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Hexaborane(10). Self-Consistent Field Wave Function, Localized Orbitals, and Relationships to Chemical Properties

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A minimum basis set of Slater orbitals for B_6H_{10} yields an SCF wave function in which atomic charges are −0.02 (e) on B1 (apex), 0.07 on B2, 0.06 on B3,B6, and 0.04 on B4,B5. Net hydrogen charges are −0.07 on H1 (apex), −0.04 on H2, −0.04 on H3,H6, −0.09 on H4,H5, 0.03 on bridge H23,H26, and 0.02 on bridge H34,H56. Localized orbitals, obtained by maximizing $D = \Sigma_i(\phi_i\phi_i|\phi_i\phi_i)$, yield uniquely central three-center bonds B1–B3–B4 and B1–B5–B6 and single bonds B1–B2 and B4–B5. The short B4–B5 bond is especially strongly localized. Asymmetry is predicted in the bridge H atom bonding and positions. Relationships of these results to probable chemical behavior of B_6H_{10} and to the isoelectronic carboranes and ions are discussed.

In the past 20 years, the theoretical chemistry of the boron hydrides has undergone an expansion which has paralleled and complemented the advances made in the experimental chemistry of these fascinating molecules. The early three-center bond theory[2] was given more quantitative expression by the semiempirical extended Hückel[3] (EH) method, which was first developed in studies of boron hydrides. Later, nonempirical molecular orbital (NEMO) calculations[4] were developed and carried out, using parameters taken from model self-consistent field (SCF) results. More recently, full SCF calculations have been carried out on B_2H_6[5] and on B_4H_{10}, B_5H_9, and B_5H_{11}.[6] These calculations confirmed several experimental findings and predicted a number of others. In addition, analysis of the wave functions using localized orbitals[5,7] has provided new insights into hybridization, valence structures, and other properties of electron-deficient molecules. In this paper we complete the SCF-localized orbital stage in the theoretical investigation of the smaller boron hydrides, by presenting the results of SCF and localization (LMO) calculations on B_6H_{10} and by comparing the results with those of earlier calculations on this molecule. We also make some predictions relating to the undeveloped chemistry of B_6H_{10} and hope ultimately that boron chemistry can be brought to the degree of systematization and sophistication which now characterizes the chemistry of carbon and its compounds.

Following a very brief description of the SCF calculation on B_6H_{10} and the localization procedure, we examine here BHB asymmetries, relationships between valence structures and localized molecular orbitals (bonds), energy-related quantities, dipole and bond moments, magnetic properties, reactivity indices, and, finally, the relationships of the results on B_6H_{10} to the isoelectronic carboranes and boron hydride ions.

Procedure

The LCAO–SCF calculations were carried out with a modified version of the program described by Stevens.[8] Each unique integral was calculated to five decimal places in atomic units. The computation time on the IBM 7094, Model I, was approximately 9 hr. The localization was carried out using the program previously described[7] but now adapted for the IBM 360/65. About 3 hr was required for this localization calculation.

The boron framework geometry was taken from a refinement,[9] carried out in this laboratory, of the original X-ray diffraction structure.[10] Since the hydrogen positions were not determined to high accuracy by the X-ray data, idealized[6,11] distances and angles were employed. Boron–hydrogen bridge (B–H–B) bonds were assumed to be symmetric, with all B–H_b distances equal to 1.322 Å,[12] in order to test the experimental asymmetries in B–H–B′ bonds involving nonequivalent borons, as described below. The coordinates of the unique atoms are given in Table I, and the labeling of the atoms is shown in Figure 1.

The basis set for the SCF calculation consisted of Slater-type orbitals 1s on hydrogen and 1s, 2s, and 2p on boron. All exponents were taken from an optimized calculation for diborane.[5] They were 1.147 for terminal hydrogen, 1.209 for bridge hydrogen, and 4.680, 1.443, and 1.477 for boron 1s, 2s, and 2p, respectively. As we have noted previously,[6] use of such a minimum basis set is justified to some extent in electron-deficient molecules by the favorable ratio of basis functions to electron pairs, although polarization at the hydrogen atoms may be poorly described by a single 1s basis function.

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TABLE I

UNIQUE COORDINATES FOR B_6H_{10}[a] (AU)

	x	*y*	*z*
B1	0.0000	4.2817	5.1927
B2	0.0000	5.2498	2.0157
B3	2.6572	3.6347	3.3167
B4	1.5149	1.2190	5.2521
H1	0.0000	5.9894	6.6727
H2	0.0000	7.4439	1.4737
H3	4.6697	4.5378	3.8082
H4	3.2320	0.1472	6.2572
H23	1.7215	3.7490	1.0030
H34	2.5888	1.1625	3.0028

[a] *yz* is the symmetry plane.

