carbonylation. Compound **9** contains a square pyramid of five osmium atoms with an $Os(CO)_3$ capping group. It seems reasonable to expect that the analogous $Ru_6(CO)_{17}(\mu_4\text{-}S)$ could be prepared by the decarbonylation of **3**; however, this has not yet been achieved.

The addition of yet another ruthenium carbonyl fragment results in the formation of $Ru_7(CO)_{19}(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (**4**). This product was made independently by the addition of a mononuclear fragment to **3**. The structure of **4** shows that it contains two $Ru(CO)_4$ groups which bridge diametrically opposed basal edges of the square pyramid and was formed by the replacement of a second bridging CO ligand in **3** with a $Ru(CO)_4$ group. The osmium homologue of **4** has not yet been reported. The closest related osmium compound is $Os_7(CO)_{19}(\mu_4\text{-}S)$ which contains a sulfur-bridged square pyramid of five osmium atoms that is fused to a trigonal-bipyramidal cluster of five osmium atoms through a triangular face.[13]

Compounds **2**, **3**, and **4** can be degraded by treatment with CO at 98 °C. Curiously, small amounts of **4** were formed in the degradation of **3** and small amounts of **3** and **4** were obtained in the degradation of **2**. The degradation reactions will lead to the formation of mononuclear ruthenium fragments which could be added to unreacted clusters. It is believed that under suitable conditions cluster enlargement and degradation will be ongoing and competing reactions in solutions that contain the appropriate species. These transformations are summarized in Scheme I.

Acknowledgment. The research was supported by the National Science Foundation under Grant No. CHE-8612862.

Registry No. 1, 105121-22-0; **2A**, 111976-49-9; **2B**, 111976-50-2; 3, 111976-47-7; 4, 111976-48-8; $Ru(CO)_5$, 16406-48-7.

Supplementary Material Available: Labeling diagram and a table of bond angles for molecule B of **3** and tables anisotropic thermal parameters (*U* values) for **2**–**4** (9 pages); listings of structure factor amplitudes for **2**–**4** (89 pages). Ordering information is given on any current masthead page.

AM1 Calculations for Compounds Containing Boron

Michael J. S. Dewar,* Caoxian Jie,[1] and Eve G. Zoebisch

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received July 22, 1987

AM1 has been parametrized for boron. Calculations are reported for an extensive set of boron-containing compounds. Most of the results are better than those given by MNDO. AM1 is especially successful in dealing with boron hydrides containing three-center bonds with bridging hydrogen atoms. Studies of some reactions of boron compounds have given satisfactory results.

Introduction

The chemistry of boron is particularly rich and interesting because it forms a large variety of unusual molecules containing three-center, two-electron bonds of the kind first proposed by Longuet-Higgins.[2] It also forms a number of cage compounds containing three-dimensional delocalized systems, as Longuet-Higgins[3] also first pointed out in the case of the dodecaboride dianion ($B_{12}H_{12}^{2-}$). Interest in boron chemistry is moreover not confined to theory. Hydroboration has become a major tool in chemical synthesis, and the boron halides are widely used as Lewis acid catalysts. The need for an effective theoretical treatment of boron compounds is therefore evident, and none is yet available.

Current quantum mechanical treatments have encountered major problems in attempts to interpret the structures of the boron hydrides and carboranes. Their properties are not interpreted satisfactorily at the Hartree–Fock (HF) level. Thus ab initio HF methods fail to reproduce the heat of dimerization of borane (**1**) to diborane (**2**), even if a large basis set is used, and the same is true[4] for the pyramidal geometry (**3**) of pentaborane (B_5H_9). It is necessary to use a large basis set together with adequate allowance for electron correlation. The same situation holds generally for reactions, the hydroboration of ethylene being a typical example.[5] Such procedures can be applied only to small molecules.

Similar problems arise generally in attempts to use ab initio calculations as a direct aid in chemical research. In

---

[1] On leave from Lanzhou University, Lanzhou, The People's Republic of China.

[2] Longuet-Higgins, H. C. *J. Chim. Phys.* **1949**, *46*, 268.

[3] Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1954**, *224*, 336.

[4] McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 765.

[5] Nagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536.

0276-7333/88/2307-0513$01.50/0

Table I. Optimized AM1 Parameters for Boron

optimized parameters	value	derived parameters	value
U_{ss} (eV)	−34.492 870	E_{el} (eV)	−63.717 265 0
U_{pp} (eV)	−22.631 525	D_D (au)	0.910 762 2
ζ_s (au)	1.611 709	Q_Q (au)	0.787 422 3
ζ_p (au)	1.555 385	A_M (au)	0.389 195 1
β_s (eV)	−9.599 114	A_D (au)	0.504 515 2
β_p (eV)	−6.273 757	A_Q (au)	0.567 885 6
α (Å^{-1})	2.446 909		
G_{ss} (eV)	10.590 000		
G_{pp} (eV)	8.860 000		
G_{sp} (eV)	9.560 000		
G_{p2} (eV)	7.860 000		
H_{sp} (eV)	1.810 000		

Parameters for Gaussian Terms

	B–X[a]	B–H	B–C	B–halogen
K_1	0.182 613	0.412 253	0.261 751	0.359 244
K_2	0.118 587	−0.149 917	0.050 275	0.074 729
K_3	−0.073 280			
L_1	6.000 000	10.000 000	8.000 000	9.000 000
L_2	6.000 000	6.000 000	5.000 000	9.000 000
L_3	5.000 000			
M_1	0.727 592	0.832 586	1.063 995	0.819 351
M_2	1.466 639	1.186 220	1.936 492	1.574 414
M_3	1.570 975			

[a] Elements other than carbon, hydrogen, or halogen.

many cases the procedures developed here (MINDO/3[6], MNDO[7], and AM1[8]) have proved satisfactory substitutes, providing results comparable with those from high level ab initio methods at a very small fraction of the cost in computing time. However, while MNDO parameters for boron are available[9] and while applications to the boron hydrides[10] and carboranes,[11] and to the reactions of boron hydrides with olefins[12] and carbonyl compounds,[13] have proved useful, MNDO resembles ab initio HF methods in failing to account adequately for the stabilities of nonclassical molecules.

MNDO is known[7] to overestimate repulsive interactions between atoms at separations greater than ca. 1.5 times the corresponding covalent bond distance, a failing which leads to various systematic errors.[14] This failing, and the accompanying errors, have been overcome in the "third generation" treatment, AM1.[8] This correction led moreover to the elimination of several other apparently unrelated errors, for example, the overestimation of the stabilities of compounds containing four-membered rings. It seemed reasonable to hope that the same might be true for the errors for compounds containing three-center bonds. We therefore decided to determine AM1 parameters for boron. Here we report our results.

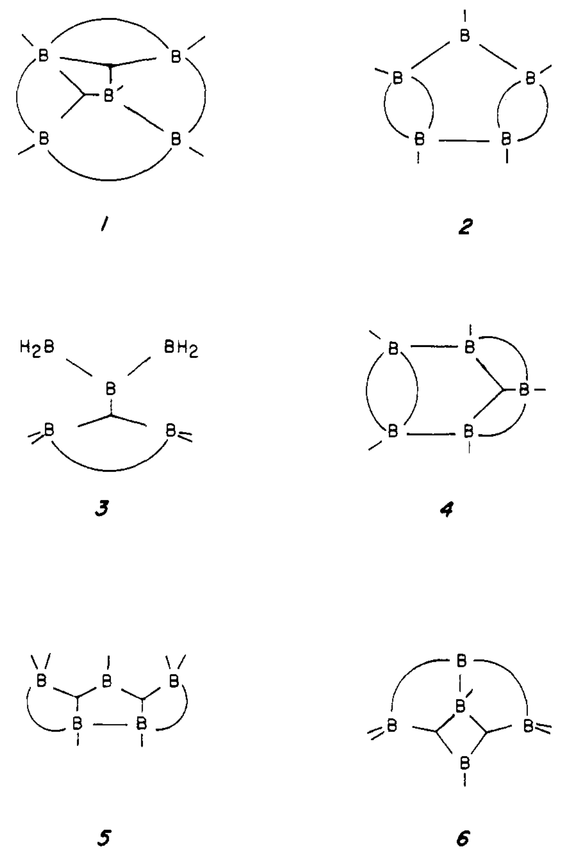


Figure 1.

