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Optimization of Parameters for Semiempirical Methods II. Applications

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# Optimization of Parameters for Semiempirical Methods II. Applications

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MNDO/AM1-type parameters for twelve elements have been optimized using a newly developed method for optimizing parameters for semiempirical methods. With the new method, MNDO-PM3, the average difference between the predicted heats of formation and experimental values for 657 compounds is 7.8 kcal/mol, and for 106 hypervalent compounds, 13.6 kcal/mol. For MNDO the equivalent differences are 13.9 and 75.8 kcal/mol, while those for AM1, in which MNDO parameters are used for aluminum, phosphorus, and sulfur, are 12.7 and 83.1 kcal/mol, respectively. Average errors for ionization potentials, bond angles, and dipole moments are intermediate between those for MNDO and AM1, while errors in bond lengths are slightly reduced.

## INTRODUCTION

The set of approximations developed by Dewar and Thiel used in the modified neglect of diatomic overlap (MNDO) method forms an excellent theoretical framework for modeling molecular systems. Earlier optimizations were limited by available computational power. Thus, the "optimized" parameters did not fully reflect the power of the theoretical model. Even the current parameters, while more completely optimized, are limited in that any errors in experimental data are reflected in the values of the parameters. Further, the large number of almost zero eigenvalues resulting from diagonalization of the parameter Hessian matrix indicate that insufficient constraints have been imposed to unambiguously define the global minimum in parameter space. Two avenues are open for resolving this problem. A systematic survey of physical phenomena such as hyperpolarizabilities, vibrational frequencies, higher ionization potentials (IP), activation barriers, etc. might reveal deficiencies in the parameters which could be rectified by reparameterization. Alternatively, the functional form of the parameters could be studied to determine if simpler functions, namely ones with fewer parameters, could be used. This may be relevant in the case of hydrogen, for example, in which the radii of the two gaussians are almost identical.

Nevertheless, as a member of the MNDO/AM1 family, the current parameter set is likely to prove a useful research tool. In order to allow future discussion of the parameter sets it is proposed that the new set be called MNDO-PM3, for modified neglect of diatomic overlap, parametric method 3, the first two being MNDO itself, and AM1, a reparameterized MNDO with modified core-core interaction terms.

## APPLICATION TO SYSTEMS

Various sets of parameters were obtained using the new procedure for optimizing parameters for semiempirical methods (see the preceding article). In order to adequately assess the predictive power of these parameter sets, a large number of systems were examined, sampling as wide a range of chemistry as possible. As with MNDO<sup>1</sup>, MINDO/3<sup>2</sup>, and AM1<sup>3</sup>, the parameters were optimized to reproduce four gas-phase molecular properties: heats of formation, dipole moments, ionization potentials, and molecular geometries; only these quantities will be surveyed here. In most instances, calculated results will be compared with experiment; however, in a few cases, mostly involving geometries, the results of high-level *ab initio* calculations will be used. As the current parameter sets are derived for the MNDO theoretical method, of which AM1 is a de-

rivative, results from MNDO and AM1 calculations are presented for comparison. For the MNDO calculation, standard MNDO parameter sets were used for H<sup>1</sup>, C<sup>1</sup>, N<sup>1</sup>, O<sup>1</sup>, F<sup>4</sup>, Al<sup>5</sup>, Si<sup>6</sup>, P<sup>6</sup>, S<sup>7</sup>, Cl<sup>8</sup>, Br<sup>9</sup>, and I<sup>10</sup>, while for the AM1 calculation, only the AM1 parameter sets for H<sup>3</sup>, C<sup>3</sup>, N<sup>3</sup>, O<sup>3</sup>, F<sup>11</sup>, Si<sup>12</sup>, Cl<sup>11</sup>, Br<sup>11</sup>, and I<sup>11</sup> were used. For systems involving Al, P, and S, mixed parameter sets were used in the AM1 calculations. MNDO parameters were used for Al, P, and S, and AM1 parameters were used for all other elements. The resulting AM1 errors for compounds containing Al, P, or S were similar to those for MNDO. This allowed a full comparison of the new parameters with those of both MNDO and AM1. The assumption will be made that the experimental data are completely accurate, although, as we will see in the discussion, this assumption is questionable for a limited number of systems.

As a large amount of data is presented in the tables, they are structured to permit rapid location of any given compound. The position within any table involving individual compounds of a specific compound is determined only by its empirical formula in a manner similar to that in Cox and Pilcher.<sup>13</sup> The occurrence and precedence of each element within the empirical formula is in the order H > C > O > N > S > F > Cl > Br > I > Al > Si > P. Thus, C<sub>3</sub>H<sub>8</sub> will occur before C<sub>4</sub>H<sub>6</sub>, and CH<sub>4</sub>S (thiomethane) will occur before HCl. The order of occurrence of a compound within a set having the same empirical formula is random.

### CHOICE OF SURVEY MOLECULES

The choice of molecules to use in comparing parameter sets or methods is by no means obvious. MNDO was parameterized using 34 molecules for the C—H—N—O set<sup>1</sup> and up to a few tens of molecules for the other elements<sup>4-10</sup>, while for AM1 slightly over a hundred molecules were used in the parameterization of the C—H—N—O set.<sup>3</sup> No hypervalent compounds were used for either MNDO or AM1. In the current parameterization, several hundred compounds were used at different times in the optimization. In general, any compound for which the properties were badly reproduced using the emerging parameter set was used in the

next stage of the optimization. In other words, the procedure for optimizing the parameters was designed so as to minimize errors for systems with large errors. As a result, differences between calculated and observed  $\Delta H_f$  and errors in dipoles, IPs, and geometries using the new parameters could be expected to be lower than those for MNDO or AM1.

No valid conclusions regarding the "value" of any parameter set or method may be drawn from a knowledge of which molecules and ions were used in the parameterization and surveys. However, when a survey is carried out with only a small number of compounds, and the compounds used in the survey were also those used in the parameterization, the applicability of the parameters to a wider range of systems is suspect. This was not the case for the parameterization of MNDO, AM1, or the current MNDO-PM3. The value of any semiempirical method depends only on the ability of that method to reproduce experimental observations in a survey, not on the particular set of molecules used for optimizing the parameters. If the survey shows that the method achieves a certain level of accuracy, then it follows logically that the method will also be predictive.

Clearly, any survey cannot be exhaustive. In the  $\Delta H_f$  survey presented here, for example, the homologous series of the alkanes is truncated at nonane. However, the predicted values for properties of many compounds not contained in the survey, among them decane and undecane, may reasonably be inferred by extrapolation from those represented here. Conversely, at present, very little may be inferred as to the predictive power of the new parameters when applied to any systems which are not represented in the survey. This is not true for MNDO, for which a large body of knowledge has been accumulated over the past several years.

All results presented here are for optimized geometries for which either the  $\Delta H_f$  did not drop by more than 0.000001 kcal/mol over 10 cycles of optimization or the gradient norm had dropped below 0.02 kcal/mol/Å. In about 20% of the compounds surveyed the molecular geometries were defined using symmetry relations between bond lengths, bond angles, and torsion angles. Invoking symmetry relationships may unwittingly

constrain the geometry at an arbitrary point on the energy surface. To prevent this potential error, in each case in which symmetry was used the magnitude of the residual forces acting on all atoms was calculated. A prerequisite for symmetry to be used in the definition of any molecular geometry was that the scalar of the residual forces vector had to be below an arbitrarily defined preset limit.

## HEATS OF FORMATION

Experimental and calculated values for the  $\Delta H_f$  of gas-phase compounds are presented in Tables I and II and a statistical analysis is presented in Table III. For all elements except phosphorus, the standard state used is the most stable allotrope at 298 K. Because red phosphorus is not well characterized, recent compendia of thermochemical data, such as the NBS<sup>14</sup> and JANAF<sup>15</sup> tables, are now based on the white allotrope. To allow facile comparison of phosphorus data, the standard state for phosphorus used in this work is the white allotrope. This redefinition lowers the observed heats of formation by approximately 4.2 kcal/mol per phosphorus atom in the compound.

Many calculated heats of formation have been reported in the literature for MNDO<sup>16</sup> and AM1<sup>3</sup>; however, in order to maintain internal consistency, all MNDO and AM1 results reported here were obtained by direct calculation using a modified version of MOPAC 4.00.<sup>17</sup> Earlier calculated heats of formation were deemed unsuitable for two reasons. First, triangular conditions for the  $p$ - $p$  two-electron one-center and  $\pi$ - $\pi$  two-electron two-center integrals were not imposed. This was corrected<sup>17</sup> in 1983 by use of the expressions:

$$\langle pp'|pp' \rangle = 1/2(\langle pp|pp \rangle - \langle pp|p'p' \rangle)$$

and

$$\langle \pi\pi'|\pi\pi' \rangle = 1/2(\langle \pi\pi|\pi\pi \rangle - \langle \pi\pi|\pi'\pi' \rangle)$$

which introduced changes in calculated  $\Delta H_f$  of about 1 kcal/mol. Secondly, the Davidson-Fletcher-Powell optimization technique<sup>18,19</sup> sometimes fails to locate stationary points on the potential energy hypersurface. To a large measure this has been corrected by the BFGS method.<sup>20</sup> The heat of association of water in forming the dimer was reported<sup>3</sup> using the DFP optimizer as -3.5 kcal/mol,

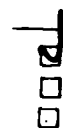
with the BFGS optimizer a heat of dimerization of -5.5 kcal/mol is obtained. *Ab initio* calculations indicate that the heat of dimerization of water is about -5.5 kcal/mol.<sup>21</sup>

Ideally, in order for the standard deviation to be a useful guide to the probable difference between the experimental and calculated  $\Delta H_f$  to be expected for a new molecule, the incidence of differences between calculated and experimental  $\Delta H_f$  should fall on a normal distribution. This may be quantified by calculating the ratio of  $\chi^2$  (the significance) for the actual distribution to the average value expected by chance. For the new method, MNDO, and AM1 these ratios are 3.1, 8.5, and 9.7, respectively, indicating that the difference distribution obtained using the new method is significantly nearer to a normal distribution than those for either MNDO or AM1. For all three methods the majority of the large differences are positive, as can be seen in Figure 1.

## SPECIFIC COMPOUNDS

While differences between calculated and observed  $\Delta H_f$  for normal valent compounds are only slightly reduced, there is a dramatic reduction in the hypervalent compounds. This is most vividly demonstrated in the heats of formation of sulfuric acid and for the halogen pentafluorides. These results are obtained using the MNDO basis set, which does not include any "d" orbitals.

One phosphorus compound,  $P_4O_6$ , is of particular interest. There have been two very different experimental values reported for  $\Delta H_f(P_4O_6)$ :  $-512 \pm 8$  kcal/mol,<sup>22</sup> and  $-378 \pm 6$  kcal/mol,<sup>23</sup> based on red phosphorus, and  $-529.2$  and  $-398.7$  kcal/mol, based on white phosphorus. From mass spectral studies of the phosphorus oxides a value<sup>24</sup> of  $-405 \pm 17$  kcal/mol for  $\Delta H_f(P_4O_6)$  was indicated. AM1 calculations indicate that the  $-398.7$  kcal/mol value is more likely to be correct, while the new parameter set indicates the  $-529.2$  kcal/mol value. The SINDO1 method,<sup>25</sup> which uses  $d$  orbitals, predicts  $\Delta H_f(P_4O_6)$  to be  $-554.1$  kcal/mol at 0 K. When the phosphorus parameters were optimized using  $-398.7$  kcal/mol as the  $\Delta H_f$  of  $P_4O_6$ , the value of the error function,  $S$ , remained very high. To obtain a lower  $S$  the other experimental value had to be used.



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or

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Table I. Comparison of experimental and calculated heats of formation for normal-valent molecules.

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
H	Hydrogen (+)	365.7	353.6	-12.1	-39.0	-50.8	a
H <sub>2</sub>	Hydrogen .....	0.0	-13.4	-13.4	0.7	-5.2	b
CH	Methidyne	142.4	146.8	4.4	1.2	2.6	c
CH <sub>2</sub>	Methylene, triplet	92.3	75.6	-16.7	-15.0	-11.5	d
CH <sub>2</sub>	Methylene, singlet	99.8	113.2	13.4	7.6	11.1	d
CH <sub>3</sub>	Methyl radical	34.8	29.8	-5.0	-9.0	-3.5	d
CH <sub>3</sub>	Methyl (+) .....	261.0	256.5	-4.5	-17.1	-8.6	e
CH <sub>4</sub>	Methane	-17.9	-13.0	4.9	5.9	9.1	f
C <sub>2</sub> H <sub>2</sub>	Acetylene	54.2	50.7	-3.5	3.7	0.6	d
C <sub>2</sub> H <sub>3</sub>	Vinyl	59.6	63.3	3.7	4.2	5.2	h
C <sub>2</sub> H <sub>3</sub>	Vinyl (+)	266.0	263.9	-2.1	-0.3	-4.5	h
C <sub>2</sub> H <sub>4</sub>	Ethylene .....	12.4	16.6	4.2	2.9	4.0	f
C <sub>2</sub> H <sub>4</sub>	Ethylene, radical cation	257.0	248.7	-8.3	-18.7	-13.1	i
C <sub>2</sub> H <sub>4</sub>	Methylmethylene	90.3	88.6	-1.7	-1.9	-2.6	j
C <sub>2</sub> H <sub>5</sub>	Ethyl radical	25.0	17.3	-7.7	-12.2	-6.9	k
C <sub>2</sub> H <sub>5</sub>	Ethyl (+) (classical)	216.0	222.5	6.5	3.7	0.8	l
C <sub>2</sub> H <sub>5</sub>	Ethyl (+) (nonclassical).....	216.0	232.1	16.1	18.7	10.3	l
C <sub>2</sub> H <sub>6</sub>	Ethane	-20.2	-18.1	2.1	0.5	2.8	f
C <sub>3</sub>	Carbon, trimer	196.0	206.6	10.6	24.3	16.4	d
C <sub>3</sub> H <sub>3</sub>	Propynyl (+)	281.0	275.3	-5.7	-15.6	-7.3	i
C <sub>3</sub> H <sub>3</sub>	Cyclopropenyl (+)	257.0	269.8	12.8	15.5	19.4	i
C <sub>3</sub> H <sub>4</sub>	Allene.....	45.6	47.1	1.5	-1.7	0.5	f
C <sub>3</sub> H <sub>4</sub>	Cyclopropene	66.2	68.2	2.0	2.1	8.6	m
C <sub>3</sub> H <sub>4</sub>	Propyne	44.4	40.2	-4.2	-3.0	-1.0	f
C <sub>3</sub> H <sub>5</sub>	Allyl (+)	226.0	232.7	6.7	-4.6	0.2	i
C <sub>3</sub> H <sub>5</sub>	Allyl	40.0	39.6	-0.4	-4.6	-1.4	h
C <sub>3</sub> H <sub>5</sub>	Propenyl (+).....	237.0	238.2	1.2	3.1	-3.3	i
C <sub>3</sub> H <sub>5</sub>	Cyclopropyl (+)	235.0	261.8	26.8	23.2	25.6	i
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	12.7	16.3	3.5	-1.5	5.0	f
C <sub>3</sub> H <sub>6</sub>	Propene	4.9	6.4	1.5	0.1	1.7	f
C <sub>3</sub> H <sub>7</sub>	Propyl (+)	208.0	214.4	6.4	4.4	-0.2	i
C <sub>3</sub> H <sub>7</sub>	2-Propyl (+) .....	192.0	197.3	5.3	8.7	-0.1	l
C <sub>3</sub> H <sub>7</sub>	i-Propyl radical	16.8	5.5	-11.3	-15.4	-10.0	k
C <sub>3</sub> H <sub>8</sub>	Propane	-24.8	-23.6	1.2	-0.1	0.5	f
C <sub>4</sub> H <sub>2</sub>	Diacetylene	113.0	102.5	-10.5	-9.8	-6.9	n
C <sub>4</sub> H <sub>4</sub>	Vinylacetylene	72.8	66.4	-6.4	-7.2	-4.9	n
C <sub>4</sub> H <sub>6</sub>	1-Methylcycloprop-1-ene.....	58.2	57.4	-0.8	-4.5	6.5	f
C <sub>4</sub> H <sub>6</sub>	Bicyclobutane	51.9	69.2	17.3	12.2	26.2	f
C <sub>4</sub> H <sub>6</sub>	1,2-Butadiene	38.8	38.0	-0.8	-5.3	-1.7	f
C <sub>4</sub> H <sub>6</sub>	1-Butyne	39.5	35.7	-3.8	-3.3	-2.0	f
C <sub>4</sub> H <sub>6</sub>	2-Butyne	34.7	29.8	-4.9	-9.8	-2.7	f
C <sub>4</sub> H <sub>6</sub>	Cyclobutene.....	37.5	37.7	0.2	-6.5	8.3	m
C <sub>4</sub> H <sub>6</sub>	Methylenecyclopropane	47.9	44.5	-3.4	-10.0	-0.2	f
C <sub>4</sub> H <sub>6</sub>	1,3-Butadiene	26.0	31.0	5.0	3.0	3.9	f
C <sub>4</sub> H <sub>7</sub>	2-Butenyl (+)	200.0	212.6	12.6	7.0	6.3	i
C <sub>4</sub> H <sub>7</sub>	Cyclobutyl (+)	213.0	225.6	12.6	8.4	13.2	i
C <sub>4</sub> H <sub>8</sub>	1-Butene	-0.2	1.8	2.0	0.6	0.6	f
C <sub>4</sub> H <sub>8</sub>	cis-2-Butene .....	-1.9	-2.5	-0.6	-2.4	-0.3	f
C <sub>4</sub> H <sub>8</sub>	Cyclobutane	6.8	-3.8	-10.6	-18.7	-7.8	f
C <sub>4</sub> H <sub>8</sub>	Isobutene	-4.3	-3.3	1.0	2.3	3.1	f
C <sub>4</sub> H <sub>8</sub>	trans-2-Butene	-3.0	-3.8	-0.8	-2.1	-0.3	f
C <sub>4</sub> H <sub>9</sub>	n-Butyl (+)	201.0	208.0	7.0	5.8	-1.1	i
C <sub>4</sub> H <sub>9</sub>	1-Methyl propyl (+).....	183.0	190.8	7.8	11.0	1.0	i
C <sub>4</sub> H <sub>9</sub>	Isobutyl	4.5	-5.9	-10.4	-11.7	-7.4	k
C <sub>4</sub> H <sub>9</sub>	Isobutyl (+)	176.0	178.7	2.7	12.0	-1.2	i
C <sub>4</sub> H <sub>10</sub>	n-Butane	-30.4	-29.1	1.3	0.7	-0.8	f
C <sub>4</sub> H <sub>10</sub>	Isobutane	-32.4	-29.5	2.9	5.6	3.0	f
C <sub>5</sub> H <sub>5</sub>	Cyclopentadienyl (-) .....	21.3	15.9	-5.4	-2.4	3.9	o
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	32.1	31.8	-0.3	0.0	5.0	m
C <sub>5</sub> H <sub>8</sub>	1,2-Dimethylcyclopropene	46.4	46.7	0.3	-7.2	8.2	p
C <sub>5</sub> H <sub>8</sub>	Methylene cyclobutane	29.1	19.7	-9.4	-18.2	-4.0	q
C <sub>5</sub> H <sub>8</sub>	1,cis-3-Pentadiene	19.1	21.1	2.0	0.6	1.8	f
C <sub>5</sub> H <sub>8</sub>	Cyclopentene .....	8.3	3.0	-5.3	-8.6	-5.3	m

