

Optimization of Parameters for Semiempirical Methods. III Extension of PM3 to Be, Mg, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, and Bi

James J.P. Stewart

The Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, Colorado 80840

Received 21 May 1990; accepted 21 August 1990

Using a recently developed procedure for optimizing parameters for semiempirical methods,¹ PM3 has been extended to a total of 28 elements. Average ΔH_f errors for the newly parameterized elements are Be: 8.6, Mg: 8.4, Zn: 5.8, Ga: 14.9, Ge: 11.4, As: 8.5, Se: 11.1, Cd: 2.6, In: 11.3, Sn: 9.0, Sb: 13.7, Te: 11.3, Hg: 6.8, Tl: 6.5, Pb: 7.4, and Bi: 10.9 kcal/mol. For some elements the paucity of data has resulted in a method, which, while highly accurate, is likely to be only poorly predictive.

INTRODUCTION

Until recently, the rate determining step for obtaining parameters for semiempirical methods was determined by the time taken to optimize the parameters. When a new method was developed, parameters were normally only determined initially for four elements: H, C, N, and O. A new automatic optimization procedure¹ has been developed which changes the rate determining step to the assembly of suitable experimental reference data. Using that procedure, parameters for 12 elements were simultaneously optimized. Average errors in heats of formation for 11 of the 12 elements are less² than those obtained using MNDO or AM1, AM1 aluminum being the exception.³

Here, the PM3 method has been extended to include 13 main group metals and three transition metals. The transition metals all have filled d shells, allowing them to be considered using only a *sp* basis set. A comparison of the chemistries of these elements is presented here.

In principle, parameters for all elements available within a given method should be optimized simultaneously. In practice, serial optimization has hitherto proved necessary, for two reasons. First, the computational requirements have precluded the simultaneous optimization of parameters for many elements. Second, once a set of parameters had been made generally available, it was considered important⁴ that their value should not be changed until significant improvement has been made. Although the first obstacle to large-scale optimization of parameters has been overcome, the second reason for not optimizing all parameters for all elements simultaneously is still valid. For this reason, parameters for the original 12 elements reported earlier

were held constant while the parameters for the 16 elements reported here were optimized.

For several metals the dearth of reference data resulted in an apparent paradox: the optimized parameters allow PM3 to accurately reproduce the reference data, but the parameters are so poorly defined that the method is likely to perform poorly when used as a predictive tool. Only when enough reference data are used to uniquely define the parameter set will the accuracy of prediction equal that of the set used in the optimization of the parameters.

METHOD

The basic technique used in optimizing the parameters for the elements reported here was similar to that used earlier. In the case of cadmium, the scarcity of experimental data precluded a unique definition of the minimum in parameter space. To allow cadmium to be studied, the Gaussian core-core terms were omitted from the theoretical framework of PM3.

The optimization was carried out in the following manner: parameters for each new element were optimized using all data available for that element, but excluding data involving the other 15 new elements. A subsequent optimization was then carried out for each element in which all compounds of that element, including compounds between the element being parameterized and one or more of the other new elements, were used. This optimization used as trial parameters for the new elements the optimized parameters which had been obtained as a result of the first step. The results of these optimizations are reported in Table I.

Table I. Optimized parameters for MNDO-PM3.

	Be	Mg	Zn	Ga	Ge	As
Uss	-17.264752	-14.623688	-18.532198	-29.855593	-35.467196	-38.507424
Upp	-11.304243	-14.173460	-11.047409	-21.875371	-31.586358	-35.152415
Zs	0.877439	0.698552	1.819989	1.847040	2.237353	2.636177
Zp	1.508755	1.483453	1.506922	0.839411	1.592432	1.703889
B(s)	-3.962053	-2.071691	-0.715578	-4.945618	-5.325002	-8.232165
B(p)	-2.780684	-0.569581	-6.351864	-0.407053	-2.250157	-5.017386
Gss	9.012851	6.694300	9.677196	8.458554	5.376963	8.789001
Gsp	6.576199	6.793995	7.736204	8.925619	10.209529	5.397983
Gpp	6.057182	6.910446	4.980174	5.086855	7.671865	8.287250
Gp2	9.005219	7.090823	4.669656	4.983045	6.924266	8.210346
Hsp	0.544679	0.543300	0.600413	2.051260	1.337020	1.951034
ALP	1.593536	1.329147	1.350126	1.605115	1.972337	1.794477
K1	1.631572	2.117050	-0.111234	-0.560179	0.963173	-0.460095
L1	2.672962	6.009477	6.001478	5.623273	6.012013	1.983115
M1	1.791686	2.084406	1.516032	1.531780	2.163365	1.086793
K2	-2.110959	-2.547767	-0.132370	-0.272731	-0.959389	-0.088996
L2	1.968594	4.395370	1.995839	1.991843	5.749180	1.992944
M2	1.755871	2.063674	2.519642	2.183864	2.169372	2.140058
	Se	Cd	In	Sn	Sb	Te
Uss	-55.378135	-15.828584	-26.176205	-34.550192	-56.432196	-44.938036
Upp	-49.823076	8.749795	-20.005822	-25.894419	-29.434954	-46.314099
Zs	2.828051	1.679351	2.016116	2.373328	2.343039	4.165492
Zp	1.732536	2.066412	1.445350	1.638233	1.899992	1.647555
B(s)	-6.157822	-8.581944	-2.993319	-2.785802	-14.794217	-2.665146
B(p)	-5.493039	-0.601034	-1.828908	-2.005999	-2.817948	-3.895430
Gss	7.432591	9.206960	6.554900	10.190033	9.238277	10.255073
Gsp	10.060461	8.231539	8.229873	7.235327	5.277680	8.169145
Gpp	9.568326	4.948104	6.299269	5.673810	6.350000	7.777592
Gp2	7.724289	4.669656	4.984211	5.182214	6.250000	7.755121
Hsp	4.016558	1.656234	2.631461	1.033157	2.424464	3.772462
ALP	3.043957	1.525382	1.418385	1.699650	2.034301	2.485019
K1	0.047873		-0.343138	-0.150353	3.002028	0.033391
L1	6.007400		1.994034	6.005694	6.005342	5.956379
M1	2.081717		1.625516	1.704642	0.853060	2.277575
K2	0.114720		-0.109532	-0.044417	-0.018892	-1.921867
L2	6.008672		5.683217	2.257381	6.011478	4.973219
M2	1.516423		2.867009	2.469869	2.793311	0.524243
	Hg	Tl	Pb	Bi		
Uss	-17.762229	-30.053170	-30.322756	-33.495938		
Upp	-18.330751	-26.920637	-24.425834	-35.521026		
Zs	1.476885	6.867921	3.141289	4.916451		
Zp	2.479951	1.969445	1.892418	1.934935		
B(s)	-3.101365	-1.084495	-6.126024	-5.607283		
B(p)	-3.464031	-7.946799	-1.395430	-5.800152		
Gss	6.624720	10.460412	7.011992	4.989480		
Gsp	10.639297	11.223883	6.793782	6.103308		
Gpp	14.709283	4.992785	5.183780	8.696007		
Gp2	16.000740	8.962727	5.045651	8.335447		
Hsp	2.036311	2.530406	1.566302	0.599122		
ALP	1.529377	1.340951	1.620045	1.857431		
K1	1.082720	-1.361399	-0.122576	2.581693		
L1	6.496598	3.557226	6.003062	5.094022		
M1	1.195146	1.092802	1.901597	0.499787		
K2	-0.096553	-0.045401	-0.056648	0.060320		
L2	3.926281	2.306995	4.743705	6.001538		
M2	2.627160	2.965029	2.861879	2.427970		

RESULTS

Four properties were used in optimizing the parameters: the ΔH_f^{298} of the molecule in the gas phase, dipole moment, first ionization potential, and molecular geometry. Only results for those properties will be reported here.*

To allow comparison with MNDO⁵ and AM1,⁶ results for these methods are also presented. The specific parameter sets used are: MNDO—H⁷, C⁷, N⁷, O⁷, F⁸, Al⁹, Si¹⁰, P⁸, S¹¹, Cl¹², Ge¹³, Br¹⁴, I¹⁵, and Pb¹⁶; for

Am1—H⁶, C⁶, N⁶, O⁶, F¹⁷, Al³, Si¹⁸, P¹⁹, S²⁰, Cl¹⁷, Zn²¹, Ge¹³, Br¹⁷, Sn²², and Hg²³. Parameters for the first 12 PM3 elements are taken from the original PM3 work.¹ The AM1 parameter sets for S and Sn were those given in AMPAC 2.1.²⁴ No calculations reported here involve use of mixed parameter sets.

**Caution.* The accuracy of prediction of quantities such as vibrational frequencies, activation barriers, and higher ionization potentials is not known at this time. Until it is known how accurately the parameters reproduce these phenomena, extra care should be exercised when the parameters are used for such work.

STRUCTURE OF TABLES

As with the earlier work, the tables involved are quite large. Because of this, the tables have been structured to allow rapid location of any particular species. However, the large number of inorganic compounds made the Cox & Pilcher sequence²⁵ used earlier unsuitable here. Instead, the location of a particular species within a table is determined by the following rules. Each new element is presented in order of increasing atomic number. Within each set, the order of appearance of species is the same as that in the JANAF Thermochemical Tables.²⁶ This uses a modified Hill indexing system (*J. Am. Chem. Soc.*, **22**, 478 (1900)), and is purely alphabetic, based on the empirical formula. Compounds involving two new elements are cited for both elements: thus, germanium telluride will appear under germanium and under tellurium; however, in the statistical analysis each compound is counted only once.

HEATS OF FORMATION

Computed and observed heats of formation are presented in Table II. A summary of the average errors in ΔH_f for all species studied is given in Table III. In order to allow comparison with the first 12 PM3 elements parameterized, average errors for these elements are also presented in Table III. The averages reported in Table III are for all compounds reported here and in the earlier²⁷ work. Several faults in the earlier tables have been corrected, and about 100 more compounds have been surveyed; these additions and corrections are reflected in Table III.

The average error in ΔH_f for the newly parameterized elements is 9.6 kcal/mol, exactly the same as that for the first set of 12 elements. Preliminary attempts to determine parameters for the remaining main group elements (i.e., the alkaline metals and alkaline earths) indicate that average errors for these elements are likely to be larger than those reported here.

STATISTICAL GEOMETRIES

A comparison of experimental and computed geometries is given in Table IV, and a statistical summary of the errors in bond lengths is given in Table V. As with the ΔH_f , comparison with the original 12 elements is useful; average errors in bond lengths for the original 12 elements are also given in Table V. Average bond length and angle errors for all elements investigated are given in Table VI. With the exception of some magnesium and gallium compounds, most geometries are of useful accuracy.

DIPOLE MOMENTS AND IONIZATION POTENTIALS

Average errors (no. of compounds) in dipole moments are: PM3: 0.53D (77), MNDO: 0.75D (46), and AM1: 0.53D (42). For ionization potentials, the averages are: PM3: 0.90V (109), MNDO: 1.31 (59), and AM1 0.81 (40). The accuracy of prediction of dipole moments by PM3 is the same as that of AM1, while the prediction of ionization potentials is 11% inferior to AM1.

INDIVIDUAL ELEMENTS

Beryllium

Two possible geometries have been reported for dicyclopentadienylberyllium: a C_{5v} η^{10} ²⁸ and an η^1 - η^5 structure.²⁹ PM3 predicts a symmetric D_{5h} structure, although the beryllium atom is not rigidly held in place, the vibrational frequency for horizontal motion being only 126 cm^{-1} .

Magnesium

Four types of bonds are represented in the chemistry of magnesium: simple ionic bonds (MgF_2), covalent bonds ($\text{Mg}(\text{CH}_3)_2$), nonclassical bonds (η^{10} - Cp_2Mg), and dative bonds ($\text{CH}_3\text{MgBr}(\text{Et}_2\text{O})_2$). All four types are reproduced by PM3.

Although all four magnesium dihalides are observed to be linear,³⁰ PM3 predicts the $X\text{-Mg-X}$ angle to be 109.9° (fluoride), 154.9° (chloride), 165.8° (bromide) and 180.0° (iodide). An attempt was made to generate a set of magnesium parameters which would predict the observed angle; this was not successful, and further work is obviously needed. That a limited sp basis set should not only predict MgF_2 to be strongly bent, but also that it should remain bent despite efforts to make it linear, is unexpected, and may indicate a limitation in either the parameterization or the NDDO approximation.

Zinc

Most of zinc chemistry is relatively simple: zinc is almost always two coordinate, with the ligand-zinc-ligand angle being 180°. Some nonclassical structures do exist, however, examples being the pentahapto complexes involving cyclopentadienyl rings. Both PM3 and AM1 correctly predict the η^5 structure of cyclopentadienylmethylzinc, and the η^1 - η^5 structure of bis(pentamethylcyclopentadienyl)zinc, Figure 1.

Gallium

Average PM3 ΔH_f errors for gallium compounds are very large. No obvious reason for this is apparent,

although faulty optimization or inaccurate experimental data are the prime suspects.

Germanium

Of all metals reported here, the largest number of experimental reference data is available for germanium. It is likely that the predictive power of PM3 when applied to germanium compounds will be the

same as for the set reported here. A recent³¹ X-ray structure of 2,2,5,5-tetramethyl-1,3-diseleno-2-germacyclohexane has been published. This structure is qualitatively reproduced by PM3 (Fig. 2). In it, both germanium and selenium have organometallic and intermetallic bonds. Of the compounds investigated, this had the most complicated structure.

The ground state of the germanium atom is incorrectly predicted by PM3 to be $4s^4p^3$. Attempts

Table II. Comparison of experimental and calculated heats of formation.