TABLE II

B_6H_{10} MOLECULAR ORBITALS AND EIGENVALUES

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	1A'	1A"	2A'	3A'	4A'	2A"	5A'	3A"	6A'	7A'	4A"	8A'	9A'	5A"	10A'	11A'	6A"	12A'	7A"	13A'
	-7.6451	-7.6304	-7.6304	-7.5535	-7.5525	-7.5518	-1.0163	-0.8431	-0.8065	-0.6901	-0.6453	-0.6053	-0.5766	-0.5392	-0.5049	-0.4878	-0.4594	-0.4578	-0.4406	-0.3426
B1 1S	-0.0920	0.0000	0.0029	-0.9849	0.1322	0.0000	0.1031	0.0000	-0.0394	-0.1538	0.0000	-0.0065	-0.0228	0.0000	0.0250	-0.0420	0.0000	0.0362	0.0000	-0.0250
2S	0.0034	0.0000	-0.0048	-0.0299	0.0084	0.0000	-0.1817	0.0000	0.0947	0.4079	0.0000	0.0336	0.0579	0.0000	-0.0800	0.1175	0.0000	-0.1045	0.0000	0.1099
2PX	0.0000	0.0034	0.0000	0.0000	0.0000	0.0018	0.0000	0.1027	0.0000	0.0000	0.0013	0.0000	0.0000	0.0896	0.0000	0.0000	-0.0051	0.0000	0.4026	0.0000
Y	0.0012	0.0000	0.0004	0.0018	-0.0034	0.0000	0.0578	0.0000	-0.1103	0.0230	0.0000	0.1444	0.0038	0.0000	-0.0697	0.2966	0.0000	-0.0610	0.0000	-0.2854
Z	-0.0025	0.0000	0.0019	0.0042	0.0007	0.0000	0.0880	0.0000	0.0433	-0.0449	0.0000	0.0719	-0.0734	0.0000	-0.1500	0.0418	0.0000	-0.3783	0.0000	0.1356
B2 1S	-0.9939	0.0000	-0.0121	0.0016	-0.0006	0.0000	0.1097	0.0000	0.1320	-0.0294	0.0000	0.0012	0.0890	0.0000	-0.0280	-0.0057	0.0000	-0.0358	0.0000	0.0070
2S	-0.0290	0.0000	-0.0042	0.0038	-0.0005	0.0000	-0.2172	0.0000	-0.3326	0.0830	0.0000	0.0021	-0.2712	0.0000	0.0796	0.0196	0.0000	0.1210	0.0000	-0.0326
2PX	0.0000	0.0029	0.0000	0.0000	0.0000	-0.0001	0.0000	0.1263	0.0000	0.0000	0.2524	0.0000	0.0000	-0.0999	0.0000	0.0000	-0.1653	0.0000	0.0840	0.0000
Y	0.0037	0.0000	0.0012	-0.0004	0.0001	0.0000	0.0986	0.0000	0.0684	0.0640	0.0000	0.1813	-0.2817	0.0000	0.2850	-0.0098	0.0000	-0.0564	0.0000	0.0026
Z	-0.0013	0.0000	-0.0018	0.0028	-0.0004	0.0000	-0.0505	0.0000	0.0335	0.1712	0.0000	0.0121	0.1529	0.0000	0.0370	0.1156	0.0000	0.2795	0.0000	-0.2736
B3 1S	-0.0087	-0.7028	0.7028	0.0020	0.0011	0.0017	0.0998	-0.1286	0.0043	0.0194	-0.0417	-0.0681	-0.0598	-0.0468	-0.0131	0.0239	-0.0256	-0.0153	-0.0209	-0.0051
2S	0.0025	-0.0209	0.0208	0.0041	0.0019	0.0026	-0.1952	0.3076	-0.0087	-0.0530	0.1181	0.2056	0.1800	0.1427	0.0459	-0.0690	0.0883	0.0448	0.0790	0.0218
2PX	-0.0018	0.0025	-0.0025	-0.0022	-0.0003	-0.0006	0.0986	-0.0551	0.0253	-0.0812	-0.0313	0.2201	0.0036	0.2318	-0.0319	-0.1376	0.0381	-0.1001	-0.2963	-0.0417
Y	0.0015	0.0011	-0.0009	0.0006	-0.0013	-0.0013	0.0237	-0.0647	-0.0972	0.1221	0.1552	0.0621	-0.0071	0.1550	-0.1114	-0.1325	-0.1605	0.0833	0.0655	-0.1147
Z	-0.0007	0.0003	-0.0004	0.0020	0.0013	0.0017	0.0047	-0.0099	0.1065	0.1137	-0.1395	0.0605	0.0164	0.1583	0.0679	-0.0125	0.0511	0.0775	0.2332	0.1244
B4 1S	0.0002	-0.0018	0.0015	-0.0938	-0.6966	-0.7028	0.0713	-0.0681	-0.1129	0.0154	0.0807	0.0214	0.0776	0.0073	0.0393	0.0396	0.0520	-0.0011	-0.0223	0.0294
2S	0.0000	0.0021	-0.0021	0.0005	-0.0175	-0.0241	-0.1242	0.1437	0.2569	-0.0439	-0.2048	-0.0503	-0.2291	-0.0156	-0.1306	-0.1146	-0.1498	0.0004	0.0854	-0.1104
2PX	0.0000	0.0006	-0.0007	-0.0013	-0.0020	0.0021	0.0277	0.0650	-0.0517	-0.0795	-0.1175	0.1594	0.0402	0.0022	-0.0286	0.2548	-0.1399	0.1869	-0.0323	0.2905
Y	-0.0000	0.0016	-0.0014	0.0019	-0.0029	-0.0018	-0.0526	0.0468	0.0438	0.0820	0.0050	-0.0232	0.0929	0.0277	0.1029	-0.0690	0.1289	-0.0762	0.1750	0.3158
Z	-0.0000	-0.0008	0.0008	0.0005	0.0018	0.0023	0.0420	-0.0633	-0.0403	0.0621	0.0280	0.0283	-0.0703	0.0579	-0.1907	-0.0620	-0.2032	0.0684	0.0083	0.1314
B5 1S	0.0002	0.0018	0.0015	-0.0938	-0.6966	0.7028	0.0713	0.0681	-0.1129	0.0154	-0.0807	0.0214	0.0776	-0.0073	0.0393	0.0396	-0.0520	-0.0011	0.0223	0.0294
2S	0.0000	-0.0021	-0.0021	0.0005	-0.0175	0.0241	-0.1242	-0.1437	0.2569	-0.0439	0.2048	-0.0503	-0.2291	0.0156	-0.1306	-0.1146	0.1498	0.0004	-0.0854	-0.1104
2PX	-0.0000	0.0006	0.0007	0.0013	0.0020	0.0021	-0.0277	0.0650	0.0517	0.0795	-0.1175	-0.1594	-0.0402	0.0022	0.0286	-0.2548	-0.1399	-0.1869	-0.0323	-0.2905
Y	-0.0000	-0.0016	-0.0014	0.0019	-0.0029	0.0018	-0.0526	-0.0468	0.0438	0.0820	-0.0050	-0.0232	0.0929	-0.0277	0.1029	-0.0690	-0.1289	-0.0762	-0.1750	0.3158
Z	-0.0000	0.0008	0.0008	0.0005	0.0018	-0.0023	0.0420	0.0633	-0.0403	0.0621	-0.0280	0.0283	-0.0703	-0.0579	-0.1907	-0.0620	0.2032	0.0684	-0.0083	0.1314
B6 1S	-0.0087	0.7028	0.7028	0.0020	0.0011	-0.0017	0.0998	0.1286	0.0043	0.0194	0.0417	-0.0681	-0.0598	0.0468	-0.0131	0.0239	0.0256	-0.0153	0.0209	-0.0051
2S	0.0025	0.0209	0.0208	0.0041	0.0019	-0.0026	-0.1952	-0.3076	-0.0087	-0.0530	-0.1181	0.2056	0.1800	-0.1427	0.0459	-0.0690	-0.0883	0.0448	-0.0790	0.0218
2PX	0.0018	0.0025	0.0025	0.0022	0.0003	-0.0006	-0.0986	-0.0551	-0.0253	0.0812	-0.0313	-0.2201	-0.0036	0.2318	0.0319	0.1376	0.0381	0.1001	-0.2963	0.0417
Y	0.0015	-0.0011	-0.0009	0.0006	-0.0013	0.0013	0.0237	0.0647	-0.0972	0.1221	-0.1552	0.0621	-0.0071	-0.1550	-0.1114	-0.1325	0.1605	0.0833	-0.0655	-0.1147
Z	-0.0007	-0.0003	-0.0004	0.0020	0.0013	-0.0017	0.0047	0.0099	0.1065	0.1137	0.1395	0.0605	0.0164	-0.1583	0.0679	-0.0125	-0.0511	0.0775	-0.2332	0.1244
H1	-0.0001	0.0000	0.0001	0.0044	-0.0006	0.0000	-0.0335	0.0000	0.0189	0.1940	0.0000	0.1243	-0.0035	0.0000	-0.1837	0.3160	0.0000	-0.3961	0.0000	-0.0961
H2	0.0043	0.0000	-0.0000	-0.0001	0.0000	0.0000	-0.0396	0.0000	-0.1142	0.0554	0.0000	0.1302	-0.4209	0.0000	0.3303	-0.0234	0.0000	-0.0439	0.0000	0.0839
H3	0.0001	0.0031	-0.0031	-0.0001	0.0000	-0.0000	-0.0347	0.0904	-0.0037	-0.0267	0.0702	0.2903	0.1121	0.3624	-0.0286	-0.2343	0.0390	-0.0043	-0.1644	-0.0839
H4	0.0000	0.0000	0.0000	0.0005	0.0032	0.0033	-0.0228	0.0546	0.0788	-0.0563	-0.1641	0.0713	-0.1781	0.0116	-0.2432	0.0859	-0.4022	0.2226	-0.0656	0.0808
H5	0.0000	-0.0000	0.0000	0.0005	0.0032	-0.0033	-0.0228	-0.0546	0.0788	-0.0563	0.1641	0.0713	-0.1781	-0.0116	-0.2432	0.0859	0.4022	0.2226	0.0656	0.0808
H6	0.0001	-0.0031	-0.0031	-0.0001	0.0000	0.0000	-0.0347	-0.0904	-0.0037	-0.0267	-0.0702	0.2903	0.1121	-0.3624	-0.0286	-0.2343	-0.0390	-0.0043	0.1644	-0.0839
H23	0.0042	0.0030	-0.0030	-0.0003	0.0001	0.0001	-0.1293	0.1532	-0.2098	-0.1625	0.2807	-0.0803	-0.0093	-0.1924	-0.1855	-0.0438	-0.1325	-0.1528	-0.1077	0.0958
H26	0.0042	-0.0030	-0.0030	-0.0003	0.0001	-0.0001	-0.1293	-0.1532	-0.2098	-0.1625	-0.2807	-0.0803	-0.0093	0.1924	-0.1855	-0.0438	0.1325	-0.1528	0.1077	0.0958
H34	0.0001	0.0029	-0.0028	0.0002	0.0030	0.0031	-0.0958	0.2035	0.1217	-0.2222	-0.1710	0.0550	0.0270	-0.1478	0.1734	0.2042	0.2214	-0.0791	-0.1742	-0.1017
H56	0.0001	-0.0029	-0.0028	0.0002	0.0030	-0.0031	-0.0958	-0.2035	0.1217	-0.2222	0.1710	0.0550	0.0270	0.1478	0.1734	0.2042	-0.2214	-0.0791	0.1742	-0.1017