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
C <sub>5</sub> H <sub>8</sub>	Bicyclo(2.1.0)-pentane	37.3	37.8	0.5	-7.1	8.8	p
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene	25.3	26.6	1.3	-0.7	-0.5	f
C <sub>5</sub> H <sub>8</sub>	Spiropentane	44.3	43.1	-1.2	-10.6	6.2	f
C <sub>5</sub> H <sub>8</sub>	1,trans-3-Pentadiene	18.1	21.3	3.2	1.0	2.5	f
C <sub>5</sub> H <sub>9</sub>	Cyclopentyl (+)	188.0	193.5	5.5	6.2	-2.1	r
C <sub>5</sub> H <sub>10</sub>	1-Pentene	-5.3	-4.0	1.3	0.3	-1.4	f
C <sub>5</sub> H <sub>10</sub>	2-Methyl-1-butene	-8.6	-7.9	0.7	2.1	1.8	f
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	-10.1	-12.2	-2.1	-0.4	0.1	f
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	-6.6	-3.9	2.7	4.3	2.2	f
C <sub>5</sub> H <sub>10</sub>	cis-2-Pentene	-7.0	-7.7	-0.7	-2.3	-1.9	f
C <sub>5</sub> H <sub>10</sub>	cis-Dimethylcyclopropane	1.3	1.4	0.1	-3.4	3.5	p
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	-18.3	-23.9	-5.6	-12.2	-10.5	m
C <sub>5</sub> H <sub>10</sub>	trans-2-Pentene	-7.9	-8.7	-0.8	-2.4	-1.8	f
C <sub>5</sub> H <sub>11</sub>	1-Pentyl (+)	194.0	202.4	8.4	7.9	-1.2	i
C <sub>5</sub> H <sub>11</sub>	2-Pentyl (+)	173.0	184.6	11.6	15.5	3.4	i
C <sub>5</sub> H <sub>11</sub>	2-Ethylisopropyl (+)	156.0	171.9	15.9	25.6	10.5	i
C <sub>5</sub> H <sub>11</sub>	Neopentyl (+)	188.0	171.8	-16.2	-6.4	-21.5	t
C <sub>5</sub> H <sub>12</sub>	2-Methylbutane	-36.8	-34.4	2.4	6.8	1.4	f
C <sub>5</sub> H <sub>12</sub>	Neopentane	-40.3	-35.8	4.5	15.7	7.5	f
C <sub>5</sub> H <sub>12</sub>	n-Pentane	-35.1	-34.5	0.6	0.7	-2.9	f
C <sub>6</sub> H <sub>6</sub>	Benzene	19.8	23.5	3.6	1.5	2.2	f
C <sub>6</sub> H <sub>6</sub>	Fulvene	47.5	56.2	8.7	6.2	15.2	f
C <sub>6</sub> H <sub>8</sub>	1,3-Cyclohexadiene	25.4	20.4	-5.0	-10.9	-7.9	f
C <sub>6</sub> H <sub>10</sub>	2,3-Dimethyl-1,3-butadiene	10.8	14.0	3.2	4.3	6.6	f
C <sub>6</sub> H <sub>10</sub>	Cyclohexene	-1.1	-4.9	-3.8	-8.8	-9.0	f
C <sub>6</sub> H <sub>10</sub>	1,5-Hexadiene	20.1	21.1	1.0	-0.5	-2.3	f
C <sub>6</sub> H <sub>10</sub>	1,2-Dimethylcyclobutene	19.8	16.2	-3.6	-13.4	7.2	p
C <sub>6</sub> H <sub>10</sub>	Bicyclopropyl	30.9	36.1	5.2	-2.2	8.6	f
C <sub>6</sub> H <sub>11</sub>	1-Methylcyclopentyl (+)	165.0	174.5	9.5	13.6	2.4	i
C <sub>6</sub> H <sub>11</sub>	Cyclohexyl (+)	177.0	185.1	9.1	9.9	-2.8	r
C <sub>6</sub> H <sub>12</sub>	Cyclohexane	-29.5	-31.0	-1.5	-5.3	-9.0	m
C <sub>6</sub> H <sub>14</sub>	n-Hexane	-39.9	-39.9	0.0	0.8	-4.9	f
C <sub>7</sub> H <sub>7</sub>	Benzyl (+)	216.0	227.4	11.4	2.0	6.1	u
C <sub>7</sub> H <sub>7</sub>	Tropylium (+)	209.0	221.0	12.0	-1.3	1.4	v
C <sub>7</sub> H <sub>8</sub>	Cycloheptatriene	43.2	42.5	-0.7	-9.4	-4.9	m
C <sub>7</sub> H <sub>8</sub>	Norbornadiene	59.7	58.8	-0.9	3.2	8.0	p
C <sub>7</sub> H <sub>8</sub>	Toluene	12.0	14.1	2.1	1.6	2.4	f
C <sub>7</sub> H <sub>11</sub>	2-Norbornyl (+)	182.0	208.5	26.5	31.1	21.0	i
C <sub>7</sub> H <sub>12</sub>	Norbornane	-12.4	-13.7	-1.3	2.0	-2.0	w
C <sub>7</sub> H <sub>16</sub>	n-Heptane	-44.9	-45.3	-0.5	1.0	-6.8	f
C <sub>8</sub> H <sub>8</sub>	Cubane	148.7	113.8	-34.9	-49.6	2.5	f
C <sub>8</sub> H <sub>8</sub>	Styrene	35.3	39.2	3.9	2.3	3.4	f
C <sub>8</sub> H <sub>10</sub>	Ethylbenzene	7.2	9.5	2.3	1.6	1.5	f
C <sub>8</sub> H <sub>14</sub>	Bicyclo(2.2.2)-octane	-24.1	-27.8	-3.7	-2.2	-11.9	w
C <sub>8</sub> H <sub>18</sub>	n-Octane	-49.9	-50.8	-0.8	1.4	-8.6	f
C <sub>9</sub> H <sub>20</sub>	n-Nonane	-54.7	-56.2	-1.5	1.5	-10.7	f
C <sub>10</sub> H <sub>8</sub>	Azulene	73.5	81.3	7.8	-1.4	10.9	f
C <sub>10</sub> H <sub>8</sub>	Naphthalene	36.1	40.7	4.6	2.2	4.5	f
C <sub>10</sub> H <sub>16</sub>	Adamantane	-31.9	-34.6	-2.7	5.5	-11.3	x
C <sub>14</sub> H <sub>10</sub>	Anthracene	55.2	61.7	6.5	3.6	7.7	f
C <sub>14</sub> H <sub>10</sub>	Phenanthrene	49.5	55.0	5.5	6.2	7.9	f
HO	Hydroxide (-)	-33.2	-17.5	15.7	27.4	19.1	o
HO	Hydroxyl radical	9.5	3.0	-6.5	-9.0	-8.6	y
H <sub>2</sub> O	Water	-57.8	-53.4	4.4	-3.1	-1.4	d
H <sub>3</sub> O	Hydronium (+)	138.9	159.1	20.2	-4.7	4.6	d
CO	Carbon monoxide	-26.4	-19.7	6.7	20.5	20.7	d
CHO	HCO	10.4	-9.3	-19.7	-10.8	-11.4	d
CHO	HCO (+)	199.0	176.9	-22.1	-14.1	-11.5	y
CH <sub>2</sub> O	Formaldehyde	-26.0	-34.1	-8.1	-6.9	-5.5	f
CH <sub>2</sub> O	Hydroxymethylene (trans)	53.2	50.5	-2.8	-6.8	-5.0	j
CH <sub>2</sub> O	Hydroxymethylene (cis)	58.5	50.1	-8.4	-12.2	-11.3	j
CH <sub>3</sub> O	Methoxy (-)	-36.0	-37.9	-1.9	-3.7	-2.5	o
CH <sub>3</sub> O	Methoxy	-0.5	-6.8	-6.3	0.3	-3.2	k

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
CH <sub>3</sub> O	CH <sub>2</sub> OH (+)	168.0	166.3	-1.7	-12.4	-6.7	i
CH <sub>4</sub> O	Methanol	-48.1	-51.9	-3.8	-9.3	-8.9	f
C <sub>2</sub> H <sub>2</sub> O	Ketene.....	-11.4	-9.2	2.2	4.6	5.7	f
C <sub>2</sub> H <sub>2</sub> O	HCCOH	36.0	23.2	-12.8	-16.7	-11.5	j
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	-39.7	-44.2	-4.5	-2.5	-1.8	f
C <sub>2</sub> H <sub>4</sub> O	Ethylene oxide	-12.6	-8.1	4.5	-2.9	3.6	f
C <sub>2</sub> H <sub>5</sub> O	Ethoxy (-)	-47.5	-44.8	2.8	2.2	2.0	o
C <sub>2</sub> H <sub>6</sub> O	Ethanol.....	-56.2	-56.8	-0.6	-6.8	-6.5	f
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	-44.0	-48.3	-4.3	-7.2	-9.2	f
C <sub>3</sub> H <sub>6</sub> O	Acetone	-51.9	-53.3	-1.4	2.5	2.7	f
C <sub>3</sub> H <sub>6</sub> O	Propanal	-45.5	-49.3	-3.8	-2.5	-2.8	f
C <sub>3</sub> H <sub>6</sub> O	Trimethylene oxide	-19.3	-26.7	-7.5	-17.9	-6.3	f
C <sub>3</sub> H <sub>8</sub> O	Isopropanol	-65.1	-64.0	1.1	-0.3	-2.9	f
C <sub>3</sub> H <sub>8</sub> O	Propanol.....	-61.2	-63.6	-2.4	-6.3	-9.4	f
C <sub>4</sub> H <sub>4</sub> O	Furan	-8.3	-4.0	4.3	-0.3	11.3	f
C <sub>4</sub> H <sub>6</sub> O	2-Butenal	-24.0	-27.1	-3.1	-3.4	-1.6	f
C <sub>4</sub> H <sub>6</sub> O	Divinyl ether	-3.3	-0.7	2.5	0.5	4.1	f
C <sub>4</sub> H <sub>8</sub> O	2-Butanone CH <sub>3</sub> eclipsed	-57.0	-57.4	-0.4	2.9	1.9	z
C <sub>4</sub> H <sub>8</sub> O	Butanal.....	-48.9	-54.7	-5.8	-3.9	-6.2	f
C <sub>4</sub> H <sub>8</sub> O	Tetrahydrofuran	-44.0	-51.3	-7.3	-15.3	-14.4	f
C <sub>4</sub> H <sub>10</sub> O	Diethyl ether	-60.3	-59.6	0.7	0.1	-4.7	f
C <sub>4</sub> H <sub>10</sub> O	<i>t</i> -Butanol	-74.7	-71.3	3.4	10.4	3.1	f
C <sub>5</sub> H <sub>8</sub> O	Cyclopentanone	-46.0	-37.2	8.8	9.6	9.9	f
C <sub>5</sub> H <sub>10</sub> O	Tetrahydropyran.....	-53.4	-57.4	-4.0	-8.6	-13.7	f
C <sub>5</sub> H <sub>12</sub> O	3-Pentanol	-75.2	-73.8	1.4	1.7	-5.5	f
C <sub>6</sub> H <sub>5</sub> O	Phenoxy (-)	-40.5	-44.1	-3.6	-1.7	-0.5	o
C <sub>6</sub> H <sub>6</sub> O	Phenol	-23.0	-21.7	1.4	-3.6	0.8	f
C <sub>6</sub> H <sub>10</sub> O	Cyclohexanone	-54.0	-60.2	-6.1	-6.1	-9.3	f
C <sub>7</sub> H <sub>6</sub> O	Benzaldehyde.....	-8.8	-10.6	-1.8	-0.8	-0.1	f
C <sub>7</sub> H <sub>8</sub> O	Anisole	-17.3	-14.6	2.7	-0.4	1.4	f
C <sub>10</sub> H <sub>8</sub> O	1-Naphthol	-5.1	-4.1	1.0	-1.7	2.9	f
C <sub>10</sub> H <sub>8</sub> O	2-Naphthol	-10.1	-4.6	5.5	0.4	6.3	f
O <sub>2</sub>	Oxygen (singlet)	22.0	18.4	-3.6	-9.9	-21.3	aa
O <sub>2</sub>	Oxygen (triplet).....	0.0	-4.2	-4.2	-15.3	-27.0	b
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	-32.5	-40.8	-8.3	-5.7	-2.8	d
CO <sub>2</sub>	Carbon dioxide	-94.1	-85.0	9.0	19.0	14.2	d
CHO <sub>2</sub>	Formic acid anion	-106.6	-110.9	-4.3	5.0	-2.8	o
CH <sub>2</sub> O <sub>2</sub>	Formic acid	-90.5	-94.4	-3.9	-2.1	-6.9	c
C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	<i>trans</i> Glyoxal.....	-50.7	-64.3	-13.6	-10.7	-8.0	f
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Acetic acid anion	-122.5	-119.7	2.8	12.5	7.1	o
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-103.3	-102.0	1.3	2.2	0.3	f
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	-83.6	-87.0	-3.4	-1.9	-7.5	n
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Dimethyl peroxide	-30.1	-34.1	-4.0	1.8	3.1	f
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Ethylene glycol.....	-93.9	-95.2	-1.3	-12.2	-13.6	f
C <sub>3</sub> O <sub>2</sub>	Carbon suboxide	-22.4	-24.0	-1.6	-1.1	7.8	f
C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	<i>beta</i> -Propiolactone	-67.6	-70.6	-3.0	-3.3	-3.4	f
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propionic acid	-108.4	-106.4	2.0	2.1	-0.7	f
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	-97.9	-94.1	3.8	4.3	1.5	n
C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	Dimethoxymethane.....	-83.3	-87.4	-4.1	-11.1	-20.0	f
C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	Diacetyl	-78.2	-83.4	-5.2	-0.6	3.3	f
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	Diethyl peroxide	-46.1	-40.0	6.1	7.0	7.7	f
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	Acetylacetone	-90.5	-91.6	-1.1	6.3	4.8	f
C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	<i>p</i> -Benzoquinone	-29.3	-31.5	-2.3	-3.5	4.2	f
C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	Benzoic acid.....	-70.1	-66.2	3.9	2.4	2.1	f
O <sub>3</sub>	Ozone	34.1	51.1	17.0	14.4	3.7	d
C <sub>4</sub> H <sub>2</sub> O <sub>3</sub>	Malic anhydride	-95.2	-90.1	5.1	6.7	18.8	f
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	Acetic anhydride	-137.1	-135.0	2.1	4.5	5.4	f
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Oxalic acid	-175.0	-174.0	1.0	-0.1	2.6	f
H <sub>2</sub> N	Amidogen	45.5	35.4	-10.1	-8.5	-7.1	d
H <sub>3</sub> N	Ammonia.....	-11.0	-3.1	7.9	4.6	3.7	d
H <sub>4</sub> N	Ammonium (+)	155.0	153.4	-1.6	9.6	-4.4	bb
CN	Cyanide	104.0	128.0	24.0	25.3	10.4	d
CHN	Hydrogen cyanide	32.3	33.0	0.7	3.0	-1.3	d