Procedure

The AM1 parameters for boron were determined in the usual way,[6-8] by a least-squares fit to selected properties of a selected set (basis set) of molecules, using standard AM1 parameters for the "organic" elements[8] (C, H, O, N) and the halogens,[15] together with an improved optimization procedure that has been recently developed.[16] This involves the minimization of an error function (SSQ), defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The best values for the weighting factors are found by trial and error, on the basis of the chemical acceptability of the final results. The experimental values used in the parametrization included heats of formation, ionization potentials, dipole moments, and geometries. The minimization of SSQ uses a derivative optimization method, based on the Davidon Fletcher Powell (DFP) algorithm.[17] The first derivatives of the heats of formation and ionization energies with respect to the parameters were calculated analytically, while the derivatives of the dipole moment and geometries were calculated by finite difference. The derivatives of the energy at the experimental geometry were used as a measure of the deviation of the calculated geometry from experiment.

---

(6) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

(7) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(8) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(9) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

(10) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569.

(11) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662.

(12) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1075.

(13) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 7499.

(14) For example, MNDO fails to reproduce hydrogen bonds and it leads to activation energies that are too large in the case of reactions where the transition states contain unusually long bonds; see, e.g.: Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.* **1983**, *105*, 7152, 7161.

(15) Dewar, M. J. S.; Zoebisch, E. G., in course of publication.

(16) Stewart, J. J. P., unpublished results.

(17) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Davidon, W. C. *Ibid.* **1968**, *10*, 406.

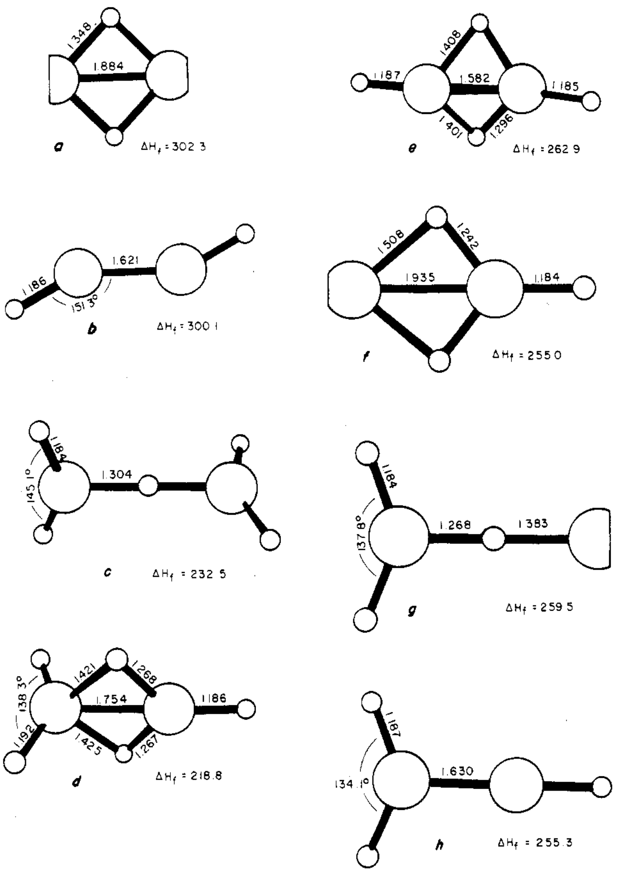


Figure 2. Geometries calculated by AM1 for cationic boron hydrides.

The calculations were carried out by using the standard AM1 procedure and parameters, as implemented in the AMPAC[18] package of computer programs. The only quantities in AM1 that depend on the period to which an atom belongs are the relevant overlap integrals. AMPAC provides for their calculation for all elements. Calculations for open-shell species were carried out by using the "half electron" method.[19]

Results and Discussion

A. Parameters. Our attempts to parametrize AM1 for boron naturally focused not only on heats of formation but also on geometrical structures, in particular those of nonclassical species. However, we soon encountered problems when we tried to use just one set of parameters for boron, as was done for most of the other elements in MNDO and AM1. While we used the basic AM1 parameters (U_{ss}, U_{pp}, ζ_s, ζ_p, β_s, β_p, α), we also included additional unique Gaussian-type functions in the core–core repulsion terms (CRT[8]) for boron–hydrogen, boron–halogen (F, Cl, Br, and I), and boron–carbon bonds.

The final parameters are shown in Table I. The one-center, two-electron parameters (g and h) were kept constant at their MNDO values.[8] The object of the additional Gaussians was to improve the character of the potential energy function between two atoms at short distances. In certain cases the MNDO CRT function was found not to increase as rapidly as experiment indicates.

Results for various properties of a number of boron-containing molecules are shown in Tables I–XIII, those used in the final parametrization being indicated by asterisks (Tables II and V).

B. Heats of Formation, Dipole Moments, and Ionization Potentials. Table II compares with experiment the calculated values for the heats of formation, dipole moments, and ionization potentials (IP) of more than 70 molecules containing boron. The IPs were estimated from HOMO energies, using Koopmans' theorem. The molecules included the 45 treated in the parametrization of MNDO. Table III compares the average unsigned errors in the calculated values with those given by MNDO.

The superiority of the AM1 heats of formation is obvious. The major improvements are for compounds containing boron–oxygen and boron–halogen bonds. The mean absolute error in the calculated heat of formation is similar to that for compounds containing only the organic elements,[8] the halogens,[15] and silicon.[20] While the errors in the MNDO heats of formation were greater than 30 kcal/mol in nine cases, only three examples occur among the much larger number of molecules treated by AM1. These were for $B(N(CH_3)_2)_3$ (+31.6 kcal/mol), the BH_2 radical (+30.0 kcal/mol), and $H_2B_2O_3$ (+36 kcal/mol). The discrepancy for $H_2B_2O_3$ may well be due[9] to error in the experimental value. This molecule was therefore omitted in calculating the mean error (Table III).

As Table III shows, the average error in the AM1 ionization potentials is less than half that for MNDO (0.46 vs 0.98 eV). This improvement is probably due mainly to the use of different values of ζ and β for the s and p AOs in AM1.

Table IV compares the calculated and observed higher ionization energies for some molecules whose photoelectron spectra have been studied in detail. The results are generally satisfactory.

The average error in the AM1 dipole moments is also approximately half that than in MNDO ones (0.32 vs. 0.62 D). As Table II shows, there are large improvements in dipole moments of some important complexes, in particular $BH_3{\cdot}CO$, $BH_3{\cdot}N(CH_3)_3$, and $BH_3{\cdot}NH_3$. The error in the dipole moment for $BH_3{\cdot}CO$ has been reduced from 1.16 D in MNDO to 0.26 D in AM1. One reason for this improvement may be the general superiority of the AM1 geometries; see the next section. The error in the B–C bond length in $BH_3{\cdot}CO$ has, for example, been reduced from −0.039 to −0.004 Å. Almost all the AM1 values for the dipole moments of boron hydrides are better than those calculated with MNDO.