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
BERYLLIUM							
Be	Beryllium, atom	77.0	77.0	0.0	0.0		a
BeBr	Beryllium bromide	28.7	22.5	-6.2	-0.1		b
BeBr ₂	Beryllium dibromide	-54.8	-53.5	1.3	11.8		b
BeCl	Beryllium chloride	14.5	5.7	-8.8	-10.8		b
BeCl ₂	Beryllium dichloride	-86.1	-86.5	-0.4	-3.7		b
BeF	Beryllium fluoride	-41.8	-50.1	-8.3	-10.9		c
BeF ₂	Beryllium difluoride	-189.7	-187.3	2.4	-2.2		c
BeH	Beryllium hydride (+)	276.4	252.9	-23.5	-37.8		b
BeH	Beryllium hydride	75.6	82.8	7.2	-15.3		c
BeHO	Beryllium hydroxide	-27.4	-26.3	1.1	1.2		b
BeH ₂	Beryllium dihydride	30.0	50.3	20.3	-24.4		b
BeH ₂ O ₂	Beryllium di-hydroxide	-161.8	-141.5	20.3	25.4		b
BeI	Beryllium iodide	40.6	31.3	-9.3	1.3		b
BeI ₂	Beryllium diiodide	-15.3	-14.4	0.9	-8.6		b
BeO	Beryllium oxide	32.6	53.0	20.4	6.0		b
Be ₂	Beryllium, dimer	152.3	136.7	-15.6	-26.9		b
Be ₂ O _F ₂	Be(OF) ₂	-287.9	-278.2	9.7	1.8		b
Be ₂ O	Beryllium oxide	-15.0	-19.7	-4.7	40.5		b
Be ₃ O ₃	Be ₃ O ₃	-251.9	-255.1	-3.2	71.8		b
MAGNESIUM							
MgBr	Magnesium bromide	-8.4	-21.8	-13.4			b
MgBr ₂	Magnesium dibromide	-72.4	-67.8	4.6			b
Mg ₂ Br ₄	Magnesium dibromide, dimer	-183.5	-181.2	2.3			b
C ₁₀ MgH ₁₀	Dicyclopentadienyl magnesium	32.6	31.6	-1.0			d
MgCl	Magnesium chloride	-10.3	-32.9	-22.6			b
MgCl ₂	Magnesium dichloride	-93.8	-82.4	11.4			b
Mg ₂ Cl ₄	Magnesium dichloride, dimer	-228.1	-232.1	-4.0			b
MgF	Magnesium fluoride	-56.6	-71.3	-14.7			b
MgF ₂	Magnesium difluoride	-173.0	-160.7	12.3			c
Mg ₂ F ₄	Magnesium difluoride, dimer	-410.7	-408.4	2.3			b
MgH	Magnesium hydride	40.5	41.8	1.3			b
MgH ₂ O ₂	Magnesium di-hydroxide	-135.0	-128.8	6.2			b
MgI ₂	Magnesium diiodide	-41.1	-44.6	-3.5			c
Mg	Magnesium (++)	561.3	555.1	-6.2			c
Mg	Magnesium (+)	213.1	217.9	4.8			c
Mg	Magnesium, atom	35.0	35.0	0.0			a
MgN	Magnesium nitride	69.0	104.0	35.0			b
MgO	Magnesium oxide	14.0	12.1	-1.9			b
MgS	Magnesium sulfide	62.0	42.4	-19.6			b
Mg ₂	Magnesium, dimer	68.8	70.1	1.3			c
ZINC							
CZnH ₃	Methylzinc (+)	215.1	228.9	13.8	12.6	9.3	c
C ₂ ZnH ₆	Dimethylzinc (+)	221.7	234.0	12.3	31.5	11.9	c
C ₂ ZnH ₆	Dimethylzinc	12.7	8.2	-4.5	7.2	7.2	c
C ₄ ZnH ₁₀	Diethylzinc	12.1	5.6	-6.5	0.9	2.1	c
C ₆ ZnH ₁₄	Di-n-propylzinc	-2.9	-1.4	1.5	7.5	5.4	d
C ₈ ZnH ₁₈	Di-n-butylzinc	-11.9	-11.5	0.4	7.2	0.8	d
ZnCl ₂	Zinc dichloride (+)	207.7	207.9	0.2	28.6	11.7	c
ZnCl ₂	Zinc dichloride	-63.6	-52.8	10.8	14.9	9.0	c
ZnH	Zinc hydride	54.4	56.9	2.5	-11.2	-3.4	a
ZnS	Zinc sulfide	48.3	51.5	3.2	18.2	30.0	f
ZnSe	Zinc selenide	56.7	54.5	-2.2			f
ZnTe	Zinc telluride	61.0	48.3	-12.7			f
Zn	Zinc (++)	665.1	662.8	-2.3	55.1	64.4	c
Zn	Zinc (+)	249.5	235.4	-14.1	-9.8	-5.2	c
Zn	Zinc, atom	31.2	31.2	0.0	0.0	0.0	a

Table II. (Continued)

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
GALLIUM							
GaBr	Gallium bromide	-11.7	-31.6	-19.9			c
C3GaH9	Trimethyl gallium	-10.8	-4.4	6.4			c
C6GaH15	Triethylgallium	-14.7	-33.8	-19.1			f
C12GaH27	Tributylgallium	-53.0	-73.5	-20.5			f
GaCl	Gallium chloride	-19.1	-21.2	-2.1			c
GaCl3	Gallium trichloride	-107.0	-79.7	27.3			c
GaH3NC13	GaCl3-NH3	-150.1	-128.1	22.0			c
Ga2Cl6	Ga2Cl6	-233.1	-251.9	-18.8			c
GaF	Gallium fluoride	-60.2	-46.2	14.0			c
Ga	Gallium (+++)	1390.2	1387.4	-2.8			c
Ga	Gallium (++)	680.5	698.9	18.4			c
Ga	Gallium (+)	205.9	205.5	-0.4			c
Ga	Gallium, atom	65.4	65.4	0.0			a
Ga	Gallium (-)	57.0	42.6	-14.4			b
GaH	Gallium hydride	52.7	67.6	14.9			c
GaHO	Gallium hydroxide	-27.4	-32.0	-4.6			c
GaI	Gallium iodide	6.9	-12.9	-19.8			c
GaO	Gallium oxide	66.8	35.3	-31.5			c
Ga2	Gallium, dimer	104.8	82.6	-22.3			c
Ga2I6	Ga2Br6	-76.0	-61.7	14.3			c
Ga2S	Ga2S	5.0	40.2	35.2			e
GERMANIUM							
C3GeH9Br	Trimethylbromogermane	-53.1	-47.8	5.3	14.9	12.1	g
GeBr	Germanium bromide	56.3	42.9	-13.4	-13.4	-13.0	c
GeBr2	Germanium dibromide	-15.0	-4.1	10.9	75.2	5.5	c
GeBr4	Germanium tetrabromide	-71.7	-66.7	5.0	37.7	2.3	c
CGe	Germanium carbide	151.0	178.6	27.6	73.4	52.6	c
C3GeH9Cl	Trimethylchlorogermane	-63.8	-60.1	3.7	1.8	5.2	g
C3GeH9	Trimethylgermanium (+)	165.0	176.5	11.5	-2.3	15.5	g
C3GeH9	Trimethylgermanium	2.2	-12.1	-14.3	-2.4	-3.8	g
C4GeH12	Tetramethylgermanium	-32.0	-34.3	-2.3	-0.8	5.8	g
C4GeH12O4	Tetramethoxygermanium	-230.4	-245.9	-15.5	-3.1	-22.2	h
C5GeH14O	Ethoxytrimethylgermane	-87.8	-91.3	-3.5	-0.4	-2.2	g
C5GeH15N	Dimethylaminetrimethylgermane	-29.1	-41.4	-12.3	-3.9	1.2	g
C6GeSnH18	GeMe3-SnMe3	-39.7	-32.2	7.5	10.3	24.2	g
C6Ge2H18	GeMe3-GeMe3	-62.5	-52.0	10.5	38.6	21.3	i
C6Ge2H18O	Bis(trimethylgermanium) oxide	-127.0	-122.5	4.5	8.9	15.9	g
C7GeH18	t-Butyltrimethylgermane	-55.7	-51.3	4.5	16.7	9.8	g
C8GeH20	Tetraethylgermanium	-38.6	-55.9	-17.3	-18.6	-21.9	f
C12GeH28	Tetrapropylgermanium	-54.2	-78.3	-24.1	-21.1	-33.2	f
C24GeH20	Tetraphenylgermanium	106.5	113.2	6.7	-16.4	-13.8	f
GeCl	Germanium chloride	37.1	27.7	-9.4	-19.7	-17.4	c
GeCl2	Germanium dichloride	-42.0	-31.8	10.2	-8.5	-2.0	c
GeCl4	Germanium tetrachloride (+)	156.8	132.9	-23.9	34.6	4.3	c
GeCl4	Germanium tetrachloride	-118.5	-127.6	-9.1	-7.3	-20.2	c
GeF	Germanium fluoride	-8.0	-3.3	4.7	-8.4	-11.7	c
GeF2	Germanium difluoride	-121.0	-107.6	13.4	-2.8	0.4	c
GeF4	Germanium tetrafluoride	-284.4	-290.3	-5.9	10.2	21.1	j
Ge	Germanium, atom	89.5	61.7	-27.8	0.0	0.0	a
GeH4	Germane	21.7	32.1	10.4	-8.2	7.3	c
GeI2	Germanium diiodide	11.2	-3.5	-14.7	49.2	21.6	c
GeI4	Germanium tetraiodide	-13.6	-6.7	6.9	70.7	17.3	c
GeO	Germanium oxide	-11.0	-5.9	5.2	11.9	20.3	c
GeTe	Germanium telluride	42.0	67.0	25.0			k
Ge2	Germanium, dimer	113.1	95.3	-17.8	77.6	15.5	c
Ge2H6	Digermane	38.8	45.6	6.8	8.1	0.3	c
Ge3H8	Trigermane	54.2	60.4	6.2	21.1	-12.4	c
ARSENIC							
As	Arsenic (++)	731.3	720.3	-11.0			c
As	Arsenic, atom	72.3	72.3	0.0			a
AsBr3	Arsenic tribromide	-31.6	-20.3	11.3			e
C3AsH9	Trimethylarsine	2.8	-14.9	-17.7			d
C3AsH9O3	Trimethyl arsenite	-131.1	-139.3	-8.2			d
C6AsH15	Triethylarsine	13.4	-20.4	-33.8			d
C6AsH15O3	Triethyl arsenite	-156.8	-155.2	1.6			d
C9AsH21O3	Tri-n-propyl arsenite	-173.7	-171.0	2.7			d
C18AsH15	Triphenylarsine	97.6	107.9	10.3			f

Table II. (Continued)

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
AsCl	Arsenic chloride	10.5	15.7	5.2			l
AsCl3	Arsenic trichloride	-62.5	-70.2	-7.7			c
AsF3	Arsenic trifluoride	-187.8	-190.2	-2.4			c
AsF5	Arsenic pentafluoride	-295.6	-287.8	7.8			e
AsH3	Arsine	15.9	12.7	-3.2			c
AsI3	Arsenic triiodide	6.9	27.3	20.4			l
AsN	Arsenic nitride	46.9	70.2	23.2			c
AsS	Arsenic sulfide	48.5	46.4	-2.1			e
AsSe	Arsenic selenide	49.5	55.7	6.2			e
AsTe	Arsenic telluride	54.7	61.1	6.4			e
As2	Arsenic, dimer	53.1	45.7	-7.5			c
As3	Arsenic, trimer	62.5	69.0	6.5			e
As4	Arsenic, tetramer	34.4	34.4	0.1			c
As4O6	Arsenic trioxide	-289.0	-287.9	1.1			c
SELENIUM							
AsSe	Arsenic selenide	49.5	55.7	6.2			e
BiSe	Bismuth selenide	42.0	54.9	12.9			c
SeBr2	Selenium dibromide	-5.0	-4.5	0.5			e
Se2Br2	BrSeSeBr	6.9	-14.2	-21.1			l
CSe2	Carbon diselenide	61.4	64.9	3.5			d
C4SeH10	Diethylselenium	-13.7	10.1	23.8			d
SeCl2	Selenium dichloride	-8.0	-37.9	-29.9			e
SeOF2	Seleninyl difluoride	-121.6	-134.3	-12.7			l
SeF4	Selenium tetrafluoride	-194.0	-209.0	-15.0			l
SeF6	Selenium hexafluoride	-267.0	-267.3	-0.3			k
SeH2	Hydrogen selenide	7.1	22.6	15.5			c
InSe	Indium selenide	56.0	57.7	1.7			e
SeO	Selenium oxide	14.8	20.1	5.3			l
SeO2	Selenium dioxide	-53.9	-30.0	23.9			k
Se	Selenium, atom	54.3	54.3	0.0			a
SeSi	Silicon selenide	48.5	62.3	13.8			e
SnSe	Tin selenide	28.9	49.1	20.2			e
ZnSe	Zinc selenide	56.7	54.5	-2.2			e
Se2	Selenium, dimer	33.0	36.0	3.0			l
Se3	Selenium, trimer	42.1	32.8	-9.3			e
CADMIUM							
C2CdH6	Dimethylcadmium (+)	223.2	218.2	-5.0			c
C2CdH6	Dimethylcadmium	25.8	30.6	4.8			d
C4CdH10	Diethylcadmium	25.5	25.9	0.4			d
Cd	Cadmium, atom	26.7	26.7	0.0			a
INDIUM							
InBr	Indium bromide	-13.6	-17.5	-3.9			k
InBr3	Indium tribromide	-67.4	-59.9	7.5			c
C3InH9	Trimethyl indium	40.8	13.2	-27.6			d
InCl	Indium chloride	-18.0	-13.3	4.7			k
InCl3	Indium trichloride	-89.4	-72.8	16.6			c
In2Cl3	In2Cl3	-103.6	-106.8	-3.2			c
InF	Indium fluoride	-48.6	-34.9	13.7			k
InH	Indium hydride	51.5	52.4	0.9			k
InI	Indium iodide	1.8	-7.2	-9.0			k
InI3	Indium triiodide	-28.8	-18.2	10.6			c
In	Indium (+++)	1272.0	1256.6	-15.4			c
In	Indium (++)	624.0	653.0	29.0			c
In	Indium (+)	187.3	200.5	13.2			c
In	Indium, atom	58.0	58.0	0.0			a
InO	Indium oxide	92.5	53.0	-39.5			c
InSb	Indium antimonide	82.3	80.1	-2.2			c
InSb2	Indium diantimonide	75.0	58.6	-16.4			c
InSe	Indium selenide	56.0	57.7	1.7			e
In2	Indium, dimer	91.0	90.3	-0.8			c
TIN							
C3SnH9Br	Trimethyltin bromide	-33.6	-35.0	-1.4	8.6	6.9	m
C12SnH27B	Tri-n-butyltin bromide	-65.7	-76.6	-10.9	0.9	-19.4	d
SnBr	Tin bromide	24.0	14.6	-9.4	-7.8	-14.8	n
SnBr2	Tin dibromide	-29.0	-45.7	-16.7	-9.2	-20.6	n
SnBr4	Tin tetrabromide	-75.2	-60.3	14.9	44.7	-9.8	c
C3SnH3Cl3	Methyltin trichloride	-99.8	-83.6	16.2	11.6	-5.0	f
C2SnH6Cl2	Dimethyltin dichloride	-71.0	-51.7	19.3	4.9	10.9	o
C2SnH5Cl3	Ethyltin trichloride	-102.0	-87.6	14.4	8.7	-9.5	f

