MNDO Calculations for Compounds Containing Aluminum and Boron

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Parametrization of MNDO for aluminum and comparisons of calculated molecular properties with experimental values indicate the general usefulness of MNDO to study aluminum-containing compounds. Although results are not as good as for molecules containing only C, H, N, and O, they are nevertheless accurate enough to be useful, especially when predictive biases noted in this article are considered. Inclusion of the d orbital in the MNDO scheme may improve the aluminum results. Results for boron-containing molecules not previously reported are also reported in this article.

I. INTRODUCTION

The MNDO method[1] seems to be the best[2] theoretical procedure currently available for studying the chemical properties of larger molecules and a number of investigations[3-7] have shown it to be accurate enough to provide useful information. Calculations of this kind are at present limited to compounds containing hydrogen and the second-period elements Be through F,[3-6] only one of which (Be) is a metal. This limitation is doubly unfortunate because the chemistry of metals is an area of major current interest and practical importance and because beryllium is one of the least interesting metals in this connection, studies of its chemistry having been hampered severely by fears concerning its toxicity.

Since MNDO has recently[7] been extended with success to the nonmetallic elements Si through Cl, of the third period, we decided to try to parametrize it for aluminum, a metal of major importance whose chemistry has been studied in great detail and one of the few metals that can be treated in terms of an sp^3 valence shell. There have been several recent *ab initio* calculations on some aluminum-containing species.[8-10] Here we report the results of our investigations and calculations for a wide variety of aluminum compounds. In addition, some molecules containing boron have been calculated which were not included in the original boron article.[5] The results are compared with experimental results obtained from the JANNAF Thermochemical Tables.[11]

II. PARAMETRIZATION

The previously described method[1] was used to obtain the aluminum parameters given in Table I. Parameters for all other atoms were held constant at their previously determined values.[3-7] The properties used in the parametrization were the heats of formation and, where available, the dipole moments, the ionization potentials, and the bond lengths of ten molecules containing aluminum (Table II). The parametrization scheme routinely uses all of these parameters. All calculations on radicals were carried out with the "half-electron" method of the MNDO program. The parameters

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Table I. MNDO parameters for aluminum.

	Optimized		Derived
U_{ss}, eV	-23.807097	H_f^A, Kcal mol^{-1}	79.49
U_{pp}, eV	-17.519878	E_{el}^A, eV	-44.48407
ζ_s, ζ_p, au	1.444161	D_1, Å	0.740431
β_s, β_p, eV	-2.670284	D_2, Å	0.613135
α, Å^{-1}	1.868839	ρ_0, Å	0.889903
		ρ_1, Å	1.003893
		ρ_2, Å	0.720237

obtained in this way are reasonably consistent with those obtained for the other third-period elements Si through Cl,[7] although it should be noted that the Slater orbital exponent for silicon is less than that found for aluminum, contrary to expectation. As with all the third-period elements, first vertical

Table II. Calculated properties for parametrization set of compounds containing aluminum.

	ΔH_{298}^o, kcal mol^{-1}			Ionisation Potential, eV	Dipole Moment, D
	Calc.	Obs.	Error		
AlCl	-28.0	-12.3	-15.7	8.86 (8.5)[b]	2.45 (1-2)[c]
AlClO	-68.9	-83.2±5[a]	+14.3	11.71	1.37
AlCl$_3$	-140.7	-139.7±0.7	- 1.0	13.08 (12.01)[d]	
AlF	-83.6	-63.5±0.8	-20.1	8.62	0.31 (1.53)[e]
AlF$_3$	-291.4	-289.0±0.6	- 2.4	14.56	
AlH	46.0	62.0±5	-16.0	7.74 (8.4)[f]	0.08 (0.17)[g]
AlOH	-61.1	-43.0±3[a]	-18.1	8.00	2.56
Al$_2$Cl$_6$	-295.9	-309.6±0.8	+13.7	13.15	
Al$_2$F$_6$	-631.5	-629.5±4	- 2.0	14.45	
Al(CH$_3$)$_3$	-40.0	-20.9[h]	-19.1	10.67 (9.76)[d]	

[a] Assumed value.
[b] Estimated value, J. Berkowitz and J. L. Dehmer, *J. Chem. Phys.*, **57**, 3194 (1972).
[c] D. Lide, *J. Chem. Phys.*, **42**, 1013 (1965).
[d] G. K. Barker, M. F. Lappert, J. B. Pedley, G. J. Sharp, and N. P. C. Westwood, *J. Chem. Soc. Dalton Trans.*, 1765 (1975).
[e] F. J. Lovas and E. Tiemann, *J. Phys. Chem. Ref. Data*, **3**, 609 (1974).
[f] Calculated value, P. Rosmus and W. Meyer, *J. Chem. Phys.*, **66**, 13 (1977).
[g] Calculated value, P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **45**, 1063 (1966).
[h] M. B. Smith, *J. Organomet. Chem.*, **76**, 171 (1974).