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
CH <sub>3</sub> N	Methyl amine anion	30.5	21.7	-8.8	-7.0	2.6	o
CH <sub>4</sub> N	CH <sub>3</sub> -NH	37.0	27.3	-9.7	-4.3	-2.9	k
CH <sub>3</sub> N	CH <sub>2</sub> -NH <sub>2</sub> (+)	178.0	185.3	7.3	8.8	-1.7	k
CH <sub>5</sub> N	Methylamine	-5.5	-5.2	0.3	-2.1	-1.9	f
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	20.9	23.3	2.4	-1.7	-1.6	cc
C <sub>2</sub> H <sub>3</sub> N	Methyl isocyanide	35.6	54.7	19.1	24.8	14.8	cc
C <sub>2</sub> H <sub>5</sub> N	Ethyleneimine (Azirane)	30.2	31.6	1.4	-5.1	2.9	f
C <sub>2</sub> H <sub>6</sub> N	Me <sub>2</sub> N (-)	24.7	7.8	-16.9	-16.2	-2.3	o
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	-11.4	-12.5	-1.1	-1.8	-3.8	f
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	-6.6	-7.9	-1.3	0.0	1.0	f
C <sub>3</sub> H <sub>3</sub> N	Acrylonitrile	44.1	50.2	6.1	-0.3	0.9	f
C <sub>3</sub> H <sub>5</sub> N	Ethyl cyanide	12.1	18.5	6.4	1.7	0.9	n
C <sub>3</sub> H <sub>9</sub> N	Isopropylamine	-20.0	-18.8	1.3	3.7	0.7	f
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	-6.6	-10.9	-4.3	3.8	4.9	f
C <sub>3</sub> H <sub>9</sub> N	<i>n</i> -Propylamine	-16.8	-17.9	-1.1	-1.4	-5.3	f
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	25.9	27.1	1.2	6.6	14.0	f
C <sub>4</sub> H <sub>9</sub> N	Pyrrolidine	-0.8	-12.0	-11.2	-15.0	-9.6	f
C <sub>4</sub> H <sub>11</sub> N	<i>t</i> -Butylamine	-28.9	-25.2	3.7	13.4	7.7	f
C <sub>5</sub> H <sub>5</sub> N	Pyridine	34.6	30.4	-4.2	-5.8	-2.6	f
C <sub>6</sub> H <sub>7</sub> N	Aniline	20.8	21.3	0.5	0.9	-0.3	f
C <sub>7</sub> H <sub>5</sub> N	Phenyl cyanide	51.5	58.5	7.0	0.5	1.9	f
NO	Nitrogen oxide	21.6	14.8	-6.8	-21.7	-20.4	d
NO	NO (+)	237.0	238.2	1.2	-6.4	-8.8	d
CNO	NCO	38.1	32.4	-5.7	-1.0	0.8	d
CHNO	Hydrogen isocyanate	-24.3	-15.3	9.0	13.5	9.1	d
CH <sub>3</sub> NO	Formamide	-44.5	-41.8	2.7	4.3	-0.3	dd
C <sub>3</sub> H <sub>7</sub> NO	Dimethylformamide	-45.8	-44.6	1.2	8.4	8.9	f
NO <sub>2</sub>	Nitrogen dioxide	7.9	-1.0	-8.9	-12.5	-22.9	d
NO <sub>2</sub>	Nitrogen dioxide (+)	233.0	208.4	-24.6	7.6	-11.9	k
HNO <sub>2</sub>	Nitrous acid, <i>trans</i>	-18.8	-14.9	3.9	-21.9	-20.6	d
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	-17.9	-15.9	2.0	21.2	8.0	f
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	-15.8	-9.1	6.7	-20.9	-16.0	f
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Nitroethane	-23.5	-20.9	2.6	20.2	6.6	f
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Glycine	-93.7	-96.0	-2.3	-2.0	-7.8	f
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	1-Nitropropane	-30.0	-26.8	3.2	21.9	6.2	f
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitropropane	-33.2	-27.1	6.1	26.9	11.6	f
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	Alanine	-111.4	-101.1	10.3	12.7	6.4	f
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	1-Nitrobutane	-34.4	-32.1	2.3	21.6	4.0	f
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	2-Nitrobutane	-39.1	-31.9	7.2	29.0	10.9	f
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene	15.4	14.5	-0.9	20.4	9.9	n
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitrotoluene	9.3	4.7	-4.6	20.6	7.9	ee
NO <sub>3</sub>	Nitrate anion	-74.7	-93.3	-18.6	7.7	-14.2	ff
NO <sub>3</sub>	Nitrate radical	17.0	22.9	5.9	27.9	16.2	d
HNO <sub>3</sub>	Nitric acid	-32.1	-38.0	-5.9	14.6	-5.4	d
CH <sub>3</sub> NO <sub>3</sub>	Methyl nitrate	-29.1	-32.4	-3.3	16.7	-2.2	f
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Ethyl nitrate	-36.8	-36.4	0.5	18.9	-0.4	f
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Nitroethanol	-75.1	-61.4	13.7	29.0	10.5	gg
N <sub>2</sub>	Nitrogen	0.0	17.6	17.6	8.3	11.2	b
H <sub>2</sub> N <sub>2</sub>	Diazene	36.0	37.8	1.8	-4.1	-4.5	hh
H <sub>4</sub> N <sub>2</sub>	Hydrazine	22.8	20.6	-2.1	-8.6	-9.1	d
CH <sub>2</sub> N <sub>2</sub>	Diazomethane	71.0	61.0	-10.0	-3.7	-8.4	f
CH <sub>2</sub> N <sub>2</sub>	<i>N=N-CH<sub>2</sub></i>	79.0	91.7	12.7	-6.6	7.8	ii
CH <sub>2</sub> N <sub>2</sub>	Methylhydrazine	22.6	17.9	-4.7	-8.2	-5.3	f
C <sub>2</sub> N <sub>2</sub>	Cyanogen	73.8	77.5	3.7	-7.2	-5.9	f
C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	1,1-Dimethylhydrazine	20.0	15.1	-4.9	-1.9	4.0	f
C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	1,2-Dimethylhydrazine	22.0	15.6	-6.4	-7.0	-0.5	f
C <sub>4</sub> N <sub>2</sub>	Dicyanoacetylene	126.5	128.1	1.6	-15.1	-6.7	f
C <sub>4</sub> H <sub>2</sub> N <sub>2</sub>	Fumaronitrile	81.3	86.0	4.7	-6.6	-5.3	f
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyridazine	66.5	56.0	-10.5	-22.9	-11.2	f
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrimidine	47.0	38.0	-9.0	-12.0	-3.1	f
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	46.9	39.3	-7.6	-9.1	-2.7	f
C <sub>6</sub> H <sub>14</sub> N <sub>2</sub>	azo- <i>n</i> -Propane	8.6	5.8	-2.8	-6.0	4.3	jj
N <sub>2</sub> O	Nitrous oxide	19.6	25.4	5.8	11.4	8.9	d



Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	<i>n</i> -Nitrodimethylamine	-3.2	1.3	4.5	25.5	24.9	n
C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	Para nitroaniline	16.2	10.7	-5.5	19.4	5.3	f
N <sub>2</sub> O <sub>3</sub>	Dinitrogen trioxide	19.8	23.7	3.9	-6.1	2.1	d
N <sub>2</sub> O <sub>4</sub>	Dinitrogen tetroxide	2.2	8.3	6.2	27.8	22.9	d
CH <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	Dinitromethane .....	-13.3	-11.9	1.4	41.2	16.2	gg
C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	1,1-Dinitroethane	-24.1	-17.4	6.7	47.3	21.5	gg
C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	1,2-Dinitroethane	-22.9	-19.6	3.3	42.9	12.9	gg
C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	1,1-Dinitropropane	-25.9	-22.0	3.9	45.3	16.7	f
C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	1,3-Dinitropropane	-31.6	-26.6	5.0	44.5	12.8	gg
C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	2,2-Dinitropropane .....	-27.0	-23.0	4.0	50.2	21.5	gg
C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	1,1-Dinitrobutane	-34.1	-27.2	6.9	48.9	18.1	gg
C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	1,4-Dinitrobutane	-38.9	-32.7	6.2	45.8	11.2	gg
C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	<i>m</i> -Dinitrobenzene	11.3	9.2	-2.1	43.9	21.8	f
N <sub>2</sub> O <sub>5</sub>	Dinitrogen pentoxide	2.7	-19.0	-21.7	31.5	3.0	d
N <sub>3</sub>	Azide .....	99.0	106.0	7.0	3.4	8.4	y
HN <sub>3</sub>	Hydrazoic acid	70.3	75.3	5.0	2.8	5.5	cc
CHN <sub>3</sub> O <sub>6</sub>	Trinitromethane	-3.2	-4.7	-1.5	61.9	28.2	kk
C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>6</sub>	1,1,1-Trinitroethane	-12.4	-10.0	2.4	68.8	33.5	gg
C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	1,1,1-Trinitropropane	-18.4	-8.1	10.3	76.0	36.9	gg
C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	2,4,6-Trinitrotoluene .....	12.9	3.3	-9.6	61.8	28.4	f
C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>9</sub>	Glycerol trinitrate	-88.6	-76.6	12.0	80.2	17.4	f
CH <sub>2</sub> N <sub>4</sub>	[1 - H]Tetrazole	79.9	86.3	6.3	-26.1	29.7	f
CN <sub>4</sub> O <sub>8</sub>	Tetranitromethane	18.5	6.4	-12.1	76.5	34.6	gg
C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>12</sub>	Pentaerythritol tetranitrate	-92.5	-98.2	-5.7	102.9	-2.8	f
S	S (-)	16.8	20.7	3.9	29.8	29.8	d
HS	HS (-) Ion .....	-17.1	-15.9	1.2	24.0	25.6	ll
HS <sup>-</sup>	Hydrogen sulfide	33.3	38.2	4.9	4.0	5.0	d
H <sub>2</sub> S	Hydrogen sulfide	-4.9	-0.9	4.0	8.7	8.9	d
CS	Carbon sulfide	67.0	97.3	30.3	37.5	32.9	d
CH <sub>3</sub> S	Thiomethanol	-5.4	-5.5	-0.1	-1.9	2.1	f
C <sub>2</sub> H <sub>4</sub> S	Thiirane .....	19.7	28.8	9.1	-0.9	12.6	f
C <sub>2</sub> H <sub>6</sub> S	Thioethanol	-11.0	-8.7	2.3	-2.4	2.4	f
C <sub>2</sub> H <sub>6</sub> S	Dimethyl thioether	-8.9	-11.0	-2.1	-8.1	-0.9	f
C <sub>3</sub> H <sub>6</sub> S	Thietane	14.6	7.5	-7.1	-19.7	-6.6	f
C <sub>3</sub> H <sub>8</sub> S	Isopropanthiol	-18.1	-13.3	4.8	1.9	5.2	d
C <sub>3</sub> H <sub>8</sub> S	1-Propanthiol .....	-16.2	-14.1	2.1	-1.9	0.8	f
C <sub>4</sub> H <sub>4</sub> S	Thiophene	27.6	30.7	3.1	-1.1	9.1	f
C <sub>4</sub> H <sub>6</sub> S	Tetrahydrothiophene	-8.1	-10.4	-2.3	-16.0	-7.9	f
C <sub>4</sub> H <sub>10</sub> S	Butanethiol	-21.1	-19.5	1.6	-1.8	-1.1	d
C <sub>6</sub> H <sub>6</sub> S	Thiophenol	26.9	27.7	0.8	-3.5	2.8	f
C <sub>6</sub> H <sub>12</sub> S	Cyclohexanethiol .....	-23.0	-20.6	2.4	-2.7	-4.2	m
SO	Sulfur monoxide (triplet)	1.2	-13.6	-14.8	3.0	20.8	d
CSO	Carbon oxysulfide	-33.8	-23.8	10.1	11.0	20.1	f
C <sub>2</sub> H <sub>4</sub> SO	Thiolacetic acid	-43.5	-38.9	4.6	2.1	9.0	ii
CHNS	Hydrogen isothiocyanate	30.0	39.5	9.5	13.4	12.0	d
C <sub>2</sub> H <sub>3</sub> NS	Methyl isothiocyanate .....	38.3	36.1	-2.2	-1.4	4.3	cc
C <sub>2</sub> H <sub>3</sub> NS	Methyl thiocyanate	27.1	28.3	1.2	-4.0	2.9	cc
S <sub>2</sub>	Sulfur dimer	30.8	28.7	-2.1	4.0	4.0	d
H <sub>2</sub> S <sub>2</sub>	Hydrogen disulfide	3.7	8.6	4.9	2.8	1.2	cc
CS <sub>2</sub>	Carbon disulfide	28.0	36.9	8.9	8.9	18.7	d
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	Ethanedithiol-1,2 .....	-2.2	1.2	3.4	-4.1	2.9	d
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	2,3-Dithiabutane	-5.6	-4.8	0.8	-9.2	-1.7	f
C <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	S <sub>2</sub> (CN) <sub>2</sub>	82.3	78.5	-3.8	-11.7	-3.9	f
H <sub>2</sub> S <sub>3</sub>	Hydrogen trisulfide	7.3	26.4	19.1	1.1	-0.7	cc
C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	2,3,4-Trithiapentane	0.0	-6.9	-6.9	-13.2	-6.0	mm
C <sub>3</sub> H <sub>4</sub> S <sub>3</sub>	1,3-Dithiolan-2-thione .....	22.7	40.4	17.7	-11.3	15.8	d
S <sub>4</sub>	Sulfur tetramer	34.8	55.2	20.4	11.0	11.0	d
H <sub>2</sub> S <sub>4</sub>	Hydrogen tetrasulfide	10.6	-0.3	-10.9	0.0	-1.7	cc
H <sub>2</sub> S <sub>5</sub>	Hydrogen pentasulfide	13.8	2.0	-11.9	66.2	-0.7	cc
S <sub>8</sub>	S <sub>8</sub>	24.0	18.2	-5.8	-0.7	-0.7	d
F	Fluoride (-) .....	-61.0	-31.2	29.8	43.9	64.4	d
HF	Hydrogen fluoride	-65.1	-62.8	2.4	5.4	-9.1	d
CF	Fluoromethylidyne	61.0	54.0	-7.0	-22.4	-23.0	d