Table II. (Continued)

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
C2SnH8	Dimethylstannane	21.0	12.4	-8.6	-15.2	-1.2	c
C3SnH9Cl	Trimethyltin chloride	-46.4	-39.9	6.5	2.3	-7.3	g
C3SnH9I	Trimethyltin iodide	-19.7	-20.5	-0.8	10.9	20.2	g
C3SnH10	Trimethyltin hydride	5.0	0.1	-4.9	-10.8	3.7	c
C4SnH12	Diethyltin dihydride	11.0	4.8	-6.2	-13.8	-3.3	c
C4SnH12	Tetramethyltin	-4.5	-12.8	-8.3	-12.3	2.0	c
C5SnH14	Ethyltrimethyltin	-7.0	-16.4	-9.4	-13.6	-1.5	f
C5SnH15N	Dimethylaminetrimethyltin	-4.3	-9.1	-4.8	7.1	16.5	g
C6SnH15Cl	Triethyltin chloride	-46.2	-50.4	-4.2	-10.2	-11.2	f
C6GeSnH18	GeMe3-SnMe3	-39.7	-32.2	7.5	10.3	24.2	g
C6SnH16	Propyltrimethyltin	-11.2	-21.5	-10.3	-14.1	-3.8	f
C7SnH18	t-Butyltrimethyltin	-16.0	-24.1	-8.1	0.1	1.4	f
C8SnH20	Tetraethyltin	-10.9	-27.2	-16.3	-21.0	-15.6	c
C9SnH14	Phenyltrimethylstannane	26.7	23.5	-3.2	-6.7	2.6	f
C24SnH20	Tetraphenyltin	114.4	122.1	7.8	23.6	13.4	d
SnCl	Tin chloride	16.0	7.6	-8.4	-21.6	-18.1	n
SnCl2	Tin dichloride	-56.4	-55.5	0.9	-25.7	-19.7	n
SnCl4	Tin tetrachloride	-112.7	-101.2	11.5	12.7	-20.2	c
SnF	Tin fluoride	-9.0	-17.5	-8.5	-11.4	4.6	n
SnF2	Tin difluoride	-116.0	-111.4	4.6	1.4	32.7	n
SnH	Tin hydride	49.0	63.3	14.3	0.7	13.7	n
SnH4	Tin tetrahydride (stannane)	38.9	35.5	-3.4	-8.4	3.2	c
SnI	Tin iodide	36.0	29.4	-6.6	0.4	4.3	n
SnI2	Tin diiodide	2.0	-15.2	-17.2	3.4	10.3	n
SnO	Tin oxide	3.6	4.5	0.9	9.6	27.6	c
SnS	Tin sulfide	28.5	37.7	9.2	-15.3	4.1	c
SnSe	Tin selenide	28.9	49.1	20.2			e
Sn	Tin, atom	72.2	72.2	0.0	0.0	0.0	a
SnTe	Tin telluride	38.4	53.6	15.2			k
ANTIMONY							
SbBr3	Antimony tribromide	-46.5	-36.5	-10.0			c
C3SbH9	Trimethylstibine	7.7	-0.3	-8.0			f
C6SbH15	Triethylstibine	10.4	-23.0	-33.4			f
C18SbH15	Triphenylstibine	104.1	98.6	-5.5			f
SbOCl	Antimony oxychloride	-25.5	-7.1	18.4			c
SbCl	Antimony chloride	-6.2	13.3	19.5			c
SbCl2	Antimony dichloride	-18.5	-34.3	-15.8			c
SbCl3	Antimony trichloride	-75.0	-72.4	2.6			c
SbCl5	Antimony pentachloride	-94.2	-91.6	2.6			c
SbF	Antimony fluoride	-11.3	-0.7	10.6			c
SbH3	Stibine	34.7	58.1	23.4			c
InSb	Indium antimonide	82.3	80.1	-2.2			c
InSb2	Indium diantimonide	75.0	58.6	-16.4			c
SbN	Antimony nitride	63.7	102.5	38.8			c
SbO	Antimony oxide	47.7	36.0	-11.8			c
Sb	Antimony (++)	646.0	616.9	-29.2			c
Sb	Antimony (+)	263.5	272.0	8.5			c
Sb	Antimony, atom	63.2	63.2	0.0			e
Sb2	Antimony, dimer	56.3	70.5	14.2			c
Sb4	Antimony, tetramer	49.0	51.5	2.5			c
TELLURIUM							
TeAl	Aluminum telluride	63.9	52.8	-11.1			e
AsTe	Arsenic telluride	54.7	61.1	6.4			e
BiTe	Bismuth telluride	42.8	43.1	0.3			c
TeBr2	Tellurium dibromide	2.6	-23.9	-26.5			l
TeCl2	Tellurium dichloride	-27.0	-33.3	-6.3			e
TeCl4	Tellurium tetrachloride	-49.5	-55.9	-6.4			l
TeF	Tellurium fluoride	-20.8	-35.1	-14.3			e
TeF2	Tellurium difluoride	-92.0	-110.6	-18.6			e
TeF4	Tellurium tetrafluoride	-226.5	-212.8	13.7			l
TeF6	Tellurium hexafluoride	-327.0	-334.1	-7.1			l
Te2F10	Te2F10	-554.4	-543.7	10.7			e
GeTe	Germanium telluride	42.0	67.0	25.0			k
TeH2	Hydrogen telluride	23.8	23.8	0.0			k
TeO	Tellurium oxide	17.8	36.5	18.7			e
TeO2	Tellurium dioxide	-14.8	-14.8	0.0			l
Te2O2	Tellurium oxide dimer	-26.0	-44.4	-18.4			e
SnTe	Tin telluride	38.4	53.6	15.2			k
Te	Tellurium, atom	47.0	47.0	0.0			e
ZnTe	Zinc telluride	61.0	48.3	-12.7			e
Te2	Tellurium, dimer	38.0	52.6	14.6			e

Table II. (Continued)

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
MERCURY							
CHgH3Br	Methylmercuric bromide	-4.4	-1.1	3.3	7.2	-6.6	c
C2HgH5Br	Ethylmercuric bromide	-7.2	-7.7	-0.5	11.2	-7.7	c
HgBr	Mercury bromide	24.9	10.7	-14.2	-10.1	-28.4	p
HgBr2	Mercury dibromide	-20.4	-26.9	-6.5	23.5	-23.5	p
CHgH3Cl	Methylmercuric chloride	-12.5	-3.4	9.1	-5.5	0.0	c
CHgH3	Methylmercury	40.0	45.9	5.9	-11.1	-1.8	c
C2HgH5Cl	Ethylmercuric chloride	-15.0	-9.8	5.2	-1.7	-1.4	c
C2HgH5I	Ethylmercuric iodide	3.3	2.9	-0.4	11.1	13.8	c
C2HgH6	Dimethylmercury (+)	233.9	243.1	9.2	-3.7	-3.6	c
C2HgH6	Dimethylmercury	22.3	28.4	6.1	-10.1	-12.2	c
C2HgN2	Mercuric cyanide	91.0	93.1	2.1	-21.9	-6.7	c
C4HgH10	Diethylmercury	17.8	15.8	-2.0	-5.6	-6.1	c
C6HgH5Cl	Phenylmercuric chloride	24.8	32.3	7.5	5.0	1.6	b
C6HgH14	Diisopropylmercury	9.7	2.7	-7.0	13.2	6.1	d
C6HgH14	Di-n-propylmercury	8.2	5.6	-2.6	-3.3	-0.4	d
C8HgH18	Di-n-butylmercury	-7.8	-5.1	2.8	4.6	2.0	d
C8HgH18	Diisobutylmercury	-9.2	-10.2	-1.0	19.4	9.9	d
C12HgH10	Diphenylmercury	93.8	98.4	4.6	7.8	7.4	d
HgCl	Mercury chloride	20.1	4.9	-15.2	-26.4	-22.8	c
HgCl2	Mercury dichloride	-35.0	-32.7	2.3	-2.0	-9.9	p
HgF	Mercury fluoride	1.0	-7.2	-8.2	-25.5	-11.7	c
HgF2	Mercury difluoride	-70.2	-51.0	19.2	3.3	16.0	p
HgH	Mercury hydride	57.2	48.1	-9.1	-19.4	-1.3	c
Hg	Mercury (++)	690.8	681.2	-9.7	-11.5	-5.5	c
Hg	Mercury (+)	256.8	271.5	14.7	-34.4	-31.3	c
Hg	Mercury, atom	14.7	14.7	0.0	0.0	0.0	a
HgI2	Mercury diiodide	-4.1	-4.2	-0.1	25.2	23.2	c
Hg2	Mercury, dimer (+)	244.3	237.4	-6.9	-27.6	-23.6	c
Hg2	Mercury, dimer	26.0	25.9	-0.1	4.2	2.0	c
THALLIUM							
TlBr	Thallium bromide (+)	203.3	214.8	11.5			c
TlBr	Thallium bromide	-9.0	-19.1	-10.1			c
TlCl	Thallium chloride (+)	209.0	211.6	2.6			c
TlCl	Thallium chloride	-16.2	-13.4	2.8			c
Tl2Cl2	Thallium chloride dimer	-49.4	-48.6	0.8			c
TlI	Thallium iodide	1.7	-12.7	-14.4			c
Tl	Thallium (+++)	1347.8	1349.9	2.1			c
Tl	Thallium (++)	658.4	656.9	-1.5			c
Tl	Thallium (+)	185.9	205.1	19.2			c
Tl	Thallium, atom	43.5	43.5	0.0			a
LEAD							
PbBr	Lead bromide	17.0	7.0	-10.0	-10.9		b
PbBr2	Lead dibromide	-25.0	-30.7	-5.7	-8.9		b
C3PbH9	Trimethyllead (+)	200.1	209.9	9.9	11.8		i
C3PbH9	Trimethyllead	46.7	62.0	15.4	-10.8		i
C4PbH12	Tetramethyllead	32.5	30.0	-2.5	-6.4		c
C6Pb2H18	Hexamethyldiplumbane	38.7	49.7	11.0	6.8		i
C7PbH18	t-Butyltrimethyllead	6.9	14.0	7.1	19.6		i
C8PbH20	Tetraethyllead	26.2	8.6	-17.5	-15.5		c
PbCl	Lead chloride (+)	178.2	174.4	-3.8	-18.4		b
PbCl	Lead chloride	3.6	1.7	-1.9	-18.9		b
PbCl2	Lead dichloride (+)	195.1	179.5	-15.6	-6.0		b
PbCl2	Lead dichloride	-41.6	-39.7	1.9	-35.4		b
PbF	Lead fluoride	-19.2	-21.0	-1.8	-3.4		b
PbF2	Lead difluoride	-104.0	-89.6	14.4	9.8		b
PbH	Lead hydride	56.5	54.2	-2.3	-15.8		p
PbH4	Lead tetrahydride (plumbane)	59.7	58.8	-0.9	3.4		q
PbI	Lead iodide	25.8	13.5	-12.3	0.4		b
PbI2	Lead diiodide	-0.8	-17.2	-16.5	9.5		b
PbO	Lead oxide	16.8	21.3	4.5	12.3		r
Pb	Lead (+)	219.0	217.9	-1.1	-0.6		c
Pb	Lead, atom	46.6	46.6	0.0	0.0		a
PbS	Lead sulfide	31.5	39.9	8.4	-12.9		b
Pb2	Lead, dimer	79.5	73.8	-5.8	-6.9		b

Table II. (Continued)

Empirical Formula	Chemical Name	Heat of Formation		Difference			Ref.
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
BISMUTH							
Bi	Bismuth (++)	606.1	588.8	-17.3			c
Bi	Bismuth (+)	219.1	237.9	18.8			c
Bi	Bismuth, atom	50.1	50.1	0.0			a
C3BiH9	Trimethylbismuth	46.1	43.1	-3.0			d
C6BiH15	Triethylbismuth	51.6	25.6	-26.0			d
C18BiH15	Triphenylbismuth	138.6	135.9	-2.7			d
BiCl	Bismuth chloride	6.0	17.8	11.8			e
BiCl3	Bismuth trichloride	-63.5	-42.6	20.9			c
BiF	Bismuth fluoride	-7.0	7.1	14.1			e
BiSe	Bismuth selenide	42.0	54.9	12.9			c
BiTe	Bismuth telluride	42.8	43.1	0.3			c
Bi2	Bismuth, dimer	52.5	55.2	2.7			c

References

- a: "CRC Handbook of Chemistry and Physics," 60th Edition, R. C. Weast, (Ed.), CRC Press, Boca Raton, FL, 1980.
- b: M. W. Chase, C. A. Davies, J. R. Downey, D. R. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, J. Phys. Chem. Ref. Data 14, Suppl. 1 (1985).
- c: D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, J. Phys. Chem. Ref. Data Suppl. 11, 2 (1982).
- d: J. O. Cox, G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970.
- e: I. Barin, O. Knacke, O. Kubaschewski, "Thermochemical Properties of Inorganic Compounds", Springer-Verlag, Berlin, 1977.
- f: G. M. Kolyakova, I. B. Rabinovich, E. N. Zoria, Dokl. Akad. Nauk SSSR, 209, 616 (1973).
- g: J. C. Baldwin, M. F. Lappert, J. B. Pedley, J. S. Poland, J. Chem. Soc., Dalton Trans., 1943 (1972).
- h: J. B. Pedley, G. Rylance, "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds," Sussex University, 1977.
- i: M. F. Lappert, J. B. Pedley, J. Simpson, T. R. Spalding, J. Organomet. Chem., 29, 195 (1971).
- j: CODATA, J. Chem. Thermodyn., 10, 903 (1978).
- k: D. D. Wagman, W. H. Evans, V. B. Parker, T. Hawlow, S. M. Bailey, R. H. Schumm, Natl. Bur. Stand. (U.S.), Tech. Note, No 270-3 (1968) and "Errata in NBS Technical Note 270-8" (1981).
- l: G. Ditter, U. Niemann, Philips J. Res., 37, 1 (1982).
- m: H. A. Skinner, Adv. Organomet. Chem., 2, 49 (1964).
- n: "Gmelins Handbuch der anorganischen Chemie", Zinn, Thiel Cl, Verlag Chemie, GMBH, Weinheim, 1972.
- o: G. A. Nash, H. A. Skinner, W. F. Stack, Trans. Faraday Soc., 61, 640 (1965).
- p: D. R. Stull, H. Prophet, Natl. Stand., Ref. Data Ser. (U.S., Natl. Bur. Stand.) NSRDS-NBS 37, 1971.
- q: F. E. Saalfeld, H. Svec, J. Inorg. Chem., 2, 46 (1963).
- r: M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, L. C. Walker, J. Phys. Chem. Ref. Data, 3, 311, (1974).

to force the configuration to $4s^2 4p^2$ resulted in a significant increase in error for the other species. The incorrect atomic configuration was preferred as the lesser of two evils.