Table III.   Heats of formation for all molecules.

Molecule	ΔH_f° Calculated Kcal Mol^{-1}	ΔH_f° Experimental Kcal Mol^{-1}	Error
$AlBO_2$	-146.2	-129.4 ± 4	-17.0
$AlCl$	- 28.0	- 12.3	-15.7
$AlCl^+$	174.7	206 ± 10	-31.3
$AlClF\cdot$	-124.9	-117 ± 15	- 7.9
$AlClF^+$	63.4	66 ± 30	- 2.6
$AlClF_2$	-241.8	-238.8 ± 1.5	- 3.0
$AlClO$	- 68.9	- 83.2 ± 5.0(a)	+14.3(a)
$AlCl_2\cdot$	- 74.8	- 67 ± 5	- 7.8
$AlCl_2^+$	118.7	115 ± 18	+ 3.7
$AlCl_2^-$	-130.9	-115 ± 25(a)	-15.9(a)
$AlCl_2F$	-191.6	-189.0 ± 1.5	- 2.6
$AlCl_3$	-140.7	-139.70 ± 0.70	- 1.0
AlF	- 83.6	- 63.5 ± 0.8	-20.1
AlF^+	114.8	165.4 ± 6	-50.6
$AlFO$	-113.7	-139 ± 4	+25.3
$AlF_2\cdot$	-171.2	-166 ± 10	- 5.2
AlF_2^+	14.1	22 ± 15	- 7.9
AlF_2^-	-209.6	-217 ± 20	+ 7.4
AlF_3	-291.4	-289.035 ± 0.6	- 2.4
$AlF_2O\cdot$	-202.6	-265 ± 7	+62.4
AlF_2O^-	-257.9	-313 ± 25	+55.1
AlF_4^-	-440.7	-476 ± 25	+ 35.3
AlH	46.0	62.0 ± 5.0	- 16.0
$AlOH$	- 61.1	- 43 ± 3 (a)	- 18.1 (a)
$AlOH^+$	121.5	130 ± 26 (a)	- 8.5 (a)
$AlOH^-$	- 41.1	- 55 ± 23 (a)	+ 13.9 (a)
AlO_2H	- 93.9	-110 ± 15 (a)	+ 16.1 (a)
AlN	140.7	104 ± 20	+ 36.7
$AlO\cdot$	- 1.9	16.4 ± 2	- 18.3
AlO^-	- 55.9	- 64.0 ± 4	+ 8.1
AlO^+	222.9	237.7 ± 5	- 14.8
$AlO_2\cdot$	- 14.6	- 44.9 ± 5	+ 30.3
AlO_2^-	- 90.6	- 140.9 ± 7	+ 50.3

Table III (*continued from previous page*)