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
CH <sub>2</sub> F	Fluoromethyl (+)	200.3	200.3	0.0	-17.5	-19.9	nn
CH <sub>3</sub> F	Fluoromethane	-56.8	-53.8	3.0	-4.1	-4.2	oo
CH <sub>3</sub> F	Trifluoromethane (+).....	233.3	228.2	-5.1	-10.1	-29.3	nn
C <sub>2</sub> HF	Fluoroacetylene	30.0	18.1	-11.9	-14.3	-14.8	d
C <sub>2</sub> H <sub>3</sub> F	Fluoroethylene	-32.5	-28.6	3.9	-2.0	-1.5	pp
C <sub>2</sub> H <sub>4</sub> F	CH <sub>3</sub> CHF (+)	166.0	172.9	6.9	-1.3	-8.9	qq
C <sub>2</sub> H <sub>5</sub> F	Fluoroethane	-62.9	-60.2	2.7	-2.2	-3.4	f
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	-69.4	-66.8	2.6	2.8	-0.4	f
C <sub>6</sub> H <sub>5</sub> F	Fluorobenzene .....	-27.8	-20.2	7.5	2.5	4.4	f
OF	FO	26.1	21.2	-4.9	-4.4	-3.5	rr
HOF	Hypofluorous acid	-23.5	-29.2	-5.7	4.9	0.9	ss
COF	COF	-42.3	-55.0	-12.7	-7.7	-13.6	g
CHOF	HCOF	-90.0	-88.8	1.2	1.2	-2.9	d
C <sub>2</sub> H <sub>3</sub> OF	Acetyl fluoride .....	-106.4	-98.7	7.7	9.9	7.6	f
C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> F	<i>p</i> -Fluorobenzoic acid	-118.4	-108.9	9.5	5.3	6.4	f
CNF	Cyanogen fluoride	8.6	6.5	-2.1	-10.9	-13.0	d
NOF	Nitrosyl fluoride	-15.7	-3.3	12.4	-9.1	-10.8	d
SF	SF	-4.1	-11.6	-7.5	4.8	12.5	d
F <sub>2</sub>	Fluorine .....	0.0	-21.7	-21.7	7.3	-22.5	b
CF <sub>2</sub>	Difluoromethylene	-45.0	-49.1	-4.1	-20.2	-23.0	g
CHF <sub>2</sub>	Difluoromethyl (+)	142.4	145.5	3.1	-10.0	-20.5	nn
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	-108.1	-103.8	4.4	-3.6	-8.0	f
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane (+)	185.2	180.4	-4.8	-6.8	-33.6	nn
C <sub>2</sub> F <sub>2</sub>	Difluoroacetylene .....	5.0	-11.6	-16.6	-26.0	-24.6	d
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	gem-Difluoroethylene	-80.5	-73.0	7.5	-3.1	-2.2	f
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	CH <sub>3</sub> CF <sub>2</sub> (+)	107.0	122.2	15.2	9.6	-1.7	qq
C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	1,1-Difluoroethane	-118.8	-111.9	6.9	5.4	0.2	f
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	<i>o</i> -Difluorobenzene	-70.3	-63.1	7.2	-0.3	3.9	f
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	<i>m</i> -Difluorobenzene .....	-74.0	-63.3	10.7	3.1	6.1	f
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	<i>p</i> -Difluorobenzene	-73.3	-63.3	10.0	2.3	5.3	f
OF <sub>2</sub>	Difluorine oxide	5.9	-4.8	-10.7	12.3	4.6	d
COF <sub>2</sub>	Carbonyl fluoride	-152.7	-141.6	11.1	14.1	6.4	f
NF <sub>2</sub>	NF <sub>2</sub> (-)	-29.5	-31.0	-1.5	-14.1	4.3	uu
NF <sub>2</sub>	NF <sub>2</sub> .....	10.1	11.9	1.8	-24.9	-16.5	d
N <sub>2</sub> F <sub>2</sub>	<i>cis</i> -Difluorodiazene	16.4	28.0	11.6	-18.6	4.4	d
N <sub>2</sub> F <sub>2</sub>	<i>trans</i> -Difluorodiazene	19.4	29.2	9.8	-17.0	11.9	d
SF <sub>2</sub>	Sulfur difluoride	-70.9	-91.9	-21.0	18.0	28.4	d
S <sub>2</sub> F <sub>2</sub>	FSSF	-80.4	-73.8	6.6	39.1	49.7	d
S <sub>2</sub> F <sub>2</sub>	SSF <sub>2</sub> .....	-95.9	-56.1	39.8	111.4	110.0	d
CF <sub>3</sub>	Trifluoromethyl (-)	-163.4	-178.8	-15.4	-15.4	-15.4	uu
CF <sub>3</sub>	Trifluoromethyl	-112.4	-132.1	-19.7	-24.7	-30.4	d
CF <sub>3</sub>	Trifluoromethyl (+)	99.3	99.6	0.3	1.6	-17.2	nn
CHF <sub>3</sub>	Trifluoromethane	-166.3	-162.0	4.3	2.5	-6.2	f
CHF <sub>3</sub>	Trifluoromethane (+).....	151.9	149.4	-2.5	6.8	-30.7	nn
C <sub>2</sub> HF <sub>3</sub>	Trifluoroethylene	-117.3	-121.5	-4.2	-13.8	-13.3	f
C <sub>2</sub> H <sub>2</sub> F <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub>	-123.6	-131.2	-7.6	-6.0	-7.8	vv
C <sub>2</sub> H <sub>2</sub> F <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> (+)	114.0	122.3	8.3	7.2	0.4	qq
C <sub>2</sub> H <sub>2</sub> F <sub>3</sub>	CH <sub>2</sub> F.CF <sub>2</sub> (+)	81.0	92.7	11.7	1.4	-11.9	qq
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1-Trifluoroethane .....	-178.0	-172.3	5.7	13.6	5.4	f
C <sub>7</sub> H <sub>5</sub> F <sub>3</sub>	Trifluoromethylbenzene	-143.2	-134.9	8.3	15.7	8.8	f
C <sub>2</sub> HO <sub>2</sub> F <sub>3</sub>	Trifluoroacetic acid	-255.0	-244.0	11.0	16.9	12.3	f
NF <sub>3</sub>	Nitrogen trifluoride	-31.6	-24.4	7.2	-2.6	-8.4	d
C <sub>2</sub> NF <sub>3</sub>	Trifluoroacetonitrile	-118.4	-115.1	3.3	5.2	-1.1	d
H <sub>4</sub> F <sub>4</sub>	Hydrogen fluoride tetramer	-282.9	-280.2	2.7	38.6	-30.2	d
CF <sub>4</sub>	Carbon tetrafluoride .....	-223.3	-225.1	-1.8	9.1	-2.4	f
C <sub>2</sub> F <sub>4</sub>	Tetrafluoroethylene	-157.9	-168.2	-10.3	-17.0	-16.9	f
COF <sub>4</sub>	Trifluoromethyl hypofluorite	-182.8	-187.3	-4.5	19.5	5.1	d
N <sub>2</sub> F <sub>4</sub>	Tetrafluorohydrazine	-2.0	-0.5	1.5	-17.7	7.8	d
C <sub>6</sub> HF <sub>5</sub>	Pentafluorobenzene	-192.5	-188.6	3.9	-9.2	0.5	f
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane .....	-321.2	-317.8	3.4	21.6	8.0	d
C <sub>6</sub> F <sub>6</sub>	Hexafluorobenzene	-228.5	-229.3	-0.8	-14.9	-2.6	f
C <sub>3</sub> OF <sub>6</sub>	Perfluoroacetone	-325.2	-340.0	-14.8	3.3	-6.4	ww

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
SF <sub>6</sub>	Sulfur hexafluoride	-291.4	-304.6	-13.2	320.7	294.0	d
C <sub>3</sub> F <sub>8</sub>	Perfluoro cyclobutane	-369.5	-379.2	-9.7	5.8	2.3	f
Cl	Chloride (-)	-55.9	-51.2	4.7	1.2	18.2	d
HCl	Hydrogen chloride	-22.1	-20.5	1.6	6.8	-2.5	d
CCl	Chloromethylidyne	111.3	105.3	-6.1	-3.9	-10.2	g
CHCl	Chloromethylene	80.0	83.2	3.2	0.9	-2.3	d
CH <sub>2</sub> Cl	Methyl chloride	-20.0	-14.7	5.3	-2.5	1.0	d
C <sub>2</sub> HCl	Chloroacetylene	51.1	46.6	-4.5	1.5	-3.3	d
C <sub>2</sub> H <sub>3</sub> Cl	Chloroethylene	8.6	9.7	1.1	-3.7	-2.7	d
C <sub>2</sub> H <sub>5</sub> Cl	Chloroethane	-26.8	-22.1	4.7	-2.0	0.6	ff
HOCl	Hypochlorous acid	-17.8	-34.3	-16.5	2.1	-4.0	d
COCl	COCl	-15.0	-16.1	-1.1	-0.6	-0.4	d
C <sub>7</sub> H <sub>5</sub> OCl	Benzoyl chloride	-26.1	-18.4	7.7	2.7	10.4	f
CNCl	Cyanogen chloride	31.6	31.6	0.0	1.7	-7.0	d
NOCl	Nitrosyl chloride	12.4	4.5	-7.9	-16.6	-7.7	d
SCl	SCl	41.8	28.6	-13.2	-25.3	-25.9	g
FCl	Chlorine fluoride	-12.1	-21.7	-9.6	20.3	1.6	d
HFCl	Hydrogen chloride fluoride (-)	-142.0	-137.0	5.0	15.8	15.9	xx
CH <sub>2</sub> FCl	Fluorochloromethane	-62.6	-57.5	5.0	-5.4	-2.7	d
COFCl	Carbonyl fluoride chloride	-102.0	-93.6	8.4	9.8	10.0	d
CHF <sub>2</sub> Cl	Difluorochloromethane	-115.6	-109.7	5.9	1.2	1.4	f
CF <sub>3</sub> Cl	Trifluorochloromethane	-169.2	-169.3	-0.1	9.6	6.6	d
Cl <sub>2</sub>	Chlorine	0.0	-11.6	-11.6	-10.7	-14.2	b
HCl <sub>2</sub>	Hydrogen dichloride (-)	-142.0	-111.0	31.0	47.2	47.6	xx
CCl <sub>2</sub>	Dichloromethylene	57.0	57.5	0.5	0.6	-8.5	d
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	-23.0	-17.1	5.8	-5.1	-2.9	f
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	<i>gem</i> -Dichloroethylene	0.6	4.0	3.4	-3.2	-3.9	d
C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub>	<i>cis</i> -Dichloroethylene	1.0	4.0	3.0	-3.6	-4.3	d
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	<i>trans</i> -Dichloroethylene	1.2	3.6	2.4	-4.9	-4.6	d
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1,1-Dichloroethane	-30.9	-26.5	4.4	-1.6	-0.2	ff
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1,2-Dichloroethane	-31.0	-24.7	6.3	-5.4	-2.8	ff
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>o</i> -Dichlorobenzene	7.1	11.1	4.0	1.5	2.1	f
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>m</i> -Dichlorobenzene	6.1	10.2	4.1	0.5	2.1	f
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>p</i> -Dichlorobenzene	5.3	10.1	4.8	1.1	2.7	f
OCl <sub>2</sub>	Chlorine monoxide	25.0	-16.2	-41.2	6.3	-5.5	d
COCl <sub>2</sub>	Carbonyl chloride	-52.6	-49.1	3.5	0.0	5.3	d
SCl <sub>2</sub>	Sulfur dichloride	-4.2	-10.9	-6.7	-19.7	-20.7	d
S <sub>2</sub> Cl <sub>2</sub>	ClSSCl	-4.0	-7.7	-3.7	-16.8	-17.6	d
CHFCl <sub>2</sub>	Fluorodichloromethane	-67.7	-62.0	5.7	-1.5	2.5	dd
CF <sub>2</sub> Cl <sub>2</sub>	Difluorodichloromethane	-117.5	-116.1	1.4	7.3	10.5	d
CCl <sub>3</sub>	Trichloromethyl	21.0	1.6	-19.4	-20.5	-25.7	g
CHCl <sub>3</sub>	Chloroform	-24.7	-20.9	3.8	-4.3	-4.3	dd
C <sub>2</sub> HCl <sub>3</sub>	Trichloroethylene	-2.0	-2.3	-0.3	-4.4	-6.4	d
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	1,1,1-Trichloroethane	-35.5	-31.9	3.6	4.0	3.6	f
CFCl <sub>3</sub>	Fluorotrichloromethane	-69.0	-67.3	1.7	3.8	8.1	d
CCl <sub>4</sub>	Carbon tetrachloride	-22.9	-26.0	-3.1	-2.6	-5.2	d
C <sub>2</sub> Cl <sub>4</sub>	Tetrachloroethylene	-2.7	-8.1	-5.4	-5.3	-9.7	f
C <sub>2</sub> Cl <sub>6</sub>	Hexachloroethane	-34.5	-36.5	-2.0	7.1	-1.3	f
C <sub>6</sub> Cl <sub>6</sub>	Hexachlorobenzene	-8.6	-9.1	-0.5	6.0	0.8	f
Br	Bromide (-)	-52.3	-56.2	-3.9	14.8	31.9	d
HBr	Hydrogen bromide	-8.7	5.3	14.0	12.4	-1.8	d
HBr	HBr (+)	261.1	274.7	13.6	16.8	-12.3	yy
CBr	Bromomethylidyne	125.9	138.4	12.5	1.6	0.9	g
CH <sub>3</sub> Br	Bromomethane	-9.1	-2.0	7.1	-1.3	2.9	f
C <sub>2</sub> H <sub>3</sub> Br	Bromoethylene	18.7	23.8	5.1	-2.9	-0.8	f
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	-15.2	-11.4	3.8	-1.8	2.1	f
C <sub>3</sub> H <sub>3</sub> Br	3-Bromopropene	10.9	15.3	4.4	-2.1	1.5	zz
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	-20.5	-16.7	3.8	-1.5	0.6	f
C <sub>3</sub> H <sub>7</sub> Br	2-Bromopropane	-23.5	-20.9	2.6	2.8	5.6	aaa
C <sub>6</sub> H <sub>5</sub> Br	Bromobenzene	25.2	31.0	5.8	-1.3	1.5	f
HOBr	Hypobromous acid	-20.0	-33.9	-13.9	-2.7	-4.7	bbb
COBr	COBR	20.5	-10.2	-30.7	-28.8	-25.6	g