	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
	14A'	8A"	15A'	9A"	16A'	17A'	10A"	18A'	11A"	19A'	12A"	20A'	13A"	21A'	14A"	22A'	15A"	23A'	24A'	16A"
	0.1580	0.1874	0.3768	0.4049	0.4417	0.4934	0.5062	0.5324	0.5488	0.5801	0.6006	0.6353	0.6522	0.6775	0.7117	0.7459	0.7616	0.7705	0.8139	0.9249
B1 1S	-0.0075	0.0000	0.0313	0.0000	-0.0140	-0.0320	0.0000	0.0565	0.0000	-0.2365	0.0000	-0.0363	0.0000	-0.0133	0.0000	0.0450	0.0000	0.0650	-0.0578	0.0000
2S	0.0500	0.0000	-0.1657	0.0000	0.1201	0.1889	0.0000	-0.3379	0.0000	1.5214	0.0000	0.2369	0.0000	0.0985	0.0000	-0.3223	0.0000	-0.4598	0.4345	0.0000
2PX	0.0000	0.0100	0.0000	-0.6348	0.0000	0.0000	0.2134	0.0000	0.5654	0.0000	-0.3759	0.0000	0.2957	0.0000	-0.2484	0.0000	-0.5526	0.0000	0.0000	-0.3066
Y	-0.0755	0.0000	0.4533	0.0000	0.1331	-0.3157	0.0000	0.3673	0.0000	-0.0360	0.0000	0.0691	0.0000	-0.3485	0.0000	0.0407	0.0000	0.3577	0.9708	0.0000
Z	0.0757	0.0000	-0.3016	0.0000	0.4117	0.1613	0.0000	-0.2589	0.0000	-0.3774	0.0000	0.4196	0.0000	0.5508	0.0000	0.4821	0.0000	0.4571	0.4002	0.0000
B2 1S	0.0643	0.0000	-0.0763	0.0000	-0.0623	-0.1725	0.0000	-0.0517	0.0000	0.0482	0.0000	0.0719	0.0000	-0.1323	0.0000	-0.0321	0.0000	-0.0032	0.0049	0.0000
2S	-0.2438	0.0000	0.4564	0.0000	0.4117	1.0767	0.0000	0.3696	0.0000	-0.2988	0.0000	-0.4774	0.0000	0.9110	0.0000	0.2451	0.0000	0.0309	-0.0473	0.0000
2PX	0.0000	-0.3596	0.0000	0.7875	0.0000	0.0000	-0.4395	0.0000	0.3074	0.0000	-0.2526	0.0000	0.5009	0.0000	0.1127	0.0000	-0.3788	0.0000	0.0000	0.0295
Y	0.2511	0.0000	-0.2211	0.0000	0.2700	-0.4082	0.0000	0.4816	0.0000	0.3277	0.0000	-0.2132	0.0000	-0.1237	0.0000	0.8156	0.0000	-0.4334	-0.2735	0.0000
Z	0.5185	0.0000	-0.0284	0.0000	-0.0262	0.2599	0.0000	0.2090	0.0000	-0.3040	0.0000	0.7736	0.0000	0.1993	0.0000	0.1283	0.0000	0.3138	-0.4018	0.0000
B3 1S	-0.0402	-0.0126	0.0109	0.0536	-0.0008	0.1391	0.0854	0.0403	0.0936	0.0445	0.0257	0.0621	0.0749	-0.0810	-0.0923	-0.0048	-0.0207	-0.0211	-0.0147	-0.0099
2S	0.2230	0.0721	-0.0611	-0.3353	0.0321	-0.8893	-0.5441	-0.2586	-0.5775	-0.2777	-0.1918	-0.4145	-0.5163	0.5559	0.6423	0.0435	0.1767	0.1656	0.0999	0.0785
2PX	0.0713	0.1482	0.1673	0.1125	0.1043	0.1472	-0.0651	0.3578	0.5671	0.3181	-0.3979	0.0547	-0.3110	0.3163	0.0610	-0.6407	-0.3095	0.1334	-0.2469	0.2330
Y	-0.1272	-0.3744	-0.4749	-0.0951	0.4636	-0.0444	0.0305	-0.0099	0.2191	-0.1384	0.2405	-0.1038	-0.5256	-0.3547	-0.3171	-0.2957	0.3250	0.1432	-0.1082	0.1657
Z	-0.4646	-0.0595	0.3385	0.3803	0.1633	-0.1772	0.3260	-0.0709	-0.0602	-0.0184	-0.4032	0.2002	0.0259	0.0461	0.2537	0.1807	0.4544	0.3636	-0.3802	0.2079
B4 1S	0.0175	-0.0094	-0.0145	-0.0373	-0.0270	0.0121	-0.0435	-0.0710	-0.0674	0.0736	-0.1537	-0.0387	0.0371	0.0215	-0.0795	0.0428	0.0565	0.0662	-0.0429	-0.0361
2S	-0.0941	0.0446	0.0695	0.2030	0.2073	-0.0620	0.2745	0.4082	0.4672	-0.4721	1.0289	0.2858	-0.2335	-0.1353	0.5549	-0.3144	-0.3942	-0.5114	0.3041	0.3585
2PX	-0.0597	0.0305	-0.1157	0.2393	0.1566	0.0403	-0.0393	0.0048	-0.0111	-0.1438	-0.1357	0.2261	-0.3547	0.0137	-0.2642	-0.1788	0.0762	-0.5283	0.0349	-1.0857
Y	0.1359	0.3910	-0.0320	0.2746	-0.0302	0.1443	-0.2369	0.4601	0.0245	-0.1978	0.2284	-0.1341	-0.1298	-0.3401	-0.6202	-0.0911	-0.0202	0.3071	0.2057	0.3244
Z	0.3421	0.2978	0.4430	-0.1440	0.1677	-0.0385	-0.3362	-0.3248	0.2800	-0.0425	0.0416	-0.1220	0.3402	-0.1874	0.2619	0.0596	0.5943	-0.0753	-0.1211	-0.1680
B5 1S	0.0175	0.0094	-0.0145	0.0373	-0.0270	0.0121	0.0435	-0.0710	0.0674	0.0736	0.1537	-0.0387	-0.0371	0.0215	0.0795	0.0428	-0.0565	0.0662	-0.0429	0.0361
2S	-0.0941	-0.0446	0.0695	-0.2030	0.2073	-0.0620	-0.2745	0.4082	-0.4672	-0.4721	-1.0289	0.2858	0.2335	-0.1353	-0.5549	-0.3144	0.3942	-0.5114	0.3041	-0.3585
2PX	0.0597	0.0305	0.1157	0.2393	-0.1566	-0.0403	-0.0393	-0.0048	-0.0111	0.1438	-0.1357	-0.2261	-0.3547	-0.0137	-0.2642	0.1788	0.0762	0.5283	-0.0349	-1.0857
Y	0.1359	-0.3910	-0.0320	-0.2746	-0.0302	0.1443	0.2369	0.4601	-0.0245	-0.1978	-0.2284	-0.1341	0.1298	-0.3401	0.6202	-0.0911	0.0202	0.3071	0.2057	-0.3244
Z	0.3421	-0.2978	0.4430	0.1440	0.1677	-0.0385	0.3362	-0.3248	-0.2800	-0.0425	-0.0416	-0.1220	-0.3402	-0.1874	-0.2619	0.0596	-0.5943	-0.0753	-0.1211	0.1680
B6 1S	-0.0402	0.0126	0.0109	-0.0536	-0.0008	0.1391	-0.0854	0.0403	-0.0936	0.0445	-0.0257	0.0621	-0.0749	-0.0810	0.0923	-0.0048	0.0207	-0.0211	-0.0147	0.0099
2S	0.2230	-0.0721	-0.0611	0.3353	0.0321	-0.8893	0.5441	-0.2586	0.5775	-0.2777	0.1918	-0.4145	0.5163	0.5559	-0.6423	0.0435	-0.1767	0.1658	0.0999	-0.0785
2PX	-0.0713	0.1482	-0.1673	0.1125	-0.1043	-0.1472	-0.0651	-0.3578	0.5671	-0.3181	-0.3979	-0.0547	-0.3110	-0.3163	0.0610	0.6407	-0.3095	-0.1334	0.2469	0.2330
Y	-0.1272	0.3744	-0.4749	0.0951	0.4636	-0.0444	-0.0305	-0.0099	-0.2191	-0.1384	-0.2405	-0.1038	0.5256	-0.3547	0.3171	-0.2957	-0.3250	0.1432	-0.1082	-0.1657
Z	-0.4646	0.0595	0.3385	-0.3803	0.1633	-0.1772	-0.3260	-0.0709	0.0602	-0.0184	0.4032	0.2002	-0.0259	0.0461	-0.2537	0.1807	-0.4544	0.3636	-0.3802	-0.2079
H1	-0.0792	0.0000	-0.0313	0.0000	-0.5063	0.0112	0.0000	0.0919	0.0000	-0.5499	0.0000	-0.4274	0.0000	-0.1380	0.0000	-0.1521	0.0000	-0.2527	-0.9092	0.0000
H2	0.0935	0.0000	-0.0711	0.0000	-0.5276	-0.1661	0.0000	-0.5878	0.0000	-0.1902	0.0000	0.5710	0.0000	-0.2678	0.0000	-0.6778	0.0000	0.3598	0.1363	0.0000
H3	-0.1333	-0.0370	0.0191	0.0674	-0.3408	0.4320	0.2949	-0.1495	-0.2376	-0.0519	0.3972	0.1596	0.6457	-0.3716	-0.2566	0.4860	-0.0276	-0.2613	0.2027	-0.2403
H4	-0.0004	0.0023	-0.2758	-0.1289	-0.3768	0.0793	-0.0791	0.1414	-0.3887	0.2689	-0.3356	-0.2800	0.1303	0.0094	-0.4386	0.1879	-0.1315	0.6382	-0.0083	0.5768
H5	-0.0004	-0.0023	-0.2758	0.1289	-0.3768	0.0793	0.0791	0.1414	0.3887	0.2689	0.3356	-0.2800	-0.1303	0.0094	0.4386	0.1879	0.1315	0.6382	-0.0083	-0.5768
H6	-0.1333	0.0370	0.0191	-0.0674	-0.3408	0.4320	-0.2949	-0.1495	0.2376	-0.0519	-0.3972	0.1598	-0.6457	-0.3716	0.2566	0.4860	0.0276	-0.2613	0.2027	0.2403
H23	-0.0247	0.3669	0.0115	0.0695	0.0324	-0.2746	0.7613	0.2883	0.1198	0.2662	-0.1833	0.6089	-0.1088	-0.3218	-0.0670	0.2117	0.2831	0.0798	-0.4375	0.1032
H26	-0.0247	-0.3669	0.0115	-0.0695	0.0324	-0.2746	-0.7613	0.2883	-0.1198	0.2662	0.1833	0.6069	0.1088	-0.3218	0.0670	0.2117	-0.2831	0.0798	-0.4375	-0.1032
H34	0.1229	-0.3099	0.0640	-0.1238	0.4372	0.3296	-0.1258	-0.3264	0.4182	0.1344	-0.0576	-0.1990	0.2256	-0.4976	-0.3708	-0.0150	0.6341	0.3047	-0.2638	0.1575
H56	0.1229	0.3099	0.0640	0.1238	0.4372	0.3296	0.1258	-0.3264	-0.4182	0.1344	0.0576	-0.1990	-0.2256	-0.4976	0.3708	-0.0150	-0.6341	0.3047	-0.2638	-0.1575

Electronic energy = -332.9127 au
Nuclear repulsion = 179.3953 au
Total energy = -153.5174 au

Kinetic energy = 153.9499 au
-E/T = 0.9972
ε (HFMO) = -0.383 au
I.P.[a] = .342 au

[a] T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 581 (1964).

Convergence of the localization calculation to a true maximum of the self-repulsion energy[13] was verified by two procedures:[7,14] (a) by applying random unitary transformations to our starting (canonical) set of orbitals and (b) by investigating the curvature of the second-order energy surface. These checks are described in more detail below.

The SCF wave functions and energies are tabulated in Table II. Results of the localization calculation are shown in Table III. The set of localized orbitals obtained for B_6H_{10} corresponds most closely to the valence structure shown in Figure 2a, with smaller contributions from some of the other structures of Figure 2.

Results and Discussion

Population Analysis.—A Mulliken population analysis[15] of our wave function shows that the present calcu-

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[13] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963).

[14] M. D. Newton, E. Switkes, and W. N. Lipscomb, to be submitted for publication.

[15] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1958).

TABLE III

LOCALIZED ORBITALS FOR B_6H_{10}

Bond				Bond length, Å			Population			Hybridization sp^x			Delocalizn,[a]
A	A′	A″		A–A″	A′–A″	A″–A	A	A′	A″	A	A′	A″	%
B1	(inner shell)		(1)[b]	...	...	...	2.00	...	...	...	...	...	3.7
B2	(inner shell)		(1)	...	...	...	2.00	...	...	...	...	...	3.5
B3	(inner shell)		(2)	...	...	...	2.00	...	...	...	...	...	3.5
B4	(inner shell)		(2)	...	...	...	2.00	...	...	...	...	...	3.6
B1	H1	...	(1)	1.20	...	...	0.93	1.09	...	1.49	...	...	6.8
B2	H2	...	(1)	1.20	...	...	0.97	1.05	...	1.38	...	...	6.5
B3	H3	...	(2)	1.20	...	...	0.96	1.05	...	1.42	...	...	6.3
B4	H4	...	(2)	1.20	...	...	0.92	1.10	...	1.60	...	...	7.1
B2	H23	B3	(2)	1.32	1.32	1.74	0.55	0.99	0.48	3.69	...	3.37	9.6
B3	H34	B4	(2)	1.32	1.32	1.74	0.58	1.01	0.42	3.57	...	7.25	10.4
B1	B2	...	(1)	1.74	...	...	0.69	0.83	...	7.33	2.86	...	16.6
B4	B5	...	(1)	1.60	...	...	1.00	1.00	...	1.70	1.70	...	10.6
B1	B3	B4	(2)	1.75	1.74	1.80	0.72	0.67	0.57	2.67	2.63	4.71	13.8

[a] See eq 1. [b] Number of symmetry-equivalent bonds.