Molecule	ΔH_f^0 Calculated Kcal Mol^{-1}	ΔH_f^0 Experimental Kcal Mol^{-1}	Error
Al_2O_2	-108.0 (O=Al-O-Al)	-104 ± 10	-4.0
$Al_2O_2^+$	78.7 (O=Al-O-Al)	126 ± 16	-47.3
Al_2O	-71.7	-31.2 ± 5	-40.5
Al_2O^+	109.0	159.45 ± 7	-50.5
Al_2F_6	-631.5	-629.45 ± 4	-2.0
Al_2Cl_6	-295.9	-309.64 ± 0.8	$+13.7$
BCl	9.1	33.8 ± 4.0	-24.7
BCl_3	-87.7	-96.31 ± 0.50	8.6
BCl^+	275.0	295 ± 10 (a)	-20.0 (a)
$BCl_2 \cdot$	-27.5	-19.0 ± 3.0	-8.5
BCl_2^+	180.1	161.1 ± 0.6	19.0
BCl_2^-	-91.8	-35.0 ± 25 (a)	-56.8 (a)
BCl_2F	-144.3	-154 ± 5	9.7
$BClF_2$	-201.7	-211.6 ± 5	9.9
$BClF \cdot$	-86.2	-75.0 ± 7 (a)	-11.2 (a)
BClO	-92.4	-75.6 ± 7.0	-16.8
BCl_2H	-58.3	-59.3 ± 1	1.0
B_2Cl_4	-116.7	-116.9 ± 1.2	0.2
$B_3O_3Cl_3$	-352.6	-390.0 ± 2	37.4
BF_2O	-189.6	-200 ± 15	10.4
BF	-63.2	-27.7 ± 3.3	-35.5
B_2 (exp. triplet)	189.4 (186.4)^t	195 ± 6.4	-8.6
BN (exp. triplet)	138.9 (137.9)^t	114 ± 30	23.9
HBO	-68.6	-47.4 ± 3.0	-21.2
HBO^-	-53.7	-58.4 ± 24	4.7
HBO^+	235.9	283.8 ± 12	-47.9
BO_2^-	-161.5	-166 ± 6	4.5
$B(OH)_2 \cdot$	-108.3	-114 ± 15	5.7
B_2O	-45.5	23 ± 25	-68.5
B_2O_2 (O-B-B-O)	-138.2	-109.0 ± 2.0	-29.2
B_2F_4O	-436.0	-453.65 ± 2	17.7
$B_3FH_2O_3$	-356.9	-382 ± 6	25.1
$B_3F_2HO_3$	-441.6	-475 ± 15	33.4

Table III (*continued from previous page*)

Molecule	ΔH°_f Calculated Kcal Mol^{-1}	ΔH°_f Experimental Kcal Mol^{-1}	Error
Al(CH$_3$)$_3$	− 40.0	− 20.9	− 19.1
AlH(CH$_3$)$_2$	− 19.1	− 6.4	− 12.7
AlCl(CH$_3$)$_2$	− 76.8	− 79.9	3.1

(a) = Assumed value.

[t] Triplet.

ionization potentials are predicted to be too high. This effect is due to the neglect in MNDO of specific interactions between the valence electrons and the core 1s, 2s, and 2p electrons, and was noted previously for the second-period elements[3] where the energies of orbitals with a high degree of 2s char-

acter were predicted to be too negative due to the neglect of interactions with the 1s core electrons. This effect could not be removed during the aluminum parametrization, except at the expense of increased errors elsewhere. Removal of the ionization potentials from the parametrization
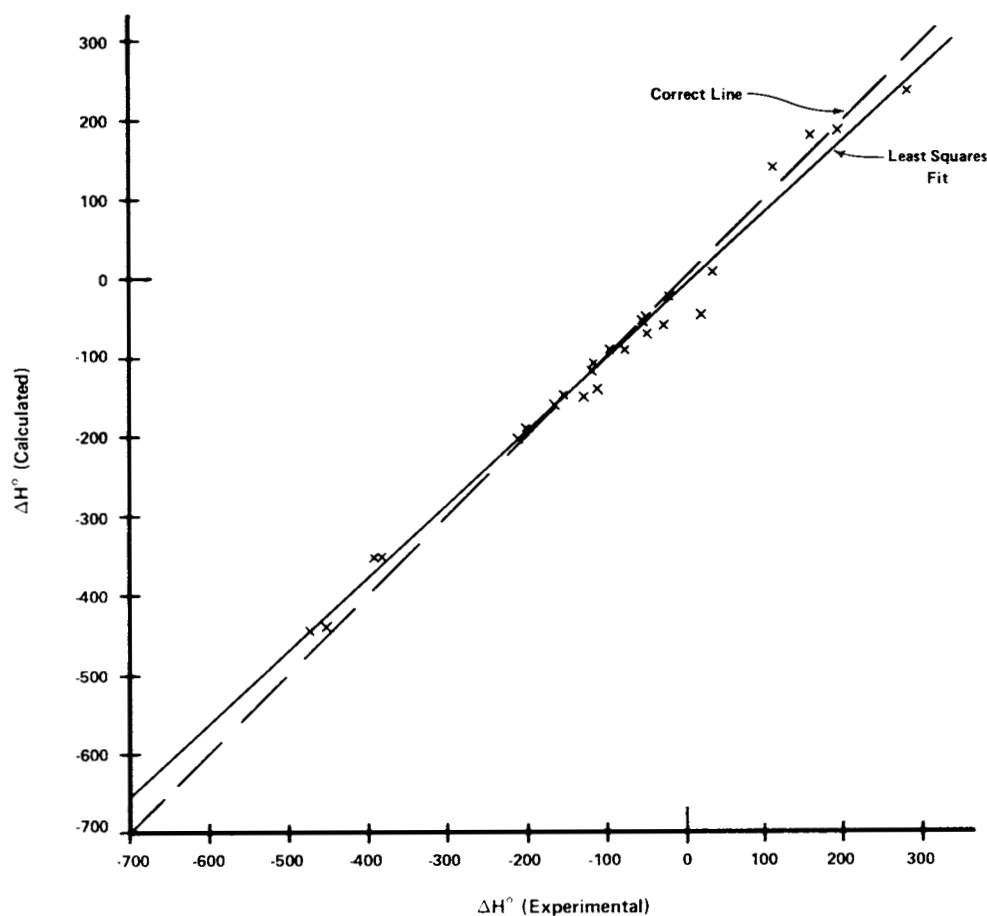

