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Ground States of Molecules. 41.¹ MNDO Results for Molecules Containing Boron

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Abstract: Heats of formation, molecular geometries, ionization potentials, and dipole moments, calculated by the MNDO method, are reported for a wide variety of boron compounds. The results are much better than those from MINDO/3, especially for the boron hydrides. Calculated proton affinities also agree well with experiment.

Boron is a particularly interesting element from a theoretical standpoint because of its propensity to form "nonclassical" molecules, in particular the boron hydrides and carboranes. When the MINDO/3 method was developed² in these laboratories, attempts were therefore naturally made to extend it to boron and a set of parameters was included in the original paper,^{2a} with, however, a warning that they were only preliminary. Later study showed them in fact to give very poor results and determined efforts were therefore made³ to develop better ones, using an improved parametrization procedure³ that had been developed here. All these attempts, however, failed. Every choice of parameters led to gross errors in one or more calculated heats of formation and in the geometries calculated for one or more of the boron hydrides. Since MINDO/3 had proved remarkably successful^{2,4} for other elements of the first row, we concluded that the problem with boron must be due to the simplifying assumptions made in the INDO⁵ approximation, in particular the neglect of one-center overlap.

This assumption is avoided in the NDDO⁶ approximation and recent work here has led to the development of a semi-empirical treatment (MNDO⁷) based on it. MNDO has proved generally superior to MINDO/3 in most connections, in particular those where MINDO/3 had failed due to its neglect of one-center overlap.

We therefore decided to parametrize MNDO for boron; the present paper reports the results obtained by this treatment for a number of boron compounds.

Experimental Section

Procedure. The parametrization followed the procedure described previously⁷ by fitting 49 properties of a set of standard molecules. These comprised 10 heats of formation, 22 bond lengths, 10 bond angles, 3 ionization potentials, and 4 dipole moments. The parameters obtained in this way are listed in Table I. The ten compounds used in the parametrization are shown in Table II. Geometry optimizations were carried out, as described previously,⁷ by minimizing the energy with respect to all relevant geometrical parameters.

Results and Discussion

(A) **Heats of Formation.** Table II compares with experiment the heats of formation calculated by MNDO and by

MINDO/3 (with the original parameters^{2a}) for the ten molecules of the basis set. As usual, these were chosen to be as "difficult" as possible in order to ensure that the parameters would give the best overall fit to compounds of different types. While the MINDO/3 values are clearly very poor, the MNDO ones are reasonably satisfactory. The only compound for which the MNDO error exceeds 20 kcal/mol is BH (error, -36.1 kcal/mol) and MNDO is known² to give relatively poor results for diatomic molecules.

Tables III, IV, and V summarize the MNDO results for 45 molecules, divided for convenience into categories. Most of the experimental values listed for comparison are taken from a paper by Guest and Pedley⁸ where a least-squares procedure was used to find the best mutually self-consistent set of heats of formation. The absolute average error in the MNDO values (Table III) is greater than that found previously¹ for compounds containing H, C, N, and O but it is not excessive. Apart from BH, the only differences greater than 30 kcal/mol are for H₂B₂O₃ (1; +57.5), B₃O₃(OH)₃ (2; +40.6), B(NMe₂)₃ (3; +33.6), and Me₃B⁻N⁺Me₃ (4; +44.1). The errors in the last two cases might have been expected since MNDO is known¹ to overestimate steric repulsions in crowded molecules. In the case of 1, the experimental value⁹ for the heat of for-

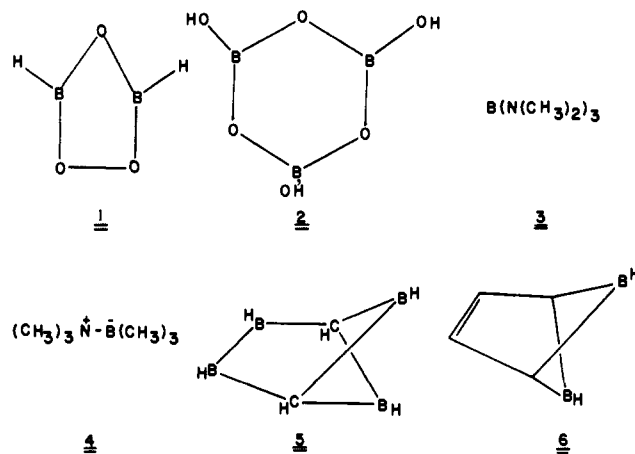


Table I. MNDO Parameters for Boron

Optimized parameters		Derived parameters	
U_{ss} , eV	-34.547130	H_f^A , kcal/mol	135.70
U_{pp} , eV	-23.121690	E_1^A , eV	-64.315 950
ξ , au	1.506801	D_1 , Å	0.506 893
β_s , eV	-8.252054	D_2 , Å	0.430 113
α , Å ⁻¹	2.134993	ρ_0 , Å	0.679 822
		ρ_1 , Å	0.539 446
		ρ_2 , Å	0.476 128

Table II. Comparison of Errors in the Heats of Formation of the Basis Molecules, Calculated by MINDO/3 and MNDO

Molecule	Error in calcd heat of formation, kcal/mol	
	MINDO/3 ^a	MNDO ^b
BH	-54.8	-36.1
B ₂ H ₆	4.5	-10.2
B ₄ H ₁₀	-8.2	-5.4
B ₅ H ₉	-99.8	13.8
BH ₃ CO	-20.0	-19.8
B ₃ N ₃ H ₆	-85.8	-8.9
B ₂ H ₅ N(CH ₃) ₂	-12.9	12.5
B(OH) ₃	-4.2	0.7
B(CH ₃) ₃	16.3	-10.3
B ₂ O ₃	44.8	0.7

^a Reference 2. ^b See Table IV.

mation is almost certainly much too negative. A reasonable thermochemical argument (see Appendix) leads to a value more positive by over 40 kcal/mol and in reasonable agreement with the MNDO value.

It should of course be remembered that thermochemical data for organoboron compounds are not only scanty but also in general much less reliable than values for other organic molecules.

(B) Molecular Geometries. Table VI compares the MNDO geometries with experiment. Here the experimental data are reliable and the agreement with them is generally good. Thus the average errors in the calculated lengths of two-center bonds to boron, other than BH, are little greater than those¹ for other second period elements. The calculated lengths of BH bonds are systematically too small, by 0.031 Å. A corresponding correction leaves only very small residual errors (Table VII).

The average errors in the lengths of multicenter bonds in the boron hydrides were greater. This was not surprising because the position of the "central" atom in such a bond is much less clearly defined than that of an atom in a "normal" classical molecule. In the latter, displacement of the atom in question involves compression and/or stretching and/or bending of one or more two-center bonds from equilibrium. In the former, movement of the central atom to or fro along the bond increases one bonding interaction at the expense of another. Such displacements should therefore occur correspondingly more easily. However, they should have little effect on the overall geometries and the structures calculated by MNDO for the boron hydrides seemed indeed in excellent agreement with experiment.

When we came to the carboranes, problems arose. The carboranes with molecular formulas $C_nB_{6-n}H_{8-n}$ can exist either in octahedral geometries or as pentagonal pyramids and MNDO was not too successful in its choice between them.