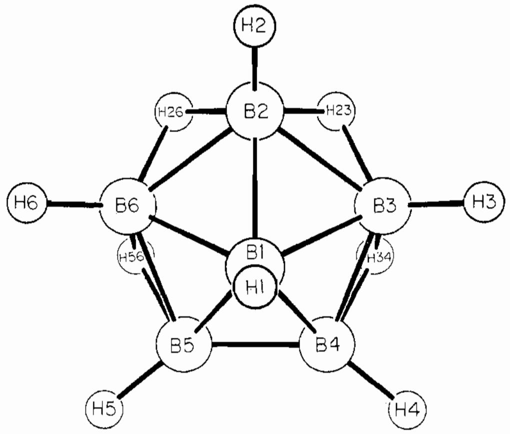

Figure 1.—B_6H_{10}.

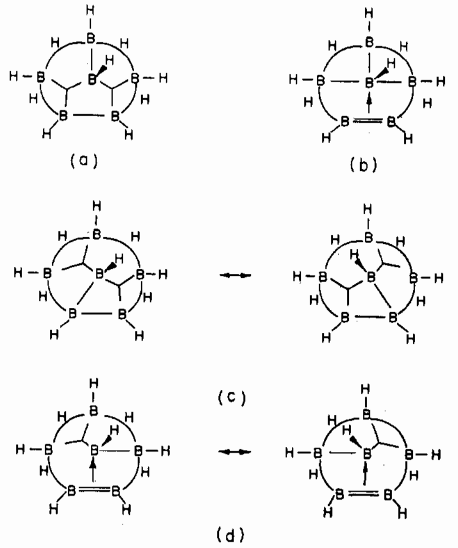

Figure 2.—Some possible valence structures for B_6H_{10}.

lation differs from earlier calculations on this molecule. In Table IV we give the Mulliken atomic charges for the unique atoms in B_6H_{10} calculated by three-center theory,[3] the EH method,[3] NEMO,[16] and our SCF calculation. As expected, the introduction of self-consistency greatly reduces the magnitudes of the calculated charge separations. More surprising is the result that there are some changes in the relative ordering of the atomic charges as the sophistication of the calculation increases.

TABLE IV

MULLIKEN ATOMIC CHARGES FOR B_6H_{10}

Atom	3 center[a]	Extended Hückel		NEMO[d]	SCF[e]
B1	−0.72	+0.02[b]	−0.12[c]	−0.21	−0.02
B2	+0.36	−0.36[b]	−0.07[c]	+0.08	+0.07
B3	+0.35	+0.24[b]	+0.30[c]	+0.07	+0.06
B4	−0.17	+0.20[b]	+0.28[c]	−0.16	+0.04
H1	...	...	...	0.00	−0.07
H2	...	...	...	+0.04	−0.04
H3	...	...	...	+0.03	−0.04
H4	...	...	...	−0.03	−0.09
H23	...	...	...	+0.09	+0.03
H34	...	...	...	+0.07	+0.02

[a] Reference 3, all structures. [b] Reference 3, method I. [c] Reference 3, method II; terminal and bridge H atoms have different Coulomb integrals. [d] Reference 16. [e] Present work.

The bond overlap populations shown in Table V are somewhat less dependent upon the method of calculation, since they are largely determined by the molecular geometry. However, some differences between methods still occur. Since total electron densities are

TABLE V

BOND STRENGTHS IN B_6H_{10}

Bond	Distance, Å	3 center[a]	EH[b]	NEMO[c]	SCF[d]	SCF[e]
B1–B2	1.74	0.74	0.52	0.43	0.45	0.120
B1–B3	1.75	0.75	0.52	0.43	0.48	0.121
B1–B4	1.80	0.77	0.44	0.42	0.34	0.105
B2–B3	1.74	0.61	0.45	0.38	0.35	0.104
B3–B4	1.74	0.67	0.44	0.38	0.38	0.110
B4–B5	1.60	1.00	1.00	0.78	0.88	0.173
B2–H23	1.32	...	...	0.42	0.41	0.112
B3–H23	1.32	...	...	0.37	0.36	0.106
B3–H34	1.32	...	...	0.43	0.45	0.120
B4–H34	1.32	...	...	0.41	0.33	0.100
B1–H1	1.20	...	...	0.84	0.82	0.173
B2–H2	1.20	...	...	0.87	0.83	0.176
B3–H3	1.20	...	...	0.85	0.83	0.175
B4–H4	1.20	...	...	0.81	0.82	0.172

[a] Mulliken population, ref 3, all structures. [b] Mulliken population, ref 3, method I. [c] Mulliken population, ref 16. [d] Mulliken population, present work. [e] Electron density (e^-/au^3), present work.

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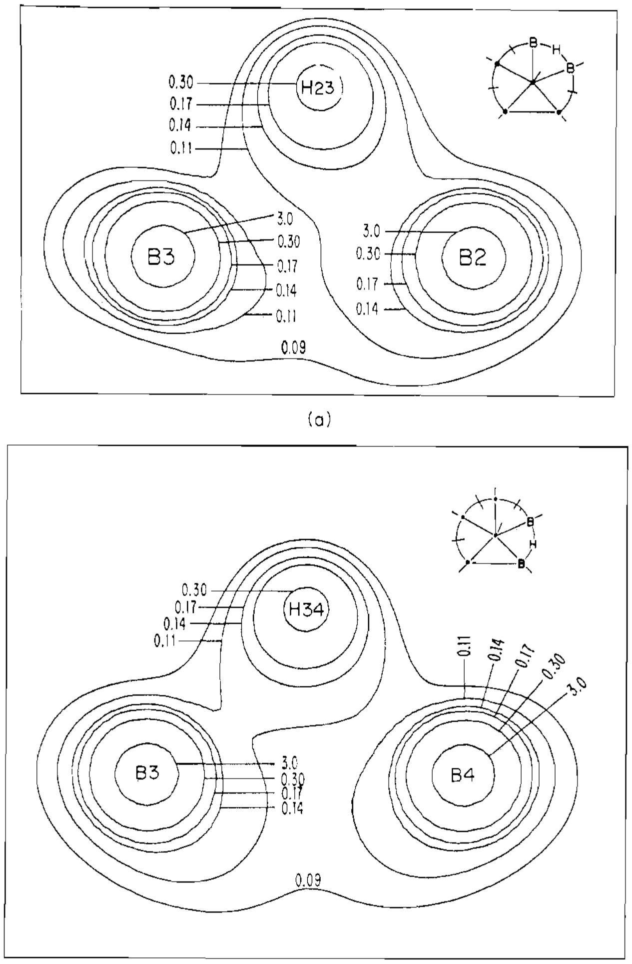
(16) F. P. Boer, "Molecular and Valence Structures of Boron Compounds," Ph.D. Thesis, Harvard University, 1965.

independent of the method of partitioning employed in the analysis, they may provide a more reliable guide to bond strengths than the Mulliken or other analyses usually presented. We have therefore included in Table V the electron density at the midpoint of each bond as another measure of bonding.

B–H–B Bridge Asymmetries.—One justification for the use of overlap populations as a measure of bonding has been that in some situations there is correlation with observed bond lengths.[15,17] Often the reasoning behind this explanation is somewhat circular, since most calculations employ experimental geometries and since the nature of the overlap population makes it strongly dependent upon overlap integrals and hence upon distances between atoms. In order to avoid this type of prejudice and to test the overlap population–bond length correlation for bonds involving bridge H atoms, we employed a geometry in this calculation which had symmetric B–H–B bridges. In addition, if one accepts at least a rough population–length relation for these bonds, this calculation provides a test of the reliability of the experimental determination of the bridge hydrogen positions, which were rather uncertain in the original work.[10] Studies of the asymmetric bridges in B_4H_{10} and B_5H_{11}[6,7] had previously suggested that such an analysis can indeed give information about the direction of bridge asymmetry.

The B–H_b distances obtained in the original X-ray study,[10] in which the molecule failed to refine as a rigid body, were 1.32, 1.48, 1.31, and 1.35 Å for B2–H23, B3–H23, B3–H34, and B4–H34, respectively. A further refinement[9] gave a decrease in all B–H_b distances but kept the directions of asymmetry unchanged.[18] Thus, experiment suggests that the B2–H23–B3 bridge is the more asymmetric and that H23 lies closer to B2 than to B3, while H34 lies closer to B3 than to B4. Both the overlap populations and the midpoint densities in Table V are in agreement with the experimental directions of asymmetry. The populations in the B–H–B localized orbitals (Table III) are also asymmetric in the experimental direction. Figure 3 shows the contours of total electron density in the two nonequivalent B–H–B bridge planes.

The present calculation appears to disagree both with intuition and with results of previous calculations[6,7] in placing the bridge hydrogens closer to the borons bearing more positive net Mulliken charges. A more detailed population analysis shows, however, that this discrepancy is due to the crudeness of the total Mulliken charges as a measure of such subtle population differences. If we include only the "relevant change," *i.e.*, only the contributions to the net Mulliken charge arising from the interaction of the boron atom with itself and with the bridge-bonded hydrogen, then both hydrogens do lie closer to the more negative (less positive) borons.