Figure 1. Calculated versus experimental heats of formation of aluminum-containing species. Least-squares fit: slope = 0.923, intercept = −10.3.

Table IV. Errors in heats of formation by class of compounds.

| Class (No.)	Average Absolute Error Kcal Mol^{-1}	Standard Deviation of Absolute Error Kcal Mol^{-1}	Average Error Kcal Mol^{-1}
ALUMINUM COMPOUNDS			
All (36)	20.3	18.2	-1.9
Basis Set Members (10)	12.2	7.5	-6.6
All AlCl Compounds (11)	8.4	9.0	-4.7
All AlF Compounds (15)	19.3	21.4	+5.4
All AlO Compounds (13)	32.6	19.5	+3.0
All Diatomics (9)	23.5	13.4	-13.6
All Triatomics (12)	20.0	18.6	-0.5
All Tetramers (9)	21.6	25.7	+4.5
All Pentamers (6) and Higher	14.3	12.2	+3.1
All Radicals (10)	31.2	20.9	-12.6
All Uncharged Radicals (6)	22.0	21.9	+8.9
All Cations (8)	26.1	21.3	-25.2
All Non-Radical Cations (4)	7.3	5.5	-5.4
All Anions (5)	31.2	22.7	+31.3
BORON COMPOUNDS			
All (25)	19.6	16.0	-2.7
All BCl Compounds (10)	13.6	11.3	+3.6
All BF Compounds (7)	20.2	11.2	+10.1
All BO Compounds (14)	24.3	18.1	-4.4
All Diatomics (4)	23.2	11.1	-11.2
All Triatomics (8)	23.9	22.8	-16.8
All Tetramers (7)	12.3	8.8	-0.9
All Pentamers and Higher (6)	19.9	14.9	+19.9
All Radicals (4)	16.7	20.9	-11.5
All Uncharged Radicals (2)	7.1	2.0	-1.4
All Cations (2)	33.5	20.4	-14.5
All Anions (2)	4.6	0.1	+4.6
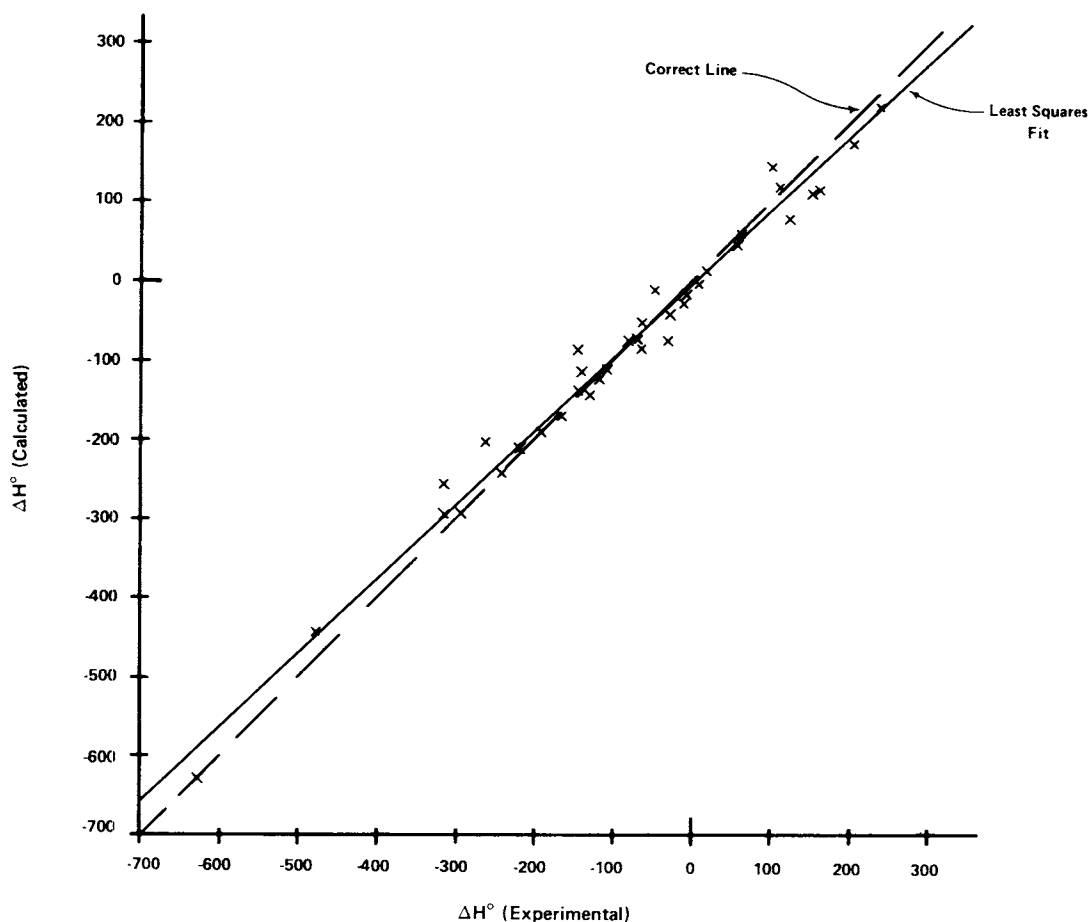
Figure 2. Calculated versus experimental heats of formation for boron-containing species. Least-squares fit: slope = 0.923, intercept = −8.24.