Arsenic

With the exception of triethylarsine, the thermochemistry and stereochemistry of arsenic is predicted with satisfying accuracy. As with triethylphosphine and triethylstibine, the experimental ΔH_f of triethylarsine is unexpectedly large (13.4 kcal/mol) particularly when compared to the trimethylarsine (2.8 kcal/mol). PM3 predicts the triethyl derivative to be 5.5 kcal/mol more stable than the trimethyl. If this compound is ignored, the av-

erage error for arsenic compounds drops to 7.4 kcal/mol.

Selenium

Along with tellurium, selenium forms the widest range of types of bonds, bonding to 12 different elements, ranging from the highly ionic, SeOF_2 , to the 100% covalent Se_2 . In addition, oxidation states from -2 (H_2Se) to +6 (SeF_6) are reproduced.

Cadmium

Because of the paucity of experimental data on cadmium compounds, the number of reference data available used is very small. As a result, the ensuing

Table III. Statistical analysis of ΔH_f errors.

Element	No.	PM3	No.	MNDO	No.	AM1
First 12 PM3 elements (Revised)						
H	570	6.9 (1.2) [13.2]	569	13.8 (5.6) [26.7]	569	8.2 (0.6) [14.9]
C	558	6.4 (1.3) [9.5]	557	13.6 (4.7) [24.3]	557	8.2 (0.4) [11.9]
N	156	9.0 (-2.5) [20.8]	156	19.5 (9.6) [29.5]	156	12.2 (1.4) [22.5]
O	315	9.3 (-0.5) [14.3]	314	32.4 (26.1) [70.3]	314	14.7 (5.9) [26.8]
F	153	9.3 (1.9) [13.9]	154	44.5 (36.7) [88.2]	154	23.5 (7.7) [51.8]
Al	50	15.6 (0.9) [21.7]	50	22.5 (3.3) [32.8]	50	13.5 (3.2) [19.8]
Si	79	10.1 (1.9) [14.2]	80	23.5 (14.2) [35.4]	80	17.7 (7.1) [38.2]
P	73	14.8 (-3.1) [23.8]	73	38.4 (24.7) [55.4]	73	22.1 (7.2) [37.0]
S	125	14.4 (1.6) [25.0]	125	51.6 (37.7) [88.8]	125	21.4 (-6.9) [34.7]
Cl	107	10.0 (-0.6) [15.7]	107	32.1 (22.4) [96.4]	107	18.0 (3.6) [36.4]
Br	71	12.9 (2.5) [18.4]	71	28.2 (16.6) [46.8]	71	21.8 (5.4) [37.7]
I	76	12.0 (-0.1) [17.9]	76	31.6 (12.3) [62.2]	76	26.0 (3.2) [53.8]
Totals:	886	9.6 (0.1) [17.4]	886	23.7 (13.3) [55.2]	886	14.2 (1.8) [30.0]
All 28 PM3 elements						
H	676	7.3 (1.0) [13.0]	644	13.4 (4.9) [25.6]	631	8.2 (0.7) [14.6]
Be	19	8.6 (0.2) [11.5]	19	15.8 (1.0) [24.0]		
C	643	6.8 (1.0) [9.9]	620	13.3 (4.5) [23.6]	614	8.3 (0.6) [12.0]
N	163	9.3 (-1.8) [20.8]	159	19.4 (9.3) [29.3]	159	12.1 (1.4) [22.4]
O	344	9.4 (-0.6) [14.3]	326	31.8 (25.7) [69.1]	319	14.7 (6.0) [26.7]
F	182	9.4 (1.7) [13.5]	166	41.8 (33.8) [84.9]	161	23.0 (7.7) [50.8]
Mg	20	8.4 (-0.3) [12.2]				
Al	51	15.5 (0.7) [21.6]	50	22.5 (3.3) [32.8]	50	13.5 (3.2) [19.8]
Si	80	10.2 (2.1) [14.2]	80	23.5 (14.2) [35.4]	80	17.7 (7.1) [38.2]
P	73	14.8 (-3.1) [23.8]	73	38.4 (24.7) [55.4]	73	22.1 (7.2) [37.0]
S	131	14.3 (1.8) [24.8]	128	50.7 (36.8) [87.8]	127	21.3 (-6.5) [34.6]
Cl	158	10.2 (-0.1) [15.0]	133	28.5 (17.3) [86.8]	127	16.8 (2.2) [33.8]
Zn	15	5.8 (0.2) [7.9]	13	15.8 (12.5) [21.4]	13	12.3 (11.0) [20.8]
Ga	21	14.9 (-2.4) [18.1]				
Ge	35	11.4 (-0.7) [13.4]	34	20.5 (12.5) [30.7]	34	13.8 (1.8) [17.7]
As	23	8.5 (0.4) [11.8]				
Se	20	11.1 (2.1) [14.3]				
Br	101	11.9 (0.4) [16.7]	88	26.1 (15.4) [43.5]	84	20.5 (3.2) [35.1]
Cd	4	2.6 (0.0) [3.5]				
In	18	11.3 (-0.5) [15.6]				
Sn	37	9.0 (-0.1) [10.5]	35	10.8 (-1.6) [13.9]	35	10.9 (1.0) [13.8]
Sb	20	13.7 (1.4) [17.3]				
Te	20	11.3 (-0.8) [13.4]				
I	94	11.5 (-1.0) [16.9]	87	29.8 (12.7) [59.0]	83	25.1 (4.3) [51.8]
Hg	29	6.8 (-0.2) [8.7]	29	11.6 (-3.5) [15.0]	29	9.5 (-3.9) [13.2]
Tl	10	7.4 (-0.7) [9.2]				
Pb	23	7.3 (-1.5) [9.0]	23	10.6 (-4.2) [13.1]		
Bi	12	10.9 (2.7) [13.8]				
Totals:	1201	9.6 (0.0) [16.3]	1038	22.3 (11.7) [51.6]	996	13.9 (1.7) [28.8]
Errors are in kcal/mol.						
Errors, in order, are: unsigned average, (signed average), [root mean square].						

parameters allow the available data to be reproduced with unprecedented accuracy. An unfortunate consequence of the small number of reference data is that the parameter set could not be well defined, and it is highly likely that the predictive power of PM3 when applied to cadmium compounds will be very poor. Because of the small number of reference data, the Gaussian parameters for cadmium were omitted.

Indium

With the exception of the In-X-In angles for the oxide and selenide, all indium geometries are in good

agreement with experiment. PM3 predicts the In-X-In angles to be 180°. This fault does not occur in In₂Te, but does occur in Ga₂O.

Tellurium

Tellurium exhibits oxidation states of -2, 0, 1, 2, 3, 4, 5, and 6. Three hypervalent compounds are represented here: TeO₃, TeF₆, and Te₂F₁₀. Te₂F₁₀ is predicted as having a *D_{4d}* structure with an unusually long Te-Te bond (3.18 Å). The total bonding between the two TeF₅ groups is quite large: 0.943, composed of a bond³² of order 0.690 to the other tellurium, four bonds of order 0.053 to the nearer fluorine atoms,

and long distance bonds of order 0.039 to the distant axial fluorine.

Lead

An inconsistency in the reported value of the ΔH_f of PbCl_4 has been found. The JANAF tables give the

$\Delta H_f(g)$ of PbCl_4 as -132.0 ± 20 kcal/mol,²⁶ while the National Bureau of Standards reports³³ a value of -78.7 kcal/mol for the $\Delta H_f(l)$. As heats of vaporization are always positive, the $\Delta H_f(g)$ must be more positive than -78.7 kcal/mol. PM3 predicts the $\Delta H_f(g)$ of PbCl_4 to be -61.8 Kcal/mol. This suggests that the NBS value is likely to be more accurate than the JANAF value.

Table IV. Comparison of experimental and calculated molecular geometries.

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	MNDO-PM3	Errors MNDO	AM1	Ref.
BERYLLIUM								
BeBr ₂	Beryllium dibromide	Be-Br	1.910	1.814	-0.096	0.102		a
C ₅ BeH ₅ Cl	Cyclopentadienylberyllium chloride	C-H	1.090	1.084	-0.006	-0.005		b
		Be-ring	1.485	1.683	0.198	0.068		
		Be-Cl	1.839	1.770	-0.069	0.118		
		Be-Cl	1.770	1.744	-0.026	0.143		a
BeCl ₂	Beryllium dichloride	Be-Cl	1.770	1.744	-0.026	0.143		a
BeF	Beryllium fluoride	Be-F	1.361	1.373	0.012	0.098		a
BeF ₂	Beryllium difluoride	Be-F	1.400	1.402	0.002	0.060		a
BeH	Beryllium hydride (+)	Be-H	1.312	1.273	-0.039	-0.065		a
BeH	Beryllium hydride	Be-H	1.343	1.307	-0.036	-0.054		a
BeI	Beryllium iodide	Be-I	2.132	2.223	0.091	0.023		a
BeI ₂	Beryllium diiodide	Be-I	2.120	2.069	-0.051	0.001		a
BeO	Beryllium oxide	Be-O	1.331	1.304	-0.027	0.004		a
BeS	Beryllium sulfide	Be-S	1.741	1.652	-0.089	-0.105		a
MAGNESIUM								
C ₁₀ MgH ₂₅ O	EtMgBr.(Et ₂ O) ₂	Mg-Br	2.480	2.422	-0.058			c
		Mg-C	2.160	1.891	-0.269			
		C-Mg-Br	124.0	106.3	-17.7			
		Mg-O	2.060	1.871	-0.189			
		O-Mg-C	95.6	99.3	3.7			
		Mg-O	2.030	1.871	-0.159			
		O-Mg-Br	104.0	110.6	6.6			
		Mg-Br	2.360	2.355	-0.005			
		Mg-Br	2.340	2.352	0.012			
		Mg-Cl	2.199	1.875	-0.324			
MgCl ₂	Magnesium dichloride	Mg-Cl	2.186	1.887	-0.299		a	
		Cl-Mg-Cl	180.0	156.7	-23.3		d	
MgF	Magnesium fluoride	Mg-F	1.750	1.754	0.004		a	
MgF ₂	Magnesium difluoride	Mg-F	1.771	1.762	-0.009		d	
MgH	Magnesium hydride	Mg-H	1.730	1.687	-0.043		a	
MgI ₂	Magnesium diiodide	Mg-I	2.520	2.421	-0.099		a	
MgO	Magnesium oxide	Mg-O	1.749	1.780	0.031		a	
MgS	Magnesium sulfide	Mg-S	2.143	2.358	0.215		a	
Mg ₂	Magnesium, dimer	Mg-Mg	3.9	5.1	1.2		a	
ZINC								
ZnBr ₂	Zinc dibromide	Zn-Br	2.204	2.095	-0.109	0.031	-0.093	d
C ₂ ZnH ₆	Dimethylzinc	Br-Zn-Br	180.0	180.0	0.0	0.0	0.0	
		Zn-C	1.930	1.937	0.007	-0.046	-0.031	e
C ₄ ZnH ₁₀	Diethylzinc	C-Zn-C	180.0	180.0	0.0	0.0	0.0	
		Zn-C	1.950	1.965	0.015	0.000	-0.021	e
		C-C-Zn	114.5	100.5	-14.0	0.0	-0.6	
C ₆ ZnH ₈	Cyclopentadienylmethylzinc	C-Zn-C	180.0	180.0	0.0	0.0	0.0	
		C-C	1.438	1.436	-0.002	0.080	0.000	f
		C-Zn	2.280	2.342	0.062	-0.359	0.078	
		Zn-C(H ₃)	1.903	1.946	0.043	-0.022	-0.023	
C ₆ ZnH ₁₄	Di-n-propylzinc	C-C-C	113.6	112.9	-0.7	1.8	-3.2	e
		Zn-C	1.952	1.972	0.020	-0.043	-0.019	
		Zn-C-C	114.5	101.0	-13.5	3.8	-1.1	
		C-Zn-C	180.0	180.0	0.0	0.0	0.0	
ZnCl ₂	Zinc dichloride	Zn-Cl	2.062	2.064	0.002	0.053	0.005	d
ZnF ₂	Zinc difluoride	Cl-Zn-Cl	180.0	180.0	0.0	0.0	0.0	
		Zn-F	1.742	1.740	-0.002	-0.062	0.006	d
ZnI ₂	Zinc diiodide	F-Zn-F	180.0	180.0	0.0	0.0	0.0	
		Zn-I	2.401	2.404	0.003	-0.019	-0.055	d
		I-Zn-I	180.0	180.0	0.0	0.0	0.0	
GALLIUM								
GaBr	Gallium bromide	Ga-Cl	2.352	2.394	0.042			g
GaH ₃ NBr ₃	Gallium tribromide-ammonia	Ga-N	2.081	1.845	-0.236			h
		Ga-Br	2.288	2.302	0.014			
		Br-Ga-Br	116.1	116.0	-0.1			
Ga ₂ Br ₆	Ga ₂ Br ₆	Ga-Br(b)	2.450	2.434	-0.016			i
CGaH ₃ Cl ₃	GaMeCl ₃ (-)	Ga-Br(t)	2.250	2.234	-0.016			
		Ga-Cl	2.220	2.289	0.069			
		Ga-C	1.930	1.813	-0.117			j