C. Molecular Geometries. Table V compares the AM1 geometries with experiment while Table VI compares the average errors for different kinds of bonds with those given by MNDO. AM1 clearly gives much better results for most bond types, the improvement being especially marked for B–H, B–C, B–B, and B–F bonds.

A dramatic improvement was found for the boron hydrides. AM1 correctly reproduced their symmetric "nonclassical" structures, with full geometry optimization and without any need to impose symmetry constraints. Their calculated force constants showed them to be min-

---

(18) Available from the Quantum Chemistry Program Exchange (QCPE), program 506.

(19) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

(20) Dewar, M. J. S.; Jie, C. *Organometallics*, **1987**, *6*, 1486.

Table II. Calculated Heats of Formation, Ionization Potentials, and Dipole Moments for Molecules Containing Boron

	ΔH_f (kcal/mol)			dipole moment (D)			IP (eV)		
compd	AM1	obsd[a]	error	AM1	obsd[b]	error	AM1	obsd[b]	error
BH	82.3	107.4	-25.1	0.84	1.27[c]	-0.43	8.96		
BH_2	75.7	45.7[d]	30.0				8.20		
BH_3	26.2*	23.9	2.3				11.86		
B_2	202.9	198.4	4.5				6.12		
B_2H_6	5.3*	8.4	-3.1				11.39	11.89[e]	-0.50
B_4H_{10}	3.4*	15.8	-12.4	0.94*	0.56[f]	0.38	10.90	11.50	-0.60
B_5H_9	28.9*	17.5	11.4	2.29*	2.13	0.16	9.98*	10.52	-0.54
1-$(CH_3)B_5H_8$	18.8			2.12	1.93	0.19	9.54	10.20	-0.66
B_5H_{11}	12.5	24.7	-12.2	1.88			10.41		
B_6H_{10}	23.8*	22.6	1.2	2.69			9.49		
$B_{10}H_{14}$	13.7	7.5	6.2	2.91			9.87	10.15	-0.28
$B(CH_3)_3$	-24.8*	-29.7	4.8				10.90*	10.90[e]	0.00
$B(C_2H_5)_3$	-40.4	-37.7	-2.7				10.38	10.20[e]	0.18
$B(C_3H_7)_3$	-58.3	-58.0[d]	-0.3				10.23		
$B(C_4H_9)_3$	-76.7	-69.4[d]	-7.3				10.20		
CB_5H_7	101.1			1.16	1.43	-0.27	10.32		
CB_5H_9	39.7			1.70	1.53	0.17	9.75		
2,3,4,5-$C_4B_2H_6$	95.4			0.27			8.74		
1,2-$C_2B_4H_6$	104.3			0.85	1.50	-0.65	9.94		
1,5-$C_2B_3H_5$	75.3						10.85	10.88	-0.03
1,6-$C_2B_4H_6$	138.0						9.09	9.87	-0.78
BO	0.8	6.0	-5.2	1.57			12.34		
BO_2	-70.7	-71.7	1.0				14.23		
B_2O_2 (O-B-O-B)	-111.9	-108.6	-3.3	2.31			12.02		
OB_2O (O-B-B-O)	-133.1	-109.0[c]	-24.1				14.57		
$B(OH)_3$	-251.6*	-237.4	-14.2				12.78		
B_2O_3	-206.9*	-201.5	-5.4	1.06			13.56		
BH_3CO	-11.1*	-26.6	15.5	2.06*	1.80	0.26	11.30*	11.92	-0.62
$H_3B_3O_3$	-286.3*	-288.8	2.5				12.34		
H_2BOH	-73.4	-69.4[d]	-4.0	1.34			11.17		
$HB(OH)_2$	-166.2	-153.1[d]	-13.1	1.54			12.54		
$CH_3B(OH)_2$	-177.7			1.60	1.16	0.44	12.31		
$(CH_3)_2BOH$	-101.0			1.34	1.53	-0.19	11.05		
$B_2(OH)_4$	-313.7	-315.0[d]	1.3				11.42		
$HB(OCH_3)_2$	-144.3	-138.4	-5.9	1.50			11.13		
$B(OCH_3)_3$	-215.8*	-214.9	-0.9				11.15		
$B(OC_2H_5)_3$	-233.5	-239.5	6.0				11.07		
$B(OC_3H_7)_3$	-252.7	-259.4[d]	6.7				10.88		
OBOH	-138.4	-134.2	-4.2	2.78			12.95		
$B_3O_3(OH)_3$	-529.0	-543.6	14.6				13.02		
$HBO_2(CH_2)_2$	-138.0			1.71	2.28	-0.57	10.95		
$N(CH_2CH_2O)_3B$	-176.1			8.30			10.12	9.80	0.32
$C_6H_5B(OH)_2$	-135.5	-151.8[d]	16.3	3.29			10.02		
$B_3N_3H_6$	-141.9*	-122.2	-19.9				10.61*	10.14[e]	0.47
$B_2H_5NH_2$	-39.5			2.83	2.67	0.16	11.06		
$B_2H_5N(CH_3)_2$	-20.6*	-27.9[h]	7.3	2.90*	2.77	0.13	10.89		
H_3B-NH_3 (elipsed)	-17.9			5.81			9.91		
H_3B-NH_3 (staggered)	-19.3			5.77*	5.22[i]	0.55	9.94*	10.33[j]	-0.39
$(CH_3)_3B-NH_3$	-54.5	-54.1	-0.4	5.03			9.72		
$H_3B-N(CH_3)_3$	3.7	-20.3	24.0	5.27	4.84	0.43	9.87		
$(CH_3)_3B-N(CH_3)_3$	-25.9	-52.6	26.7	4.54			9.66		
$(CH_3)_2B-N(CH_3)_2$	-39.3			1.18			9.51	8.90	0.61
$C_5H_5N-BH_3$	34.7			6.40			9.56	9.72	-0.16
p-$CH_3C_5H_4NBH_3$	26.4			6.92			9.43	9.50	-0.07
p-$OCH_3C_5H_4NBH_3$	-4.2			7.12			9.35	9.30	0.05
p-$NO_2C_5H_4NBH_3$	44.3			1.40			10.13	10.27	-0.14
$B(N(CH_3)_2)_3$	-34.3	-65.9[h]	31.6				8.48	7.60	0.88
BF	-56.5	-29.2	-27.3	0.19	0.50[k]	-0.31	11.49		
BF_3	-272.1*	-271.6	-0.6				14.94*	15.95[e]	-1.01
HBF_2	-182.4	-176.6[d]	-5.8	1.23	0.97[k]	0.26	12.69		
F_2BOH	-264.7	-260.7	-4.0	1.58	1.48	0.28	13.68		
BF_2O	-198.6	-200.0[g]	-1.4	0.18			15.47		
FBO	-149.2	-145.0	-4.2	1.46			13.81		
F_2BCCH	-124.0			1.66	1.88[k]	-0.22	11.87		
F_2BCHCH_2	-164.2	-171.0	6.8	1.91	1.74	0.17	11.12		
CH_3BF_2	-193.1	-199.0	5.9	1.67	1.60[k]	0.07	12.40		
B_2F_4	-352.9*	-344.0	-8.9				12.10*	13.26[e]	-1.15
$B_3O_3F_3$	-553.8*	-567.7	13.9				13.78		
$FB(OH)_2$	-258.2	-249.5	-8.7	1.61			13.02		
$B_3O_3H_2F$	-377.9	-382.6	4.7	1.43			12.44		
$B_3O_3HF_2$	-468.6	-475.8	7.2	1.45			13.11		
$(CH_3)_2O-BF_3$	-326.1	-328.2	-2.1	1.53			10.73		
$C_6H_5BF_2$	-155.2			2.03			9.94		
BBr	37.2	56.9	-19.7	2.56			10.25		
BBr_3	-50.0*	-49.1	-0.9				11.26*	10.65[e]	0.61