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
C <sub>2</sub> H <sub>3</sub> OBr	Acetyl bromide	-45.6	-43.5	2.1	2.4	11.3	f
C <sub>7</sub> H <sub>5</sub> OBr	Benzoyl bromide	-11.6	-7.7	4.0	0.7	12.9	f
CNBr	Cyanogen bromide	43.3	53.7	10.4	-2.3	-10.8	f
NOBr	Nitrosyl bromide	19.6	6.6	-13.0	-17.8	1.7	d
SBr	SBr	56.1	48.3	-7.8	-26.7	-28.0	g
FBr	Bromine fluoride	-14.0	-21.3	-7.3	8.2	6.8	d
CF <sub>3</sub> Br	Bromotrifluoromethane	-155.1	-157.9	-2.8	8.5	10.5	d
ClBr	Bromine chloride	3.5	-3.2	-6.7	-13.0	-14.1	J
ClBr	Bromine chloride (+)	261.0	247.6	-13.4	4.8	-14.6	ff
CCl <sub>3</sub> Br	Trichlorobromomethane	-9.3	-14.1	-4.8	-5.8	-5.4	f
Br <sub>2</sub>	Bromine	7.4	4.9	-2.5	-9.1	-12.7	d
Br <sub>2</sub>	Bromine (+)	253.5	263.0	9.5	12.5	-7.7	yy
CBr <sub>2</sub>	Dibromomethylene	84.3	104.9	20.6	7.8	5.7	g
CH <sub>2</sub> Br <sub>2</sub>	Dibromomethane	-3.5	7.9	11.4	-1.6	2.5	ccc
COBr <sub>2</sub>	Carbonyl bromide	-20.1	-25.3	-5.2	-11.5	2.3	f
SBr <sub>2</sub>	Sulfur dibromide	48.0	24.9	-23.1	-48.2	-48.5	g
S <sub>2</sub> Br <sub>2</sub>	S <sub>2</sub> Br <sub>2</sub>	25.1	21.8	-3.3	-23.6	-23.5	g
C <sub>2</sub> F <sub>4</sub> Br <sub>2</sub>	1,2-Dibromotetrafluoroethane	-189.0	-191.3	-2.3	18.6	27.8	aaa
CBr <sub>3</sub>	Tribromomethyl	64.7	64.2	-0.5	-35.8	-37.8	g
CHBr <sub>3</sub>	Bromoform	4.4	17.5	13.1	-1.3	2.0	ccc
CBr <sub>4</sub>	Carbon tetrabromide	35.1	32.9	-2.2	-21.3	-19.2	g
I	Iodide (-)	-46.5	-64.6	-18.1	40.1	44.3	d
HI	Hydrogen iodide	6.3	28.8	22.5	9.4	1.6	d
CI	Iodomethylidene	144.8	145.5	0.7	7.1	6.2	g
CH <sub>3</sub> I	Methyl iodide	3.4	9.4	6.0	-1.5	2.3	f
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	-2.0	2.1	4.1	-2.5	0.9	f
C <sub>3</sub> H <sub>5</sub> I	Allyl iodide	22.8	30.2	7.4	-3.3	-0.4	f
C <sub>3</sub> H <sub>5</sub> I	E-1-Iodo-1-propene	22.3	25.4	3.2	-7.8	-2.6	m
C <sub>3</sub> H <sub>5</sub> I	Z-1-Iodo-1-propene	20.7	29.2	8.6	-5.4	-0.2	m
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane	-7.1	-3.0	4.2	-2.2	-0.7	f
C <sub>3</sub> H <sub>7</sub> I	2-Iodopropane	-9.8	-5.3	4.5	2.3	4.1	f
C <sub>4</sub> H <sub>9</sub> I	1-Butyl iodide	-12.0	-8.3	3.7	-2.0	-2.7	f
C <sub>4</sub> H <sub>9</sub> I	2-Iodo-2-methylpropane	-17.2	-12.5	4.7	10.7	8.9	m
C <sub>6</sub> H <sub>5</sub> I	Iodobenzene	39.4	44.7	5.3	-6.9	-1.3	m
C <sub>6</sub> H <sub>11</sub> I	Iodocyclohexane	-11.9	-11.7	0.2	-5.0	-8.1	m
C <sub>7</sub> H <sub>7</sub> I	<i>o</i> -Iodotoluene	31.7	38.8	7.1	-4.7	0.1	m
C <sub>7</sub> H <sub>7</sub> I	<i>m</i> -Iodotoluene	31.9	35.3	3.4	-7.1	-1.4	m
C <sub>7</sub> H <sub>7</sub> I	<i>p</i> -Iodotoluene	29.1	35.3	6.2	-4.4	1.3	f
C <sub>7</sub> H <sub>7</sub> I	Benzyl iodide	25.1	37.6	12.5	3.6	5.8	f
COI	COI	63.5	-2.9	-66.4	-62.5	-58.8	g
C <sub>2</sub> H <sub>3</sub> OI	Acetyl iodide	-30.2	-29.9	0.3	3.3	9.5	m
C <sub>3</sub> H <sub>5</sub> OI	1-Iodo-2-propanone	-31.2	-26.5	4.7	-1.6	0.2	m
C <sub>7</sub> H <sub>5</sub> OI	Benzoyl iodide	2.5	8.0	5.5	2.6	11.6	m
CNI	Cyanogen iodide	53.7	63.5	9.8	-14.1	-11.1	m
NOI	Nitrosyl iodide	26.8	18.2	-8.6	-5.9	5.5	d
SI	SI	73.1	58.0	-15.1	-26.4	-28.2	g
FI	Iodine fluoride	-22.6	-8.0	14.6	13.4	13.5	d
CF <sub>3</sub> I	Trifluoroiodomethane	-140.5	-137.9	2.5	12.3	7.9	m
ClI	Iodine chloride	4.6	10.8	6.2	-11.4	-9.2	dd
BrI	Iodine bromide	9.8	15.6	5.9	-2.5	-3.8	d
I <sub>2</sub>	Iodine	14.9	20.7	5.8	6.3	4.9	d
Cl <sub>2</sub>	Diiodomethylene	120.4	121.6	1.2	-15.5	1.2	g
CH <sub>2</sub> I <sub>2</sub>	Diiodomethane	27.0	33.5	6.5	-10.2	-5.5	yy
C <sub>2</sub> H <sub>2</sub> I <sub>2</sub>	E-1,2-Diiodoethene	49.6	55.0	5.4	-14.3	-5.5	m
C <sub>2</sub> H <sub>2</sub> I <sub>2</sub>	z-1,2-Diiodoethene	49.6	60.5	11.0	-14.5	-6.1	m
C <sub>2</sub> H <sub>4</sub> I <sub>2</sub>	1,2-Diiodoethane	16.0	23.3	7.4	-4.4	-0.2	m
C <sub>3</sub> H <sub>6</sub> I <sub>2</sub>	1,2-Diiodopropane	8.5	20.8	12.3	-1.2	1.2	f
C <sub>4</sub> H <sub>8</sub> I <sub>2</sub>	1,2-Diiodobutane	2.7	16.1	13.4	3.7	3.5	f
C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	<i>o</i> -Diiodobenzene	60.2	73.8	13.7	-15.4	-6.1	m
COI <sub>2</sub>	Carbonyl iodide	9.6	-1.5	-11.1	-15.1	-3.0	g
SI <sub>2</sub>	Sulfur diiodide	81.9	51.6	-30.3	-52.4	-55.9	g
S <sub>2</sub> I <sub>2</sub>	S <sub>2</sub> I <sub>2</sub>	59.0	46.3	-12.7	-26.7	-30.1	g
Cl <sub>3</sub>	Triiodomethyl	117.3	105.7	-11.6	-68.0	-52.7	g

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
CHI <sub>3</sub>	Iodoform	50.4	60.6	10.2	-18.4	-12.6	ccc
Cl <sub>4</sub>	Carbon tetraiodide	108.2	102.7	-5.5	-61.3	-54.0	g
Al	Al (+)	218.1	279.8	61.7	-24.2	-24.2	d
HAL	AlH	62.0	70.1	8.1	-16.0	-7.4	d
C <sub>3</sub> H <sub>9</sub> Al	Trimethylaluminum	-20.9	-5.7	15.2	-19.2	21.8	f
AlO	AlO (-).....	-64.4	-50.9	13.5	8.6	34.8	d
AlO	AlO	16.0	-7.8	-23.9	-17.8	9.1	d
AlO	AlO (+)	237.3	202.4	-34.9	-14.2	11.3	d
HALO	AlOH (-)	-55.0	-105.7	-50.7	13.9	32.0	d
HALO	Al-O-H	-43.0	-33.4	9.6	-18.1	8.3	d
HALO	AlOH (+).....	130.0	129.3	-0.7	59.2	60.7	d
HALO	H-Al=O	-8.0	2.2	10.2	-13.7	15.3	d
AlO <sub>2</sub>	AlO <sub>2</sub> (-) ion	-116.0	-117.1	-1.1	25.5	59.3	d
AlO <sub>2</sub>	AlO <sub>2</sub>	-20.6	-37.4	-16.8	6.2	47.9	d
HALO <sub>2</sub>	AlO <sub>2</sub> H	-110.0	-105.1	4.9	16.2	57.5	d
AlN	Aluminum nitride.....	125.0	75.5	-49.5	15.9	30.0	d
AlF	Aluminum fluoride	-63.5	-50.1	13.4	-20.1	4.8	d
AlF	AlF (+)	165.4	160.4	-5.0	-50.6	-27.1	d
AlOF	AlFO	-139.0	-124.7	14.3	25.4	71.2	d
AlF <sub>2</sub>	AlF <sub>2</sub> (-) ion	-217.0	-229.6	-12.6	7.4	56.8	d
AlF <sub>2</sub>	AlF <sub>2</sub> .....	-166.0	-162.7	3.3	-5.1	42.6	d
AlF <sub>2</sub>	AlF <sub>2</sub> (+)	22.0	29.0	7.0	-7.8	37.7	d
AlOF <sub>2</sub>	AlF <sub>2</sub> O (-) Ion	-311.6	-286.0	25.6	53.7	118.1	d
AlOF <sub>2</sub>	AlF <sub>2</sub> O	-265.0	-208.5	56.5	62.5	124.6	d
AlF <sub>3</sub>	Aluminum trifluoride	-289.0	-291.5	-2.5	-2.3	71.3	d
AlF <sub>4</sub>	AlF <sub>4</sub> (-) ion.....	-476.0	-469.2	6.8	35.4	135.9	d
AlCl	Aluminum chloride	-12.3	-5.5	6.8	-15.5	-13.4	d
AlCl	Aluminum chloride (+)	206.0	198.7	-7.3	-31.2	-33.8	d
AlOCl	AlClO	-83.2	-72.4	10.8	14.5	38.0	d
AlFCl	AlClF	-117.0	-116.0	1.0	-7.7	17.9	d
AlFCl	Aluminum chloride fluoride....	66.0	74.9	8.9	-2.5	17.4	d
AlF <sub>2</sub> Cl	AlClF <sub>2</sub>	-238.8	-234.6	4.2	-2.8	46.1	d
AlCl <sub>2</sub>	AlCl <sub>2</sub> (-) ion	-115.0	-145.0	-30.0	-15.6	-5.0	d
AlCl <sub>2</sub>	Aluminum dichloride	-67.0	-68.2	-1.2	-7.6	-6.1	d
AlCl <sub>2</sub>	AlCl <sub>2</sub> (+)	115.0	124.3	9.3	3.9	-4.4	d
AlFCl <sub>2</sub>	AlCl <sub>2</sub> F.....	-189.0	-178.0	11.0	-2.4	21.8	d
AlCl <sub>3</sub>	Aluminum trichloride	-139.7	-122.1	17.6	-0.6	-2.3	d
AlBr <sub>3</sub>	Aluminum tribromide	-98.1	-85.8	12.3	37.8	8.7	d
AlI	AlI	16.2	49.3	33.1	15.0	14.9	d
AlI <sub>3</sub>	Aluminum triiodide	-46.2	-39.9	6.3	57.8	51.1	d
Al <sub>2</sub>	Al <sub>2</sub> .....	116.4	79.6	-36.8	14.9	14.9	d
Al <sub>2</sub> O	Al <sub>2</sub> O	-34.7	-28.6	6.1	-37.0	16.1	d
Al <sub>2</sub> O	Al <sub>2</sub> O (+)	155.9	168.4	12.6	-46.8	2.3	d
Al <sub>2</sub> O <sub>2</sub>	Al <sub>2</sub> O <sub>2</sub>	-94.3	-87.6	6.8	-13.5	60.9	d
Al <sub>2</sub> F <sub>6</sub>	Al <sub>2</sub> F <sub>6</sub>	-629.5	-631.4	-1.9	-2.1	148.9	d
Al <sub>2</sub> Cl <sub>6</sub>	Al <sub>2</sub> Cl <sub>6</sub> .....	-309.7	-311.2	-1.5	14.4	7.9	d
Al <sub>2</sub> Br <sub>6</sub>	Al <sub>2</sub> Br <sub>6</sub>	-224.0	-224.9	-0.9	91.4	26.7	d
Al <sub>2</sub> I <sub>6</sub>	Al <sub>2</sub> I <sub>6</sub>	-117.0	-117.4	-0.4	124.4	107.2	d
HSi	SiH	86.3	94.6	8.3	3.9	3.5	ff
H <sub>2</sub> Si	Silylene (singlet)	61.1	72.8	11.7	3.2	6.7	ddd
H <sub>2</sub> Si	Silylene (triplet)	6.5	-2.9	-9.4	-2.7	-30.7	eee
H <sub>3</sub> Si	Silyl (-).....	14.0	-2.8	-16.8	32.5	-15.8	fff
H <sub>3</sub> Si	Silyl	46.4	42.9	-3.5	-9.5	-20.1	ggg
H <sub>3</sub> Si	Silyl (+)	234.1	223.3	-10.8	-43.3	-11.2	fff
H <sub>4</sub> Si	Silane	8.2	12.5	4.3	-7.0	-4.1	d
CH <sub>3</sub> Si	Methylsilyl	30.5	23.3	-7.2	-11.5	-21.5	ggg
CH <sub>3</sub> Si	Methylsilane.....	-7.8	-3.6	4.2	-5.8	-3.0	m
C <sub>2</sub> H <sub>6</sub> Si	Vinylsilane	-1.9	19.7	21.6	8.2	13.3	ff
C <sub>2</sub> H <sub>5</sub> Si	Dimethylsilyl	14.3	3.9	-10.4	-13.6	-21.8	ggg
C <sub>2</sub> H <sub>5</sub> Si	Ethylsilane	-15.0	-10.2	4.8	-6.7	-1.5	hhh
C <sub>2</sub> H <sub>6</sub> Si	Dimethylsilane	-20.0	-20.8	-0.8	-9.2	-5.6	m
C <sub>3</sub> H <sub>9</sub> Si	Trimethylsilyl.....	-0.8	-14.9	-14.1	-16.9	-22.1	ggg
C <sub>3</sub> H <sub>9</sub> Si	Trimethylsilane	-37.4	-37.3	0.1	-6.9	-1.9	m