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	Errors			Ref.
					MNDO-PM3	MNDO	AM1	
C2GaH6Cl2	GaMe2Cl2(-)	Ga-Cl	2.280	2.355	0.075			j
		Ga-C	1.980	1.826	-0.154			
C3GaH9Cl	GaMe3Cl(-)	Ga-Cl	2.380	2.404	0.024			j
		Ga-C	2.050	1.857	-0.183			
GaCl	Gallium chloride	Ga-Cl	2.202	2.307	0.105			g
Ga2H4Cl2	Ga2Cl2H4	Ga-Ga	3.241	3.824	0.583			k
		Ga-Cl	2.349	2.407	0.058			
GaH3NC13	Gallium trichloride-ammonia	Ga-H	1.559	1.598	0.039			
		Ga-N	2.057	2.417	0.360			h
		Ga-Cl	2.142	2.375	0.233			
		Cl-Ga-Cl	116.4	120.3	3.9			
GaCl4	GaCl4(-)	Ga-Cl	2.170	2.216	0.046			j
Ga2Cl6	Ga2Cl6	Ga-Cl(b)	2.300	2.360	0.060			i
		Ga-Cl(t)	2.100	1.889	-0.211			
GaF	Gallium fluoride	Ga-F	1.774	1.783	0.009			g
GaF3	Gallium trifluoride	Ga-F	1.725	1.713	-0.012			d
GaH	Gallium hydride	Ga-H	1.663	1.648	-0.015			g
GaI	Gallium iodide	Ga-I	2.575	2.539	-0.036			g
GaI3	Gallium triiodide	Ga-I	2.458	2.577	0.119			d
Ga2O	Gallium(I) oxide	Ga-O	1.824	1.796	-0.028			h
		Ga-O-Ga	142.9	180.0	37.1			
GERMANIUM								
C3GeH9Br	Bromotrimethylgermane	Ge-Br	2.323	2.362	0.039	0.051	-0.054	b
		Ge-C	1.936	1.948	0.012	-0.006	0.056	
		Br-Ge-C	106.3	106.4	0.1	0.6	4.2	
GeH3Br	Bromogermane	Ge-Br	2.297	2.333	0.036	0.070	-0.040	h
		Ge-H	1.527	1.503	-0.024	-0.050	0.026	
		H-Ge-Br	106.3	108.1	1.8	0.7	3.2	
GeBr2	Germanium dibromide	Ge-Br	2.337	2.323	-0.014	0.044	-0.123	l
		Br-Ge-Br	101.2	112.5	11.3	9.8	9.2	
CGeH3Br3	Tribromomethylgermane	Ge-C	1.889	1.936	0.047	0.037	0.133	h
		Ge-Br	2.276	2.333	0.057	0.075	-0.010	
		C-Ge-Br	111.6	110.6	-1.0	-1.4	-5.9	
		C-H	1.120	1.092	-0.028	-0.014	-0.015	
GeBr4	Germanium tetrabromide	Ge-Br	2.272	2.315	0.043	0.130	-0.003	m
		Ge-Cl	2.135	2.163	0.028	0.097	0.001	b
CGeH3Cl3	Trichloromethylgermane	C-Ge-Cl	106.0	110.7	4.7	5.6	4.1	
		Ge-F	1.739	1.736	-0.003	0.003	-0.023	n
		Ge-C	1.927	1.962	0.035	0.005	0.044	
		C-Ge-F	106.1	107.5	1.4	1.5	-1.8	
CGeH5F	Methylgermanium fluoride dihydride	Ge-H	1.523	1.510	-0.013	-0.038	0.016	
		C-Ge-H	113.9	109.7	-4.2	-2.4	-2.9	
		Ge-C	1.904	1.950	0.046	0.032	0.065	h
		Ge-F	1.714	1.714	0.000	0.024	-0.007	
CGeH3F3	Trifluoromethylgermane	F-Ge-C	113.2	113.2	0.0	0.8	1.3	
		Ge-C	1.919	1.835	-0.084	-0.061	-0.031	b
		C-N	1.155	1.158	0.003	0.011	0.008	
CGeH3NO	Germyl isocyanate	Ge-H	1.532	1.515	-0.017	-0.048	0.007	o
		Ge-N	1.831	1.842	0.011	0.000	-0.028	
CGeH3NS	Germyl isothiocyanate	Ge-H	1.520	1.518	-0.002	-0.039	0.021	h
		Ge-N	1.817	1.832	0.015	0.035	-0.010	
		H-Ge-N	106.9	110.0	3.1	0.9	1.3	
		C-N	1.144	1.213	0.069	0.049	0.054	
CGeH6	Methylgermane	Ge-C	1.945	1.955	0.010	-0.018	0.042	p
		Ge-H	1.529	1.505	-0.024	-0.046	0.016	
		C-H	1.083	1.090	0.007	0.024	0.022	
C2GeH6Cl2	Dimethylgermanium dichloride	Ge-Cl	2.143	2.183	0.040	0.099	-0.004	q
		Cl-Ge-Cl	105.0	107.0	2.0	1.1	3.5	
		Ge-C	1.928	1.941	0.013	-0.002	0.053	
		C-Ge-Cl	108.0	108.7	0.7	0.7	0.9	
C2GeH6F2	Dimethylgermanium difluoride	Ge-F	1.739	1.725	-0.014	0.004	-0.029	r
		F-Ge-F	105.4	103.7	-1.7	-3.7	-4.2	
		Ge-C	1.928	1.956	0.028	0.008	0.038	
		C-Ge-F	107.4	109.7	2.3	2.4	1.8	
C2GeH8	Ethylgermane	Ge-C	1.949	1.957	0.008	-0.008	0.055	b
		C-C	1.545	1.493	-0.052	-0.025	-0.056	
		Ge-C-C	112.2	105.2	-7.0	5.0	-1.1	
		Ge-H	1.522	1.506	-0.016	-0.039	0.023	
C2GeH8	Dimethylgermane	H-Ge-C	109.7	109.6	-0.1	0.2	-2.0	
		Ge-H	1.532	1.505	-0.027	-0.046	0.012	s
		H-Ge-H	108.7	108.8	0.1	0.6	5.3	
		Ge-C	1.950	1.957	0.007	-0.020	0.034	
C3GeH9Cl	Trimethylchlorogermane	C-Ge-C	110.0	109.4	-0.6	0.8	-3.2	
		Ge-Cl	2.170	2.203	0.033	0.088	-0.026	t
		Ge-C	1.940	1.950	0.010	-0.010	0.039	
		C-Ge-Cl	106.6	107.1	0.5	0.1	1.4	

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	Errors			Ref.
					MNDO-PM3	MNDO	AM1	
C3GeH10	Trimethylgermane	Ge-H	1.522	1.504	-0.018	-0.033	0.021	b
		Ge-C	1.947	1.959	0.012	-0.013	0.035	
		H-Ge-C	109.3	109.6	0.3	-0.5	1.6	
C4GeH12	Tetramethylgermanium	Ge-C	1.945	1.960	0.015	-0.007	0.036	u
		C-H	1.120	1.090	-0.030	-0.013	-0.014	
C6Ge2H18O	Bis(trimethylgermanium) oxide	Ge-O	1.770	1.786	0.016	-0.016	0.079	v
		Ge-O-Ge	141.0	125.1	-15.9	39.2	-18.9	
		Ge-C	1.980	1.975	-0.005	-0.038	-0.011	
C7GeSe2H1	Tetramethyldiselenagermacyclohexane	Se-C	1.972	1.993	0.021			w
		Ge-Se	2.350	2.399	0.049			
		Ge-Se-C	92.4	114.6	22.2			
		Se-Ge-Se	103.2	87.7	-15.5			
		Ge-C'	1.967	1.947	-0.020			
		Ge-C''	1.953	1.962	0.009			
		C'-Ge-C''	111.5	119.7	8.2			
GeF3Cl	Chlorotrifluorogermane	Ge-Cl	2.067	2.134	0.067	0.234	0.105	b
		Ge-F	1.688	1.703	0.015	0.063	0.015	
		F-Ge-F	107.5	107.6	0.1	-0.3	-1.9	
GeH3Cl	Chlorogermane	Ge-Cl	2.150	2.197	0.047	0.099	-0.018	p
		Ge-H	1.537	1.504	-0.033	-0.060	0.010	
		H-Ge-H	111.0	110.1	-0.9	0.8	1.0	
GeCl2	Germanium dichloride	Ge-Cl	2.186	1.981	-0.205	0.028	-0.089	d
		Cl-Ge-Cl	100.4	179.6	79.2	4.4	13.8	
GeHCl3	Trichlorogermane	Ge-Cl	2.114	2.153	0.039	0.155	0.015	b
GeCl4	Germanium tetrachloride	Ge-Cl	2.113	2.149	0.036	0.158	0.023	x
GeF	Germanium fluoride	Ge-F	1.749	1.711	-0.038	-0.016	-0.092	y
GeH3F	Fluorogermane	Ge-F	1.734	1.738	0.004	0.025	-0.019	h
		Ge-H	1.523	1.513	-0.010	0.003	0.017	
		F-Ge-H	106.0	109.9	3.9	2.4	2.4	
		Ge-F	1.732	1.695	-0.037	-0.017	-0.062	
GeH3PSF2	Difluoro(germylthio)phosphine	F-Ge-F	97.2	112.0	14.8	-2.0	-1.8	h
		Ge-S	2.256	2.288	0.032	-0.047	0.057	
		P-S	2.115	2.104	-0.011	-0.160	-0.011	
		Ge-S-P	99.0	125.2	26.2	32.6	17.6	
		Ge-H	1.538	1.506	-0.032	-0.063	0.006	
		S-Ge-H	110.0	113.4	3.4	-3.6	-1.2	
		P-F	1.590	1.555	-0.035	-0.034	-0.052	
Ge2H6P2F2	1,1-Difluoro-2,2-digermyldiphosphane	S-P-F	99.9	113.2	13.3	5.5	9.4	h
		P-F	1.581	1.549	-0.032	-0.028	-0.052	
		P-P	2.177	2.115	-0.062	-0.209	-0.288	
		P-P-F	98.9	107.1	8.2	7.1	0.5	
		Ge-P	2.320	2.210	-0.110	-0.141	-0.167	
		Ge-P-F	95.7	129.2	33.5	31.8	30.3	
		Ge-P-Ge	98.6	111.1	12.5	20.0	12.4	
		Ge-H	1.512	1.513	0.001	-0.035	0.018	
		Ge-I	2.508	2.472	-0.036	0.139	-0.075	
		GeH3I	Iodogermane	Ge-I	2.508	2.472	-0.036	
GeH3N3	Germylazide	Ge-H	1.497	1.515	0.018	0.032	0.056	z
		Ge-N	1.866	1.831	-0.035	0.058	-0.007	
GeH4	Germane	Ge-H	1.527	1.506	-0.021	-0.002	0.019	aa
GeH6Si	Germylsilane	Ge-Si	2.357	2.404	0.047	-0.016	0.000	b
		Ge-H	1.529	1.497	-0.032	-0.047	0.020	
		Si-H	1.483	1.488	0.005	-0.104	-0.026	
		Ge-I	2.500	2.469	-0.031	0.108	-0.091	
		Ge-O	1.625	1.637	0.012	-0.033	-0.003	
GeI4	Germanium tetraiodide	Ge-I	2.500	2.469	-0.031	0.108	-0.091	i
GeO	Germanium oxide	Ge-O	1.625	1.637	0.012	-0.033	-0.003	g
GeS	Germanium sulfide	Ge-S	2.012	1.973	-0.039	-0.048	0.020	g
GeSe	Germanium selenide	Ge-Se	2.135	1.927	-0.208			b
GeTe	Germanium telluride	Ge-Te	2.340	2.002	-0.338			g
Ge2H6	Digermane	GeGe	2.403	2.393	-0.010	2.242	-0.036	p
		GeH	1.541	1.502	-0.039	1.574	0.007	
		HGeH	106.4	110.3	3.9	-15.8	1.8	
Ge3H9P	Trigermylphosphine	P-Ge	2.306	2.235	-0.071	-0.106	-0.204	h
		Ge-P-Ge	95.7	109.0	13.3	24.1	25.4	
		Ge-H	1.490	1.506	0.016	0.034	0.034	
		P-Ge-H	110.3	116.0	5.7	-3.0	-4.1	
ARSENIC								
AsBr3	Arsenic tribromide	As-Br	2.323	2.315	-0.008			h
		Br-As-Br	99.8	100.3	0.5			
C3AsF9	Triperfluoromethylarsine	As-C	2.053	2.081	0.028			i
		C-As-C	100.0	99.5	-0.5			
C3AsH9	Trimethylarsine	As-C	1.960	1.976	0.016			i
		C-As-C	96.0	99.7	3.7			
C3AsN3	Arsenic tricyanide	As-C	1.900	1.868	-0.032			i
		C-As-C	92.0	98.5	6.5			
		As-C-N	171.0	175.6	4.6			
AsCl3	Arsenic trichloride	As-Cl	2.161	2.163	0.002			i
		Cl-As-Cl	98.7	99.8	1.1			
AsF3	Arsenic trifluoride	As-F	1.706	1.706	0.000			i
		F-As-F	96.2	95.9	-0.3			