properties did not change the overall results appreciably.

III. RESULTS AND DISCUSSION

Heats of Formation

Table II presents the calculated and observed heats of formation (ΔH_f° at 25°C) for the ten molecules selected for the parametrization. The average absolute error is 12.2 kcal/mol and the average error is −6.6 kcal/mol, indicating that the predictions give results in which the molecules are too stable in comparison with experiment.

Table III compares the calculated and experimental heats of formation for all molecules which were studied, and Table IV summarizes the results by classes of compounds. In Table IV, results do not include compounds for which only an assumed experimental value was available. These assumed "experimental" values are denoted with an (a) in the tables to indicate that they are estimated by comparison with closely related systems.[11]

The errors given in Tables III and IV are clearly in excess of those for compounds which contain only C, H, N, and O.[3] However, they are not very different from the set of boron compounds calculated previously by Dewar.[5] The apparently worse agreement for the aluminum compounds may be due at least in part to the large number of radicals which were not predicted very well for this set of compounds.

Several trends became apparent in Table IV for both sets of compounds. First, the compounds

Table V. Molecular geometries.

Molecule	Parameter	Calculated[1]	Experimental[1]
$AlBO_2$	Al–O	1.632	1.66(a)
	O–B	1.288	1.36(a)
	B=O	1.193	1.20(a)
	⟩Al–O–B	179.8°	145°(a)
	⟩O–B=O	180.0°	180°(a)
AlCl	Al–Cl	2.075	2.1298
AlCl⁺	Al–Cl	2.004	2.05(a)
AlClF·	Al–Cl	2.081	2.10(a)
	Al–F	1.570	1.65(a)
	⟩Cl–Al–F	125.2°	120°(a)
AlClF⁺	Al–Cl	2.006	2.05(a)
	Al–F	1.532	1.60(a)
	⟩Cl–Al–F	179.9°	180°(a)
$AlClF_2$	Al–Cl	2.090	2.06(a)
	Al–F	1.587	1.63(a)
	⟩Cl–Al–F	121.8°	120°(a)
	⟩F–Al–F	116.7°	120°(a)
AlClO	Al–Cl	2.048	2.14(a)
	Al–O	1.483	1.62(a)
	⟩O–Al–Cl	180.0°	180°(a)
$AlCl_2$	Al–Cl	2.056	2.10(a)
	⟩Cl–Al–Cl	132.1°	120°(a)
$AlCl_2^+$	Al–Cl	1.994	2.05(a)
	⟩Cl–Al–Cl	180.0°	180°(a)
$AlCl_2^-$	Al–Cl	2.177	2.15(a)
	⟩Cl–Al–Cl	105.5°	105°(a)
$AlCl_2F$	Al–Cl	2.080	2.06(a)
	Al–F	1.579	1.63(a)
	⟩F–Al–Cl	120.4°	120°(a)
	⟩Cl–Al–Cl	119.1°	120°(a)
$AlCl_3$	Al–Cl	2.065	2.06
	⟩Cl–Al–Cl	120.0°	120°
AlF	Al–F	1.560	1.654
AlF⁺	Al–F	1.533	1.605(a)