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
C <sub>4</sub> H <sub>12</sub> Si	Diethylsilane	-43.6	-32.6	11.0	-0.5	7.3	iii
C <sub>4</sub> H <sub>12</sub> Si	Tetramethylsilane	-55.7	-53.7	2.0	-3.4	3.6	jjj
C <sub>5</sub> H <sub>12</sub> Si	1,1-Dimethylsilacyclobutane	-33.7	-35.6	-1.9	-14.7	-3.5	m
C <sub>6</sub> H <sub>16</sub> Si	Triethylsilane	-39.5	-55.4	-15.9	-24.5	-15.2	iii
C <sub>8</sub> H <sub>20</sub> Si	Tetraethylsilane	-64.4	-77.9	-13.5	-17.8	-7.4	iii
SiO	Silicon monoxide	-23.9	-26.0	-2.1	1.3	21.8	g
C <sub>3</sub> H <sub>10</sub> SiO	Trimethylsilicon hydroxide	-119.4	-115.4	4.0	-2.5	8.9	f
SiO <sub>2</sub>	Silicon dioxide	-73.0	-88.9	-15.9	50.1	5.5	d
SiF	Silicon fluoride	1.7	-20.9	-22.6	-30.5	-27.8	ff
H <sub>3</sub> SiF	Fluorosilane	-90.0	-77.4	12.6	-6.4	4.2	kkk
SiOF	SiOF	-136.1	-107.5	28.6	56.1	30.1	g
SiF <sub>2</sub>	Silicon difluoride	-141.2	-154.9	-13.7	-23.7	-13.4	kkk
H <sub>2</sub> SiF <sub>2</sub>	Difluorosilane	-189.0	-175.2	13.8	-3.5	7.5	kkk
SiOF <sub>2</sub>	SiOF <sub>2</sub>	-231.0	-229.4	1.6	42.4	10.3	d
SiF <sub>3</sub>	Trifluorosilyl	-245.0	-260.3	-15.3	-3.9	-22.8	ggg
HSiF <sub>3</sub>	Trifluorosilane	-287.0	-280.2	6.8	1.9	6.1	d
SiF <sub>4</sub>	Silicon tetrafluoride	-386.0	-390.6	-4.6	15.6	4.0	kkk
SiCl	Silicon chloride	45.3	29.8	-15.5	-15.6	-18.0	ff
H <sub>3</sub> SiCl	Chlorosilane	-32.4	-27.6	4.8	-11.5	-5.3	kkk
C <sub>2</sub> H <sub>7</sub> SiCl	Chlorodimethylsilane	-69.9	-63.7	6.2	-3.1	-0.1	iii
C <sub>3</sub> H <sub>9</sub> SiCl	Chlorotrimethylsilane	-84.6	-81.6	3.0	-2.8	-0.2	f
SiOCl	SiOCl	-86.7	-59.0	27.7	44.2	28.6	g
SiCl <sub>2</sub>	Silicon dichloride	-40.6	-49.4	-8.8	-5.7	-6.1	kkk
H <sub>2</sub> SiCl <sub>2</sub>	Dichlorosilane	-75.3	-69.5	5.8	-8.2	-5.4	kkk
CH <sub>4</sub> SiCl <sub>2</sub>	Dichloromethylsilane	-96.0	-88.9	7.1	-1.4	-2.5	f
C <sub>2</sub> H <sub>6</sub> SiCl <sub>2</sub>	Dichlorodimethylsilane	-109.5	-108.1	1.4	-1.8	-5.8	m
SiOCl <sub>2</sub>	SiOCl <sub>2</sub>	-167.7	-121.2	46.5	73.6	49.4	g
SiCl <sub>3</sub>	Trichlorosilyl	-76.0	-94.8	-18.8	-13.5	-40.0	ggg
HSiCl <sub>3</sub>	Trichlorosilane	-119.3	-112.7	6.6	1.4	-5.8	kkk
CH <sub>3</sub> SiCl <sub>3</sub>	Trichloromethylsilane	-131.2	-132.9	-1.7	0.6	-12.4	m
SiCl <sub>4</sub>	Silicon tetrachloride	-158.4	-156.4	2.0	10.8	-12.5	d
SiBr	Silicon bromide	50.0	41.0	-9.0	7.8	-3.0	ff
H <sub>3</sub> SiBr	Bromosilane	-15.3	-16.0	-0.7	-2.7	-5.8	lll
C <sub>3</sub> H <sub>9</sub> SiBr	Trimethylbromosilane	-70.0	-68.5	1.5	7.7	3.6	f
SiOBr	SiOBr	-71.4	-47.1	24.3	42.8	31.1	g
SiBr <sub>2</sub>	Silicon dibromide	-9.6	-27.4	-17.8	20.8	3.6	kkk
H <sub>2</sub> SiBr <sub>2</sub>	Dibromosilane	-43.2	-47.2	-4.0	11.2	-2.6	kkk
SiOBr <sub>2</sub>	SiOBr <sub>2</sub>	-137.4	-94.1	43.3	86.0	60.0	g
SiBr <sub>3</sub>	Silicon tribromide	-56.1	-60.8	-4.7	41.1	-9.6	g
HSiBr <sub>3</sub>	Tribromosilane	-72.5	-79.6	-7.1	30.1	2.3	lll
SiBr <sub>4</sub>	Silicon tetrabromide	-99.3	-107.9	-8.6	48.9	4.8	ff
SiI	Silicon iodide	76.4	71.0	-5.4	15.5	4.1	g
H <sub>3</sub> SiI	Iodosilane	-0.5	0.9	1.4	11.5	5.4	kkk
SiOI	SiOI	-53.3	-47.9	5.4	37.7	43.3	g
SiI <sub>2</sub>	Silicon diiodide	22.0	24.0	2.0	60.1	35.5	kkk
H <sub>2</sub> SiI <sub>2</sub>	Diiodosilane	-9.1	-12.4	-3.3	32.1	14.1	d
SiOI <sub>2</sub>	SiOI <sub>2</sub>	-99.4	-50.2	49.2	89.7	80.7	g
SiI <sub>3</sub>	Silicon triiodide	0.5	4.7	4.2	44.9	11.9	g
HSiI <sub>3</sub>	Triiodosilane	-17.8	-9.0	8.8	51.9	21.7	kkk
SiI <sub>4</sub>	Silicon tetraiodide	-26.4	-14.2	12.2	68.8	28.0	d
Si <sub>2</sub>	Silicon dimer	140.9	135.7	-5.2	74.4	-1.4	g
H <sub>6</sub> Si <sub>2</sub>	Disilane	17.1	17.9	0.8	5.3	-0.9	mmm
C <sub>6</sub> H <sub>18</sub> Si <sub>2</sub>	Hexamethylidisilane	-85.8	-83.2	2.7	12.1	19.7	m
C <sub>6</sub> H <sub>18</sub> Si <sub>2</sub> O	Hexamethylidisiloxane	-185.8	-182.8	3.0	-8.8	18.1	f
C <sub>6</sub> H <sub>19</sub> Si <sub>2</sub> N	Hexamethylidisilazane	-113.9	-120.8	-6.9	-9.7	-4.1	f
Si <sub>2</sub> Cl <sub>6</sub>	Hexachlorodisilane	-243.5	-229.7	13.8	30.8	1.9	mmm
Si <sub>2</sub> Br <sub>6</sub>	Hexabromodisilane	-182.8	-164.7	18.1	116.9	38.9	g
Si <sub>3</sub>	Silicon trimer	152.2	152.8	0.6	15.0	32.7	g
H <sub>8</sub> Si <sub>3</sub>	Si <sub>3</sub> H <sub>8</sub>	28.9	21.7	-7.2	2.9	-4.3	ff
HP	Phosphinidene	60.6	73.4	12.8	27.9	31.4	d
H <sub>2</sub> P	Phosphino	30.1	29.3	-0.8	1.3	6.8	d

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
H <sub>3</sub> P	Phosphine	1.3	0.2	-1.1	2.6	8.3	d
CP	Carbon phosphide	107.5	119.6	12.1	22.1	28.7	d
CHP	Methinophosphine	35.8	46.5	10.7	6.4	14.9	d
CH <sub>3</sub> P	Methylphosphine.....	-7.0	-9.5	-2.5	-7.7	2.0	nnn
C <sub>2</sub> H <sub>7</sub> P	Ethylphosphine	-12.0	-11.7	0.3	-9.1	-0.2	nnn
C <sub>2</sub> H <sub>7</sub> P	Dimethylphosphine	-15.0	-19.6	-4.6	-17.1	-3.2	nnn
C <sub>3</sub> H <sub>9</sub> P	Trimethylphosphine	-22.5	-29.8	-7.3	-25.7	-8.1	f
C <sub>4</sub> H <sub>11</sub> P	Diethylphosphine	-25.0	-23.3	1.7	-20.0	-6.5	nnn
C <sub>6</sub> H <sub>15</sub> P	Triethylphosphine.....	-11.8	-36.7	-24.9	-53.0	-37.1	f
PO	Phosphorus oxide	-2.9	-19.5	-16.6	-18.1	7.6	g
NP	Phosphorus nitride	25.0	32.9	7.9	8.9	25.3	d
PF	Phosphorus fluoride	-20.8	-20.4	0.4	10.9	0.0	g
POF	POF	-111.8	-124.0	-12.2	-2.4	31.8	g
PF <sub>2</sub>	Phosphorus difluoride.....	-119.0	-144.4	-25.4	-19.0	11.2	g
PF <sub>3</sub>	Phosphorus trifluoride	-229.1	-252.2	-23.1	-0.2	40.5	d
PCl	Phosphorus chloride	25.6	28.9	3.3	10.8	7.3	g
POCl <sub>1</sub>	POCl	-64.7	-76.4	-11.7	-10.1	14.2	g
PCl <sub>2</sub>	Phosphorus dichloride	-21.3	-40.1	-18.8	-28.1	-31.5	g
PCl <sub>3</sub>	Phosphorus trichloride	-69.0	-88.5	-19.5	-27.4	-31.5	d
PBr	Phosphorus bromide.....	43.0	34.9	-8.1	-13.6	-17.7	dd
POBr	POBr	-50.2	-59.9	-9.7	-3.7	23.0	g
PBr <sub>2</sub>	Phosphorus dibromide	6.7	0.4	-6.3	-16.0	-20.4	g
PBr <sub>3</sub>	Phosphorus tribromide	-34.9	-28.2	6.7	-3.2	-4.9	d
PI	PI, triplet	54.6	51.0	-3.6	-3.1	12.6	g
POI	POI.....	-33.4	-43.6	-10.2	8.8	31.9	g
PI <sub>2</sub>	Phosphorus diiodide	41.3	36.6	-4.7	-4.8	-8.6	g
PI <sub>3</sub>	Phosphorus triiodide	25.1	31.3	6.2	-0.3	-7.4	g
P <sub>2</sub>	Phosphorus dimer	42.8	32.0	-10.8	-1.7	-1.7	g
H <sub>4</sub> P <sub>2</sub>	P <sub>2</sub> H <sub>4</sub>	5.0	-3.7	-8.7	-7.9	-5.3	ff
P <sub>4</sub>	Phosphorus tetramer.....	31.1	42.9	11.8	5.1	5.1	g
P <sub>4</sub> O <sub>6</sub>	Phosphorus trioxide	-529.2	-511.0	18.2	8.1	162.8	d

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While this cannot be construed as proof, it indicated that the  $-529.2$  value is likely to be more correct. Unfortunately, we see from this that different semiempirical methods can give very different results when applied to even relatively simple systems. This problem will not be resolved until accurate values for heats of formation are available from either high-level *ab initio* calculations<sup>26</sup> or new experimental measurements.

As we have seen, in a few instances very large differences between experimental and calculated  $\Delta H_f$  were obtained using MNDO-PM3. In attempting to identify the source of these large differences it is useful to do a comparative analysis with similar compounds. However, in certain of these instances there are no closely related compounds available for comparison. In such cases it is informative to investigate hypothetical reactions of



Table II. Comparison of experimental and calculated heats of formation for hypervalent molecules.

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
C <sub>2</sub> H <sub>6</sub> SO	Dimethyl sulfoxide	-36.1	-38.8	-2.7	40.0	41.2	a
C <sub>4</sub> H <sub>10</sub> SO	Diethyl sulfoxide.....	-49.1	-46.6	2.5	41.5	42.1	a
SO <sub>2</sub>	Sulfur dioxide	-71.0	-50.8	20.2	75.4	98.0	b
C <sub>2</sub> H <sub>6</sub> SO <sub>2</sub>	Dimethyl sulfone	-89.1	-76.3	12.8	142.8	142.1	a
C <sub>4</sub> H <sub>10</sub> SO <sub>2</sub>	Diethyl sulfone	-102.5	-80.8	21.7	143.1	142.0	a
SO <sub>3</sub>	Sulfur trioxide	-94.6	-104.8	-10.2	153.1	177.7	b
C <sub>2</sub> H <sub>6</sub> SO <sub>3</sub>	Dimethyl sulfite.....	-115.5	-130.0	-14.5	50.4	56.4	a
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	-175.7	-181.4	-5.8	172.2	177.7	b
C <sub>2</sub> H <sub>6</sub> SO <sub>4</sub>	Dimethyl sulfate	-164.1	-172.1	-8.0	158.6	162.7	a
O <sub>2</sub> F	Fluorine dioxide	3.0	12.9	9.9	21.1	6.0	b
NO <sub>2</sub> F	Fluorine nitrite	-26.0	-25.6	0.4	26.7	4.7	b
NO <sub>3</sub> F	Fluorine nitrate.....	2.5	-6.1	-8.6	25.5	11.2	b
SOF	SOF	-63.3	-74.4	-11.1	35.0	51.7	c
SO <sub>2</sub> F	SO <sub>2</sub> F	-113.2	-102.5	10.7	127.2	143.8	c
SOF <sub>2</sub>	Thionyl fluoride	-130.0	-138.2	-8.2	84.3	96.1	b
SO <sub>2</sub> F <sub>2</sub>	Sulfuryl fluoride	-181.3	-184.3	-3.0	203.3	211.4	b
NOF <sub>3</sub>	F <sub>3</sub> NO.....	-39.0	-26.6	12.4	61.8	24.4	b
SF <sub>3</sub>	Sulfur trifluoride	-130.0	-134.3	-4.3	89.9	97.1	c
SOF <sub>3</sub>	SOF <sub>3</sub>	-185.1	-176.5	8.6	180.2	183.5	c
SF <sub>4</sub>	Sulfur tetrafluoride	-182.4	-185.3	-2.9	135.9	138.9	b
SOF <sub>4</sub>	SOF <sub>4</sub>	-235.5	-236.3	-0.8	269.1	255.4	c
SF <sub>5</sub>	Sulfur pentafluoride (-).....	-291.0	-303.0	-12.0	159.4	169.0	d
SF <sub>5</sub>	Sulfur pentafluoride	-217.1	-232.5	-15.4	208.2	198.7	b
O <sub>2</sub> Cl	Chlorine dioxide	25.0	1.5	-23.5	111.0	80.9	b
NO <sub>2</sub> Cl	Nitryl chloride	2.9	-13.0	-15.9	14.4	11.7	b
SOCl	SOCl	-17.4	-31.1	-13.7	1.5	17.6	c
SO <sub>2</sub> Cl	SO <sub>2</sub> Cl.....	-66.4	-57.3	9.1	92.3	111.4	c
O <sub>3</sub> FCl	Perchloryl fluoride	-5.1	14.6	19.7	328.4	251.6	b
F <sub>3</sub> Cl	Chlorine trifluoride	-38.0	-22.1	15.9	116.7	58.2	b
F <sub>5</sub> Cl	Chlorine pentafluoride	-54.0	-54.0	0.0	258.8	144.5	b
SOCl <sub>2</sub>	Thionyl chloride	-50.8	-47.6	3.2	28.6	43.1	e
SO <sub>2</sub> Cl <sub>2</sub>	Sulfuryl chloride.....	-86.2	-62.3	23.9	79.9	99.0	b
SCl <sub>3</sub>	Sulfur trichloride	8.8	-19.1	-27.9	-41.3	-37.5	c
SOCl <sub>3</sub>	SOCl <sub>3</sub>	-47.5	-46.5	1.0	49.9	60.8	c
SCl <sub>4</sub>	Sulfur tetrachloride	-0.7	-19.8	-19.1	-32.6	-25.5	c
SOCl <sub>4</sub>	SOCl <sub>4</sub>	-55.7	-59.3	-3.6	22.7	33.6	c
SCl <sub>5</sub>	Sulfur pentachloride.....	-8.6	9.2	17.8	4.3	11.4	c
SCl <sub>6</sub>	Sulfur hexachloride	-19.8	10.3	30.1	138.1	132.8	c
OBr	BrO	30.1	20.8	-9.3	5.3	5.6	f
SOBr	SOBr	-4.3	-16.2	-11.9	2.2	21.1	c
SO <sub>2</sub> Br	SO <sub>2</sub> Br	-52.8	-42.9	9.9	89.5	112.7	c
F <sub>3</sub> Br	Bromine trifluoride.....	-61.1	-47.1	14.0	84.0	82.6	b
F <sub>5</sub> Br	Bromine pentafluoride	-102.5	-75.8	26.7	207.4	183.7	b
SOBr <sub>2</sub>	Thionyl bromide	-11.5	-18.6	-7.1	16.1	37.7	c
SO <sub>2</sub> Br <sub>2</sub>	Sulfuryl bromide	-59.5	-46.2	13.3	127.9	149.5	c
SBr <sub>3</sub>	Sulfur tribromide	50.2	16.4	-33.8	-51.3	-48.4	c
SOBr <sub>3</sub>	SOBr <sub>3</sub>	-8.6	-10.0	-1.4	41.4	59.5	c
SBr <sub>4</sub>	Sulfur tetrabromide.....	53.0	18.8	-34.2	-42.9	-34.1	c
SOBr <sub>4</sub>	SOBr <sub>4</sub>	-3.3	-20.7	-17.4	26.6	38.3	c
SBr <sub>5</sub>	Sulfur pentabromide	55.9	44.0	-11.9	23.5	28.1	c
SBr <sub>6</sub>	Sulfur hexabromide	58.8	78.1	19.3	107.6	104.6	c
OI	IO	41.8	31.0	-10.9	4.8	-4.9	f
SOI	SOI.....	12.7	-0.4	-13.1	7.0	20.6	c
SO <sub>2</sub> I	SO <sub>2</sub> I	-34.9	-32.0	2.9	64.5	86.7	c
F <sub>5</sub> I	Iodine pentafluoride	-200.8	-202.9	-2.1	298.8	267.9	b
F <sub>7</sub> I	Iodine heptafluoride	-229.7	-225.4	4.3	334.9	274.1	b
SOI <sub>2</sub>	Thionyl iodide	21.5	11.1	-10.4	26.6	34.9	c
SO <sub>2</sub> I <sub>2</sub>	Sulfuryl iodide.....	-26.0	-30.0	-4.0	51.7	72.8	c
SI <sub>3</sub>	Sulfur triiodide	100.3	54.7	-45.6	-60.0	-64.9	c
SOI <sub>3</sub>	SOI <sub>3</sub>	40.4	23.8	-16.6	1.7	0.1	c
SI <sub>4</sub>	Sulfur tetraiodide	120.2	83.8	-36.4	-38.0	-42.0	c
SOI <sub>4</sub>	SOI <sub>4</sub>	60.0	27.6	-32.4	-17.0	-17.8	c
SI <sub>5</sub>	Sulfur pentaiodide.....	130.9	129.6	-1.3	-1.0	-12.2	c