Table II (Continued)

	ΔH_f (kcal/mol)			dipole moment (D)			IP (eV)		
compd	AM1	obsd[a]	error	AM1	obsd[b]	error	AM1	obsd[b]	error
$BBrF_2$	-190.1	-196.0[g]	5.9	0.14			11.87		
$C_6H_5BBr_2$	-5.5	-30.5[d]	25.0	2.28			10.02		
BI_3	1.4*	17.0	2.4				10.80*	9.36[e]	1.44
BCl	13.5	35.7	-22.1	1.74			10.94		
BCl_3	-97.0*	-96.4	-0.6				12.32*	11.73[e]	0.59
$HBCl_2$	-60.7	-60.5[d]	-0.2	0.94			11.56		
CH_3BCl_2	-75.8			1.72	1.421	0.30	11.62		
$C_6H_5BCl_2$	-38.5	-63.3[d]	24.8	2.20			9.99		
$BClF_2$	-208.5	-212.7	4.2	0.04			12.74		
BCl_2F	-149.0	-154.1	5.1	0.47			12.24		
BOCl	-99.3	-75.0	-24.3	2.13			12.94		
B_2Cl_4	-124.6	-117.1	-7.5				10.98	10.97[e]	0.01
$B_3O_3H_2Cl$	-313.6	-313.8	0.2	1.32			12.01		
$B_3O_3HCl_2$	-339.8	-338.7	-1.1	1.22			12.33		
$B_3O_3Cl_3$	-364.5	-390.1	25.6				12.54		
$(CH_3O)_2BCl$	-172.4*	-177.9	5.5	0.88*	1.71[k]	-0.83	11.38		
BCl_2F	-149.0	-154.1	5.1	0.47			12.24		
$B_3N_3Cl_3H_3$	-257.0*	-237.7	-19.3				11.24*	10.55[e]	0.69

[a] Except where noted, for references see: Harmony, M. D.; Laurie, V. W.; Kuczkowsky, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 3. [b] For references see (except where noted) ref 9. [c] Thomson, R.; Dalby, F. W. *Can. J. Phys.* **1969**, *47*, 1155. [d] See footnote *b*. [e] Siegbahn, K.; Allison, D. A.; Allison, J. H. *Handbook of Spectroscopy*, Robinson, J. W., Ed.; CRC Press: Cleveland, OH, 1974; Vol. I, Section B. [f] Weaver, J. R.; Hertsch, C. W.; Parry, R. W. *J. Chem. Phys.* **1959**, *30*, 1075. [g] Stull, D. R.; Prophet, H. et al. *JANAF Thermochemical Tables*, 2nd ed.; U.S. Department of Commerce, National Bureau of Standards, 1970. [h] See footnote *b*. [i] Suenram, R. D.; Thorne, L. R. *Chem. Phys. Lett.* **1981**, *78*, 157. [j] Binkley, J. S.; Thorne, L. R. *J. Chem. Phys.* **1983**, *79*, 2932. [k] McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: el Cerrito, CA, 1974. [l] Hubbard, S. D.; Cox, A. P. *J. Mol. Spectrosc.* **1986**, *115*, 188.

Table III. Mean Unsigned Errors

average error in	examples	AM1	MNDO
heat of formation (kcal/mol)	72	9.43	13.78
dipole moment (D)	23	0.32	0.62
ionization energy (eV)	26	0.46	0.98

ima on the respective potential energy (PE) surfaces, and they were also found to be lower in energy than their unsymmetrical "classical" counterparts.

A striking example was provided by B_5H_9 (**3**) which has C_{4v} symmetry. As noted above, with the exception of one high level ab initio calculation,[4] no other procedure has ever reproduced its structure correctly. Other previous studies of **3** have calculated the C_{4v} structure only by imposing symmetry since none of them predicted it to be even a minimum on the corresponding PE surface. Table VII compares the energies calculated by AM1 for **3** and several isomers (see Figure 1) with results from other procedures.

An amusing result emerged from our attempts to improve the results for boron hybrides in AM1. Our initial parameterizations were based on a geometry for B_5H_9 derived from an early microwave study.[21] In our attempts to fit these "important" data, the corresponding geometry was heavily weighted in the optimization. Yet we were able to obtain only a marginally satisfactory agreement with it. After the parameters were determined, we discovered a more recent microwave investigation[22] of **3** which we had previously overlooked. We were happy to find that our calculated geometry was much closer to this than it had been to the original one; see Table VIII.

Table IV. Ionization Potential (eV)

molecule	calcd	exptl[a]	assign.
B_2H_6	11.38	11.89	$1b_{3g}$
	12.12	13.30	$3a_g$
	13.05	13.91	$1b_{2u}$
B_4H_{10}[b]	10.88	11.50	$5a_1$
	11.43	12.1	$3b_2$
	11.62	12.62	$2b_1$
BH_3CO	11.30	11.92	2e
	14.17	14.13	$6a_1$
	17.59	16.98	1e
$B(CH_3)_3$	10.90	10.90	
	12.48	11.50	
	12.97	13.30	
B_5H_9[b]	9.97	10.52	3e
	11.48	12.27	$4a_1$
	11.85	12.56	2e
$B_3N_3H_6$	10.57	10.14	e''
	11.17	11.42	$4e'$
	13.47	12.06	$1a_2''$
$B_3N_3Cl_3H_3$	11.24	10.55	$2e''\pi$
	11.97	11.55	
	12.00	11.95	
BF_3	14.94	15.95	$1a_2'$
	15.15	17.14	3e
	15.19	16.67	$1e''$
BCl_3	12.32	11.73	$1a_2'$
	12.52	12.66	$3e'$
	12.69	12.39	$1e''$
BBr_3	11.27	10.65	$1a_2'$
	11.58	11.36	3e
	11.74	11.71	1e
BI_3	10.80	9.36	$1a_2'$
	11.01	9.92	$3e'$
	11.12	10.36	$1e''$
B_2Cl_4	10.98	10.97	$4a_1$
	12.41	11.97	4e
	12.62	12.25	$1a_2$

[a] For references see (except where noted): *Handbook of Spectroscopy*, Robinson, J. W., Ed.; CRC Press: Cleveland, OH, 1974; Vol. I. [b] Lloyd, D. R., et al. *J. Chem. Soc., Faraday Trans. 1* **1975**, 1382.

---

(21) Switkes, E.; Epstein, I. R.; Tossell, J. A.; Stevens, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1970**, *92*, 3837.

(22) Schwock, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219.