Table V (*continued from previous page*)

Molecule	Parameter	Calculated[1]	Experimental[1]
AlFO	Al-F	1.580	1.63(a)
	Al-O	1.496	1.61(a)
	⊀F-Al-O	180.0	180°(a)
AlF$_2$·	Al-F	1.587	1.65(a)
	⊀F-Al-F	113.3°	120°(a)
AlF$_2^+$	Al-F	1.541	1.60(a)
	⊀F-Al-F	180.0°	180°(a)
AlF$_2^-$	Al-F	1.633	1.70(a)
	⊀F-Al-F	97.8°	105°(a)
AlF$_3$	Al-F	1.592	1.63+.01
	⊀F-Al-F	120.0°	120°
AlF$_2$O·	Al-F	1.588	1.63(a)
	Al-O	1.697	1.72(a)
	⊀F-Al-F	120.0°	120°(a)
	⊀O-Al-F	120.0°	120°(a)
AlF$_2$O$^-$	Al-F	1.638	1.63(a)
	Al-O	1.565	1.66(a)
	⊀F-Al-F	107.0°	120°(a)
	⊀O-Al-F	126.5°	120°(a)
AlF$_4^-$	Al-F	1.649	1.69
	⊀F-Al-F	109.4°	109.5°
AlH	Al-H	1.426	1.6477
AlOH	Al-O	1.570	1.87(a)
	O-H	0.921	0.96(a)
	⊀Al-O-H	179.8°	180°(a)
AlOH$^+$·	Al-O	1.534	1.90(a)
	O-H	0.927	0.96(a)
	⊀Al-O-H	179.4°	180°(a)
AlOH$^-$·	Al-O	1.663	1.90(a)
	O-H	0.941	0.96(a)
	⊀Al-O-H	115.2°	120°(a)
AlO$_2$H	Al=O	1.494	1.62(a)
	Al-O	1.655	1.87(a)
	O-H	0.931	0.94(a)
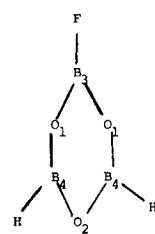
Table V (*continued from previous page*)

Molecule	Parameter	Calculated[1]	Experimental[1]
	∤O-Al=O	123.9°	180° (a)
	∤Al-O-H	175.8°	105° (a)
AlN	Al-N	1.443	1.65(a)
AlO·	Al-O	1.476	1.618
AlO⁻	Al-O	1.497	1.62(a)
AlO⁺	Al-O	1.470	1.92(a)
AlO₂·	Al-O	1.557	1.62(a)
	∤O-Al-O	180.0°	180° (a)
AlO₂⁻	Al-O	1.550	1.61(a)
	∤O-Al-O	179.9°	180° (a)
Al₂O₂	Al=O	1.497	1.72(a)
	Al-O	1.599	1.72(a)
	∤O=Al-O	180.0°	90° (a)
	∤Al-O-Al	179.3°	90° (a)

NOTE: Assumed form is a planar square. Calculated most stable form is O=Al-O-Al.

Al₂O₂⁺·	Al=O	1.482	1.66(a)
	Al-O	1.667 (Al₁-O)	1.66(a)
		1.550 (Al₂-O)	
	∤O=Al-O	179.7°	90° (a)
	∤Al-O-Al	179.9°	90° (a)

NOTE: Assumed form is a planar square. Calculated most stable form is O=Al₁-O-Al₂.