(a)

(b)

Figure 3.—Total electron densities (e^-/au^3) of bridge hydrogen bonds: (a) B2-H23-B3 plane; (b) B3-H34-B4 plane.

Our calculation, however, clearly implies that the B3–H34–B4 bridge is the more asymmetric. While the standard deviations in the X-ray determination[10] are large enough to be consistent with this conclusion, Pawley's refinement[9] makes the B3–H34–B4 bridge nearly symmetric. Perhaps a redetermination of the structure with enough data so that the molecule refines as a rigid body would resolve this apparent discrepancy between theory and experiment.

Valence Structures and LMO's.—One of the most interesting and ambiguous aspects of boron chemistry is the existence of a sizable number of often nearly equivalent valence structures consistent with a given molecular configuration. Allowing for only boron–hydrogen terminal and bridge bonds and for boron–boron two-center single and three-center open and central bonds (Figure 2), B_6H_{10} has 12 possible three-center valence structures, while $B_{10}H_{14}$ is known to have at least 111.[11] One reason for these large numbers of valence structures in the boron hydrides is, of course, the existence of several different types of boron–boron bonds, as shown in Figure 4. If one allows for the possibility of multiple B–B bonding, analogous to the carbon–carbon double and triple bonds, the number of possible structures increases greatly.

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(17) C. A. Coulson, *Proc. Roy. Soc.*, *Ser. A*, **169**, 413 (1939).

(18) Pawley,[9] although still unsuccessful, did reduce *R* from the 0.099 of ref 10 to 0.078. Pawley suggested that the problem is lack of sufficient data in the original study, giving rise to anisotropic temperature factors with no physical meaning.

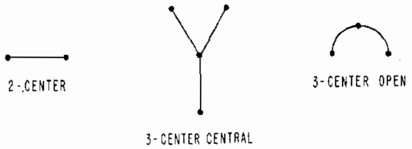

Figure 4.—Types of boron–boron framework bonds.

The localized orbital approach has proved extremely helpful in elucidating the valence structures of several other boron hydrides. The completely *ab initio* nature[5,7] of this theory lends added weight to the objectivity of its conclusions. Calculations on B_2H_6,[5] B_4H_{10},[6] B_5H_9,[6] and B_5H_{11}[6] have shown that the orbitals which maximize the self-energy

$$D = \sum_k (\phi_k\phi_k|\phi_k\phi_k) = \sum_k \int \phi_k(i)\phi_k(i)r_{ij}^{-1}\phi_k(j)\phi_k(j)\, \mathrm{d}V_i \mathrm{d}V_j$$

in these compounds are of the type postulated by the three-center bond theory. Thus, we find three-center bridge and two-center terminal boron–hydrogen bonds, boron inner shells, and two-center and three-center central boron–boron bonds, with ambiguity only in boron–boron bonds of B_5H_9. The open three-center boron–boron bond did not appear in any of these previous calculations. Also, the orbitals found in these calculations show a large degree of transferability. For example, a B–H–B orbital in B_2H_6 looks very much like a B–H–B orbital in B_5H_{11}. Thus, we expected and indeed found strongly localized BH bonds and BHB bonds in B_6H_{10}.

In addition to providing still another test of the ability of the localized orbital formulation to decide quantitatively among several valence structures, hexaborane(10) also introduces the possibility of multiple boron–boron bonding. The B4–B5 distance (1.60 Å), the shortest known in the boron hydrides, compares with a B–B distance of 1.75 Å for the single bond in B_4H_{10}. This shortening is comparable with the 0.14-Å difference between the C–C bond lengths in ethane and benzene. While it is unsafe to argue from this similarity, this comparison does raise the possibility of partial multiple bonding in B_6H_{10}. Furthermore the B4–B5 overlap population of 0.88 is 50% greater than any other previously calculated B–B population. The dihydrocarborane $B_4H_6C_2H_2$ has been shown[19] to have a structure consistent with a π-donation model in which the double-bonded borons and their attached bridge and terminal hydrogens in Figure 2b are replaced by C–H groups. One aim of the localized orbital analysis was to determine to what extent the multiple bonding of this carborane is present in its parent boron hydride.

The atomic populations in Table III show that each localized orbital is composed almost completely of contributions from the one, two, or three relevant atoms which form the inner shell or interatomic bond. The delocalization index,[7] d_i^{rms}, measures the root-mean-square deviation of the localized orbital from a renormalized truncated orbital obtained by removing all contributions from orbitals centered on atoms not directly involved in the bond (eq 1). This index is zero

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

if the orbital ϕ_i^{L} is completely localized on the atoms which form the bond and is 100% if ϕ_i^{L} and ϕ_i^{T} are mutually orthogonal. The hybridization sp^x is given, for the s and p orbitals centered on the atom of interest, by the ratio of the sum of squares of the p-orbital LCAO coefficients to the sum of squares of the s-orbital coefficients in a single localized orbital.[5]

The calculation converges unambiguously to a structure which corresponds most closely to Figure 2a. Inspection of the many-dimensional self-repulsion energy surface in the neighborhood of this structure using the second-derivative test developed by Switkes, Lipscomb, and Newton[7,14] shows that we are indeed at a relative maximum. The largest (least negative) eigenvalue of the quadratic-form matrix is -1.5×10^{-1}, showing that any infinitesimal change in the orbitals will cause the self-repulsion energy to decrease relatively sharply.

In order to search for other relative maxima and to ensure that our calculation was not prejudiced against double-bonded structures like Figures 2b and 2d or against asymmetric pairs of resonance hybrids like Figures 2c and 2d, we employed the feature of the localization program which allows for unitary transformations among the orbitals or among any subset of them. Since randomization and relocalization of the complete set of 20 orbitals would require an extremely large expenditure of computing time, we sought a subset of the full LMO basis which would make possible an economical, but still unprejudiced, search for further relative maxima in the energy surface. A detailed study of this problem in B_5H_9[7] showed that the results of the localization procedure can be influenced not only by the boron framework orbitals but also by the B–H–B and even by the B–H_t bonds. The B_6H_{10} localization, however, is expected to be far less sensitive, since its largest second-order energy eigenvalue is four orders of magnitude greater than the corresponding quantities for the B_5H_9 structures.

The eigenvector associated with this largest eigenvalue determines a "direction" in a 210-dimensional space in which the basis vectors are the interactions between pairs of LMO's. This direction gives the mixing of LMO's which is least strongly coupled to the self-repulsion energy.[5,7] We find, in agreement with earlier calculations,[7] that this eigenvector is composed mainly of contributions from boron framework and to a lesser extent from BHB–boron framework interactions. A smaller contribution also arises from the coupling between BH_t and boron framework orbitals. The coefficients of the inner-shell interactions are negligible.

The above analysis suggests that suitable subsets for our search may be (a) the 4-boron framework LMO's, (b) the 8-boron framework and BHB LMO's, and (c) the 14 valence orbital LMO's, omitting inner shells.

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(19) F. P. Boer, W. E. Streib, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1666 (1964). C–C distances are 1.419 ± 0.006 Å in $B_4H_6C_2H_2$ and 1.431 ± 0.006 Å in $B_4H_6C_2(CH_3)_2$.

The search for further maxima then proceeded as follows. (1) A set of orbitals was constructed from set (a) to correspond to the structure in Figure 2b. (2) Three different sets of orbitals were generated by randomizing set (a). (3) Set (b) was randomized. (4) Set (c) was randomized. All the above sets of starting orbitals were then subjected to the localization procedure in which only the appropriate subsets of orbitals were transformed. All converged to the same structure, that of Table III and Figure 2a. Approximate computing times for the localizations were 10 min with set (a), 35 min with set (b), and 90 min with set (c). Thus, we believe that the structure found represents the single relative maximum of the self-repulsion energy surface.

The above discussion does not deny the existence of some multiple bonding in B_6H_{10}, as part of a more complex description. It does say that the best single localized bond picture, according to the self-energy criterion, is that of Figure 2a and not one having a double bond between B4 and B5. However, we recognize that this is an oversimplified picture. As Table III shows, the two single bonds in B_6H_{10} are by no means equivalent. The B1–B2 bond resembles the "normal" boron–boron single bond of B_4H_{10} in having significant contributions from atoms not involved in the bond. Comparison of the appropriate delocalization indices[7] shows that the B4–B5 bond is much more highly localized than any previously studied boron–boron bond. The existence of a strengthened single bond is in marked contrast to the situation found in the hydrocarbons, where Newton, Switkes, and Lipscomb[14] obtained two and three equivalent "bent bond" localized orbitals for the double and triple bonds in ethylene and acetylene, respectively. These considerations, plus the increased electron density in the B4–B5 bond, as shown in Figure 5, justify our speaking of a partial double bond. Although this objective localization procedure unambiguously rejects the notion of a double-bond π-donation structure as the preferred valence structure, qualitative and quantitative measures of bonding do require a distinction between the B4–B5 bond in B_6H_{10} and "normal" two-center B–B bonds such as those found in B_4H_{10} and in B_6H_{10} (B1–B2).

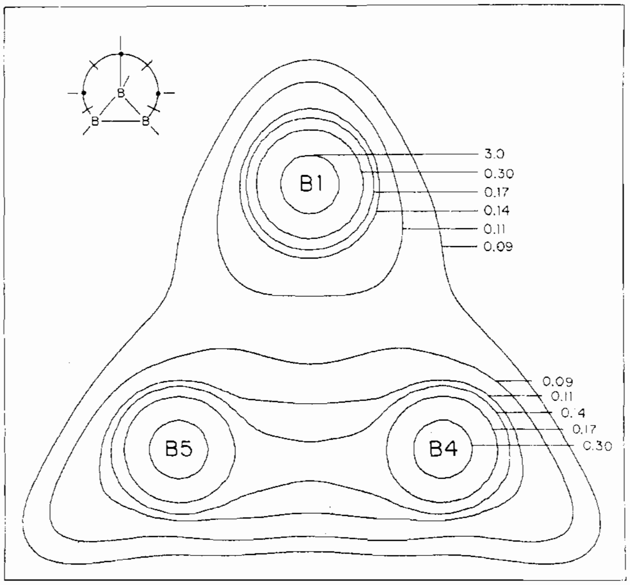

Figure 5.—Total electron density (e^-/au^3) in the B1–B4–B5 plane.