Table V. Calculated and Observed Geometrical Parameters

molecule	point group	geometries calcd (obsd)	ref^a
BH	$C_{\infty v}$	BH 1.220 (1.236)	*b*
BH_2	C_{2v}	BH 1.198 (1.18), HBH 128.0 (131)	
BH_3	D_{3h}	BH 1.190	
B_2	$D_{\infty h}$	BB 1.732 (1.59)	*b*
B_2H_6*	D_{2d}	BB 1.754 (1.775), BHb 1.330 (1.339), BHt 1.191 (1.196)	
B_4H_{10}	C_{2v}	B_1B_3 1.658 (1.750), B_1B_2 1.839 (1.845), B_1Hb 1.268 (1.330), B_2Hb 1.412 (1.430), BHt 1.191 (1.19)	*b*
B_5H_9*	C_{4v}	B_1B_2 1.667 (1.690), B_2B_3 1.816 (1.803), BHb 1.346 (1.352), BHt 1.185 (1.186), B_1Ht 1.177 (1.181)	*c*
B_5H_{11}	C_s	B_1B_3 1.727 (1.721), B_1B_2 1.783 (1.852), B_2B_3 1.750 (1.720), B_4B_6 1.845 (1.772), B_2Hb 1.439 (1.319), B_3Hb 1.269 (1.340), B_3Ha 1.331 (1.341), B_2Ht 1.191 (1.193), 1.195 (1.213), B_1Ht 1.211 (1.190)	
B_6H_{10}	C_s	B_1B_4 1.830 (1.808), B_1B_3 1.698 (1.755), B_1B_2 1.718 (1.757), B_4B_5 1.519 (1.603), B_3B_4 1.759 (1.746), B_2B_3 1.799 (1.784), B_3Ha 1.340 (1.503), B_2Ha 1.316 (1.322), B_3Hb 1.349 (1.319), B_4Hb 1.327 (1.319), B_1Ht 1.183 (1.196), BHt 1.187 (1.196)	
$B_{10}H_{14}$	C_{2v}	B_1B_3 1.790 (1.770), B_1B_2 1.740 (1.776), B_2B_5 1.810 (1.79), B_7B_8 1.777 (1.973), B_5B_6 1.813 (1.775), B_2B_6 1.660 (1.720), B_6Hb 1.353 (1.347), B_5Hb 1.315 (1.298)	
$B(CH_3)_3$	D_{3h}	BC 1.537 (1.578)	
$B(C_2H_5)_3$	C_3	BC 1.547	
1,5-$C_2B_3H_5$	D_{3h}	BC 1.565 (1.556), BB 1.924 (1.853), CH 1.073 (1.071), BH 1.177 (1.183)	
CB_5H_7	C_s	C_1B_2 1.605 (1.60), C_1B_4 1.649 (1.63), B_2B_6 1.891 (1.89), B_4B_6 1.678 (1.70), B_4B_5 1.736 (1.72), B_3B_4 1.662 (1.70), B_2B_3 1.884 (1.87), B_2Hb 1.379	
CB_5H_9	C_s	B_1B_3 1.871 (1.782), B_1B_4 1.695 (1.781), B_3B_4 1.778 (1.759), B_4B_5 1.863 (1.830), B_1C_2 1.648, B_3Ha 1.320, B_4Ha 1.357, B_4Hb 1.337, C_2B_3 1.510	
1,2-$C_2B_4H_6$	C_{2v}	C_1C_2 1.613 (1.540), C_1B_3 1.607 (1.627), C_1B_4 1.675 (1.605), B_3B_4 1.765 (1.721), B_4B_6 1.649 (1.752)	
$C_4B_2H_6$	C_s	B_1B_6 1.949 (1.886), B_1C_2 1.592 (1.709), B_1C_3 2.344 (1.697), C_2B_6 1.592 (1.541), C_4C_5 1.513 (1.436), C_3C_4 1.370 (1.424)	
2,4-$C_2B_5H_7$	C_{2v}	B_1C_2 1.683 (1.708), B_1B_3 1.869 (1.818), B_1B_5 1.792 (1.815), C_2B_6 1.617 (1.563), C_2B_3 1.554 (1.546), B_5B_6 1.594 (1.651)	
BO	$C_{\infty v}$	BO 1.168 (1.204)	*b*
BO_2	$D_{\infty h}$	BO 1.225 (1.263)	*b*
HBO	$C_{\infty v}$	BH 1.166 (1.17), BO 1.170 (1.19)	
B_2O_2 (O–B–B–O)	$D_{\infty h}$	BO 1.168 (1.20), BB 1.507 (1.70)	*d*
B_2O_2 (O_1–B_2–O_3–B_4)	C_s	B_2O_1 1.177, B_2O_3 1.306, O_3B_4 1.347, OBO 177.2, BOB 120.9	
B_2O_3*	C_{2v}	BOa 1.340 (1.36), BO 1.171 (1.20), BOaB 105.0	*d*
$B(OH)_3$	C_{3h}	BO 1.348	
BH_3CO	C_{3v}	BC 1.530 (1.534), BH 1.205 (1.221), HBC 103.3 (103.8)	*e*
$H_3B_3O_3$	D_{3h}	BO 1.357 (1.380), BH 1.187 (1.192)	
H_2BOH	C_s	BH 1.194, 1.192, BO 1.331, HBO 121.4, 114.0, HOB 109.0, 107.4	
$HB(OH)_2$	C_s	BH 1.187, BO 1.341, 1.356, HOB 119.6, 127.2	
$B_2(OH)_4$	D_{2h}	BB 1.631, BO 1.351, OBB 125.7, HBO 106.6	
$HB(OCH_3)_2$	C_s	BH 1.187, BO 1.349, 1.367, HBO 118.2, 127.4	
$B(OCH_3)_3$	C_3	BO 1.359 (1.367), OC 1.428 (1.424), COB 116.7	
$B(OC_2H_5)_3$	C_3	BO 1.359, OC 1.434, BOC 117.9	
OBOH	C_s	BO 1.175, BO(H) 1.322, OBO 175.8	
$B_3O_3(OH)_3$	C_{3h}	BO 1.360, BO(H) 1.333, OBO 119.1	
$N(CH_2CH_2O)_3B$	C_3	BN 1.749, NC 1.474, BO 1.436, BNC 102.4, NBO 105.8	
$B_3N_3H_6$	D_{3h}	BN 1.399 (1.435), BH 1.205 (1.258), NH 0.977 (1.050), NBN 121.2 (117.7), BNB 118.7 (121.1)	
$B_2H_5NH_2$ (ϵ = tilt of BH_2 plane)	C_{2v}	BN 1.525 (1.558), BHb 1.348 (1.355), BB 1.909 (1.916), BHt 1.199 (1.193), HBH 121.0 (121), ϵ 15.2 (16.8)	
$B_2H_5N(CH_3)_2$*	C_{2v}	BN 1.560 (1.544), BB 1.912 (1.916), BHb 1.341 (1.369), BHt 1.199 (1.191), HBH 118.2, ϵ 15.0 (16.7)	
BH_3CNCH_3	C_3	BC 1.545 (1.566), NCH_3 1.402 (1.416), CN 1.174 (1.155), HBC 105.7 (103.8)	*f*
BH_3–NH_3(staggered)	C_{3v}	BN 1.562 (1.672), BH 1.209 (1.210), NH 1.007 (1.014), HBN 105.5 (104.5), BNH 108.5 (110.3)	*g*
BH_3–NH_3(elipsed)	C_{3v}	BN 1.572, BH 1.209, NH 1.007, HBN 105.8, HNB 108.7	
$(CH_3)_3B$–NH_3	C_3	BN 1.611, BC 1.576, CBN 107.2, HNB 107.7	
$(CH_3)_3N$–BH_3	C_3	BN 1.658 (1.638), BH 1.207 (1.211), NC 1.474 (1.483), CNB 108.9 (109.9), HBN 103.9 (105.3)	*b*
$(CH_3)_3N$–$B(CH_3)_3$	C_3	BN 1.735 (1.80), BC 1.572 (1.56), NC 1.475 (1.47), CNB 109.6, CBN 107.0	
$B(N(CH_3)_2)_3$	C_3	BN 1.449, NC 1.429, CNB 122.1	
BF	$C_{\infty v}$	BB 1.278 (1.263)	*b*
BF_3	D_{3h}	BF 1.306 (1.309)	*h*
HBF_2	C_{2v}	BH 1.193 (1.189), BF 1.307 (1.311), HBF 123.6 (118.3)	
F_2BOH	C_s	BF 1.306 (1.31), BO 1.352 (1.34), OH 0.962 (0.94), FBO 120.0 (123), HOB 107.5 (114)	*b*
$FB(OH)_2$	C_s	BF 1.276, BO 1.348, 1.360, OBF 119.5, 122.7	
BF_2O	C_{2v}	BO 1.356 (1.40), BF 1.303 (1.3)	*b*
FBO	$C_{\infty v}$	BF 1.283, BO 1.175, FBO 180	
F_2BC–CH	C_{2v}	BF 1.308 (1.323), BC 1.511 (1.513), FBC 123.1 (121.8), CC 1.197 (1.206)	*b*
F_2BCH–CH_2	C_s	BF 1.310, BC 1.544, CC 1.328, FBC 124.8	
CH_3BF_2	C_s	BC 1.549 (1.559), BF 1.311 (1.324), FBF 112.6 (116.0)	*i*
B_2F_4	D_{2h}	BB 1.649, BF 1.306, FBB 123.4	
$B_3O_3F_3$	D_{3h}	BO 1.362, BF 1.293	
$PHBF_2$	C_{2v}	BF 1.310 (1.33), BC 1.550 (1.55), FBF 112.5 (116)	*j*