Table II. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
SI <sub>6</sub>	Sulfur hexaiodide	158.9	167.0	8.1	48.7	32.2	c
C <sub>4</sub> H <sub>12</sub> SiF	SiMe <sub>4</sub> F (-) C <sub>3v</sub> symmetry	-147.5	-122.4	25.1	33.5	23.5	d
SiF <sub>5</sub>	SiF <sub>5</sub> (-)	-507.1	-504.4	2.7	17.7	3.6	d
SiF <sub>4</sub> Cl	SiF <sub>4</sub> Cl (-)	-465.3	-465.2	0.1	17.5	8.0	d
SiCl <sub>5</sub>	SiCl <sub>5</sub> (-) .....	-237.2	-254.6	-17.4	-19.3	-30.4	d
C <sub>3</sub> H <sub>9</sub> PO	Trimethylphosphine oxide	-102.2	-82.7	19.5	59.3	78.9	a
PO <sub>2</sub>	Phosphorus dioxide	-71.0	-76.7	-5.7	24.0	61.8	c
CH <sub>5</sub> PO <sub>3</sub>	Methylphosphonic acid	-240.5	-213.3	27.2	25.2	51.5	a
C <sub>2</sub> H <sub>7</sub> PO <sub>3</sub>	Ethylphosphonic acid	-239.4	-218.5	20.9	19.9	43.4	a
C <sub>3</sub> H <sub>9</sub> PO <sub>3</sub>	Trimethyl phosphite .....	-168.3	-192.2	-23.9	-38.0	-3.5	a
C <sub>6</sub> H <sub>15</sub> PO <sub>3</sub>	Triethyl phosphite	-195.9	-208.5	-12.6	-27.5	3.3	a
C <sub>6</sub> H <sub>15</sub> PO <sub>4</sub>	Triethyl phosphate	-284.5	-252.9	31.6	75.0	104.8	a
C <sub>2</sub> H <sub>6</sub> PO <sub>2</sub> F	Methyl methylphosphono- fluoridate	-197.3	-207.6	-10.3	51.4	80.5	g
C <sub>3</sub> H <sub>8</sub> PO <sub>2</sub> F	Ethyl methylphosphono- fluoridate	-205.8	-212.3	-6.5	53.9	82.6	g
C <sub>4</sub> H <sub>10</sub> PO <sub>2</sub> F	<i>n</i> -Propyl methylphosphono- fluoridate .....	-210.2	-217.4	-7.2	53.9	80.7	g
C <sub>4</sub> H <sub>10</sub> PO <sub>2</sub> F	<i>i</i> -Propyl methylphosphono- fluoridate	-214.6	-216.7	-2.1	60.8	87.2	g
C <sub>5</sub> H <sub>12</sub> PO <sub>2</sub> F	<i>i</i> -Propyl ethylphosphono- fluoridate	-219.8	-217.5	2.2	59.4	85.2	g
C <sub>5</sub> H <sub>12</sub> PO <sub>2</sub> F	<i>s</i> -Butyl methylphosphono- fluoridate	-220.1	-221.2	-1.1	63.2	86.8	g
C <sub>5</sub> H <sub>12</sub> PO <sub>2</sub> F	<i>n</i> -Butyl methylphosphono- fluoridate	-215.1	-222.9	-7.8	53.8	78.4	g
C <sub>6</sub> H <sub>14</sub> PO <sub>2</sub> F	Neopentyl methylphosphono- fluoridate .....	-224.2	-226.6	-2.4	70.4	87.8	g
POF <sub>2</sub>	POF <sub>2</sub>	-213.6	-188.9	24.7	61.7	99.0	c
CH <sub>3</sub> POF <sub>2</sub>	Methylphosphonodifluoride	-233.2	-225.3	7.9	86.1	119.8	g
POF <sub>3</sub>	Phosphorus oxyfluoride	-289.5	-297.7	-8.2	90.0	132.2	h
PF <sub>4</sub>	Phosphorus tetrafluoride (-)	-325.0	-332.1	-7.1	22.8	66.2	d
PF <sub>4</sub>	Phosphorus tetrafluoride .....	-287.9	-303.9	-16.0	53.3	93.9	c
PF <sub>5</sub>	Phosphorus pentafluoride	-381.1	-386.9	-5.8	132.3	166.3	b
PF <sub>6</sub>	Phosphorus hexafluoride (-)	-522.0	-508.5	13.5	152.4	194.3	d
POCl <sub>2</sub>	POCl <sub>2</sub>	-109.9	-94.8	15.1	33.9	51.2	c
CH <sub>3</sub> POCl <sub>2</sub>	Methylphosphonodichloride	-124.1	-128.9	-4.8	48.7	62.9	g
POCl <sub>3</sub>	Phosphorus oxychloride	-132.8	-140.2	-7.4	53.2	58.7	h
PSCl <sub>3</sub>	Phosphorus thiochloride .....	-91.0	-60.2	30.8	62.6	53.6	b
PCl <sub>4</sub>	Phosphorus tetrachloride	-80.5	-102.8	-22.3	-22.7	-30.8	c
PCl <sub>5</sub>	Phosphorus pentachloride	-89.6	-111.6	-22.0	47.7	36.1	h
POBr <sub>2</sub>	POBr <sub>2</sub>	-78.3	-50.8	27.5	26.4	70.1	c
POBr <sub>3</sub>	Phosphorus oxybromide	-97.0	-80.2	16.8	68.3	84.6	b
PSBr <sub>3</sub>	Phosphorus thiobromide .....	-67.2	-7.8	59.4	85.7	83.3	b
PBr <sub>4</sub>	Phosphorus tetrabromide	-17.4	-17.4	0.0	-11.9	-10.7	c
PBr <sub>5</sub>	Phosphorus pentabromide	-11.0	-27.1	-16.1	42.8	73.3	c
POI <sub>2</sub>	POI <sub>2</sub>	-40.1	-35.2	4.9	19.5	42.8	c
POI <sub>3</sub>	Phosphorus oxyiodide	-39.7	-8.3	31.4	71.3	79.3	c
PI <sub>4</sub>	Phosphorus tetraiodide .....	60.2	44.7	-15.5	-36.1	-47.1	c
PI <sub>5</sub>	Phosphorus pentaiodide	97.7	88.5	-9.2	-16.0	-36.1	c
P <sub>4</sub> O <sub>10</sub>	Phosphorus pentoxide	-694.1	-712.6	-18.5	262.4	444.7	b

<sup>a</sup>J. O. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.

<sup>b</sup>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).

<sup>c</sup>G. Ditter and U. Niemann, *Philips J. Res.*, 37, 1 (1982).

<sup>d</sup>J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, 107, 766 (1985).

<sup>e</sup>D. D. Wagman, W. H. Evans, V. B. Parker, T. Hawlow, S. M. Bailey, and R. H. Schumm, Natl. Bur. Stand. (U.S.), Tech. Note, No 270-3 (1968) and "Errata in NBS Technical Note 270-8" (1981).

<sup>f</sup>NBS Technical Note 270-3, Jan. 1968.

<sup>g</sup>E. C. Penski and E. S. Domalski, CRDEC-TR-87063 (1987).

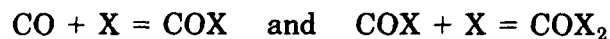
<sup>h</sup>D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data Suppl.* 11, 2, 1982.

Table III. Statistical analysis of difference between experimental and calculated heats of formation.

Type of compounds	No. of compounds	Averages (unsigned)			Average (signed)			Root mean square		
		PM3	MNDO	AM1	PM3	MNDO	AM1	PM3	MNDO	AM1
Hydrogen	465	6.3	12.9	11.2	1.5	4.8	5.0	8.6	24.1	23.5
Carbon	463	6.2	12.8	11.1	1.1	3.4	3.9	8.8	23.1	22.1
Nitrogen	118	6.9	18.8	9.9	0.2	10.1	4.1	9.4	26.9	12.9
Oxygen	255	9.7	31.7	33.5	0.1	25.0	28.8	13.9	54.7	61.3
Fluorine	148	8.9	41.9	46.6	1.5	34.1	38.4	12.0	80.3	79.7
Aluminum	46	14.7	23.9	38.6	2.6	6.7	33.2	21.2	34.2	53.3
Silicon	78	10.1	22.4	14.5	1.9	13.0	3.6	14.2	32.9	20.8
Phosphorus	71	12.5	37.3	53.6	-0.5	23.8	44.8	16.1	55.1	83.0
Sulfur	101	12.0	50.3	53.5	-1.4	36.9	41.5	16.2	79.8	81.7
Chlorine	105	9.6	23.0	22.3	0.2	12.8	10.6	13.3	51.1	41.4
Bromine	70	11.5	28.8	27.1	1.1	17.1	14.9	15.7	47.1	44.7
Iodine	77	10.7	30.3	27.3	0.2	12.9	11.8	15.9	61.1	54.0
Set of Compounds used in Refs. 3 and 16	138	4.4	6.2	5.5	0.0	-1.4	0.7	6.3	9.1	7.3
Compounds of C, H, N, O, only	276	5.7	11.2	7.5	0.4	3.8	1.4	7.9	18.5	10.5
Nitro compounds	29	5.2	39.6	15.7	2.5	38.1	14.5	6.2	44.1	18.5
Organophosphorus-V compounds	15	10.9	53.9	75.6	3.6	50.2	75.6	14.3	56.7	80.1
Normal valent compounds	657	7.8	13.9	12.7	0.7	3.3	3.7	11.4	25.1	24.3
Hypervalent	106	13.6	75.8	83.1	-0.8	67.2	74.7	17.3	104.5	110.0
All compounds	763	8.6	22.5	22.4	0.5	12.1	13.6	12.4	45.5	46.8
All compounds except Al, P, and S	547	7.1	15.5	11.5	0.9	6.6	2.9	10.1	35.1	26.5

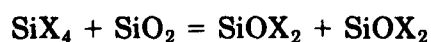
these compounds involving reactants or products having accurately determined  $\Delta H_f$ 's. These may be illustrated by reactions involving the radicals resulting from addition of a halide radical to carbon monoxide.

All three methods predict COBr and COI to be considerably more stable than that observed experimentally. As the  $\Delta H_f$  of CO and heat of atomization of the halogens<sup>27</sup> (F: 18.9, Cl: 29.0, Br: 26.7, I: 25.5 kcal/mol) are known, the heats of the reactions



can be estimated (F: -34.8, -129.3; Cl: -17.6, -66.6; Br: 20.2, -67.3; I: 64.4, -79.4). For iodine this indicates that the two C—I bonds differ in strength by 143.8 kcal/mol. Computationally, these bonds are predicted to be of comparable strength. As with  $\text{P}_4\text{O}_6$ , further work will be required to resolve this conflict.

The differences between the experimental and calculated values of  $\Delta H_f$  for three of the oxyhalides of silicon are large and positive. This difference is vividly illustrated by investigating the metathetical reaction



for which the calculated and experimental  $\Delta H_f$  and  $\Delta H_r$  are presented in Table IV. As these reactions are metathetic it is unlikely that the heats of reaction would be very large. As a result of the unexpectedly large value for the observed  $\Delta H_r$ , and the small predicted  $\Delta H_r$ , we postulate that the experimental  $\Delta H_f$  for  $\text{SiOCl}_2$ ,  $\text{SiOBr}_2$ , and  $\text{SiOI}_2$  are incorrect, and that the correct values lie nearer to -121.2, -94.1, and -50.2 kcal/mol, respectively.

In certain cases involving homologous series the accuracy of prediction of related compounds are of interest. Thus, all the  $\Delta H_f$  of the alkyl phosphines are reproduced accurately with the exception of triethylphosphine (Table V).

Large errors have been reported for the calculated MNDO and AM1  $\Delta H_f$  of nitro and polynitro organics.<sup>28</sup> For 26 nitro-organic compounds and three organic nitrates, the average calculated differences in  $\Delta H_f$  for PM3, MNDO, and AM1, respectively, are 5.2, 39.6, and 15.7 kcal/mol. It should be noted that for MNDO and AM1 the errors were systematic, and that by subtracting a constant for each nitro group a considerably improved result could be obtained.

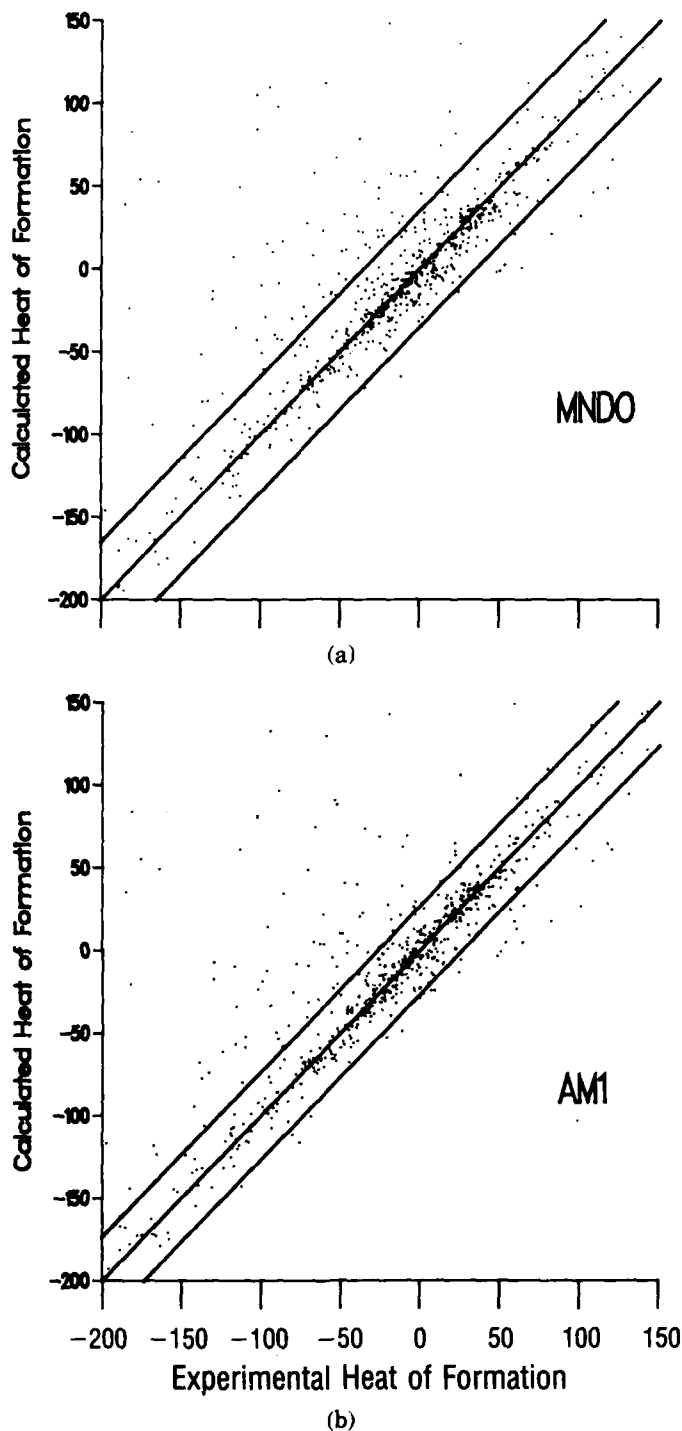


Figure 1. Calculated and experimental heats of formation for all compounds surveyed.