The other results of the localization calculation are in good agreement with the general features found in other boron hydrides.[5,7] Inner shells are strongly localized and highly coupled to the self-repulsion energy. Boron–terminal hydrogen bonds are well localized, are quite transferable, and have a slight $B^{\delta+}$–$H^{\delta-}$ polarity. Boron–bridge hydrogen bonds are less well localized and less strongly coupled to the self-repulsion energy. Their relation to bond asymmetries is discussed above. Finally, we have again failed to find any evidence for the occurrence of open three-center bonds in these neutral boron hydrides.

Energetics.—The total energies and virial ratio are given in Table II. Atomization energies for this calculation and for the NEMO calculation[16] are presented in Table VI. As in an earlier paper[6] we find that the use of molecular exponents for our reference atoms gives atomization energies in good agreement with experiment. Koopmans' ionization potentials and the observed ionization potentials are shown in Table II. Table VII gives a comparison of the diagonal SCF Hamiltonian matrix elements and the α's used by Boer.[16] We see that the diagonal elements are substantially different for different boron atoms and confirm that a simple ω technique is not capable of reproducing these differences in boron compounds. The

TABLE VI

ATOMIZATION ENERGIES (AU)

A				$A/A_{B_2H_6}$			
SCF[a]	SCF[b]	Exptl[c]	NEMO[d]	SCF[a]	SCF[b]	Exptl[c]	NEMO[d]
−1.527	−2.002	−2.091	−2.114	2.118	2.150	2.280	2.068

[a] The reference atoms use Clementi's best single-ζ exponents: $E(B) = -24.4984$, $E(H) = -0.500$. [b] The reference atoms employ B_6H_{10} molecular exponents: $E(B) = -24.4372$, $E(H_t) = -0.4892$, $E(H_{br}) = -0.4781$. [c] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961). [d] Reference 16 (partially optimized BH_3 exponents).

TABLE VII

COMPARISON OF DIAGONAL SCF HAMILTONIAN MATRIX ELEMENTS (F_{ii}) AND NEMO α's (AU'S)

SCF[a]

	q^b	F_{B1s}	F_{B2s}	F_{B2p}(av)		F_{H1s}
B1	−0.017	−7.511	−1.188	−0.287	H1	−0.441
B2	0.068	−7.642	−1.217	−0.311	H2	−0.484
B3	0.062	−7.628	−1.212	−0.304	H3	−0.475
B4	0.045	−7.549	−1.151	−0.237	H4	−0.451
					H23	−0.624
					H34	−0.590

NEMO[c]

F_{B1s}	F_{B2s}	F_{B2p}	F_{Ht}	F_{Hb}
−7.650	−1.108	−0.295	−0.459	−0.577

[a] Present work. [b] Net Mulliken atomic charges on borons. [c] Reference 16.

Hamiltonian matrix also shows large anisotropies in the boron 2p orbitals and large zero-overlap matrix elements for both 2s,2p, and 2p,2p interactions. In Boer's calculations all zero-overlap elements were neglected, and no p orbital anisotropy was allowed. We have chosen to list the 1s diagonal elements (the canonical "inner-shell" MO eigenvalues) because of our belief that they may provide a useful comparison with experimental results from photoelectron spectroscopy.[20]

The localization criterion, that is the maximization of the intraorbital Coulomb (self-repulsion) energy $\Sigma(ii|ii)$, is equivalent to the minimization of the interorbital Coulomb energy $4\Sigma_{i>j}(ii|jj)$ and the interorbital exchange energy $2\Sigma_{i>j}(ij|ij)$.[5] This exchange or "Pauli interference" term is nonclassical in nature. Its magnitude is often reduced by factors as large as 10, over that for the canonical molecular orbital method, in localization calculations. The results justify the contention[7] that the local orbital transformation provides a conceptual bridge between the Hartree–Fock wave function and the more easily visualizable notions of electron-pair bonding.

The reduction in magnitude of the exchange energy reflects both the nature of the localized orbitals and the degree of localization of the parent canonical orbitals (which are by no means the most "delocalized" possible choice of orbitals). The various energy components for B_6H_{10} are shown in Table VIII. The relative decrease in the exchange energy of B_6H_{10} is slightly less than that found for the smaller boron hydrides.[7] This phenomenon may be attributed to the somewhat lower symmetry of B_6H_{10}, which allows the canonical orbitals to be more localized than if they were more completely determined by symmetry.

TABLE VIII

ENERGY ANALYSIS FOR B_6H_{10}[a]

	Canonical	Local
Total two-electron	224.9539	224.9539
Self-repulsion[b]	16.3459	25.9455
Coulomb[c]	235.6596	226.0599
Exchange[d]	−10.7057	−1.1060
Interorbital Coulomb[e]	219.3137	200.1144

[a] All energies in atomic units (1 au = 27.21 eV). [b] $\Sigma_i(ii|ii)$. [c] $\Sigma_{i>j}4(ii|jj) + \Sigma_i(ii|ii)$. [d] $-\Sigma_{i>j}2(ij|ij)$. [e] $\Sigma_{i>j}4(ii|jj)$.

Dipole Moment.—One property for which SCF calculations can be expected to show great improvement over nonself-consistent methods is the dipole moment. By allowing for the effects on each electron of the electrostatic field of the other electrons, the SCF method avoids to a great extent the piling up of charge and hence the exaggerated dipole moments characteristic of many other methods. While the dipole moment of B_6H_{10} has not yet been measured, previous experience[6] suggests that boron hydride calculations employing basis sets of the quality used here should give dipole moments roughly twice the experimental values.

Table IX shows the dipole moment of B_6H_{10} as calculated by the SCF and by the nonself-consistent methods. We have employed the origin-invariant partitioning method of Ruedenberg[21] to analyze the total moment in terms of atomic, bond, and classical (Mulliken point charge) contributions. The reduction in the calculated value of the dipole moment due to the introduction of self-consistency is seen to be on the order of 50–100%. Improvement in the basis set can be expected to lower the calculated moment even further. Individual atomic and bond contributions are in good agreement with values obtained previously for the smaller boron hydrides.[6]

TABLE IX

DIPOLE MOMENT OF B_6H_{10}[a]

Atom[b]	z	Total	Bond[b]	z	Total
B1 (1)	−0.38	0.39	B1–B2 (1)	0.02	0.23
B2 (1)	−0.20	0.56	B1–B3 (2)	−0.18	0.24
B3 (2)	−0.43	0.52	B1–B4 (2)	−0.30	0.47
B4 (2)	−0.28	0.63	B2–B3 (2)	−0.07	0.09
			B3–B4 (2)	−0.07	0.22
			B4–B5 (1)	0.14	0.80
			B1–H1 (1)	−0.89	1.28
			B2–H2 (1)	0.40	1.27
			B3–H3 (2)	−0.12	1.29
			B4–H4 (2)	−0.72	1.30
			B2–H23 (2)	0.43	0.77
			B3–H23 (2)	0.65	0.67
			B3–H34 (2)	0.18	0.81
			B4–H34 (2)	0.63	0.66

	Classical	Atom	Bond	Total
3 center[c]	. . .	. . .	. . .	6.67
EH[d]	. . .	. . .	. . .	6.64
NEMO[e]	5.28	. . .	. . .	8.13
SCF[f]	2.09	2.01	−0.44	3.69

[a] All moments in Debye units. [b] Numbers in parentheses indicate number of symmetry-equivalent atoms or bonds. [c] Reference 3, all structures. [d] Reference 3, method I. [e] Reference 16. [f] Present work.

The net dipole moment is almost completely in the z direction, that is, from the negative apical boron toward the positive pentagonal base. The large B4–B5 bond moment pointing in toward the center of the molecule lends some credence to the π-donation picture of Figures 2b and 2d as a partial contribution to the valence structure. As in previous calculations[4,6] B–H–B bridges contribute a sizable moment in a direction opposite that of the net molecular moment.

Magnetic Properties.—The ^{11}B nmr spectrum of B_6H_{10}[22,23] has been interpreted as showing one boron at high field (σ = 51.2 ppm) and five equivalent borons at low field (σ = −15.0). The single boron at high field is clearly B1, which has a negative Mulliken charge (q_1 = −0.017) suggesting a small increased diamagnetic shielding. However, it is far more important that the 2p orbital populations on this atom show little anisotropy so that the paramagnetic contribution to the chemical shift arising from the mixing of the ground state with excited states should be smaller than that for the other boron atoms of B_6H_{10}. The electron

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(20) A. D. Baker, *Accounts Chem. Res.*, **3**, 17 (1970).

(21) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(22) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959).

(23) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

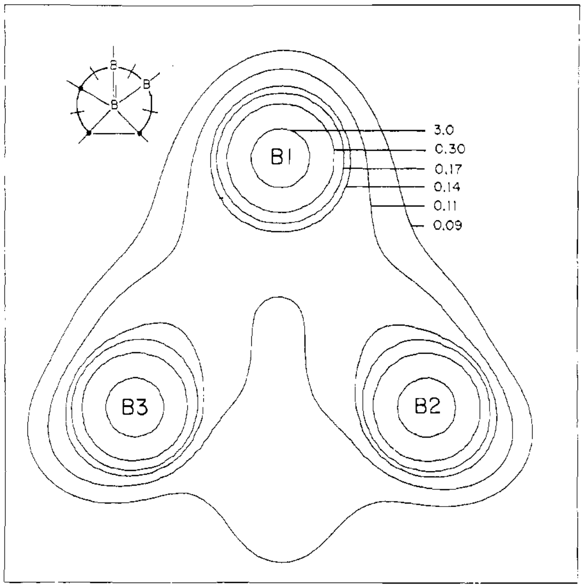

Figure 6.—Total electron density (e^-/au^3) in the B1–B2–B3 plane.

density in the B1, B2, B3 plane (Figure 6) is unexpectedly symmetric, with near-equivalent densities in the B1–B2 and B1–B3 bonds. The basal plane difference density map (Figure 7) also shows B2 and B3 to be nearly equivalent in terms of the electron density in the basal plane. These maps, as well as the more ambiguous Mulliken charges (Table III), show the similarity of B2 and B3 with regard to the ground-state electron density. Figure 7 also shows B4 and B5 to be distinguished by the large bonding density connecting them. The electron density in the plane of the B_1–B_3–B_4 bond (Figure 8) is markedly asymmetric, being considerably greater between B1 and B3 than between B4 and either of the other borons. One may think (rather crudely) of B4 having less electron density to contribute to the three-center bond because of its abnormally large contribution to the B4–B5 two-center bond.