Table V (Continued)

molecule	point group	geometries calcd (obsd)	ref[a]
$B_3O_3FH_2$	C_{2v}	BF 1.299, BH 1.188, BO 1.360	
$B_3O_3F_2H$	C_{2v}	BF 1.298, BH 1.188, BO 1.360	
$(CH_3)_2O\text{-}BF_3$	C_s	BO 3.481, OC 1.418, BF 1.307	
BBr	$C_{\infty v}$	BBr 1.895	
BBr_3*	D_{3h}	BBr 1.858 (1.87)	d
$BBrF_2$	C_{2v}	BBr 1.921, BF 1.311, FBBr 124.7	
BI_3	D_{3h}	BI 1.991	
BCl_3	D_{3h}	BCl 1.708 (1.742)	k
$HBCl_2$	C_{2v}	BH 1.196, BCl 1.701	
CH_3BCl_2	C_s	BCl 1.719 (1.753), BC 1.539 (1.557), CBCl 121.1, 120.2 (121)	l
$PhBCl_2$	C_{2v}	BC 1.539 (1.556), BCl 1.719 (1.761), ClBCl 121.0 (116.5)	m
$BClF_2$	C_{2v}	BCl 1.760 (1.728), BF 1.308 (1.315), FBCl 123.2 (121)	b
BCl_2F	C_{2v}	BCl 1.748, BF 1.304, FBCl 121.6	
BOCl	$C_{\infty v}$	BO 1.176, BCl 1.605	
B_2Cl_4	D_{2h}	BB 1.604 (1.75), BCl 1.696 (1.73), ClBB 119.0 (120)	d
$B_3O_3ClH_2$	C_{2v}	BCl 1.726, BH 1.188, BO 1.363, 1.359, 1.354	
$B_3O_3Cl_2H$	C_{2v}	BCl 1.721, BH 1.189, BO 1.365, 1.361, 1.358	
$B_3O_3Cl_3$	D_{3h}	BCl 1.712, BO 1.364	
$(CH_3O)_2BCl$	C_s	BCl 1.754, BO 1.362, ClBO 125.8	
$B_3N_3Cl_3H_3$	D_{3h}	BN 1.402, BCl 1.765, NH 0.982	
BCl_2F	C_{2v}	BCl 1.748, BF 1.304, FBCl 121.6	

[a] Except where noted, for numbering and references, see: Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231. [b] Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A., et al. *J. Phys. Chem. Ref. Data* **1979**, *8*(3), 619. [c] Schwock, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219. [d] Stull, D. R.; Prophet, H., et al. *JANAF Thermochemical Tables*; 2nd ed.; U.S. Department of Commerce, National Bureau of Standards, 1970. [e] Venkatachar, R. C.; Taylor, R. C.; Kuczkowski, R. L. *J. Mol. Struct.* **1977**, *38*, 17. [f] Stevens, J. F., Jr.; Bevan, J. W.; Curl, R. F., Jr.; Geanangel, R. A.; Hu, M. G. *J. Am. Chem. Soc.* **1977**, *99*, 1442. Bevan, J. W.; Stevens, J. F.; Curl, R. F., Jr. *J. Mol. Spectrosc.* **1979**, *78*, 514. [g] Thorne, L. R.; Suenrum, R. D.; Lovas F. J. *J. Chem. Phys.* **1983**, *78*, 167. [h] Ginn, S. G. W.; Kennedy, J. K.; Overend, J. *J. Chem. Phys.* **1968**, *48*, 1571. [i] Cox, A. P. *J. Mol. Struct.* **1983**, *97*, 61–76. [j] Christen, D.; Lister, D. G.; Sheridom, J. *J. Chem. Soc., Faraday Trans. 2* **1974**, 70, 1953–8. [k] Konaka, S.; Marata, Y.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1134–46. [l] Hubbard, S. D.; Cox, P. A. *J. Mol. Spectrosc.* **1986**, *115*, 188–214. [m] Caminati, W.; Lister, D. G. *J. Chem. Soc., Faraday Trans. 2* **1978**, 74, 896–903.

Table VI. Mean Unsigned Errors (Å) in Bond Lengths

type of bond	no. of compds	AM1	MNDO
B–H (terminal)	20	0.010	0.031
B–H (bridged)	15	0.037	0.067
B–B	24	0.045	0.055
B–C	9	0.014	0.030
B–N	6	0.047	0.029
B–O	10	0.026	0.019
B–F	9	0.009	0.021
B–Cl	5	0.035	0.031

The improvement in the treatment of nonclassical structures by AM1 has not been obtained at the expense of classical ones. As Tables II, IV, and V show, AM1 gives better results than MNDO for boron hydrides of all kinds, classical and nonclassical alike.

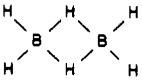
This improvement does not extend uniformly to the carboranes. Thus AM1, like MNDO,[9] fails to predict structures with the correct symmetry for CB_5H_7 and 1,6-$C_2B_4H_6$. It seems likely that AM1 still tends to underestimate the stabilities of B–B–B and/or B–C–B three-center bonds. For other carboranes, however, AM1 is much more successful; see Tables II and V. Thus in the case of 1,2-$C_2B_4H_6$, AM1 correctly predicted the octahedral structure to be the most stable and the calculated CC bond length now agrees much better with experiment, the error being 0.07 Å compared with 0.21 Å in MNDO. The heats of formation calculated by AM1 for carboranes are generally higher than the MNDO values by 20–40 kcal/mol. No experimental values are available for comparison.

D. Studies of Reactions. While hydroboration is a reaction of major practical value in synthesis, very few detailed kinetic studies have been published and most of these refer to reactions of tetrasubstituted diboranes where complications due to multiple additions of the olefin are avoided. It has been shown[23] that hydroborations probably always involve the corresponding borane, formed by initial dissociation of the diborane, and kinetic data are also available[24] for the prototypical hydroboration, i.e. the reaction of diborane (**2**) with ethylene (**4**) to form **5**. While both MNDO[12,13] and ab initio[26,27] calculations have been reported for the reaction of **2** with **4**, none of them have as yet reproduced the very low activation energy reported[24] for this reaction; see Table IX.