Al₂O	Al-O	1.606	1.72
	∤Al-O-Al	180.2°	180°±35°
Al₂O⁺·	Al-O	1.610	1.73(a)
	∤Al-O-Al	180.0°	180° (a)
Al₂F₆	Al-F	1.63	1.60(a)
	Al-F_bridge	1.80	1.77(a)
	∤F-Al-F	118.5°	120° (a)
Al₂Cl₆	Al-Cl	2.071	2.05
	Al-Cl_bridge	2.282	2.23
	∤Cl-Al-Cl	122.3°	120°
	∤Cl_b-Al-Cl_b²	85.8°	83°
BCl	B-Cl	1.7548	1.7157
BCl₃	B-Cl	1.762	1.75
	∤Cl-B-Cl	119.9°	120.0°

Table V (*continued from previous page*)

Molecule	Parameter	Calculated[1]	Experimental[1]
BCl[+]	B-Cl	1.668	1.73(a)
BCl$_2$·	B-Cl	1.720	1.73(a)
	⟩Cl-B-Cl	149.4	112.0°(a)
BCl$_2$[+]	B-Cl	1.644	1.74(a)
	⟩Cl-B-Cl	179.8°	180.0°(a)
BCl$_2$[-]	B-Cl	1.887	1.716(a)
	⟩Cl-B-Cl	112.5°	100.0°(a)
BCl$_2$F	B-Cl	1.786	1.73(a)
	B-F	1.297	1.295(a)
	⟩Cl-B-Cl	118.4°	120.0°(a)
	⟩Cl-B-F	120.8°	120.0°(a)
BClF$_2$	B-Cl	1.797	1.73(a)
	B-F	1.311	1.295(a)
	⟩F-B-Cl	121.6°	120.0°(a)
	⟩F-B-F	116.8°	120.0°(a)
BClF·	B-Cl	1.752	1.73(a)
	B-F	1.269	1.295(a)
	⟩Cl-B-F	139.6°	120.0°(a)
BClO	B-Cl	1.708	1.75(a)
	B-O	1.176	1.20(a)
	⟩Cl-B-O	180.0°	180.0°(a)
BCl$_2$H	B-Cl	1.760	1.75(a)
	B-H	1.163	1.13+0.2
	⟩Cl-B-Cl	120.2°	119.7°+3°
	⟩H-B-Cl	119.8°	120.15°+1.5°
B$_2$Cl$_4$	B-Cl	1.761	1.73+0.02
	B-B	1.647	1.75+0.01
	⟩Cl-B-Cl	119.2°	120.0°+2°
	⟩Cl-B-B	120.4°	120.0°+2°
	⟩Dihedral	90.1°	90.0°
B$_3$O$_3$Cl$_3$	B-Cl	1.770	1.75(a)
	B-O	1.380	1.36(a)
	⟩B-O-B	120.9°	120.0°(a)
	⟩Cl-B-O	118.8°	120.0°(a)
	⟩O-B-O	120.9°	120.0°(a)

Table V (*continued from previous page*)

Molecule	Parameter	Calculated[1]	Experimental[1]
BF_2O	B-F	1.314	1.30±0.05
	B-O	1.369	1.40±0.05
	∠O-B-F	117.0	117±5
	∠F-B-F	121.5	126±5
BF	B-F	1.266	1.265
B_2	B-B	1.764	-
		1.618[t]	1.589
BN	B-N	1.147	-
		1.294[t]	1.281
HBO	H-B	1.141	1.17(a)
	B-O	1.173	1.19(a)
	∠H-B-O	180.0	180(a)
HBO^-	H-B	1.224	1.25(a)
	B-O	1.222	1.37(a)
	∠H-B-O	131.1	123
HBO^+	H-B	1.168	1.19(a)
	B-O	1.310	1.25(a)
	∠H-B-O	179.8	180(a)
BO_2^-	B-O	1.234	1.25(a)
	∠O-B-O	180.0	180(a)
$B(OH)_2$·	H-O	0.974	0.97(a)
	B-O	1.329	1.27(a)
	∠H-O-B	122.4	105(a)
	∠O-B-O	137.9	180(a)
B_2O	B-O	1.304	1.26(a)
	∠B-O-B	179.1	150(a)
B_2O_2 (O-B-B-O)	O-B	1.173	1.20
	B-B	1.575	1.70
	∠O-B-B	179.9	180
$B_3FH_2O_3$	B_4-O_1	1.383	1.36(a)
	B_4-O_2	1.379	1.36(a)
	∠F-B_3-O_4	120.2	120(a)
	∠B_3-O_1-B_4	121.0	120(a)
	∠O_1-B_4-O_2	117.0	120(a)
	∠B_4-O_2-B_4	124.5	120(a)
	∠O_1-B_4-H	121.3	120(a)
	∠O_2-B_4-H	121.7	120(a)
	∠O_1-B_3-O_1	119.6	120(a)