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	Errors		AMI	Ref.
					MNDO-PM3	MNDO		
AsF5	Arsenic pentafluoride	As-F(ax)	1.711	1.685	-0.026			p
		As-F(eq)	1.656	1.661	0.005			
AsH3	Arsine	As-H	1.513	1.520	0.007			bb
		H-As-H	92.1	94.2	2.1			
AsH9Si3	Trisilylarsine	As-Si	2.353	2.371	0.018			h
		Si-As-Si	94.1	90.6	-3.5			
		Si-H	1.470	1.494	0.024			
AsI3	Arsenic triiodide	As-I	2.550	2.509	-0.041			i
		I-As-I	100.2	104.8	4.6			
SELENIUM								
CSeF2	Selenocarbonyl difluoride	C=Se	1.743	1.745	0.002			h
		C-F	1.314	1.320	0.006			
		F-C-F	107.5	105.3	-2.2			
CSeNOF5	Pentafluoro(isocyanato)selenium	Se-F	1.677	1.713	0.036			h
		Se-N	1.789	1.840	0.051			
		N=C	1.260	1.267	0.007			
		Se-N=C	116.9	130.0	13.1			
		C=O	1.187	1.167	-0.020			
CSeHN	Isoselenocyanic acid (Se=C=N-H)	N=C=O	172.9	172.3	-0.6			h
		Se=C	1.719	1.642	-0.077			
		C=N	1.191	1.196	0.005			
		Se=C=N	175.0	175.0	0.0			
		N-H	0.990	0.977	-0.013			
CSeH4	Methylselenium hydride	C=N-H	140.0	155.1	15.1			p
		CSe	1.959	1.948	-0.011			
		CH	1.088	1.093	0.005			
CSeS	Carbon sulfide selenide	SeH	1.473	1.470	-0.003			b
		C-S	1.533	1.452	-0.081			
CSe	Selenium carbide	C-Se	1.695	1.587	-0.108			g
		Se-C	1.676	1.592	-0.084			
C2SeF6	Diperfluoromethyl selenide	Se-C	1.960	2.008	0.048			i
		C-Se-C	104.0	101.6	-2.4			
C2SeH6	Ethyl selanol (anti)	Se-H	1.440	1.466	0.026			cc
		Se-C	1.962	1.956	-0.006			
		H-Se-C	93.5	99.9	6.4			
		Se-C-C	108.7	100.3	-8.4			
		Se-C	1.943	1.948	0.005			
C2SeH6	Dimethylselenium	C-Se-C	96.2	100.8	4.6			dd
		Se-C	1.950	1.945	-0.005			i
C2Se2H6	Me-Se-Se-Me	Se-Se	2.330	2.370	0.040			
		Se-Se-C	99.0	100.2	1.2			
		Se-C2	1.855	1.887	0.032			b
		C5-Se-C2	87.8	88.0	0.2			
		C2-C3	1.369	1.344	-0.025			
C4SeH4	Selenophene	Se-C2-C3	111.6	110.1	-1.5			
		C2-H	1.070	1.084	0.014			
		Se-C2-H2	121.7	121.2	-0.5			
		Se-C2	1.963	1.959	-0.004			b
		C5-Se-C2	90.7	92.2	1.5			
C4SeH8	Tetrahydroselenophene	C2-C3	1.549	1.505	-0.044			
		Se-C2-C3	104.0	103.6	-0.4			
		Se-C	1.972	1.993	0.021			w
		Ge-Se	2.350	2.399	0.049			
		Ge-Se-C	92.4	114.6	22.2			
SeOC12	Selenyl chloride	Se-Ge-Se	103.2	87.7	-15.5			
		Ge-C'	1.967	1.947	-0.020			
		Ge-C"	1.953	1.962	0.009			
		C'-Ge-C"	111.5	119.7	8.2			
		Se-O	1.614	1.634	0.020			h
SeCl12	Selenium dichloride	Se-Cl1	2.205	2.201	-0.004			
		O=Se-Cl1	106.0	103.0	-3.0			
		Cl1-Se-Cl1	96.9	98.2	1.3			
		Se-Cl1	2.157	2.164	0.007			h
		Cl1-Se-Cl1	99.6	99.7	0.1			
SeHPF2	Difluorophosphine selenide	P=Se	2.026	2.089	0.063			h
		P-F	1.557	1.552	-0.005			
		Se=P-F	116.8	115.9	-0.9			
		P-H	1.422	1.264	-0.158			
		Se=P-H	118.6	118.5	-0.1			
SeOF2	Selenyl fluoride	F-P-F	98.1	93.6	-4.5			p
		SeO	1.576	1.624	0.048			
		SeF	1.730	1.724	-0.006			
		FSeO	104.8	101.5	-3.3			
		FSeF	92.2	94.6	2.4			

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	Errors			Ref.
					MNDO-PM3	MNDO	AMI	
SeO2F2	Selenoyl fluoride	Se-F	1.685	1.705	0.020			h
		F-Se-F	94.1	95.0	0.9			
		Se-O	1.575	1.558	-0.017			
		O-Se-O	126.2	129.9	3.7			
SeF4	Selenium tetrafluoride	SeF	1.770	1.736	-0.034			i
		FSeF	169.2	140.3	-28.9			
		SeF'	1.680	1.708	0.028			
		F'SF'	100.6	111.9	11.3			
SeF6	Selenium hexafluoride	SeF	1.685	1.690	0.005			ee
Se2OF10	Bis(pentafluoroselenium)oxide	Se-O	1.679	1.713	0.034			h
		Se-O-Se	142.4	132.3	-10.1			
		Se-F(eq)	1.683	1.687	0.004			
		Se-F(ax)	1.665	1.696	0.031			
GeSe	Germanium selenide	Ge-Se	2.135	1.927	-0.208			b
SeH2	Hydrogen selenide	SeH	1.460	1.470	0.010			i
		HSeH	91.0	93.6	2.6			
SeH6Si2	Disilyl selenide	Se-Si	2.270	2.393	0.123			i
		Si-Se-Si	97.0	96.0	-1.0			
In2Se	Indium(I) selenide	In-Se	2.650	2.579	-0.071			h
		In-Se-In	113.0	179.8	66.8			
SeO	Selenium oxide	Se-O	1.663	1.602	-0.061			ff
SeO2	Selenium dioxide	SeO	1.608	1.606	-0.002			g
		OSeO	113.8	106.6	-7.2			
SeO3	Selenium trioxide	Se-O	1.688	1.538	-0.150			h
PbSe	Lead selenide	Pb-Se	2.402	2.360	-0.042			b
SeSi	Silicon selenide	Se-Si	2.058	1.974	-0.084			b
SnSe	Tin selenide	Sn-Se	2.326	2.326	0.000			b
CADMIUM								
CdBr2	Cadmium dibromide	Cd-Br	2.394	2.360	-0.034			gg
		Dimethylcadmium	Cd-C	2.112	2.035	-0.077		
C2CdH6	Dimethylcadmium	Cd-N	2.240	2.211	-0.029			hh
		Cd-S	2.570	2.569	-0.001			
CdCl2	Cadmium dichloride	Cd-Cl	2.210	2.225	0.015			i
CdF2	Cadmium difluoride	Cd-F	1.970	1.966	-0.004			i
CdI2	Cadmium diiodide	Cd-I	2.550	2.588	0.038			i
INDIUM								
InBr	Indium bromide	In-Br	2.543	2.289	-0.254			g
InCl	Indium chloride	In-Cl	2.401	2.401	0.000			g
InF	Indium fluoride	In-F	1.985	1.985	0.000			g
InH	Indium hydride	In-H	1.838	1.733	-0.105			g
InI	Indium iodide	In-I	2.729	2.711	-0.018			ii
InI3	Indium triiodide	In-I	2.641	2.646	0.005			d
		In-O	2.020	1.999	-0.021			
In2O	Indium(I) oxide	In-O-In	145.0	180.1	35.1			h
		In-Se	2.650	2.579	-0.071			
In2Se	Indium(I) selenide	In-Se-In	113.0	179.8	66.8			h
		In-Te	2.840	2.836	-0.004			
In2Te	Indium(I) telluride	In-Te-In	99.0	104.9	5.9			h
TIN								
C3SnH9Br	Trimethyltin bromide	Sn-Br	2.490	2.449	-0.041	-0.074	-0.092	jj
		Sn-C	2.170	2.114	-0.056	-0.105	-0.065	
SnH3Br	Tin bromide trihydride	Sn-Br	2.469	2.453	-0.016	-0.068	-0.076	p
		Sn-H	1.767	1.693	-0.074	-0.177	-0.147	
		H-Sn-H	112.8	114.0	1.2	-0.2	-2.2	
		Sn-Br	2.512	2.404	-0.108	-0.150	-0.137	
SnBr2	Tin dibromide	Br-Sn-Br	100.0	102.5	2.5	4.3	5.6	d
		Sn-Br	2.440	2.440	0.000	-0.056	-0.063	
SnBr4	Tin tetrabromide	Sn-C	2.140	2.187	0.047	-0.083	-0.037	h
		Sn-H	1.708	1.701	-0.007	-0.122	-0.090	
C2SnH6Cl2	Dimethyltin dichloride	H-Sn-C	109.4	110.1	0.7	1.2	0.0	ll
		Sn-Cl	2.327	2.364	0.037	-0.020	-0.027	
		Cl-Sn-Cl	106.2	105.8	-0.4	-2.2	-0.8	
		Sn-C	2.109	2.108	-0.001	-0.034	-0.018	
C2SnH8	Dimethyltin dihydride	S-Sn-Cl	108.5	108.3	-0.2	-0.8	0.3	ll
		Sn-H	1.680	1.700	0.020	-0.092	-0.062	
		Sn-C	2.150	2.177	0.027	-0.091	-0.046	
		H-Sn-C	108.0	109.7	1.7	1.2	1.1	
C3SnH9I	Trimethyltin iodide	C-Sn-C	104.8	109.4	4.6	7.6	5.6	jj
		Sn-I	2.720	2.668	-0.052	-0.168	-0.116	
C3SnH10	Trimethyltin hydride	Sn-H	1.705	1.697	-0.008	-0.116	-0.087	nm
		Sn-C	2.147	2.164	0.017	-0.086	-0.041	
		H-Sn-C	111.5	109.7	-1.8	-3.6	-2.5	
C4SnH12	Tetramethyltin	Sn-C	2.134	2.148	0.014	-0.071	-0.026	nn
		Sn-Cl	2.327	2.396	0.069	-0.018	-0.012	
SnH3Cl	Tin chloride trihydride	Sn-Cl						b

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	MNDO-PM3	Errors MNDO	AMI	Ref.
SnCl ₂	Tin dichloride	Sn-Cl	2.346	2.340	-0.006	-0.075	-0.036	d
		Cl-Sn-Cl	99.0	98.9	-0.1	3.4	0.1	
SnCl ₄	Tin tetrachloride	Sn-Cl	2.280	2.354	0.074	0.003	-0.020	oo
SnH ₃ I	Tin iodide trihydride	Sn-I	2.674	2.623	-0.051	-0.139	-0.085	b
SnH ₄	Tin tetrahydride (stannane)	Sn-H	1.701	1.701	0.000	-0.116	-0.084	pp
SnI ₂	Tin diiodide	Sn-I	2.706	2.643	-0.063	-0.210	-0.120	d
		I-Sn-I	103.8	109.5	5.7	3.3	2.0	
SnO	Tin oxide	SnO	1.833	1.839	0.006	-0.084	0.049	g
SnS	Tin sulfide	SnS	2.209	2.137	-0.072	-0.205	-0.029	g
SnSe	Tin selenide	Sn-Se	2.326	2.326	0.000			b
SnTe	Tin telluride	Sn-Te	2.523	2.572	0.049			g
ANTIMONY								
SbBr ₃	Antimony tribromide	Sb-Br	2.490	2.471	-0.020			i
		Br-Sb-Br	98.0	98.5	0.5			
C ₃ SbF ₉	Triperfluoromethylstibine	Sb-C	2.202	2.209	0.007			i
		C-Sb-C	100.0	99.2	-0.8			
SbCl ₃	Antimony trichloride	Sb-Cl	2.323	2.320	-0.003			h
		Cl-Sb-Cl	97.1	97.0	0.1			
SbCl ₅	Antimony pentachloride	Sb-Cl(ax)	2.338	2.373	0.035			d
		Sb-Cl(eq)	2.277	2.349	0.072			
SbH ₃	Stibine	Sb-H	1.707	1.701	-0.006			i
		H-Sb-H	91.3	92.4	1.1			
SbH ₉ Si ₃	Trisilylstibine	Sb-Si	2.555	2.533	-0.022			h
		Si-Sb-Si	89.0	95.0	6.0			
		Si-H	1.470	1.488	0.018			
Sb ₂	Antimony, dimer	Sb-Sb	2.590	2.300	-0.290			qq
TELLURIUM								
TeBr ₂	Tellurium dibromide	Te-Br	2.510	2.511	0.001			i
		Br-Te-Br	98.0	99.4	1.4			
TeBr ₄	Tellurium tetrabromide	Te-Br	2.680	2.532	-0.148			rr
CTeNOF ₅	Pentafluoro(isocyanato)tellurium	Te-F	1.826	1.824	-0.002			h
		Te-N	1.859	1.813	-0.046			
		Te-N=C	126.5	179.4	52.9			
C ₉ TeH ₁₃ PS	MeOPh-Te-S-P(S)(OMe) ₂	Te-C	2.114	2.092	-0.022			ss
		Te-S	2.444	2.613	0.169			
		C-Te-S	94.9	98.7	3.8			
		S-P	2.051	2.109	0.058			
		P-S-Te	103.3	94.3	-9.0			
		P=S	1.933	1.982	0.049			
		S=P-S	107.9	103.5	-4.4			
TeCl ₄	Tellurium tetrachloride	Te-Cl	2.330	2.404	0.074			rr
TeF ₆	Tellurium hexafluoride	TeF	1.815	1.816	0.001			h
Te ₂ OF ₁₀	Bis(pentafluorotellurium)oxide	Te-O	1.832	1.775	-0.057			h
		Te-O-Te	145.5	155.9	10.4			
		Te-Feq	1.820	1.811	-0.009			
		Te-Fax	1.799	1.814	0.015			
		Fax-Te-Feq	89.9	94.3	4.4			
GeTe	Germanium telluride	Ge-Te	2.340	2.002	-0.338			g
TeH ₂	Hydrogen telluride	Te-H	1.658	1.675	0.017			tt
		H-Te-H	90.3	88.3	-2.0			
In ₂ Te	Indium(I) telluride	In-Te	2.840	2.836	-0.004			h
		In-Te-In	99.0	104.9	5.9			
TeO ₂	Tellurium dioxide	Te-O	1.830	1.702	-0.128			h
PbTe	Lead telluride	Pb-Te	2.595	2.738	0.143			b
SnTe	Tin telluride	Sn-Te	2.523	2.572	0.049			g
Te ₂	Tellurium, dimer	Te-Te	2.560	2.705	0.145			g
MERCURY								
CHgH ₃ Br	Methylmercuric bromide	Hg-C	2.062	2.090	0.028	-0.079	0.015	h
		Hg-Br	2.405	2.290	-0.115	-0.021	-0.137	
		C-H	1.095	1.087	-0.008	0.013	0.011	
		Hg-C-H	109.6	109.5	-0.1	0.1	-2.2	
HgBr	Mercury bromide	Hg-Br	2.330	2.217	-0.113	0.038	-0.101	uu
HgBr ₂	Mercury dibromide	Hg-Br	2.440	2.225	-0.215	-0.077	-0.190	vv
CHgH ₃ Cl	Methylmercuric chloride	Hg-C	2.052	2.111	0.059	-0.070	-0.002	b
		Hg-Cl	2.285	2.254	-0.031	0.006	-0.031	
CHgH ₃ I	Methylmercuric iodide	Hg-C	2.069	2.077	0.008	-0.082	-0.016	h
		Hg-I	2.588	2.501	-0.087	-0.109	-0.094	
C ₂ HgF ₆	Ditrifluoromethyl mercury	Hg-C	2.101	2.101	0.000	0.162	0.110	ww
		C-Hg-C	180.0	180.0	0.0	0.4	0.5	
C ₂ HgH ₃ N	Methylmercuric cyanide	Hg-CN	2.082	2.027	-0.055	-0.148	-0.070	xx
		Hg-CH ₃	2.051	2.107	0.056	-0.068	-0.005	
		C-N	1.141	1.157	0.016	0.030	0.026	
Cl ₂ HgH ₁₀	Diphenylmercury	Hg-C	2.085	2.045	-0.040	-0.082	-0.032	yy