In the case of CB₅H₇, MNDO predicted the pentagonal pyramid to be the lower in energy by 17 kcal/mol. It has, however, been shown by microwave studies¹⁰ that the known compound has the octahedral structure. It is conceivable that

Table III. Mean Absolute Errors $\Delta(\Delta H_f^\circ)$ in the Heats of Formation of Boron Compounds

Class of compd	No.	$\Delta(\Delta H_f^\circ)$, kcal
All compds ^a	45	14.1
Boron hydrides	9	13.7
BO	15	12.2
BN	6	21.2
BC	3	12.2
Cations ^b	12	13.7

^a B₂H₂O₃ not included for these averages. ^b Including radical cations calculated by the half-electron method.

the isomers might be separated by a high-energy barrier, the stability of the known isomer being kinetic rather than thermodynamic. However, an even worse discrepancy occurs in the case of 1,6-C₂B₄H₆ where MNDO predicted the octahedral structure to be not even a local minimum on the potential surface, although this is the one observed.¹¹ The calculated geometry corresponds to a bonding situation best represented by the classical structure 5. Finally, in the case of 1,2-C₂B₄H₆, Mndo did, correctly,¹² predict the octahedral structure to be the more stable, but the length of the CC bond was overestimated by 0.21 Å. A similar problem arose in the case of C₄B₂H₆. While MNDO correctly predicted this to have a pentagonal pyramidal structure, analogous to that of B₆H₁₀ and with boron as the apical atom, the calculated carbon-(apical boron) distances are too great by 0.32 Å and the bond lengths in the C₄ moiety are incorrectly predicted to alternate strongly, the calculated lengths of the terminal bonds being of 1.519 Å (obsd¹³ 1.436 Å) while that of the central one is 1.391 Å (obsd¹³ 1.424 Å).

It seems likely that these problems arise from a tendency of MNDO to underestimate the strengths of multicenter bonds formed by σ -type overlap of AO's. This is indicated by calculations¹⁴ for "nonclassical" carbocations for which the MNDO heats of formation are too positive relative to those of their "classical" counterparts. In the case of CB₅H₇ or C₂B₄H₆, there are four such bonds in the symmetrical octahedral structures but only three in the pentagonal bipyramids. Furthermore, the geometry calculated for C₄B₂H₆ is distorted toward the classical structure 6.

At this point we realized that we had not yet completely optimized the geometry of B₅H₉. We had assumed C_{4v} symmetry and had not checked that the structure found in this way (Figure 1a) corresponded in fact to a minimum on the potential surface. Since the C_{4v} structure contains no less than seven multicenter bonds, it was clearly a good candidate for another MNDO failure. Indeed, we found that the Hessian matrix of the C_{4v} structure had three negative eigenvalues, and when the geometry was optimized without constraints, the molecule distorted to the structure indicated in Figure 1b, lower in energy by 9 kcal/mol than the C_{4v} one. Here two of the BHB three-center bonds have been replaced by two-center ones while the other two are now very unsymmetrical, and one of the BB distances to the apical boron has become very short. The structure indeed approximates to that indicated in 7, with two

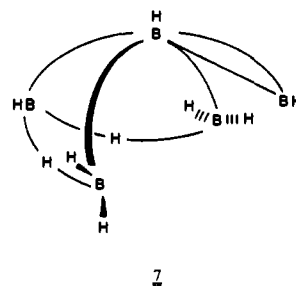


Table IV. Comparison of Calculated and Experimental Heats of Formation

Molecule	ΔH_f° , kcal mol ⁻¹			Dipole moment, D			Ionization potential, ^{cc} eV		
	Calcd	Exptl	Δ	Calcd	Exptl	Δ	Calcd	Exptl	Δ
BH	72.1	108.2 ^a	-36.1	0.49			10.10		
BH ₂	66.5	45.7 ^a	20.8						
BH ₃	11.7	23.8 ^a	-12.1	0.0			13.52		
B ₂ H ₆	-1.8	8.4 ^a	-10.2	0.0			12.78	11.83 ^b	0.95
B ₄ H ₁₀	10.2	15.6 ^a	-5.4	1.30			12.50	11.5 ^c	1.00
B ₅ H ₉	31.3	17.5 ^a	13.8	2.97	2.13 ^d	0.84	11.48	10.52 ^c	0.96
B ₅ H ₁₁	15.2	24.3 ^a	-9.3	2.33			12.02		
B ₆ H ₁₀	18.8	22.2 ^a	-3.4	2.96			10.94		
B ₁₀ H ₁₄	16.7	7.1 ^a	9.6	4.08			11.29	10.15 ^c	1.14
1,5-C ₂ B ₃ H ₅	27.5			0.0			11.48	10.88 ^e	0.60
CB ₅ H ₇	38.2			0.79	1.43 ^f	-0.64	10.96		
CB ₅ H ₉	17.6			2.13	1.53 ^g	0.60	11.18		
1,2-C ₂ B ₄ H ₆	62.3			2.25	1.50 ^h	0.75	11.36		
C ₄ B ₂ H ₆	56.3			1.65	2.26 ⁱ	-0.61	9.63		
2,4-C ₂ B ₅ H ₇	33.7			1.24	1.32 ^j	-0.08	11.61	10.94 ^e	0.67
B ₃ H ₃ O ₃	-271.7	-290.0 ^a	18.3	0.0			12.79		
B ₂ H ₂ O ₃	-142.9	-200.4 ^k	-57.5	1.02	0.96 ^l	0.06	12.47		
HBO ₂ (CH ₂) ₂	-135.7			2.09	2.28 ^m	-0.19	11.56		
B(OCH ₃) ₃	-207.8	-214.6 ⁿ	6.8	0.0			11.28		
(CH ₃) ₂ BOB(CH ₃) ₂	-144.0			0.53			10.57		
BO·	-1.5	18.4 ^a	-19.9						
BO ₂ ·	-68.7	-75.3 ^a	6.6						
B ₂ O ₂	-125.2	-108.1 ^a	-17.1	0.95			12.50		
B ₂ O ₃	-198.5	-199.2 ^a	0.7	0.81			13.14		
BO ₂ H	-133.1	-134.1 ^a	1.0	2.71			12.66		
H ₂ BOH	-78.2	-69.4 ^a	-8.8	1.53			12.15		
HB(OH) ₂	-159.4	-153.1 ^a	-6.3	1.31			12.31		
B(OH) ₃	-236.3	-237.0 ^a	0.7	0.0			12.37		
PhB(OH) ₂	-139.1	-151.8 ^a	12.7	2.56			9.60		
B ₂ (OH) ₄	-303.4	-315.0 ^a	11.6	0.0			11.20		
HB(OCH ₃) ₂	-142.0	-138.4 ⁿ	-3.6	1.18			11.31		
B(OCH ₂ CH ₃) ₃	-212.6	-239.9 ⁿ	27.3	1.85			11.09		
(CH ₃) ₂ BOH	-108.6			1.33	1.53 ^o	-0.20	11.41		
CH ₃ B(OH) ₂	-174.4			1.30	1.16 ^o	0.14	12.21		
B ₃ O ₆ H ₃	-501.8	-542.4 ^a	40.6	0.0			12.62		
B ₃ N ₃ H ₆	-131.1	-122.2 ⁿ	-8.9	0.0			10.96	10.09 ^p	0.87
(CH ₃) ₃ NBH ₃	6.3	-20.4 ⁿ	26.7	5.87	4.84 ^q	1.03	11.26		
(CH ₃) ₃ NB(CH ₃) ₃	-8.5	-52.6 ^a	44.1	5.30			10.49		
B ₂ H ₅ NH ₂	-33.2			2.95	2.67 ^r	0.28	12.59		
(CH ₃) ₂ NB ₂ H ₅	-15.4	-27.9 ⁿ	12.5	3.22	2.78 ^s	0.44	12.35		
HBN ₄ (CH ₃) ₂	5.4			2.30			10.42		
H ₃ NB(CH ₃) ₃	-52.4	-54.1 ^a	1.7	5.46			10.58		
B(N(CH ₃) ₂) ₃	-32.3	-65.9 ⁿ	33.6	0.0			9.23	7.60 ^t	1.62
NH ₃ BH ₃	-21.7			6.04			11.47	10.33 ^u	1.14
(CH ₃) ₂ NB(CH ₃) ₂	-44.5			1.60			10.36	8.9 ^t	1.46
C ₅ H ₅ N·BH ₃	22.5			7.24			10.55	9.72 ^v	0.83
p-CH ₃ C ₅ H ₄ N·BH ₃	14.4			7.46			10.46	9.50 ^v	0.96
p-OCH ₃ C ₅ H ₄ N·BH ₃	-16.7			7.28			10.45	9.30 ^v	1.15
p-NO ₂ C ₅ H ₄ N·BH ₃	46.0			2.22			11.20	10.27 ^v	0.93
N(CH ₂ CH ₂ O) ₃ B	-170.2			7.87			10.53	9.8 ^w	0.73
BH ₃ CO	-46.4	-26.6 ^a	-19.8	2.96	1.80 ^x	1.16	12.60	11.92 ^u	0.68
B(CH ₃) ₃	-40.1	-29.3 ⁿ	-10.8	0.0			11.65	10.98 ^{y,t}	0.67
(CH ₃) ₄ B ₂ H ₂	-46.4			0.0			11.76		
B(CH ₂ CH ₃) ₃	-49.1	-36.5 ⁿ	-12.6	0.0			11.26	10.4 ^{y,z}	0.86
1-CH ₃ B ₅ H ₈	18.3			2.86	1.93 ^{aa}	0.93	10.90	10.20 ^{bb}	0.70