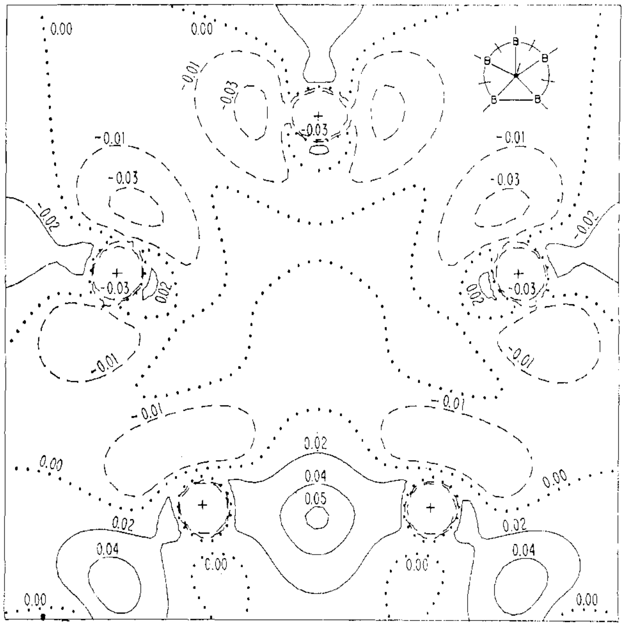

Figure 7.—Difference density (total density minus sum of atomic densities, e^-/au^3) in the pentagonal boron base plane. Dotted lines are contours of zero density. Positions of nuclei are shown by crosses.

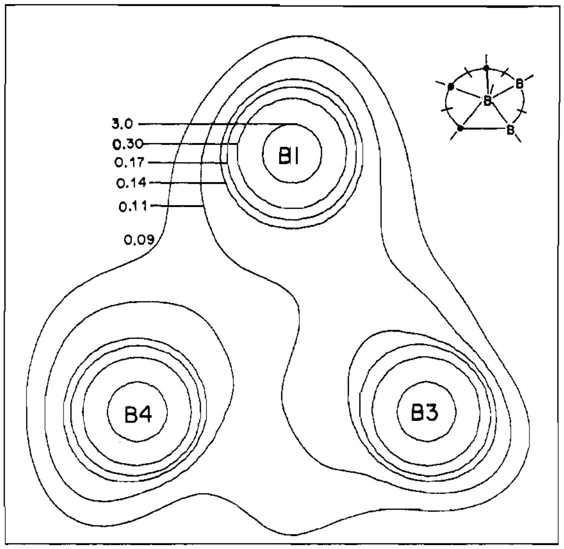

Figure 8.—Total electron density (e^-/au^3) in the B1–B3–B4 plane.

All five basal borons are positively charged and show significant p-orbital population anisotropies, consistent with their large low-field chemical shift. Therefore, similar chemical shifts for all five basal borons are suggested by our results, but the observed equivalence is not explained by a static picture. The possibility that equivalence of basal boron atoms can arise by intramolecular tautomerism[24] was realized even before the ^{11}B nmr spectrum was known. While this ^{11}B spectrum does show equivalence of the five basal B atoms, the ^1H spectrum is not without some anomalies.[25] Studies of these spectra at lower temperatures are desirable.

The published ^1H nmr spectrum[22] shows an apical terminal proton at high field, a group of bridge protons at somewhat lower field, and a low-field group of basal terminal protons. As in previous calculations[5,6] we find all terminal hydrogens to be slightly negative (more shielded diamagnetically) and all bridge hydrogens to be slightly positive (less shielded diamagnetically). We note that the basal terminal hydrogens, attached to highly anisotropic basal borons, are antishielded and interpret this effect as a consequence of paramagnetic contributions to the ^1H shift arising from the boron 2p orbital anisotropy.

Reactivity.—One of the major goals of our undertaking SCF calculations of boron hydride wave functions has been to provide sufficient data for the prediction of boron hydride reactivities using methods cur-

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[24] W. N. Lipscomb, *J. Inorg. Nucl. Chem.*, **11**, 1 (1959).

[25] R. R. Rietz, R. Schaeffer, and L. G. Snedden, *J. Amer. Chem. Soc.*, **92**, 3514 (1970).

rently available and those which are still to be developed. While few reactions of the type most suitable for theoretical treatment (single-step nucleophilic and electrophilic substitutions) have been observed in these compounds, improvements in experimental techniques and increased interest in the field make it likely that the coming years will see a number of such experiments.

Such simple indices of reactivity as atomic charges, frontier orbital populations, and free valence have given a reasonably good correlation with the scanty reactivity data available for simple substitution reactions in B_4H_{10} and B_5H_9.[6] The possibility of using the molecular integrals generated in the course of an SCF calculation like the present one as a starting point for more sophisticated treatments of reactivity is now being studied by J. A. T. and I. R. E.

Hexaborane(10) is an especially interesting molecule from the point of view of reactivity, since it has four nonequivalent borons at which reaction may occur.

We have previously[6] discussed reactivity indices for ionic substitution reactions. We considered the total charge on an atom, the atomic orbital populations in the highest filled and lowest empty molecular orbitals, and also the spatial distribution of the electron density in these orbitals. In the first approximation one expects electrophilic substitution to take place most easily at the boron atom with the greatest negative charge or at the boron with the largest population in the highest filled molecular orbital (HFMO). The greatest negative charge is at B1 but B4 and B5 have the largest HFMO atomic populations (0.61 electron each). The HFMO (no. 20) is associated primarily with the B4–B5 bond (the B4–B5 overlap population for this orbital alone is 0.34, compared to a total overlap population of 0.88). The density in this orbital is concentrated along the B4–B5 bond and an electrophile would have to approach both B4 and B5 closely in order to interact with this density. This close approach would be unfavorable due to the repulsive mixing[26] of the filled MO's of B_6H_{10} and the electrophile. Also, since the HFMO makes an important contribution to the framework bonding, charge transfer from it to an electrophile might disrupt the molecular framework. The next lower MO, no. 19, is primarily an antibonding orbital between B1, B3, and B6 with sizable H3 and bridge hydrogen coefficients and makes little contribution to the framework bonding. The B1 $2p_x$ orbital has a large coefficient and is well removed from the center of the molecule's electron density. The B1 population in this orbital is 0.54. We predict electrophilic substitution to take place at B1. Then, B3 and B6 should be fairly reactive, but electrophilic attack may result in fragmentation of the molecule.

Total charges and lowest empty molecular orbital (LEMO) populations agree in predicting that B2 will be most susceptible to nucleophilic attack (the LEMO atomic population of B2 is 0.55).

The prediction of free-radical reactivities has employed the concept of free valence.[6,27] One predicts that the most reactive atom in free-radical substitutions will be the one for which the sum of the Mulliken overlap populations between atom i and its nearest neighbors is the least. Using this index we find the following predicted order for free-radical substitutions: B2 > B3 > B4 > B1.

Although the quantities discussed above have been of some use in predicting and correlating reactivities of boron hydrides and more notably of hydrocarbons,[28] they provide rather crude indications at best. Since they are static indices, *i.e.*, they depend only upon the nature of the unperturbed molecule, their success must rest upon the validity of the assumption that the transition state for the reaction closely resembles the unperturbed reactant. Furthermore, such gross measures of atomic populations are extremely unsuited for comparisons between different types of atoms, for example, boron and carbon atoms in the carboranes.[29] Such subtle effects as possible differences in reactivity between two nonequivalent terminal hydrogens attached to the same boron atom are probably beyond the reach of these methods. One also wishes to be able to compare different types of reactions, for example, addition *vs.* substitution in olefins. Another area for future consideration is the possible cooperative rearrangement of H atoms or boron framework which may be induced by the close approach of a reactant. Boron hydrides seem to be particularly susceptible to such rearrangements.

One approach to developing a more sensitive theory of reactivity is to make use of localized rather than canonical orbitals. Questions of reactivity not involving cooperative transition states generally have to do with the relative ease of making or breaking one or at most two or three bonds. The LMO formulation allows us to treat each bond with only a small subset of the often unmanageable full set of molecular orbitals. The possibility of dealing with only one or two orbitals on each reactant makes the prospect of examining interactions between different molecules a less frightening one. Also, having each bond in the molecule represented by at least one orbital of its own means that we should find it easier to compare different types of bonds in the LMO framework.

Several possible uses of LMO's in reactivity calculations are now being studied. Here we shall present one rather simple application, the use of the energy required to remove an electron from an LMO as an index of its susceptibility to electrophilic attack. If one views electrophilic attack upon a molecule as a process in which some other species captures or removes electrons from a bond in the molecule, then it seems reasonable that the bonds most readily attacked should be those whose electrons are most easily removed. In other words, we expect a correlation between this "local

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[26] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).

[27] C. A. Coulson, *Discuss. Faraday Soc.*, **2**, 9 (1947).

[28] S.-S. Sung, O. Chalvet, and R. Daudel, *J. Chim. Phys.*, **57**, 30 (1960).