Table IV. (Continued)

Empirical Formula	Chemical Name	Geometric Variable	Exp.	Calc.	Errors		AM1	Ref.
					MNDO-PM3	MNDO		
HgCl	Mercury chloride	Hg-Cl	2.230	2.194	-0.036	0.048	0.009	a
HgCl ₂	Mercury dichloride	Hg-Cl	2.252	2.243	-0.009	0.016	-0.013	zz
HgF	Mercury fluoride	Hg-F	1.890	1.900	0.010	-0.018	0.004	uu
HgF ₂	Mercury difluoride	Hg-F	1.960	1.928	-0.032	-0.082	-0.052	uu
HgH	Mercury hydride	Hg-H	1.740	1.695	-0.045	-0.190	-0.070	a
HgI	Mercury iodide	Hg-I	2.490	3.001	0.511	-0.025	0.036	uu
HgI ₂	Mercury diiodide	Hg-I	2.554	2.474	-0.080	-0.079	-0.059	aaa
HgO	Mercury oxide	Hg-O	1.840	1.841	0.001	0.042	0.222	uu
THALLIUM								
BT102	Tl-O-B-O	Tl-O	2.420	2.395	-0.025			h
		Tl-O-B	132.0	108.1	-23.9			
		B=O	1.260	1.210	-0.050			
TlBr	Thallium bromide	Tl-Br	2.618	2.558	-0.060			b
C5TlH5	Cyclopentadienyl thallium	Tl-C	2.705	2.711	0.006			b
TlCl	Thallium chloride	Tl-Cl	2.485	2.489	0.004			b
TlF	Thallium fluoride (TlF)	Tl-F	2.084	2.084	0.000			i
Tl ₂ F ₂	Thallium fluoride dimer	Tl-F	2.290	2.286	-0.004			h
		F-Tl-F	90.0	113.4	23.4			
TlI	Thallium iodide	Tl-I	2.814	2.724	-0.090			b
LEAD								
PbBr	Lead bromide	Pb-Br	2.546	2.563	0.017	-0.080		a
PbBr ₂	Lead dibromide	Pb-Br	2.597	2.566	-0.031	-0.127		bbb
		Br-Pb-Br	99.2	102.7	3.5	2.7		
C4PbH12	Tetramethyllead	Pb-C	2.240	2.186	-0.054	-0.070		ccc
		C-H	1.080	1.093	0.013	0.021		
		H-C-Pb	104.6	110.6	6.0	4.5		
C6Pb2H18	Hexamethyldiplumbane	Pb-Pb	2.880	2.867	-0.013	-0.109		ddd
		Pb-C	2.250	2.200	-0.050	-0.073		
		Pb-Pb-C	109.5	112.4	2.9	2.2		
PbCl	Lead chloride	Pb-Cl	2.180	2.382	0.202	0.198		a
PbCl ₂	Lead dichloride	Pb-Cl	2.444	2.458	0.014	-0.064		eee
		Cl-Pb-Cl	98.3	99.6	1.3	2.4		
PbCl ₄	Lead tetrachloride	Pb-Cl	2.430	2.275	-0.155	-0.049		a
PbF	Lead fluoride	Pb-F	2.058	2.027	-0.031	-0.063		a
PbF ₂	Lead difluoride	Pb-F	2.033	2.026	-0.007	-0.038		bbb
		F-Pb-F	97.2	88.9	-8.3	-5.9		
PbH	Lead hydride	Pb-H	1.839	1.730	-0.109	-0.181		a
PbI	Lead iodide	Pb-I	2.736	2.773	0.037	-0.154		a
PbI ₂	Lead diiodide	Pb-I	2.804	2.778	-0.026	-0.206		bbb
		I-Pb-I	99.7	107.9	8.2	4.3		
PbO	Lead oxide	Pb-O	1.920	1.936	0.016	-0.039		fff
PbS	Lead sulfide	Pb-S	2.290	2.152	-0.138	-0.175		fff
PbSe	Lead selenide	Pb-Se	2.402	2.360	-0.042			b
PbTe	Lead telluride	Pb-Te	2.595	2.738	0.143			b
BISMUTH								
BiBr ₃	Bismuth tribromide	Bi-Br	2.630	2.603	-0.027			i
		Br-Bi-Br	100.0	98.7	-1.3			
C3BiH9	Trimethylbismuth	Bi-C	2.270	2.266	-0.004			i
		C-Bi-C	96.7	97.0	0.3			
BiCl ₃	Bismuth trichloride	Bi-Cl	2.425	2.419	-0.006			d
		Cl-Bi-Cl	97.3	99.9	2.6			

References

- a: M. W. Chase, C. A. Davies, J. R. Downey, D. R. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, J. Phys. Chem. Ref. Data 14, Suppl. 1 (1985).
- b: M. D. Harmony, V. W. Laurie, R. L. Kuczkowsky, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, A. G. Maki, J. Phys. Chem. Ref. Data 8, 3 (1979).
- c: L. J. Guggenberger, R. E. Rundle, J. Am. Chem. Soc., 86, 5344 (1964).
- d: M. Hargittai, Coord. Chem. Rev., 91, 35 (1988).
- e: A. Almenningen, T. U. Halgaker, A. Haaland, S. Samdal, Acta Chem. Scand., Part A. A36, 159 (1982).
- f: A. Haaland, S. Samdal, R. Seip, J. Organomet. Chem., 153, 187 (1978).
- g: K. P. Huber, G. Herzberg, "Molecular Spectra and Molecular Structure," IV. "Constants for Diatomic Molecules," Van Nostrand, Reinhold, New York, (1979).
- h: J. H. Callomon, E. Hirota, T. Iijima, K. Kuchitsu, W. J. Lafferty, "Structure Data on Free Polyatomic Molecules," Landolt-Bornstein, New Series, Group II, Vol. 15, Springer, Berlin (1977).
- i: "Structural Inorganic Chemistry", A. F. Wells, Clarendon Press, Oxford, 1984.
- k: M. J. Goode, A. J. Downs, C. R. Pulham, D. W. H. Rankin, H. E. Robertson, J. Chem. Soc. Chem. Comm., 768 (1988).

Table IV. (Continued)

- l: G. Schultz, J. Tremmel, I. Hargittai, N. D. Kagramanov, A. K. Maltsev, O. M. Nefedov, *J. Mol. Struct.*, **82**, 107 (1982).
- m: G. G. B. Souza, J. D. Wieser, *J. Mol. Struct.*, **25**, 442 (1975).
- n: M. Hayashi, S. Kaminaka, M. Fujitake, S. Miyazaki, *J. Mol. Spect.*, **135**, 289 (1989).
- o: J. D. Murdoch, D. W. H. Rankin, B. Beagley, *J. Mol. Struct.*, **31**, 291, (1976).
- p: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, C. S. Pote, "Structure Data on Free Polyatomic Molecules," Landolt-Bornstein, New Series, Group II, Vol. 7, Springer, Berlin (1976).
- q: J. E. Drake, H. L. Hencher, Q. Shem, *Can. J. Chem.*, **55**, 1104 (1977).
- r: J. E. Drake, R. T. Hemmings, J. L. Hencher, F. M. Mustoe, Q. Shem, *J. Chem. Soc., Dalton Trans.*, **394**, (1976).
- s: J. Durig, M. M. Chen, Y. S. Li, *J. Phys. Chem.*, **77**, 227 (1973), and E. C. Thomas, V. W. Laurie, *J. Chem. Phys.*, **50**, 3512 (1969).
- t: J. Durig, K. L. Hellams, *J. Mol. Struct.*, **29**, 349 (1975).
- u: J. L. Hencher, F. J. Mistoe, *Can. J. Chem.*, **53**, 3542 (1975).
- v: L. V. Vilkov, N. A. Tarensenko, *Zh. Strukt. Khim.*, **10**, 102 (1969).
- w: S. Tomoda, M. Shimoda, M. Sanami, Y. Takeuchi, Y. Litaka, *J. Chem. Soc. Chem. Comm.*, **1304** (1989).
- x: Y. Morino, Y. Nakamura, T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).
- y: S. Saito, Y. Endo, E. Hirota, *J. Mol. Spect.*, **116**, 499 (1986).
- z: P. Groner, G. M. Attia, A. B. Mohamad, J. F. Sullivan, Y. S. Li, J. R. Durig, *J. Chem. Phys.*, **91**, 1434 (1989).
- aa: R. A. Eades, D. A. Dixon, *J. Chem. Phys.*, **72**, 3309 (1980).
- bb: G. A. McRae, M. C. L. Gerry, M. Wong, I. Ozier, E. A. Cohen, *J. Mol. Spect.*, **123**, 321 (1987).
- cc: J. Nakagawa, H. Okutani, M. Hayashi, *J. Mol. Spectrosc.*, **94**, 410 (1982).
- dd: J. F. Beecher, *J. Mol. Spectrosc.*, **21**, 414 (1966).
- ee: L. S. Bartell, A. Jin, *J. Mol. Struct.*, **118**, 47 (1984).
- ff: E. H. Fink, K. D. Setzer, *J. Mol. Spect.*, **125**, 66 (1987).
- gg: V. M. Petrov, A. N. Utkin, G. V. Girichev, A. A. Ivanov, *Zh. Strukt. Khim.*, **26**, 52 (1985).
- hh: K. Ozutsumi, T. Takamuka, S. Ishiguko, H. Ohtaki, *Bull. Chem. Soc. Japan*, **62**, 1875 (1989).
- ii: S. N. Vempati, W. E. Jones, *J. Mol. Spect.*, **127**, 232 (1988).
- jj: H. A. Skinner, L. E. Sutton, *Trans. Farad. Soc.*, **44**, 164 (1944).
- kk: E. Coop, L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).
- ll: B. Beagley, K. McAloon, J. M. Freeman, *Acta Crystallogr., Sect. B*, **B30**, 444 (1974).
- mm: H. C. Clark, S. G. Furnival, J. T. Kwon, *Can. J. Chem.*, **41**, 2889 (1963).
- nn: H. Fujii, M. Kimura, *Bull. Chem. Soc. Japan*, **44**, 2643 (1970).
- oo: H. Fujii, M. Kimura, *Bull. Chem. Soc. Japan*, **43**, 1933 (1970).
- pp: G. R. Wilkinson, M. K. Wilson, *J. Chem. Phys.*, **25**, 784 (1956).
- qq: K. Balasubramanian, J. Li, *J. Mol. Spect.*, **135**, 169 (1989).
- rr: L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11 + 18, Chem. Soc., London (1958), (1965).
- ss: S. Husebye, K. Maartmann-Moe, O. Mikalsen, *Acta Chem. Scand.*, **43**, 868 (1989).
- tt: N. K. Moncur, P. D. Willson, T. H. Edwards, *J. Mol. Spectrosc.*, **52**, 380 (1974).
- uu: D. R. Stull, H. Prophet, *Natl. Stand., Ref. Data Ser. (U.S., Natl. Bur. Stand.)* NSRDS-NBS 37, 1971.
- vv: P. W. Allen, L. E. Sutton, *Acta. Crystallogr.* **3**, 46 (1950).
- ww: H. Oberhammer, *J. Mol. Struct.*, **48**, 389 (1978).
- xx: N. Iwasaki, *Bull. Chem. Soc. Japan*, **49**, 2735 (1976).
- yy: L. V. Vilkov, M. G. Anashkin, G. I. Mamaeva, *J. Struct. Chem. (Engl. Transl.)* **9**, 310 (1968).
- zz: K. Kashiwabara, S. Konaka, N. M. Kimura, *Bull. Chem. Soc. Japan*, **46**, 410 (1973).
- aaa: V. P. Spiridonov, A. G. Gershikov, B. S. Butayev, *J. Mol. Struct.*, **52**, 53 (1979).
- bbb: A. V. Demidov, A. G. Gershikov, E. Z. Zasorin, V. P. Spiridonov, A. A. Ivanov, *J. Struct. Chem.*, **24**, 9 (1983).
- ccc: T. Oyamada, T. Iijima, M. Kimura, *Bull. Chem. Soc. Japan*, **44**, 2638 (1971).
- ddd: H. A. Skinner, L. E. Sutton, *Trans. Farad. Soc.*, **36**, 1209 (1940).
- eee: I. Hargittai, *J. Mol. Struct.*, **100**, 129 (1983).
- fff: F. J. Lovas, E. Tiemann, *J. Phys. Chem. Ref. Data* **3**, 609 (1974).

Bismuth

As with the phosphorus, arsenic, and antimony analogues, triethylbismuth is predicted to have a heat of formation much lower than that observed. Since the ΔH_f of both the trimethyl and triphenyl derivatives are accurately reproduced, it is likely that the

experimental value for the ΔH_f of the triethyl derivative is incorrect.

General

The spectrum of errors in ΔH_f range from 39.5 (InO) to -37.8 kcal/mol (Sb^{3+}); this is much less than that

Table V. Average errors in calculated bond lengths (Å).

Element	PM3		MNDO		AM1	
	No.	Average Error	No.	Average Error	No.	Average Error
First 12 PM3 elements only						
Hydrogen	101	0.015	101	0.041	101	0.026
Carbon	264	0.019	264	0.024	264	0.027
Nitrogen	66	0.041	66	0.063	66	0.060
Oxygen	75	0.026	75	0.052	75	0.045
Fluorine	68	0.041	68	0.071	68	0.058
Aluminum	12	0.077	12	0.105	12	0.104
Silicon	30	0.064	30	0.080	30	0.061
Phosphorus	36	0.055	36	0.064	36	0.065
Sulfur	68	0.057	68	0.109	68	0.093
Chlorine	40	0.051	40	0.052	40	0.077
Bromine	31	0.092	31	0.085	31	0.075
Iodine	16	0.134	16	0.139	16	0.119
All 28 PM3 elements						
Hydrogen	149	0.022	133	0.057	128	0.028
Beryllium	11	0.049	11	0.070		
Carbon	341	0.023	306	0.028	302	0.028
Nitrogen	80	0.045	72	0.060	72	0.057
Oxygen	97	0.031	82	0.050	80	0.048
Fluorine	111	0.042	84	0.065	80	0.054
Magnesium	15	0.193				
Aluminum	12	0.077	12	0.105	12	0.104
Silicon	38	0.060	32	0.079	32	0.058
Phosphorus	47	0.056	42	0.071	42	0.074
Sulfur	80	0.061	74	0.110	72	0.090
Chlorine	83	0.064	61	0.063	56	0.062
Zinc	10	0.030	10	0.068	10	0.047
Gallium	26	0.110				
Germanium	69	0.037	64	0.108	64	0.040
Arsenic	11	0.017				
Selenium	42	0.040				
Bromine	62	0.075	47	0.081	44	0.078
Cadmium	7	0.028				
Indium	9	0.053				
Tin	26	0.040	24	0.098	24	0.065
Antimony	8	0.057				
Tellurium	18	0.076				
Iodine	37	0.100	29	0.124	25	0.105
Mercury	20	0.077	20	0.072	20	0.063
Thallium	6	0.027				
Lead	17	0.063	15	0.108		
Bismuth	3	0.012				

of the first 12 elements (61.7 kcal/mol (Al^+) to -142.1 (P^{2+}). In a few instances, it is likely that the experimental data are of limited accuracy, the most important of which are the ΔH_f of the trialkyl-Group V compounds. Normally, ethyl derivatives are more stable than the corresponding methyl derivative;

however, in Group V that is true only for nitrogen (Table VII). In the case of phosphorus, experimental data are available for all the methyl and ethyl phosphines. From these, Figure 3, we see that the anomaly only appears in the case of triethylphosphine. If this effect is genuine, and is also found in the chem-

Table VI. Average errors in molecular geometries.