[t] Triplet.
[1] Distances in angstroms, angles in degrees.
(a) Assumed value.

containing oxygen fare worse than the non-oxy-gen-containing compounds. Second, there seems to be a general trend with the size of the molecule. Diatomic species consistently are predicted to be too stable, while larger molecules (five atoms or more) are predicted best. In the case of the aluminum compounds, results for radicals and charged species are quite poor. In particular, the radical cations $AlCl^+$, AlF^+, $Al_2O_2^+$, and Al_2O^+ are all predicted grossly too stable. Thus, predictions for small charged or radical species are not very accurate. Both the triplet ground states of B_2 and BN are predicted correctly.

Figures 1 and 2 further clarify the predictive trends. For both classes of compounds, molecules with very negative heats of formation are predicted to be too unstable and those with positive heats of formation too stable. This trend results in the least-squares linear fits of calculated results to experimental results with slopes less than one, as shown in the figures.

Geometries

Table V displays calculated versus experimental geometries for the two sets of molecules. In the JANNAF Tables,[11] most of the "experimental" numbers for the aluminum-containing molecules are really based on comparisons with related systems. Again an (a) is used in our tables to denote these estimated values. Several general conclusions can be deduced even with many of the experimental numbers being estimated. It is apparent that bond lengths for the aluminum bonds are underpredicted. This is not the case for the boron bonds in the boron species. All kinds of boron bonds except for boron–boron bonds are predicted fairly accurately (average absolute error <0.03 Å). The average absolute error for boron–boron bonds is approximately 0.06 Å. In either case, however, there is no clear tendency of either overprediction or underprediction for boron bonds. Comparison of results for aluminum and boron species leads to the conclusion that d orbitals (currently not considered in MNDO) might be necessary to improve the accuracy of the aluminum calculations.

General molecular shapes are predicted quite well for both sets of molecules. Structures thought to be linear by comparison with related systems are generally predicted to be linear. Bond angles are usually predicted to within a few degrees.

The molecules Al_2O_2 and $Al_2O_2^+$ are quite interesting. The JANNAF Table gives an assumed

Table VI. Comparison beteen *ab initio* and MNDO results for aluminum–acetylene complexes.

Molecule	ΔH_f^o MNDO Kcal Mol^{-1}	ΔH_f^o Ab Initio[1] Kcal Mol^{-1}
HCAlCH	96.3	134.8
HCCAlH	93.2	126.6
H$_2$CCAl	78.0	113.3
Isolated HCCH + Al	136.8	134.8

[1] Calculated values from ref. 10.

square planar structure, but the MNDO calculation on both molecules predicts a linear O—Al—O—Al structure to be more stable. We considered the square planar and three open-ended structures in this calculation: O—Al—O—Al, Al—O—O—Al, and O—Al—Al—O.

The results of *ab initio* calculations using a large basis set have suggested that the π complex between an aluminum atom and acetylene is not bound.[10] The corresponding σ complex was calculated to be bound by about 8 kcal/mol, while the complex formed as a result of a 1,2 hydrogen shift was the most stable, being 21.5 kcal/mol lower in energy than the π complex. MNDO predicts a similar order of stabilities (Table VI), but also predicts the π complex to be 40.5 kcal/mol more stable than acetylene and an aluminum atom. This suggests that MNDO overestimates the stabilities of carbon–aluminum bonds.

IV. CONCLUSIONS

Calculations utilizing the MNDO method on a series of boron- and aluminum-containing molecules indicate that the method is useful in predictions of heats of formation and geometry for these compounds. However, biases in both the heats of formation predictions and geometry predictions were noted. In particular, inclusion of d orbitals in the MNDO method may be required to obtain accurate geometry predictions for aluminum-containing molecules.

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