^a See ref 8. ^b C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Am. Chem. Soc.*, **92**, 3863 (1970). ^c D. R. Lloyd, N. Lynaugh, P. J. Roberts, and M. F. Guest, *J. Chem. Soc., Faraday Trans. 1*, 1382 (1975). ^d H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, **22**, 262 (1954). ^e T. P. Fehlner, *Inorg. Chem.*, **14**, 934 (1975). ^f G. L. McKown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Am. Chem. Soc.*, **98**, 6909 (1976). ^g C. S. Cheung and R. A. Beaudet, *Inorg. Chem.*, **10**, 1144 (1971). ^h Reference 12. ⁱ Reference 13. ^j R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **43**, 2166 (1965). ^k Reference 9, see Appendix. ^l W. V. F. Brooks and R. F. Porter, *J. Chem. Phys.*, **47**, 4186 (1967). ^m J. H. Hand and R. H. Schwendeman, *ibid.*, **45**, 3349 (1966). ⁿ J. O. Cox and G. Pilsher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. ^o J. E. de Moor and G. P. van der Kelen, *J. Organomet. Chem.*, **9**, 23 (1967). ^p H. Block and W. Fuss, *Angew. Chem., Int. Ed. Engl.*, **10**, 182 (1971). ^q P. Cassoux, R. L. Kuczowski, P. S. Bryan, and R. C. Taylor, *Inorg. Chem.*, **14**, 126 (1975). ^r K. K. Lau, A. B. Burg, and R. A. Beaudet, *ibid.*, **13**, 2787 (1974). ^s E. A. Cohen and R. A. Beaudet, *ibid.*, **12**, 1570 (1963). ^t W. Fuss and H. Bock, *J. Chem. Phys.*, **61**, 1613 (1974). ^u D. R. Lloyd and N. Lynaugh, *Chem. Commun.*, 1545 (1970). ^v See ref 15. ^w S. C. Craddock, E. A. V. Ebsworth, and I. B. Muir, *J. Chem. Soc., Dalton Trans.*, 25 (1975). ^x See ref 19. ^y Band center (average of Jahn-Teller peaks). ^z A. K. Holliday, W. Reade, R. A. W. Johnstone, and A. F. Neville, *Chem. Commun.*, 51 (1971). ^{aa} E. A. Cohen and R. A. Beaudet, *J. Chem. Phys.*, **48**, 1220 (1968). ^{bb} J. A. Ullman and T. P. Fehlner, *J. Am. Chem. Soc.*, **98**, 1119 (1976). ^{cc} The calculated IP's are using Koopmans' theorem and the experimental IP's are from UV-photoelectron spectroscopy.

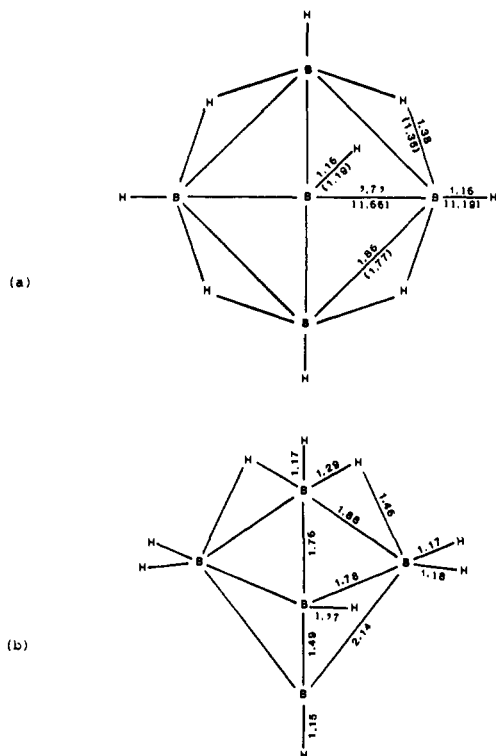


Figure 1. (a) Calculated (observed) geometry (bond lengths in Å) for the C_{4v} structure of B_5H_9 ; (b) calculated geometry for the MNDO structure for B_5H_9 .

BBB three-center bonds and two BHB three-center bonds. Two of the boron atoms are linked simultaneously by a σ -type two-center bond, and half a BBB three-center bond, involving π -type overlap.

In view of this unexpected result, we naturally rechecked the structures calculated for the other boron hydrides, but they all proved to be correct. Each corresponded to a definite local minimum on the potential surface. Since these compounds contain numerous three-center bonds, it seems likely that the cyclic four-center ones in the octahedral carboranes represent an especially unfavorable situation for MNDO.

So far no calculations of the geometries of these molecules seem to have been reported, using the RH (Roothaan-Hall: "ab initio SCF") method. It will be interesting to see if attempts in this direction meet with problems similar to those encountered by MNDO. It is well known (see ref 14) that the RH method tends to underestimate the stabilities of nonclassical carbonium ions relative to their classical isomers. The errors are serious if a minimum basis set (e.g., STO-3G) is used and persist even with basis sets of split ζ type (e.g., 4-31 G). Since MNDO gives results¹⁴ very similar to those obtained using the 4-31G basis set, it seems likely that both procedures underestimate the strengths of three-center bonds to comparable extents. If so, it may prove necessary to use a very large basis set, and perhaps also to include CI, if the geometries of the boron hydrides and carboranes are to be predicted reliably.

(C) Ionization Energies. Table IV compares calculated (MNDO) and observed first ionization energies for 19 molecules. The MNDO values are systematically too large by 0.92 eV. It is possible that this error might be corrected by changes in the U_{ss} and U_{pp} parameters. However, since the errors are small and since the relative ordering of the other occupied orbitals is well reproduced (see below), we did not think the attempt worthwhile.

Table VIII compares calculated and observed¹⁵ ionization energies for a series of pyridine-borane adducts with substit-

Table V. Comparison of Calculated and Experimental Heats of Formation of Gaseous Cations

Molecule	ΔH_f° , kcal mol ⁻¹		
	Calcd	Exptl ^a	Δ
BH^+	304	333	-29
BH_2^+	249	274	-25
BH_3^+	292	279	13
$B_2H_2^+$	324	329	-5
$B_2H_3^+$	265	285	-20
$B_2H_4^+$	273	285	-12
$B_2H_5^+$	231	232	-1
$B_2H_6^+$	268	286	-18
$(CH_3)_2B^+$	181	175	6
CH_3B^+	269	296	-27
$B_3H_2O_3^+$	-10	-7	-3
$(CH_3)_3B^+$	206.4	201.4 ^b	5

^a See ref 22. ^b M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 1433 (1976).

uents in the γ position. The order of first ionization energies is correctly reproduced ($NO_2 > H > CH_3 > OCH_3$). The photoelectron spectra indicate that the first ionization corresponds to ionization from the BH_3 moiety and that this is not split. In MNDO, the HOMO is predominantly BH_3 , mixed with the $B_1 \pi$ MO of the ring. The second highest occupied MO is the π MO of A_2 symmetry and the third a BH_3 MO, orthogonal to the π MO's of the ring. This discrepancy is due to the fact that MNDO overestimates the binding energy of electrons in MO's composed primarily of boron AO's. As a result, the BH_3 orbitals are predicted to be similar in energy to the $A_2 \pi$ MO's and the resulting interaction between them splits the BH_3 level.