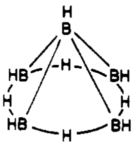
We studied several hydroboration reactions using AM1. The results are compared with those from the other procedures, and with the available experimental data, in Table

BH_3

1



2



3

$H_2C{=}CH_2$

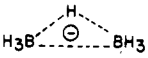
4

$H_3CCH_2BH_2$

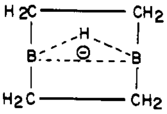
5

$H_3C\text{-}O\text{-}BH_2$

6



7



8

$(Ph_3P{=}N{=}PPh_3)^+\ (B_2H_3^-)\ (CH_2Cl_2)$

9

---

(23) See, for example, Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.

(24) Fehlner, T. P. *J. Am. Chem. Soc.* **1971**, *93*, 6366.

Table VII. Energies (kcal/mol) Calculated by Various Procedures[a] for B_5H_9 Isomers Relative to C_{4v} Structure[b]

struct in Fig 1	AM1	MNDO	PRDDO	STO-3G	6-31G	[MP2/6-31G*]
1	0.0	0.0	0.0	0.0	0.0	0.0
2	16.4	-4.4	9.5	20.6	27.1	59.4
3	27.6	-26.3	-26.4	-11.1	-0.4	46.6
4	14.4	-8.6	11.8	22.4	24.4	39.8
5	23.9	-4.0	7.7	17.8	21.6	40.1
6	19.7	-9.7	2.6	12.4	15.2	31.5

[a] PRDDO and ab initio results from ref 4. [b] The MNDO method was used to locate and optimize the six structures. All energies are related to zero for the C_{4v} structure and are in kcal/mol.

Table VIII. Calculated Bond Lengths (Å) for C_{4v} B_5H_9

bond	MNDO	PRDDO[a]	3-21G[b]	4-21G	exptl[c]	AM1	exptl[d]
B_2B_3	1.863	1.791	1.828	1.833	1.803	1.816	1.770
B_2B_1	1.712	1.648	1.709	1.710	1.690	1.667	1.659
B_2Ht	1.160	(1.208)[e]	1.174	1.171	1.186	1.185	1.195
B_1Ht	1.156	(1.201)[e]	1.175	1.170	1.181	1.177	1.190
BHb	1.384	1.356	1.349	1.354	1.352	1.346	1.351

[a] Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6595. [b] Reference 4. [c] Schwock, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219. [d] Switkes, E.; Epstein, I. R.; Tossell, J. A.; Stevens, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1970**, *92*, 3837. [e] Assumed.

Table IX. Activation Energies[a] (kcal/mol) for the Hydroboration of Ethylene by Reaction with Borane

obsd	AM1	MNDO	4-31G	6-31G**	4-31G + CI(S+D)	4-31G + CI(S+D+Q)
2 ± 3	2.9	7.6	11.7	6.7	9.7	5.6

[a] MNDO.[12] Ab initio.[5] Experiment.[24]

Table X. Geometry and Dipole Moment of CH_3OBH_2[a]

parameter	obsd[b]	AM1	4-31G*[b]
BH (cis)	1.196[c]	1.193	1.191
BH (trans)	1.196[c]	1.193	1.185
BO	1.352	1.340	1.331
CO	1.425	1.428	1.403
CH_1	1.091	1.117	1.082
CH_2	1.091	1.118	1.081
H_4BO	120.3	121.8	120.5
H_5BO	115.0	112.4	118.3
BOC	121.5	118.9	123.2
OCH	109.2	109.6	109.1
μ	1.61	1.51	

[a] Bond lengths in Å, angles in deg, and dipole moment in debyes. [b] Kawashima, Y.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* 1986, *116*, 23. [c] Assumed.

Table XI. Heats of Formation (kcal/mol) of Cations

ion	calcd	exptl[a]	Δ
BH^+	288	334[b]	-46
BH_2^+	240	274	-34
BH_3^+	273	279	-6
$B_2H_2^+$	300	329	-29
$B_2H_3^+$	260	285	-25
$B_2H_4^+$	265	285	-20
$B_2H_5^+$	232	232	0
$B_2H_6^+$	258	272[b]	14
$B_5H_9^+$	244	250[c]	-6
$B_5H_{10}^+$	202	217[d]	-15
$B_6H_{11}^+$	179	194[d]	-15
$(CH_3)_2B^+$	181	175	6
CH_3B^+	262	296	-34
$(CH_3)_3B^+$	202	201	1

[a] For references to experimental values see (except where noted) ref 9. [b] See Table II, footnote *e*. [c] Calculated from the experimental values for the heat of formation and ionization potential. [d] Lloyd, D. R.; Lynaugh, N.; Roberts, P. J.; Guest, M. F. *J. Chem. Soc., Faraday Trans. 2* **1975**, 1382.

Table XII. Proton Affinities (kcal/mol)

molecule	calcd	obsd[a]	error
B_2H_6	163.9	146 ± 5	18
B_4H_{10}	175.6	144 ± 5	31
B_5H_9	192.6	167 ± 6	25
B_6H_{10}	210.8	195 ± 8	16
1,5-$C_2B_3H_5$	175.1		
1,6-$C_2B_4H_6$	194.0	208 ± 4	-14
2,4-$C_2B_5H_7$	193.3	173 ± 1	20
$B_3N_3H_6$	209	203 ± 7	6

[a] Dixon, D. A. *Inorg. Chem.* **1980**, *19*, 593.

IX. The AM1 value for the activation energy of the reaction between **2** and **4** agrees better with experiment[24] than any of the others. In contrast to MNDO,[12] AM1 predicts a loose π-complex-like adduct type to be formed as a stable intermediate ($\Delta H = -2$ kcal/mol) *before* the transition state is reached. This conclusion agrees qualitatively with the ab initio results.[5] A detailed study of hydroboration will be reported elsewhere in due course.

AM1 calculations were also carried out for methoxyborane (**6**), which is probably the initial product in the reaction of diborane with either methanol or formaldehyde.[25] As Table X shows, the geometry and dipole moment calculated by AM1 agreed well with experiment, better indeed than the values given by an ab initio calculation.

E. Boron-Containing Ions. Table XI compares with experiment the heats of formation calculated by AM1 for a number of boron-containing cations. Two minima were found on the potential surfaces for $B_2H_2^+$ and $B_2H_5^+$ and three were found for $B_2H_3^+$. Their geometries and relative energies are shown in Figure 2. In the case of $B_2H_3^+$, AM1 predicts the most stable structure to be **f** whereas MNDO

---

(25) Kawashima, Y.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1986**, *116*, 23.

Table XIII. Calculated Structure of $(B_2H_7)^-$ Anion

method.	BH_1	BH	BH_1B	HB_1H_1	$H_3B_1H_1$
6-31G[a]	1.33	1.21	179.9	104.2	104.2
6-31G**[a]	1.34	1.21	149.9	101.3	104.3
AM1	1.30	1.21	106.2	110.9	98.9

[a] See ref 28. For numbering of atoms, see 7.

predicted it to be **h**. In view of the generally better performance of AM1, the former prediction is probably correct.

Since the AM1 ionization potentials for boron hydrides seem to be uniformly too small by 0.6 eV (see Table II), a similar error (−14 kcal/mol) might be expected in the case of the cations in Table XI. This indeed appears to be the case. The only discrepancies are for the compounds containing two methyl groups, where the HOMO is probably a CH π-type MO, and BH^+, for which a large error might be expected from analogy with other diatomic species. It should be noted that some of the experimental values come from mass spectrometric measurements of uncertain accuracy.

