isomer			1,6 isomer
	y component	Total		Total
C_1	−0.24	0.27	C_1	0.22
B_3	−0.26	0.36	B_2	0.29
B_4	−0.25	0.25	C_1–B_2	0.56
C_1–C_2	−0.59	0.59	B_2–B_3	0.63
C_1–B_3	0.27	0.63	C_1–H_1	1.05
C_1–B_4	0.14	0.52	B_2–H_2	1.21
B_3–B_4	0.43	0.60		
B_4–B_6	0.50	0.50		
C_1–H_1	0.78	1.01		
B_3–H_3	0.11	1.23		
B_4–H_4	−0.81	1.24		

Dipole Moments

The dipole moment of the less symmetric 1,2 isomer was calculated by the origin-invariant partitioning method of Ruedenberg[23] to be 2.95 D. The direction of the moment makes the side of the molecule containing the C atoms positive. This dipole moment, like those calculated using minimum basis sets for the boron hydrides,[13] is probably about twice the experimental value, which has not yet been determined.

The Ruedenberg method was also used to analyze the atomic and bond components of the dipole moment in both isomers. These results are shown in Table VII. The net contributions to the 1,2-$B_4C_2H_6$ dipole moment were 1.49 D for atomic moments, 0.32 D for bond moments, and 1.15 D for the formal (Mulliken charge) moment. The fact that the net bond moment points in the same direction as does the total moment, rather than opposing it as in the boron hydrides,[13] is due to the absence of bridge hydrogens in 1,2-$B_4C_2H_6$. As found in previous calculations,[11,13] B–H and C–H bond moments appear to be almost independent of local environment, while other types of bond and atomic moments are far more sensitive.

Conclusion

We should like to emphasize once more the unreliability of all basis-set-dependent indices in comparing different types of atoms. Thus, we avoid most possible comparisons between B and C atoms using charges, overlap populations, free valences, dipole moment components, or frontier orbital populations. This approach greatly limits the range of our conclusions. Nevertheless, by stressing the solid theoretical framework of such partitioning-invariant quantities as the total electron density, we hope to minimize the arbitrary and/or *ex post facto* interpretations often given to approximate molecular orbital calculations of this type.[24]

Acknowledgment. We wish to thank E. Switkes for helpful discussions and the Office of Naval Research for support.

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(19) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1471, 1478, 1483 (1966).

(20) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964).

(21) C. A. Coulson, *Discuss. Faraday Soc.*, **2**, 9 (1947).

(22) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

(23) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962). The total dipole moment was calculated as $\int \psi^* \mathbf{r} \psi d\tau$.

(24) NOTE ADDED IN PROOF. After submission of this work, a CNDO/2 study of several carboranes appeared: C.-C. S. Cheung, R. A. Beaudet, and G. M. Segal, *J. Amer. Chem. Soc.*, **92**, 4158 (1970). The authors calculate the 1,2 isomer of $B_4C_2H_6$ to be the more stable by 13.6 kcal/mol, and attribute this discrepancy to their use of calculated rather than experimental B–B distances. They also report a microwave determination of the dipole moment of 1,2-$B_4C_2H_6$ to give a value of 1.50 D: R. A. Beaudet and R. L. Poynter, in preparation.