Table IX compares calculated and observed ionization energies for several molecules whose photoelectron spectra have been studied in detail. Values calculated by the RH method (using the conventional scaling factor, 0.92) and by the X_α method are included for comparison. All three methods predict similar ordering of the ionizations with one exception (I_5 and I_6 of B_5H_9). Here MNDO and X_α agree. Since it seems to be generally agreed that X_α is more reliable than RH in this connection, MNDO is presumably correct.

It will be seen that the MNDO values are systematically too large and indeed similar to the unscaled RH values. We have therefore included scaled MNDO values for comparison.

(D) Dipole Moments and Charge Distributions. Calculated and observed dipole moments for 15 molecules are compared in Table IV. The average absolute error (0.51 D) is greater than that for compounds containing only H, C, N, and O.¹ The errors are moreover nearly all positive. This again suggests that our U_{ss} and U_{pp} values may be somewhat too large. It should be noted that calculated heats of formation are insensitive to changes in the U parameters and that the problems with multicenter bonding cannot be corrected by changing them. It is therefore unlikely that any useful overall improvement in MNDO could be effected by such changes.

There has been a good deal of discussion and controversy concerning the magnitude and even the signs of the formal charges in boron compounds.¹⁶ We will discuss three which have been studied extensively in this connection, namely the ammonia-borane adduct ($H_3N \cdot BH_3$), diborane (B_2H_6), and borane carbonyl (H_3BCO).

Table X compares the formal charges calculated for the two latter compounds by MNDO and by the RH method, using minimum and extended basis sets. Since the magnitudes, and even the signs, of the calculated charges are sensitive to the choice of basis set, it is difficult to know how much weight to

Table VI

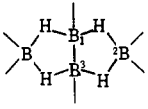
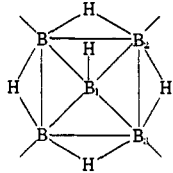
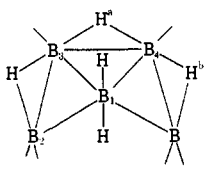
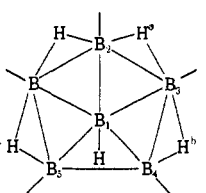
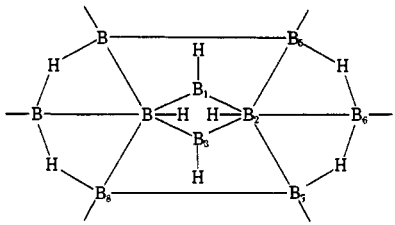
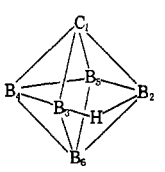
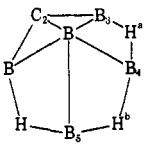
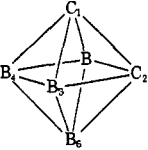
Molecule	Point groups	Calcd (obsd) values for geometrical variables ^a	Ref
BH	$C_{\infty v}$	BH 1.178 (1.236)	<i>b</i>
BH ₂	C_{2v}	BH 1.159 (1.18), HBH 126.6 (131)	<i>c</i>
BH ₃	D_{3h}	BH 1.155	
B ₂ H ₆	D_{2d}	BB 1.753 (1.775), BH _b 1.350 (1.339), BH _t 1.164 (1.196)	<i>d, e</i>
B ₄ H ₁₀	C_{2v}	B ¹ B ³ 1.752 (1.750), B ¹ B ² 1.881 (1.845), B ¹ H _b 1.258 (1.330), B ² H _b 1.514 (1.430), BH _t 1.17 (1.19)	<i>f</i>
			
B ₅ H ₉	C_{4v}	B ¹ B ² 1.712 (1.659), B ² B ³ 1.862 (1.770), BH _b 1.384 (1.351), BH _t 1.160 (1.195), B ¹ H _t 1.156 (1.190)	<i>f</i>
			
B ₅ H ₁₁	C_s	B ¹ B ³ 1.793 (1.721), B ¹ B ² 1.863 (1.852), B ³ B ⁴ 1.903 (1.772), B ² B ³ 1.761 (1.720), B ³ H _b 1.263 (1.340), B ² H _b 1.524 (1.319), B ³ H _a 1.366 (1.341), B ² H _t 1.167 (1.213), 1.165 (1.193), B ¹ H _t 1.174 (1.190), 1.214 (1.190)	<i>f</i>
			
B ₆ H ₁₀	C_s	B ¹ B ⁴ 1.908 (1.808), B ¹ B ³ 1.716 (1.755), B ¹ B ² 1.798 (1.757), B ⁴ B ⁵ 1.590 (1.603), B ³ B ⁴ 1.784 (1.746), B ² B ³ 1.866 (1.784), B ³ H _a 1.503 (1.322), B ² H _a 1.285 (1.322), B ³ H _b 1.406 (1.319), B ⁴ H _b 1.340 (1.319), B ₁ H _t 1.164 (1.196)	<i>g</i>
			
B ₁₀ H ₁₄	C_{2v}	B ¹ B ³ 1.869 (1.789), B ¹ B ² 1.797 (1.776), B ² B ⁵ 1.787 (1.735), B ⁷ B ⁸ 1.897 (1.973), B ² B ⁶ 1.868 (1.775), B ² B ⁶ 1.688 (1.720), B ⁶ H _b 1.439 (1.347), B ⁵ H _b 1.313 (1.248)	<i>h</i>
			
1,5 C ₂ B ₃ H ₅	D_{3h}	CB 1.576 (1.556), BB 1.928 (1.853), CH 1.079 (1.071), BH 1.150 (1.183)	<i>i</i>
CB ₅ H ₇	C_s	C ¹ B ² 1.656 (1.60), C ¹ B ⁴ 1.671 (1.63), B ³ B ⁶ 2.132 (1.89), B ⁴ B ⁶ 1.642 (1.70), B ⁴ B ⁵ 1.879 (1.72), B ³ B ⁴ 1.716 (1.70), B ² B ³ 1.826 (1.87), B ² H _b 1.375	<i>j</i>
			
CB ₅ H ₉	C_s	B ¹ B ³ 1.883 (1.782), B ¹ B ⁴ 1.736 (1.781), B ³ B ⁴ 1.811 (1.759), B ⁴ B ⁵ 1.897 (1.830), B ¹ C ² 1.777, B ³ H _a 1.363, B ⁴ H _a 1.378, B ⁴ H _b 1.374, C ² B ³ 1.505	<i>k</i>
			
1,2-C ₂ B ₄ H ₆	C_{2v}	C ¹ C ² 1.751 (1.540), C ¹ B ³ 1.590 (1.627), C ¹ B ⁴ 1.717 (1.605), B ³ B ⁴ 1.806 (1.721), B ⁴ B ⁶ 1.614 (1.752)	<i>l</i>
			

Table VI (Continued)