Geometric parameter	PM3		MNDO		AM1	
	No.	Error	No.	Error	No.	Error
First 12 PM3 elements						
Bond lengths (angstroms)	460	0.037	460	0.055	460	0.051
Angles (degrees)	196	4.286	196	4.305	196	3.792
All 28 PM3 elements						
Bond lengths (angstroms)	780	0.044	617	0.065	589	0.051
Angles (degrees)	324	5.480	256	4.426	250	3.904

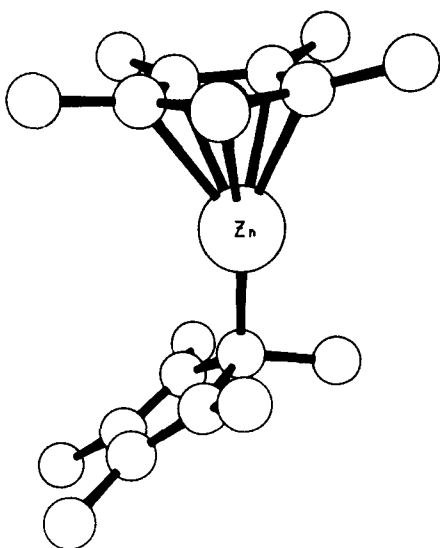


Figure 1. Geometry predicted by PM3 for Cp_2Zn .

istries of arsenic, antimony and bismuth, then a theoretical explanation must be sought. At the PM3 level no such phenomenon is predicted.

Atoms

Isolated atoms are used in semiempirical methods in the definition of the zero of energy. Consequently, their ΔH_f should be independent of the parameters. In two instances, however, (Al and Ge) the error in the ΔH_f of isolated atoms is finite. For those atoms, the ground state of the atom, as calculated by PM3, is different from that observed experimentally.

Within the optimization, the option exists to force the correct electronic configuration. However, when this was done, the overall SSQ became considerably larger than when an incorrect atomic electronic configuration was allowed. Instead of forcing the correct configuration, the atoms involved were given the default weight, and the parameters optimized. In the case of germanium the atomic configuration predicted by PM3 is $4s^1 4p^3$, i.e., the same as in normal germanium chemistry.

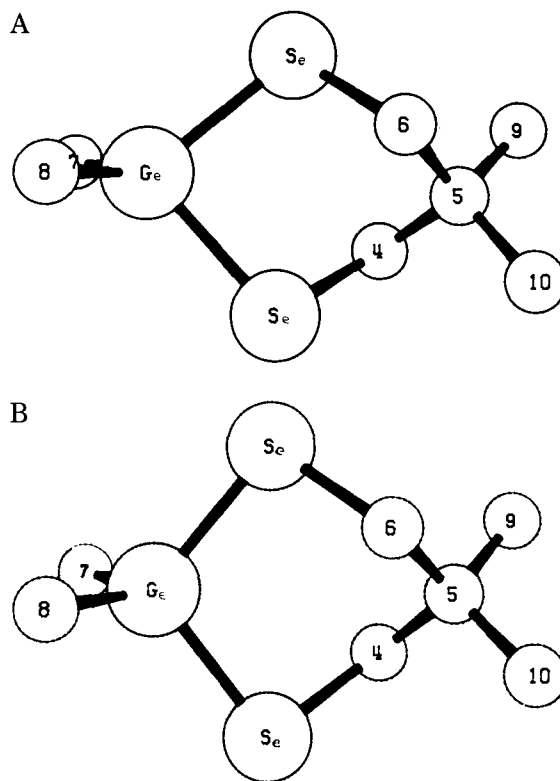


Figure 2. X-ray and PM3 geometries for 2,2,5,5-tetramethyl-1,3-diselena-2-germacyclohexane (A: PM3 geometry B: X-ray geometry³¹).

DISCUSSION

Predictive Power of MNDO/PM3

When the original 12 elements were parameterized, only about a third of the data reported²⁷ was used in the optimization calculation, the remainder being used in the surveys only. If a surveyed molecule was badly predicted, it was then added to the optimization set. This meant that, although a large number of data were "predicted," the manner in which the optimization was done predisposed the method to be as accurate in prediction as it was in reproducing the set used in the optimization. When parameters are being optimized there does not appear to be any way in which the resulting method can be demon-

Table VII. Experimental ΔH_f for group V trialkyl derivatives (kcal/mol).

Element	Trimethyl Derivative	Triethyl Derivative	Difference
Nitrogen	-5.7a	-22.1a	-15.5
Phosphorus	-22.5a	-11.8a	+10.7
Arsenic	2.8a	13.4a	+10.6
Antimony	7.7a	11.6a	+3.9
Bismuth	46.1a	51.6a	+5.5

a: J. O. Cox, G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970.

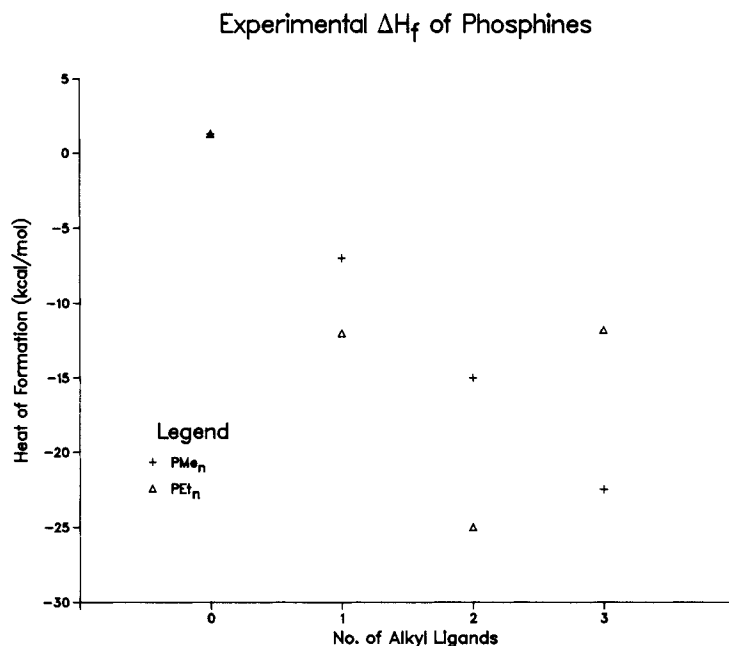


Figure 3. Experimental ΔH_f for trialkylphosphines.

strated to have predictive power: if a trial method did not have predictive power in that poor predictions were made, then the method could be improved by making use of that poor prediction. An optimum method would thus implicitly involve all available data.

In extending the method to new elements the predictive power of the first set of elements becomes apparent. If the method was not predictive, then the errors for the next set of elements, even when fully optimized parameters were used, would be much larger than for the first set.

Examination of Table III shows that the predictive power of PM3 when applied to the first 12 elements is virtually the same as the accuracy: errors in ΔH_f for seven elements became slightly larger, four became slightly smaller, and one was unchanged; similar effects are observed for the geometries, Tables V and VI. Obviously none of the compounds reported here could have been used in determining the parameters for the first set of 12 elements. Therefore it follows that the predictive accuracy of the first set of 12 elements is similar to the accuracy reported in the surveys. Differences between these tables and those in reported earlier²⁷ are due to various errors in the original work being corrected and, in the case of AM1, to new parameters being made available. No mixed parameter sets were involved in this work. A systematic error was found in the earlier work,²⁷ which is corrected in Table V presented here.

The predictive accuracy of PM3 for the set of elements reported here is likely to be less than that of the surveys given here for cadmium and bismuth, but likely to be much better for tin, selenium, and germanium. Of course, the predictive power of the current set of elements could be determined by ex-

tending PM3 to compounds containing elements which have not yet parameterized.

At the present time there is no easy way to partition errors between those resulting from theoretical limitations in the computational method and those from experimental inaccuracies. However, computational errors tend to be systematic, whereas experimental errors are random. By making post hoc corrections to the computed values, very high accuracy results can be obtained. Thus for the *n*-alkanes with more than three carbon atoms, a correction to the PM3 values of the ΔH_f of $-3.5 + 0.56$ times the number of carbon atoms results in predicted ΔH_f within 0.1 kcal/mol of experiment.

CONCLUSION

The PM3 method has been extended to a total of 28 elements with only minor loss of accuracy in geometry prediction. PM3 is based upon the NDDO³⁴ approximation, as in MNDO and AM1. In PM3, the NDDO approximation has been shown to be extremely robust, able to represent the chemistry of a large number of elements involved in a wide spectrum of bonds, ranging from purely covalent to highly ionic to the nonclassical bonds found in the cyclopentadienyl complexes to dative or donor-acceptor bonds.

In addition, PM3 has been shown that the NDDO approximation can accommodate a wide range of oxidation states, from -3 in, e.g., ammonia to $+6$ in such hypervalent systems as H_2SO_4 , H_3PO_4 , and TeF_6 .

The range of errors in ΔH_f is smaller than that found for the organic elements. This may be due to

the limited number of reference data available; if so, then, as more data become available, highly inaccurate predictions will be made. In particular, for Cd and Bi, the lack of data has resulted in a spuriously high accuracy, an accuracy which will certainly drop as more data are generated.

The parameters for the sixteen elements reported here were optimized simultaneously, but not in one large optimization of the type used for the first twelve elements. Each parameter set was optimized individually, using the previously optimized parameters and the current set of parameters for the other elements reported here. Although advocated earlier, a general optimization of all parameters for all elements being studied proved inefficient relative to the cyclic optimization used here. The main limitation of a general optimization was that a single faulty data-set could rapidly corrupt parameters for many elements, a disaster which would be avoided when serial or cyclic optimization was done. Irrespective of which scheme is used, the final parameters should be the same.

References

1. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).
2. J.J.P. Stewart, *J. Comp. Chem.*, **11**, 543 (1990).
3. M.J.S. Dewar and A.J. Holder, *Organomet.*, **9**, 508 (1990).
4. M.J.S. Dewar, E.F. Healy, A.J. Holder, and Y. Yuan, *J. Comp. Chem.*, **11**, 541 (1990).
5. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
6. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
7. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977).
8. M.J.S. Dewar and H.S. Rzepa, *J. Am. Chem. Soc.*, **100**, 777 (1978).
9. L.P. Davis, R.M. Guidry, J.R. Williams, M.J.S. Dewar, and H.S. Rzepa, *J. Comp. Chem.*, **2**, 433 (1981).
10. M.J.S. Dewar, E.F. Healy, J.J.P. Stewart, J.E. Friedheim, and G.L. Grady, *Organometallics*, **5**, 375 (1986).
11. M.J.S. Dewar and C.H. Reynolds, *J. Comp. Chem.*, **7**, 140 (1986).
12. M.J.S. Dewar and H.S. Rzepa, *J. Comp. Chem.*, **4**, 158 (1983).
13. M.J.S. Dewar and C. Jie, *Organometallics*, **8**, 1544 (1988).
14. M.J.S. Dewar and E.F. Healy, *J. Comp. Chem.*, **4**, 542 (1983).
15. M.J.S. Dewar, E.F. Healy, and J.J.P. Stewart, *J. Comp. Chem.*, **5**, 358 (1984).
16. M.J.S. Dewar, M.K. Holloway, G.L. Grady, and J.J.P. Stewart, *Organometallics*, **4**, 1973 (1985).
17. M.J.S. Dewar and E.G. Zoebisch, *J. Mol. Struct. (Theochem)*, **180**, 1 (1988).
18. M.J.S. Dewar and C. Jie, *Organometallics*, **6**, 1486 (1987).
19. M.J.S. Dewar and C. Jie, *J. Mol. Struct. (Theochem)*, **187**, 1 (1989).
20. M.J.S. Dewar and Y-C Yuan, *J. Inorg. Chem.*, submitted for publication.
21. M.J.S. Dewar and K.M. Merz, *Organometallics*, **7**, 522 (1988).
22. M.J.S. Dewar, D.R. Kuhn, and E.F. Healy, to be published.
23. M.J.S. Dewar and C. Jie, *Organometal.*, **8**, 1547 (1989).
24. D.A. Liotard, E.F. Healy, J.M. Ruiz, and M.J.S. Dewar, *Quant. Chem. Prog. Exch. Bull.*, **9**, 123 (1989).
25. J.O. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.
26. M.W. Chase, C.A. Davies, J.R. Downey, D.R. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, Third Edition, *J. Phys. Chem. Ref. Data*, **14**, Suppl. 1 (1985).
27. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 221 (1989).
28. A. Almenningen, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434, (1964). A. Haaland, *Acta Chem. Scand.*, **22**, 3030 (1968). D.A. Drew and A. Haaland, *Acta Crystallogr., Sect. B*, **28**, 3671 (1972).
29. C.H. Wong, T.Y. Lee, K.J. Chao, and S. Lee, *Acta Crystallogr., Sect. B*, **28**, 1662 (1972).
30. L. Lesiecki and J.W. Nibler, *J. Chem. Phys.* **64**, 871 (1976).
31. S. Tomoda, M. Shimoda, M. Sanami, Y. Takeuchi, and Y. Litaka, *J. Chem. Soc., Chem. Commun.*, 1304 (1989).
32. D.R. Armstrong, P.G. Perkins and J.J.P. Stewart, *J. Chem. Soc., Dalton*, **838** (1973).
33. D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, and R.L. Nutall, *J. Phys. Chem. Ref. Data Suppl.*, **11**, 2 (1982).
34. J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).