[29] I. R. Epstein, T. F. Koetzle, W. N. Lipscomb, and R. M. Stevens, to be submitted for publication.

orbital ionization energy (LOIE)"[30] and the reactivity in electrophilic substitution of the bond it represents. We recognize that this simple picture considers only the initial stages of the reaction and fails to take account of either differences among electrophiles or of changes in the activation energy due to electrophile–substrate interactions. These limitations are inherent in any static reactivity indices. They become less significant, however, when comparing reactivities toward a single electrophile of different sites on the same reactant molecule.

In Table X we give the LOIE's for B_6H_{10}. The most striking result is the position of the B4–B5 bond LMO in the gap between the first three B–H terminal bonds and the last three. The existence of a boron framework LMO with lower ionization energy than a B–H_t bond LMO is unprecedented in the lower boron hydrides[31] (except for the case of the anomalous terminal hydrogen of B_5H_{11}, which exhibits properties more typical of a bridge hydrogen). The situation resembles that found in unsaturated hydrocarbons,[31] in which CH orbitals have lower LOIE's than CC LMO's for unsaturated carbons, while this ordering is reversed for aliphatic carbon. The results in Table X should not be regarded as a firm prediction that three and only three hydrogens may undergo electrophilic substitution before the boron framework of B_6H_{10} is attacked. However, they do suggest very strongly that vigorous attack by electrophilic reagents is likely to bring about cleavage of the B4–B5 bond.

TABLE X

LOCALIZED ORBITAL IONIZATION ENERGIES[a]

Orbital	Ionization energy, au
B1–H1 (1)[b]	0.554
B4–H4 (2)	0.558
B4–B5 (1)	0.585
B3–H3 (2)	0.602
B2–H2 (1)	0.612
B1–B2–B4 (2)	0.635
B1–B2 (1)	0.640
B3–B4–H34 (2)	0.691
B2–B3–H23 (2)	0.743
B4 inner shell (2)	7.477
B1 inner shell (1)	7.482
B3 inner shell (2)	7.561
B2 inner shell (1)	7.575

[a] See footnote 30. [b] Number of symmetry-equivalent orbitals.

Another result of interest, also found in the smaller hydrides, is that B–H–B LMO's have higher ionization energies than do boron framework orbitals. Thus it seems unlikely that electrophilic substitution can be achieved at bridge positions without concurrent fragmentation of the molecule.

Related Carboranes.—Our discussion of the various possible hexaborane(10) valence structures can, with only slight modifications, be adapted to consideration of the derived carborane series with general formula $C_nB_{6-n}H_{10-n}$. In Table XI we show a systematic schematic approach to the generation of these resonance structures. Each molecule is taken to be composed of two structural units: a pentagonal basal group and the apical boron with its three associated bonds. The apical group may be placed in any of five ways, corresponding to rotations by $2\pi m/5$, $m = 0$–4.

For example, in the parent molecule B_6H_{10}, the arrangement ($m = 0$) gives rise to the structure derived from our localization calculation, Figure 2a. The $m = 1$ and $m = 4$ rotations give equivalent structures in which the B4–B5 bond is bridged by a B1–B4–B5 three-center bond. Such a structure violates the topological rules for three-center bonding and has been shown above not to be the dominant valence structure for B_6H_{10}. However, such a valence structure may be important in the carboranes, and we suggest that the topological rule violation can be overcome by noting that the structures of columns 1 and 4 are essentially equivalent to the π-donation structures of Figure 2d. That is, the structural unit of a single bond bridged by a three-center bond may be represented by a double bond with π donation toward the apex. The $m = 2$ and $m = 3$ rotations give the pair of equivalent structures shown in Figure 2c. For a given fixed arrangement of basal atoms and bonds, this method will generate all possible arrangements of two-center and central three-center bonds. Designation of a preferred structure must utilize further computational or chemical information as illustrated below. We have not considered structures involving open three-center bonds because our boron hydride calculations have not, as yet, given any evidence for their existence. Nevertheless, such structures may be of some importance in the carboranes. Note that certain structures containing open three-center bonds may be derived from combinations of the structures obtained here. For example, the structure of Figure 2b may be viewed as a resonance hybrid of the equivalent pair in Figure 2d.

Thus far, four neutral carborane derivatives of B_6H_{10} ($n = 1$–4 in the formula $C_nB_{6-n}H_{10-n}$) have been prepared and characterized. Electronegativity considerations suggest that the preferred structures will have charge concentrated on carbon or, equivalently, that carbon atoms will prefer two-center bonding while boron atoms are more likely to participate in three-center bonds. We have used this observation as a guideline to resolve any ambiguities in writing down the basal framework bonds. In CB_5H_9[32] the structure of column 3 is preferred, since it has the apical single bond to carbon. The carborane $C_2B_4H_8$[19,33] was discussed earlier as a possible structural model for multiple bonding in B_6H_{10}. In the X-ray study,[19] a structure was suggested containing an open three-center bond, which may be ex-

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[30] Our "localized orbital ionization energy" refers to the difference in energy between the Slater determinant representing the neutral molecule and the determinant for the ion formed by removing an electron from the LMO under consideration. In terms of the variation principle and state symmetry, the canonical MO's provide a physically meaningful basis for calculating ionization potentials: T. Koopmans, *Physica*, **1**, 105 (1933); M. D. Newton, *J. Chem. Phys.*, **48**, 2825 (1968). The loss of an electron from a localized orbital reflects an electronic reorganization which we postulate to occur during reaction.

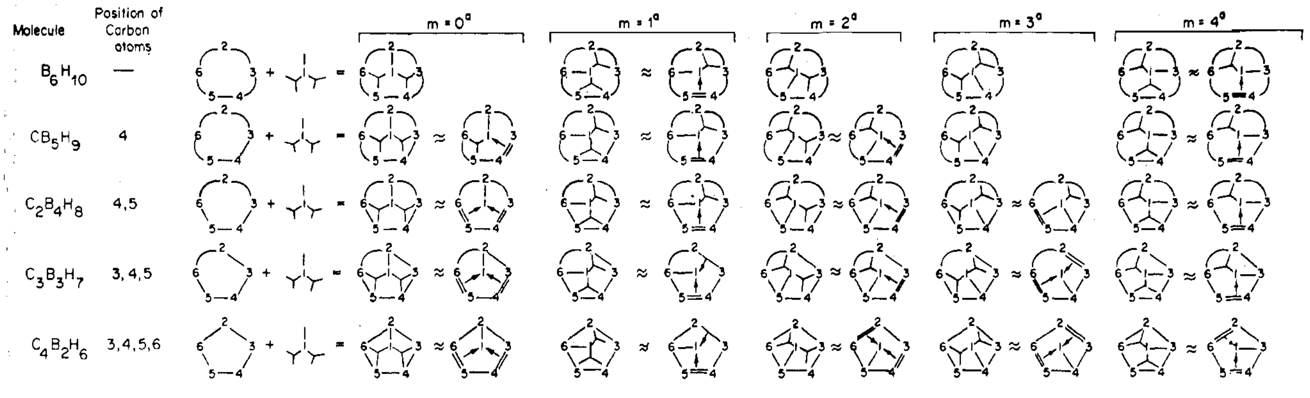
[31] I. R. Epstein and E. Switkes, unpublished calculations.

[32] T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Amer. Chem. Soc.*, **88**, 2061 (1966).

[33] T. P. Onak, *Inorg. Chem.*, **7**, 1043 (1968).

TABLE XI

VALENCE STRUCTURES FOR NEUTRAL CARBORANES RELATED TO B_6H_{10}



[a] The unit is rotated by 2πm/5 before being added to the pentagonal base unit.

pressed as a combination of the "equivalent" structures of columns 1 and 4. In $C_3B_3H_7$,[34] the preferred structures are probably those in columns 2 and 4, which minimize the formal charges. The situation in the recently prepared $C_4B_2H_6$[35] is less clear, but formal charge considerations suggest a preference for either the structures of column 0 or the equivalent pair, columns 1 and 4. The suggestion here of a π-donation model involving two double bonds would make a structural determination and comparison of C–C and C–B bond distances in this molecule extremely interesting.

The formalism developed above may also be applied to borane or carborane ions of the above species, such as $B_8H_9^-$ [36] or $B_4C_2H_7^-$.[37] An ion produced by removal of a proton from a bridge position is simply assigned those resonance structures of the parent isostructural carborane which minimize the formal charges.

Acknowledgments.—We wish to thank the National Science Foundation for predoctoral fellowships to I. R. E., J. A. T., and E. S. and the Office of Naval Research for financial support of this work.

(34) C. L. Bramlett and R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 4269 (1966).

(35) T. P. Onak and G. T. F. Wong, *ibid.*, in press; T. P. Onak, private communication, 1970.

(36) H. D. Johnson, II, Ph.D. Thesis, The Ohio State University, 1969; *Diss. Abstr.*, in press.

(37) T. P. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

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Reaction of Amino Acid Derivatives with Trihaloboranes and with Sodium Borohydride

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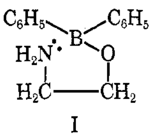
The borane, trichloroborane, and some trifluoroborane adducts of several amino acid esters were prepared. The nmr and ir spectra show them all to be amine adducts. The BF_3 adducts of methyl glycinate and of methyl β-alaninate were converted to the corresponding N-substituted borazines. Possible intramolecular coordination of ring borons by carbonyl groups in the N substituent was investigated but none could be observed. The reaction of BCl_3 with glycine gave the novel compound $B(O_2CCH_2NH_3^+)_3,(BCl_4^-)_3$.

Introduction

The intramolecular coordination of a boron atom to give a four-coordinate species has been shown in many cases to result in a material that is often much more resistant to hydrolysis than is a similar three-coordinate compound. Diphenylborinic acid is very difficult to obtain, but its β-aminoethyl ester, I, has been isolated and found to be very resistant to hydrolysis.[1] This has



I

been attributed to intramolecular coordination of the

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(1) R. L. Letzinger and I. Skoog, *J. Amer. Chem. Soc.*, **77**, 2491 (1955).