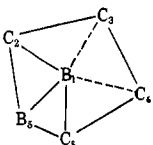
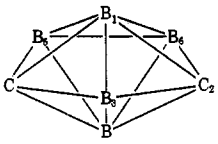
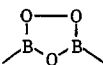
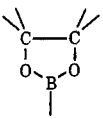
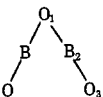
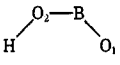
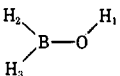
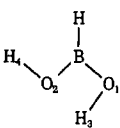
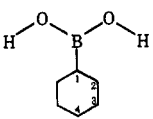
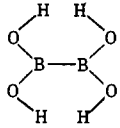
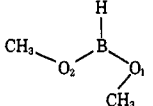
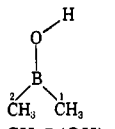
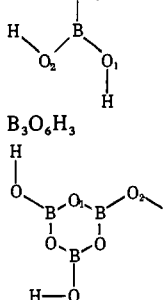
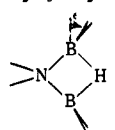
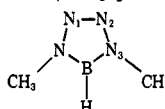
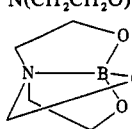
Molecule	Point groups	Calcd (obsd) values for geometrical variables ^a	Ref
$C_4B_2H_6$ 	C_3	B^1B^6 1.979 (1.886), B^1C^2 1.622 (1.709), B^1C^3 2.014 (1.697), C^2B^6 1.568 (1.541), C^4C^5 1.519 (1.436), C^3C^4 1.391 (1.424), B^6C^3 2.46	<i>m</i>
$2,4 C_2B_5H_7$ 	C_{2v}	B^1C^2 1.781 (1.708), B^1B^3 1.908 (1.818), B^1B^5 1.812 (1.815), C^2B^6 1.607 (1.563), C^2B^3 1.557 (1.546), B^5B^6 1.672 (1.651)	<i>n</i>
$B_3H_3O_3$ $B_2H_2O_3$ 	D_{3h} C_{2v}	BO 1.380 (1.380), BOB 123.4 (120.0), BH 1.171 (1.192) BO ¹ 1.387 (1.380), BO ² 1.409 (1.365), BH 1.163 (1.181), BOB 107.2 (104)	<i>o</i> <i>p</i>
$HBO_2(CH_2)_2$ 	C_{2v}	BO 1.374 (1.368), OC 1.418 (1.438), CC 1.580 (1.541), BH 1.168 (1.20)	<i>q</i>
$B(OCH_3)_3$ $(CH_3)_2BOB(CH_3)_2$	C_3 C_{2v}	BO 1.370 (1.367), OC 1.396 (1.424) BO 1.358 (1.359), BC 1.576 (1.573), BOB 145.8 (144.4)	<i>r</i> <i>s</i>
$BO\cdot$ $BO_2\cdot$ B_2O_2 $^1O^2B^3O^4B$ B_2O_3	$C_{\infty v}$ C_{2v} $C_{\infty v}$ C_{2v}	BO 1.169 BO 1.238, OBO 180.0 B^2O^1 1.184, B^2O^3 1.312, B^4O^3 1.289 B^2O^1 1.341, B^2O^3 1.181, BOB 123.2	
	C_3	BO ₁ 1.184, BO ² 1.333, O ² H 0.949, O ¹ BO ² 172.0, BO ² H 114.5	
HOBO 	C_3	BO 1.335, BH ² 1.172, BH ³ 1.168, OH ¹ 0.946, H ² BO 121.8, H ³ BO 117.5, H ¹ OB 117.5	
H_2BOH 	C_3	BO ¹ 1.366, BO ² 1.354, BH 1.177, O ¹ H 0.943, O ² H 0.945, BO ¹ H ³ 115.2, BO ² H ⁴ 115.2, O ¹ BO ² 117.6	
$HB(OH)_2$ 	C_3	BO 1.371, OH 0.945, BOH 116.5 BO 1.363, OH 0.945, C ¹ C ² 1.413, C ² C ³ 1.405, C ³ C ⁴ 1.405, C ¹ B 1.569, BOH 115.3	
$B(OH)_3$ PhB(OH) ₂ 	D_{3h} C_{2v}	BB 1.744, BO 1.363, OH 0.943, BBO 125.0, BOH 116.6	
$B_2(OH)_4$ 	C_3	BO ¹ 1.353, BO ² 1.368, CO ¹ 1.398, CO ² 1.396, BH 1.179, OBO 117.5	
$HB(OCH_3)_2$ 			

Table VI (Continued)

Molecule	Point groups	Calcd (obsd) values for geometrical variables ^a	Ref
B(OCH ₂ CH ₃) ₃ (CH ₃) ₂ BOH	C ₃ C _s	BO 1.369, OC 1.393, CC 1.545 BC ¹ 1.578, BC ² 1.573, BO 1.350, OH 0.945, C ¹ BC ² 122.9, HOB 117.8	
 CH ₃ B(OH) ₂	C _s	BO ¹ 1.360, BO ² 1.372, O ¹ H 0.946, O ² H 0.943, BC 1.578, O ¹ BO ² 115.0, HO ¹ B 118.4, HO ² B 116.2	
 B ₃ O ₆ H ₃	C _{3h}	BO ¹ 1.390, BO ² 1.354, O ² H 0.946, BO ¹ B 120.0, O ¹ BO ² 117.9, BO ² H 116.4	
B ₃ N ₃ H ₆	D _{3h}	BN 1.429 (1.435), BH 1.172 (1.258), NH .998 (1.050), NBN 118.2 (117.7), BNB 123.6 (121.1)	<i>t</i>
(CH ₃) ₃ NBH ₃	C _{3v}	BN 1.656 (1.638), CN 1.516 (1.483), BH 1.179 (1.211), CNB 109.0 (109.9), NBH 106.7 (105.3)	<i>u</i>
(CH ₃) ₃ NB(CH ₃) ₃ B ₂ H ₅ NH ₂	C _{3v} C _{2v}	BC 1.610 (1.56), BN 1.777 (1.80), CN 1.518 (1.47) BN 1.557 (1.558), BH _b 1.377 (1.355), BB 1.964 (1.916), BH _t 1.171 (1.193), HBH 119 (121), ϵ 16.1 (16.8)	<i>v</i> <i>w</i>
 ϵ = tilt of BH ₂ plane (CH ₃) ₂ NB ₂ H ₅	C _{2v}	BN 1.587 (1.544), BH _b 1.369 (1.365), BB 1.957 (1.916), BH _t 1.171 (1.191), NC 1.501 (1.488), ϵ 17.3 (16.7)	<i>x</i>
HBN ₄ (CH ₃) ₂	C _{2v}	BN 1.445 (1.413), BH 1.158 (1.195), N ₁ N ₂ 1.255 (1.291), N ₁ N ₃ 1.357 (1.376), NC 1.465 (1.454), NBN 100.3 (101.8)	<i>y</i>
 H ₃ NB(CH ₃) ₃ B(N(CH ₃) ₂) ₃ NH ₃ BH ₃ (CH ₃) ₂ NB(CH ₃) ₂ C ₂ H ₅ N·BH ₃ <i>p</i> -CH ₃ C ₆ H ₄ N·BH ₃ <i>p</i> -OCH ₂ C ₆ H ₄ N·BH ₃ <i>p</i> -NO ₂ C ₆ H ₄ N·BH ₃ N(CH ₂ CH ₂ O) ₃ B	C _{3v} C ₃ C _{3v} D _{2h} C _{2v} C _{2v} C _{2v} C ₃	BC 1.610, NH 1.016, HNB 112.1, CBN 106.4 BN 1.457, NC 1.600, CNB 122.2 BN 1.591, BH 1.179, NH 1.015, HBN 106.4, HNB 111.5 NB 1.422, CN 1.470, CB 1.575, CNB 122.1, CBN 120.6 BN 1.593 BN 1.591 BN 1.594 BN 1.596 BN 1.73, NC 1.511, BO 1.433, BNC 103.5, NBO 103.7, CC 1.568	<i>z</i> <i>aa</i> <i>bb</i>
 BH ₃ CO B(CH ₃) ₃ (CH ₃) ₄ B ₂ H ₂ B(CH ₂ CH ₃) ₃	C _{3v} D _{3h} D _{2d} C ₃	BH 1.176 (1.194), BC 1.495 (1.540), CO 1.163 (1.131) BC 1.558 (1.578) BB 1.867 (1.840), BH _b 1.365 (1.364), BC 1.582 (1.590) BC 1.573, CC 1.529	<i>z</i> <i>aa</i> <i>bb</i>