MNDO calculations[9,26] have given reasonable estimates of proton affinities for various boron hydrides. Table XII shows the results given by AM1 for some boron hydrides and related compounds. As in the MNDO studies, the experimental heat of formation (365.7 kcal/mol) was used for H^+. For species involving protonation at boron, an error of +14 kcal/mol would be expected, for the reasons indicated above. The results in Table XII are consistent with this prediction, the two exceptions being molecules which are predicted to protonate on carbon or nitrogen.

Table XIII shows our results for another interesting molecule, the $B_2H_7^-$ anion (**7**). This seems to be the only known example of a species containing an unsupported B–H–B bond.[27] While earlier ab initio calculations[28] agreed with MNDO[10] in predicting the central B–H–B linkage in **7** to be linear, an X-ray crystallographic study[27] of a closely related anion (**8**) showed it to contain a bent (140°) B–H–B bond (**8**), and recently a similar situation has been shown[29] to hold for a salt (**9**) containing **7** itself. A recent ab initio calculation,[30] using a larger basis set (6-31G**), predicted a bent geometry for **7**.

Table XII compares our AM1 results for **7** with experiment and with those from the 6-31G and 6-31G** ab initio calculations. AM1 not only predicts a bent structure for **7** but also underestimates the BHB bond angle. We also carried out AM1 calculations for linear **7**, assuming the BHB angle to be 180° but otherwise optimizing the geometry. The difference in energy between the linear and bent structures (4 kcal/mol) was greater than that (<1 kcal/mol) given by the 6-31G** calculation, reflecting the difference between the calculated BHB angles.

A bent structure would be expected for **7** since it contains a three-center, two-electron bond. The optimum structure for such a bond is one where all the three AOs overlap with one another. **7** is indeed isoelectronic with the corresponding isomer of $C_2H_7^+$ which is also predicted[31] to have a bent structure.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. AF86-0022) and the Robert A. Welch Foundation (Grant No. F-126).

Registry No. BH, 13766-26-2; BH_2, 14452-64-3; BH_3, 13283-31-3; B_2, 14452-61-0; B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7; B_5H_9, 19624-22-7; 1-$(CH_3)B_5H_8$, 19495-55-7; B_5H_{11}, 18433-84-6; B_6H_{10}, 23777-80-2; $B_{10}H_{14}$, 17702-41-9; $B(CH_3)_3$, 593-90-8; $B(C_2H_5)_3$, 97-94-9; $B(C_3H_7)_3$, 1116-61-6; $B(C_4H_9)_3$, 122-56-5; CB_5H_7, 55188-36-8; CB_5H_9, 12385-35-2; 2,3,4,5-$C_4B_2H_6$, 28323-17-3; 1,2-$C_2B_4H_6$, 20693-68-9; 1,5-$C_2B_3H_5$, 20693-66-7; 1,6-$C_2B_4H_6$, 20693-67-8; BO, 12505-77-0; BO_2, 13840-88-5; B_2O_2 (O–B–O–B), 111160-60-2; OB_2O (O–B–B–O), 13766-28-4; $B(OH)_3$, 10043-35-3; B_2O_3, 1303-86-2; BH_3CO, 13205-44-2; $H_3B_3O_3$, 289-56-5; H_2BOH, 35825-58-2; $HB(OH)_2$, 13780-71-7; $CH_3B(OH)_2$, 13061-96-6; $(CH_3)_2BOH$, 13061-97-7; $B_2(OH)_4$, 13675-18-8; $HB(OCH_3)_2$, 4542-61-4; $B(OCH_3)_3$, 121-43-7; $B(OC_2H_5)_3$, 150-46-9; $B(OC_3H_7)_3$, 688-71-1; OBOH, 13460-50-9; $B_3O_3(OH)_3$, 13460-51-0; $HBO_2(CH_2)_2$, 1942-28-5; $N(CH_2CH_2O)_3B$, 283-56-7; $C_6H_5B(OH)_2$, 98-80-6; $B_3N_3H_6$, 6569-51-3; $B_2H_5NH_2$, 39046-41-8; H_3B-NH_3, 13774-81-7; $(CH_3)_3B$-NH_3, 1830-95-1; $B_2H_5N(CH_3)_2$, 23273-02-1; H_3B-$N(CH_3)_3$, 75-22-9; $(CH_3)_3B$-$N(CH_3)_3$, 1704-27-4; $(CH_3)_2B$-$N(CH_3)_2$, 1113-30-0; C_5H_5N-BH_3, 110-51-0; *p*-$CH_3C_5H_4NBH_3$, 3999-39-1; *p*-$OCH_3C_5H_4NBH_3$, 56898-50-1; *p*-$NO_2C_5H_4NBH_3$, 56898-55-6; $B(N(CH_3)_2)_3$, 4375-83-1; BF, 13768-60-0; BF_3, 7637-07-2; HBF_2, 13709-83-6; F_2BOH, 13867-66-8; BF_2O, 38150-67-3; FBO, 23361-56-0; F_2BCCH, 23728-64-5; F_2BCHCH_2, 358-95-2; CH_3BF_2, 373-64-8; B_2F_4, 13965-73-6; $B_3O_3F_3$, 13703-95-2; $FB(OH)_2$, 14720-33-3; $B_3O_3H_2F$, 57372-62-0; $B_3O_3HF_2$, 57328-69-5; $(CH_3)_2O$-BF_3, 353-42-4; $C_6H_5BF_2$, 368-98-9; BBr, 19961-29-6; BBr_3, 10294-33-4; $BBrF_2$, 14720-23-1; $C_6H_5BBr_2$, 4151-77-3; BI_3, 13517-10-7; BCl, 20583-55-5; BCl_3, 10294-34-5; $HBCl_2$, 10325-39-0; CH_3BCl_2, 7318-78-7; $C_6H_5BCl_2$, 873-51-8; $BClF_2$, 14720-30-0; BCl_2F, 14720-31-1; BOCl, 23361-55-9; B_2Cl_4, 13701-67-2; $B_3O_3H_2Cl$, 89306-13-8; $B_3O_3HCl_2$, 89306-14-9; $B_3O_3Cl_3$, 13703-91-8; $(CH_3O)_2BCl$, 868-81-5; $B_3N_3Cl_3H_3$, 933-18-6; CH_2CH_2, 74-85-1; CH_3OBH_2, 54098-92-9; BH^+, 12258-45-6; BH_2^+, 15194-16-8; BH_3^+, 12228-16-9; $B_2H_2^+$, 111264-41-6; $B_2H_3^+$, 111160-61-3; $B_2H_4^+$, 111002-23-4; $B_2H_5^+$, 38702-72-6; $B_2H_6^+$, 58256-05-6; $B_5H_9^+$, 65982-52-7; $B_5H_{10}^+$, 111265-66-8; $B_6H_{11}^+$, 66272-80-8; $(CH_3)_2B^+$, 59414-81-2; CH_3B^+, 84863-49-0; $(CH_3)_3B^+$, 59223-53-9; $B_2H_7^+$, 27380-11-6.

---

(26) DeKock, R. L.; Jasperse, C. P. *Inorg. Chem.* **1983**, *22*, 3843.

(27) Shore, S. G.; Lawrence, S. H. *J. Am. Chem. Soc.* **1982**, *104*, 7669.

(28) Hall, J. H., Jr.; Marynick, D. C.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 3126.

(29) Clayton, W. R.; Saturnino, D. J.; Corfield, P. W. R.; Shore, S. G. *J. Chem. Soc., Chem Commun.* **1973**, 377. Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063.

(30) Sapse, A.-M.; Osorio, L. *Inorg. Chem.* **1984**, *23*, 627.

(31) (a) Dewar, M. J. S.; Bischoff, P. K. *J. Am. Chem. Soc.* **1975**, *97*, 2278. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649.