^a Bond length in Å and bond angle in deg. ^b S. H. Bauer, G. Herzberg, and J. W. C. Johns, *J. Mol. Spectrosc.*, **13**, 256 (1964). ^c G. Herzberg and J. W. C. Johns, *Proc. R. Soc. London, Ser. A.*, **298**, 142 (1967). ^d The geometries for the boron hydrides are taken from Lipscomb's symmetrized coordinates. ^e E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969). ^f E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **92**, 3837 (1970). ^g I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971). ^h See ref 16. ⁱ See ref 11. ^j See ref 10. ^k See ref *e*, Table IV. ^l See ref 12. ^m See ref 13. ⁿ See ref *h*, Table IV. ^o C. H. Chang, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1689 (1969). ^p See ref *j*, Table IV. ^q See ref *k*, Table IV. ^r G. Gundersen, *J. Mol. Struct.*, **33**, 79 (1976). ^s G. Gundersen and H. Vahrenkamp, *ibid.*, **33**, 97 (1976). ^t W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969). ^u See ref *o*, Table IV. ^v D. R. Lide, Jr., *J. Chem. Phys.*, **31**, 561 (1959). ^w See footnote *p*, Table IV. ^x See footnote *q*, Table IV. ^y C. H. Chang, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1677 (1969). ^z W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950). ^{aa} L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 3076 (1965). ^{bb} B. L. Carroll and L. S. Bartell, *Inorg. Chem.*, **7**, 219 (1968).

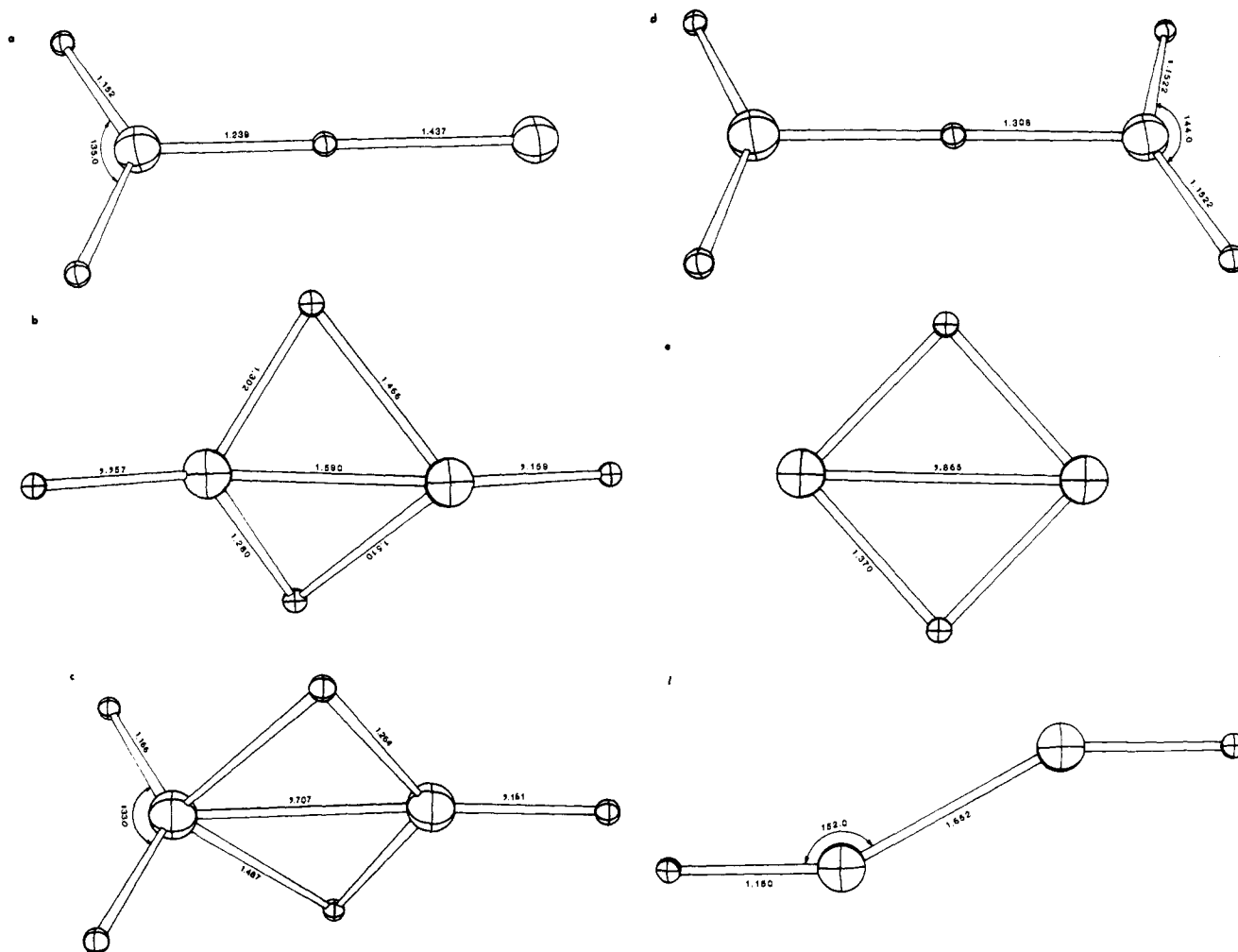


Figure 2. Geometries calculated by MNDO for cationic boron hydrides.

Table VII. Average Errors in MNDO Bond Lengths

Type of bond	Av absolute error in calcd bond lengths, Å
Two Center	
B-C	0.029
B-N	0.021
B-O	0.010
B-H	0.028 (0.013) ^a
Three Center	
B-C (carboranes)	0.053 ^b
B-B (carboranes)	0.083
B-B (boron hydrides)	0.050
B-H	0.062

^a Value in parentheses corrected for the systematic error of -0.028 Å. ^b Omitting the value for $C_4B_2H_6$; see text.

give to these values. The MNDO ones mostly lie in the same range as those given by the various RH calculations^{17,18} with one exception, the charge on oxygen in H_3BCO . According to MNDO, a net charge of $0.418 e$ flows from CO to BH_3 on formation of the adduct, nearly four times the RH estimate ($0.115 e$). Here the MNDO value is clearly in error because the corresponding dipole moment is much greater than that observed,¹⁹ because the MNDO value for the BC bond length is too small (by 0.045 Å, Table VI), and because the heat of complex formation calculated by MNDO is too negative (by 27.3 kcal/mol, Table IV). Evidently MNDO overestimates

Table VIII. Comparison of Calculated and Observed Ionization Potentials for A Complexes

X	MNDO, ^a eV		Obsd., ^b eV		$\Delta(IP_1^{MNDO} - IP_1^{obsd})$
	IP_1	IP_2	IP_1	IP_2	
H	10.55	10.71	9.72	10.63	.83
CH ₃	10.46	10.68	9.50	10.45	.96
OCH ₃	10.44	10.80	9.30	10.5	1.15
NO ₂	11.20	11.48	11.27	11.25	.93

^a Calculated via Koopmans' theorem. ^b See ref 15.

the strength of bonding in the complex and hence also the extent of the electronic reorganization accompanying in formation.

Another interesting species is the ammonia-borine adduct, $H_3N \cdot BH_3$, where there have been conflicting claims concerning the charges on nitrogen and boron. A RH calculation by Veillard and Daudel,²⁰ claimed to be near the Hartree-Fock limit, led to the predicted changes in charge on formation of the complex from $(H_3N + BH_3)$ shown in Table XI. It will be seen that the charges on boron and nitrogen change little, the main effect being a large transfer of charge ($0.25 e$) from the hydrogen atoms of ammonia to those of borine. MNDO, on the other hand, predicts a large transfer of charge ($0.30 e$) from nitrogen to boron, combined with a further transfer of $0.25 e$ from the hydrogen atoms of the ammonia moiety to boron, the charges on the borine hydrogen atoms remaining almost un-

Table IX. Higher Ionization Potentials IP

Molecule	Exptl ^a	MNDO ^b		Ab initio ^c	Assignment ^d
		Unscaled	Scaled ^e		
BH ₃ CO	11.92 ^e	12.60	11.59	11.81 ^f	2e
	14.13	15.41	14.18	14.09	2a ₁
	16.98	17.60	16.19	17.35	1e
	18.68	20.43	18.60	20.03	1a ₁
NH ₃ BH ₃	10.33 ^e	11.47	10.55	10.36 ^g	2e
	13.92	14.69	13.51	13.14	2a ₁
	17.75	19.39	17.84	18.37	1e
		21.33	19.62	18.05	1a ₁
		12.78	11.76	11.74 ⁱ	1b _{2g}
B ₂ H ₆	11.83 ^h	12.78	11.76	11.74 ⁱ	1b _{2g}
	13.33	13.97	12.85	12.93	2a _g
	13.93	14.84	13.65	13.42	1b _{3u}
	14.72	14.87	13.68	13.83	1b _{2u}
	16.09	19.17	18.13	16.03	1b _{1u}
B ₄ H ₁₀	11.5 ^j	12.50	11.50	11.11 ^j	5a ₁
	12.1	13.17	12.12	11.60	3b ₂
	12.62	13.01	11.97	12.66	2b ₁
	12.93	13.36	12.29	12.94	4a ₁
		14.28	13.14	13.17	2b ₂
	14.12	14.80	13.62	14.19	1a ₂
	14.52	15.56	14.32	14.25	3a ₁
	15.84	18.90	17.39	16.29	2a ₁
	18.1	21.96	20.20	19.21	1b ₁
	18.9	23.60	21.71	20.00	1b ₂
B ₃ N ₃ H ₆	10.09 ^k	10.96	10.08	10.21 ^l	1e''
	11.40	12.68	11.67	11.50	3e'
	12.83	14.09	12.96	13.05	1a ₂ ''
	13.72	16.02	14.74	13.81	2a ₁ '
	14.75	16.18	14.89	15.19	2e'
		17.04	15.68	15.21	1a ₂ '
	17.5	20.45	18.81	18.57	1a ₁ '
		21.57	19.84	18.08	1e'

Molecule	Exptl ^j	MNDO		X _α ^m	Ab initio	Assignment
		Unscaled	Scaled			
B ₅ H ₉	10.52	11.47	10.55	11.28	10.11	3e
	12.27	12.83	11.80	11.69	12.36	4a ₁
	12.56	13.48	12.40	13.06	13.30	2e
	14.33	15.28	14.06	13.24	14.53	1b ₁
	14.59	16.15	14.85	13.82	15.21	3a ₁
	14.83	17.19	15.81	15.16	14.67	1b ₂
	16.38	20.00	18.40	16.45	17.79	2a ₁
	18.37	23.29	21.43	18.42	20.27	1e

^a Vertical ionization potentials from UV-photoelectron spectroscopy in units of eV. ^b Calculated via Koopmans' theorem. ^c All orbitals are scaled by a factor of 0.92. ^d The numbering of the MO's refers to a valence basis set. The assignments are taken from the ab initio calculation except for B₅H₉ where the X_α assignment is used. ^e See footnote s, Table IV. ^f See ref 17. ^g D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 1044 (1969). ^h See footnote b, Table IV. ⁱ See ref 13. ^j See footnote c, Table IV. ^k See footnote n, Table IV. ^l M. F. Guest, I. H. Hillier, and I. C. Shenton, *Tetrahedron*, **31**, 1943 (1975). ^m H. J. T. Preston, J. J. Kaufman, and W. S. Koski, *Int. J. Quantum Chem., Symp.*, No. **9**, 137 (1975).

changed. Since it is difficult to see how there could be a large transfer of charge from the hydrogen atoms of ammonia to those of borine without a concomitant transfer of charge from nitrogen to boron, the MNDO values certainly do not seem less reasonable than those given by the RH calculations.

(E) **Species Observed in the Mass Spectrometer.** One possible application of semiempirical treatments such as MINDO/3 and MNDO is the interpretation of species observed in the mass spectrometer and the reactions leading to them. Such calculations could be of practical value in the interpretation of mass spectra and MINDO/3 has indeed provided valuable information in this connection, in particular concerning the rearrangements that take place in the C₇H₇⁺ and C₇H₈⁺ systems.²¹ In the case of the boron hydrides there are interesting possibilities of isomerism in the derived cations since these can be formed by loss of hydrogen from either bridging or terminal positions. We have therefore studied the structures of several such species with the results shown in Figure 2.

The vinyl cation is predicted by MNDO to have a classical

Table X. Comparison of Ab Initio and MNDO Charge Densities^a for B₂H₆ and BH₃CO

B ₂ H ₆	Minimum STO basis set ^b	Extended STO basis set ^b	MNDO
H _t	-0.067	0.023	-0.024
H _b	0.010	0.099	0.048
B	0.125	-0.145	0.000
BH ₃ CO	Ab initio ^c	Ab initio ^d	MNDO
H	-0.020	0.073	-0.017
B	-0.116	-0.334	-0.367
C	0.485	0.491	0.537
O	-0.308	-0.376	-0.119

^a MNDO charge densities were obtained by the method described in ref 5. Ab initio charge densities were obtained by a Mulliken population analysis. ^b See ref 16. ^c See ref 17. ^d See ref 18.

Table XI. Relative Changes in Charge Density between BH₃, NH₃, and BH₃NH₃ Using Ab Initio^a and MNDO Wave Functions

	Boron				Nitrogen				H _B	H _N
	2s	2p _x	2p _y	2p _z	2s	2p _x	2p _y	2p _z		
MNDO ^b	0.10	-0.04	-0.04	-0.50	0.20	-0.06	-0.06	0.22	-0.01	0.07
Ab initio	0.12	0.06	0.06	-0.25	0.00	-0.13	-0.13	0.30	-0.08	0.07

^a See ref 20. ^b The B-N bond is along the z axis.

Table XII. Comparison of Observed and Calculated Proton Affinities

	Proton affinity, kcal mol ⁻¹		
	Calcd	Exptl	Δ
(CH ₃) ₂ B=CH ₂ ⁻	360.4	365 ± 5 ^a	-5
B ₂ H ₆	136.7	147 ± 4 ^b	-10
B ₄ H ₁₀	132.3	144 ± 5 ^b	-12
B ₅ H ₉	155.3	167 ± 6 ^c	-12
B ₆ H ₁₀	174.3	>186 ^c	
B ₃ N ₃ H ₆	184.3	203 ± 7 ^d	-19

^a See footnote b, Table V. ^b R. C. Pierce and R. F. Porter, *J. Am. Chem. Soc.*, **95**, 3849 (1973). ^c J. J. Solomon and R. F. Porter, *ibid.*, **94**, 1443 (1972). ^d L. D. Betowski, J. J. Solomon, and R. F. Porter, *Inorg. Chem.*, **11**, 424 (1972).

structure, H₂C=C⁺H. The analogous boron ion, B₂H₃⁺, is on the other hand predicted to have a completely unsymmetrical structure (Figure 2a), corresponding to a proton π complex formed by H₂B·B⁺.

The structure predicted for B₂H₄⁺ (Figure 2b) is equally surprising. It corresponds to loss of two terminal hydrogen atoms from B₂H₆.

In the case of B₂H₅⁺, we found two stable isomeric species, differing only by 7 kcal/mol in energy. The more stable (Figure 2c) contains three terminal and two bridging hydrogen atoms while the other (Figure 2d) contains four terminal hydrogens and one bridging one. The two structures can be derived by loss of H⁻ from a terminal or bridging position of B₂H₆, respectively. As one might expect, loss of a bridging hydrogen is energetically less favorable.

The calculated heats of formation of these three ions agree quite well with experiment.²² B₂H₂⁺ is also predicted to occur in two stable isomeric forms (Figures 2e and 2f), one with a single bridging hydrogen, the other with two. Here, however, the observed²² heat of formation (329 kcal/mol) agrees much better with that calculated for the less stable (doubly bridged) structure, the other being lower in energy by 26 kcal/mol. It is of course possible that the former is formed more easily from diborane in the mass spectrometer, this involving merely the loss of all four terminal hydrogen atoms. We have not studied the energetics of the reactions leading from B₂H₆ to the two isomeric ions B₂H₂⁺.

(F) Proton Affinities. Table XII compares calculated and observed proton affinities for the few compounds for which experimental data are available. The agreement is satisfactory.

Summary and Conclusions

Given the problems that have arisen in previous attempts to calculate the heats of formation of boron compounds, it is gratifying to find at last a treatment which reproduces them in a reasonably satisfactory manner. The geometries of most of the "nonclassical" boron compounds also seem to be quite well reproduced, exceptions arising only in cases where the proportion of multicenter bonds is abnormally large (B₅H₉) or when cyclic four-center bonds are present (octahedral carboranes). Since the MNDO calculations can be carried out quite rapidly, including complete geometry optimization, for

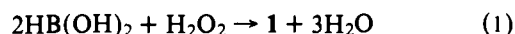
quite large molecules, the results should be of practical value in the general area of "nonclassical" boron chemistry.

Note Added in Proof. In view of a recent publication,²⁶ the triple bridged B₂H₅⁺ species was calculated and found to be 3 kcal/mol more stable than the double bridged species and 10 kcal/mol more stable than the single bridged form. In the optimized structure, *D*_{3h}, the bond lengths were BB 1.494 Å, BH_b 1.382 Å, and BH_t 1.164 Å.

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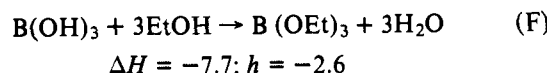
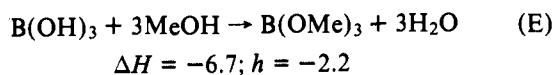
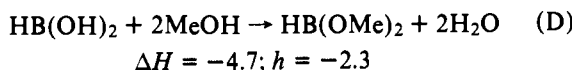
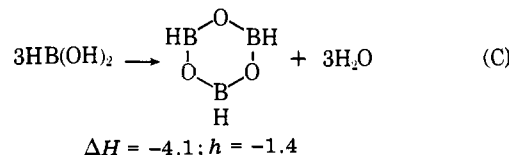
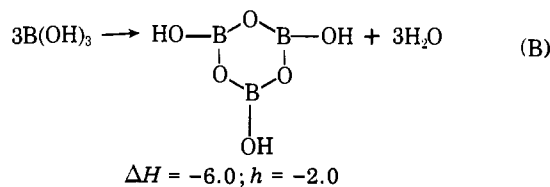
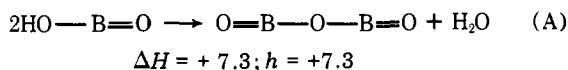
Appendix. The Heat of Formation of H₂B₂O₃ (1)

The experimental value (-153.1 kcal/mol) for the heat of formation of boronic acid (HB(OH)₂), listed in Table IV, seems reliable. Condensation of boronic acid with hydrogen peroxide gives 1;



Since the heats of formation of hydrogen peroxide (-32.5 kcal/mol) and water (-57.8 kcal/mol) are well known,²⁴ the heat of formation (ΔH_f(1)) of 1 could be found from eq 1 if the corresponding heat of reaction could be estimated.

The reactions in question involve condensation of a >BOH moiety with a hydroxy derivative, ROH, to form (>BOR + H₂O). The heat of reaction (*h*) for a number of processes of this kind can be estimated from data in Table IV; viz., (ΔH, *h* in kcal/mol):



In A, the heat of reaction is increased by the fact that the resonance energy of the reactant (HO-B=O ⇌ HO⁺=B-O⁻) is greater than that of the product.

The reverse may be the case in B and C since here the product (boroxine or trihydroxyboroxine) is potentially aromatic. However, the available evidence suggests that the aromatic stabilization energy is much less than that in benzene (20 kcal/mol).²⁵

In D-F, the inductive effects of the alkyl groups should stabilize the esters and so tend to make ΔH (and hence h) more negative. This is supported by the fact that the heat of reaction of ethanol with boric acid (F) is more negative than that of methanol (E).

In the conversion of boronic acid to **1**, neither resonance nor inductive effects should significantly affect the heat of reaction. From the examples above, it would seem that the value of h in such circumstances should be greater than zero but less than 7 kcal/mol. Since eq 1 involves loss of water from three separate pairs of OH groups, the corresponding heat of reaction should then lie between 0 and 21 kcal/mol; using this value and the heats of formation cited above, we find:

$$-165.3 \leq \Delta H_f(\mathbf{1}) \leq -144.3 \text{ kcal/mol} \quad (2)$$

This agrees reasonably well with our MNDO estimate (-142.9 kcal/mol) but is very much less than the claimed experimental value (-200.4 kcal/mol; Table IV). It seems clear that the latter must be grossly in error and that the best available estimate of the heat of formation of **1** is -155 ± 10 kcal/mol.

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CNDO Treatment for Faraday *B* Terms of Some Azaheterocycles

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Abstract: The magnetic circular dichroism (MCD) spectra of pyridine, pyridazine, pyrimidine, pyrazine, and 1,3,5-triazine were measured in the wavenumber region of 25000–50000 cm^{-1} . The transition energies, the oscillator strengths, and the Faraday *B* terms were calculated within the framework of the CNDO/S-CI approximation. The agreement between theoretical and experimental results is satisfactory. The perturbing mechanism for the Faraday *B* terms of the lowest $\pi^* \leftarrow n$ and the lowest $\pi^* \leftarrow \pi$ transitions were clarified on the basis of the calculated results.

The value of the magnetic circular dichroism (MCD) technique as a useful tool of spectral and molecular structural analysis has been confirmed extensively by an introduction of the quantum mechanical treatments of the Faraday parameters. It has been shown that the Pariser–Parr–Pople (PPP) method¹ has explained well the experimental Faraday *A* terms of aromatic organic compounds,^{2–5} which originate from the Zeeman splitting of the ground or excited electronic state. The Faraday *B* terms arising from the magnetic mixing among electronic states have also been successfully interpreted^{6–8} by the PPP method. Although the PPP method can easily treat $\pi^* \leftarrow \pi$ transitions of large aromatic systems within relatively short computer time and small computer capacity, several authors have pointed out the importance of an inclusion of all valence electrons in the molecular orbital treatment of the

Faraday parameters.^{9–12} The CNDO method,^{13,14} a semi-empirical LCAOMO–SCF procedure for all valence electrons, has advantage not only in taking account of the effects of the polarization of σ core, but also in dealing with the $\pi^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi$ transitions. Recently Sprinkel et al.¹¹ have indicated the necessity of including the $\pi^* \leftarrow \sigma$ states and interpreted that the main contribution to the Faraday *B* terms of the lowest $\pi^* \leftarrow \pi$ transition of indole comes from the magnetic coupling of the $\pi^* \leftarrow \sigma$ states around 50000 cm^{-1} with the lowest $\pi^* \leftarrow \pi$ state. The Faraday *B* terms of the vibronically induced $\pi^* \leftarrow n$ transition in formaldehyde^{10a} and the allowed ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\pi^* \leftarrow \sigma$) transition in benzene¹² have also been calculated using wave functions obtained from the CNDO approximation.

On the other hand, the electronic structures of pyridine, diazines, and 1,3,5-triazine have been investigated with the aid