### HEATS OF HYDRATION

Most reactions of biochemical interest occur in aqueous media; therefore, the ability of a computational model to simulate condensed phase reactions is of interest. Experimental values for the successive heats of hydration of an ammonium ion are known.<sup>29</sup> A comparison with calculated results is given in Table VI. From this we see that

AM1 is significantly more accurate at modeling ammonium ion hydration than either MND0 or PM3.

### HEATS OF ASSOCIATION AND HYDROGEN BONDING

The intermolecular stabilization due to molecules associating has proved difficult to accurately model using semiempirical meth-

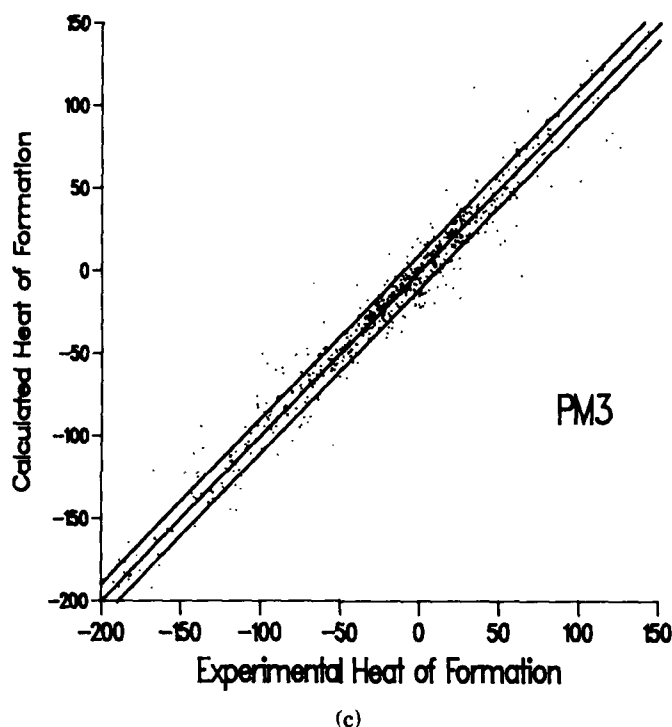


Figure 1. (continued)

ods. The model must avoid the Scylla of having everything bind together so energetically that gases become stable relative to condensation at only extremely high temperatures, and the Charybdis of having such weak intermolecular forces that almost everything is predicted to be gaseous at 298 K.

Calculated values for the heat of association for various pairs of molecules are given in Table VII. For all three methods the heat of association of systems which are gaseous at 298 K is less than 0.1 kcal/mol. MNDO underestimates all intermolecular forces, while AM1 slightly overestimates the ozone-water bond, predicting it to be slightly more stable than the water dimer. Large basis set *ab initio* calculations indicate<sup>21</sup> that in the water dimer the hydrogen bond is linear, that is, the O—H—O angle is 180°. Of the three semiempirical models the new method

is the only one to predict a water dimer to have an almost linear O—H—O bond. The various geometries predicted are shown in Figure 2.

## GEOMETRIES

Molecular geometries are presented in Table VIII. A statistical analysis is given in Tables IX–XII. In general, errors in bond lengths are reduced, while some errors in bond angles are increased. There are too few dihedral data to generalize, but a superficial indication is that the dihedral error is intermediate between MNDO and AM1. In certain important cases, errors in interatomic distances are significantly decreased.

Many force constants for torsional bending are very low compared to bond length stretching. This implies that very large

Table IV. Heats of formation and reaction for silicon oxyhalide synthesis.

X	$\Delta H_f(\text{Exp})^a$			$\Delta H_r(\text{Exp})$	$\Delta H_f(\text{Calc})$			$\Delta H_r(\text{Calc})$
	$\text{SiX}_4$	$\text{SiO}_2$	$\text{SiOX}_2$		$\text{SiX}_4$	$\text{SiO}_2$	$\text{SiOX}_2$	
F	-386.0	-73.0	-231.0	-3.0	-390.6	-88.9	-229.4	20.7
Cl	-158.4	-73.0	-167.7	-104.0	-156.4	-88.9	-121.2	2.9
Br	-99.3	-73.0	-137.4	-102.5	-107.9	-88.9	-94.1	8.6
I	-26.4	-73.0	-99.4	-99.4	-14.2	-88.9	-50.2	2.7

<sup>a</sup>For references, see Table I.

**Table V.** Heats of formation of methyl and ethyl phosphines (kcal/mol).

Compound	$\Delta H_f(\text{Exp})^a$	$\Delta H_f(\text{Calc})$	Difference
PH <sub>3</sub>	1.3	0.2	-1.1
CH <sub>3</sub> PH <sub>2</sub>	-7.0	-9.5	-2.5
(CH <sub>3</sub> ) <sub>2</sub> PH	-15.0	-19.6	-4.6
(CH <sub>3</sub> ) <sub>3</sub> P	-22.5	-29.8	-7.3
C <sub>2</sub> H <sub>5</sub> PH <sub>2</sub>	-12.0	-11.7	+0.3
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> PH	-25.0	-23.3	+1.7
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> P	-11.8	-36.7	-24.9

<sup>a</sup>For references, see Table I.

changes in torsional angle can result from very small changes in energy. In consequence, it is likely that the largest errors in geometry will be in torsional angles. However, it is unlikely that any phenomena of chemical interest will be seriously affected by these errors: even if the torsion angles were accurately reproduced, from the low force constants, we may infer that the molecular geometry would (a) be subject to large librations or internal rotations at room temperature, and (b) in the course of a chemical reaction local forces could easily change the dihedral from its equilibrium position. The former consideration is important in studies of electronic phenomena such as ultraviolet (UV) visible absorption, where Boltzmann weighting of various conformations would be necessary.

Intramolecular hydrogen bonding distances in salicylaldehydes (Fig. 3), are poorly reproduced<sup>30</sup> by MNDO and AM1. Using the new parameter set, these distances are more accurately reproduced, as is shown in Table VIII.

The geometry of the amino group in *para*-nitroaniline (PNA) is of interest. It is well established that the amino group in crystalline PNA is planar, while the geometry of gas-phase PNA has not yet been reported. The magnitude of the interaction of the NO<sub>2</sub> and NH<sub>2</sub> groups may be estimated by reference to the metathetic reaction

**Table VI.** Heats of hydration of ammonium ion.<sup>a</sup>

Hydration reaction	Heat of hydration		Error		
	Exp.	Calc.	PM3	MNDO	AM1
NH <sub>4</sub> (+) + H <sub>2</sub> O = NH <sub>4</sub> (+)H <sub>2</sub> O	-17.3	-13.5	3.8	8.8	2.0
NH <sub>4</sub> (+)H <sub>2</sub> O + H <sub>2</sub> O = NH <sub>4</sub> (+)(H <sub>2</sub> O) <sub>2</sub>	-14.7	-9.3	5.4	6.8	1.6
NH <sub>4</sub> (+)(H <sub>2</sub> O) <sub>2</sub> + H <sub>2</sub> O = NH <sub>4</sub> (+)(H <sub>2</sub> O) <sub>3</sub>	-13.4	-9.3	4.1	6.0	-1.5

<sup>a</sup>Source: P. Kebarle, *Environmental Effects on Molecular Structure and Properties*, B. Pullman, (Ed.), D. Reidel, Dordrecht, The Netherlands, 1976, p. 81.

**Table VII.** Heats of association.

Associating molecules	Heat of association (kcal)		
	PM3	MNDO	AM1
CO <sub>2</sub> -CO <sub>2</sub>	0.0	0.0	0.0
NH <sub>3</sub> -H <sub>2</sub>	0.0	0.0	0.0
O <sub>2</sub> -O <sub>2</sub>	0.0	0.0	0.0
H <sub>2</sub> -N <sub>2</sub>	0.0	0.0	0.0
H <sub>2</sub> -CO <sub>2</sub>	0.0	0.0	0.0
H <sub>2</sub> O-H <sub>2</sub> O	-3.5	-1.0	-5.5
NH <sub>3</sub> -NH <sub>3</sub>	-0.9	-0.8	-2.4
H <sub>2</sub> O-H <sub>2</sub> O (C <sub>2</sub> v)	-2.0	-1.0	-5.0
Benzene-Benzene	-3.8	0.0	-0.4
H <sub>2</sub> O-H <sub>2</sub>	-0.9	0.0	-1.1
H <sub>2</sub> O-CH <sub>4</sub>	-1.2	0.0	-1.2
CH <sub>2</sub> O-H <sub>2</sub> O	-1.6	-0.7	-3.7
H <sub>2</sub> O-CH <sub>2</sub> O	-1.6	-1.0	-4.0
H <sub>2</sub> O-CH <sub>3</sub> OH	-1.9	-0.9	-4.8
CH <sub>3</sub> OH-H <sub>2</sub> O	-1.5	-0.7	-2.7
CH <sub>2</sub> O-CH <sub>2</sub> O	-1.0	-0.8	-2.4
HCOOH-CH <sub>4</sub>	-2.3	0.1	-0.8
H <sub>2</sub> O-CO <sub>2</sub>	-0.9	-0.8	-2.7
H <sub>2</sub> O-HCOOH	-5.3	-1.0	-7.4
H <sub>2</sub> O-O <sub>3</sub>	-1.8	-1.1	-6.8
HCOOH-HCOOH	-8.6	-1.7	-6.4
H <sub>2</sub> O-NH <sub>3</sub>	-1.1	-0.5	-2.7
H <sub>2</sub> O-C <sub>3</sub> H <sub>5</sub> N	-1.7	-1.1	-3.1
NH <sub>3</sub> -CO <sub>2</sub>	-0.5	-0.4	-1.8
HCOOH-NH <sub>3</sub>	-5.3	-0.9	-4.1
NH <sub>2</sub> CHO-NH <sub>2</sub> CHO	-4.7	-2.1	-8.1
NH <sub>2</sub> COOH-NH <sub>2</sub> COOH	-1.9	-3.3	-9.0

	Nitro- Aniline + benzene = Benzene + nitroaniline			Para-	$\Delta H_f$
Exp.*	20.8	15.4	19.8	16.2	-0.2
Calc	21.3	14.5	23.5	10.7	-1.6

\*For references, see Table I.

For aniline, the out-of-plane angle, or the angle between the NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>N planes, is 37.5° ± 2°.<sup>31</sup> This, together with the fact that the calculated barrier to inversion of an -NH<sub>2</sub> group in ammonia and methylamine is 5.4 and 5.7 kcal/mol at the MP3/6-31G\*//3-21G\* level<sup>32</sup>, and the very small experimental  $\Delta H_f$ , indicates that in the gas phase PNA is nonplanar. As molecular calculations are currently limited to gas-phase systems, the geometry of crystalline PNA cannot be

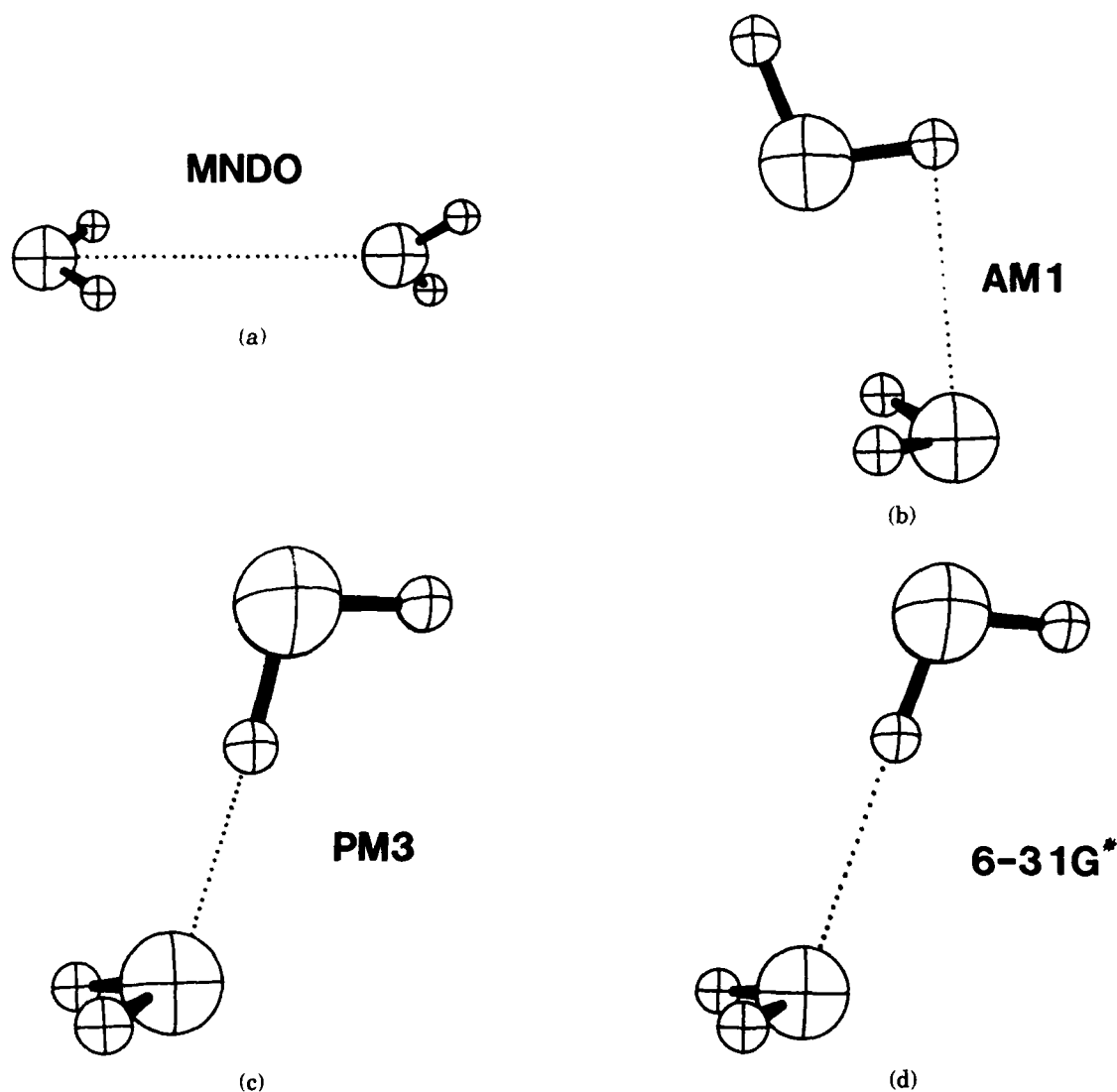


Figure 2. Calculated structures for water dimers.

calculated. However, in gas-phase PNA the  $-\text{NH}_2$  group is predicted to be pyramidal.

#### STRUCTURE OF IODINE HEPTAFLUORIDE

The geometry of  $\text{IF}_7$  is currently not known. It has been assumed, however, to be a bicapped pentagonal pyramid<sup>15</sup>. Attempts to obtain a stable structure of point group  $D_{5h}$  resulted both in very high energies and in the loss of the two axial fluorine atoms. The only stable geometry predicted for  $\text{IF}_7$  is a distorted trigonal bipyramid in which a  $\text{F}_2$  moiety is loosely associated at a distance of 2.8 Å from the iodine, as shown in Figure 4. As the geometry of  $\text{IF}_5$  and the heats of formation of  $\text{IF}_5$  and  $\text{IF}_7$  (but not  $\text{F}_2$ )

are all reproduced accurately, we predict that the geometry of  $\text{IF}_7$  is not a bicapped pentagonal pyramid, and it is likely that iodine is strongly coordinated to five fluorine atoms in a distorted trigonal bipyramid arrangement and weakly bound to a fluorine molecule.

#### DIPOLE MOMENTS

Dipole moments for 125 compounds are presented in Table XIII. The average difference between experimental and observed dipole moments is 0.38 Debye for PM3, and 0.45 and 0.35 Debye for MNDO and AM1, respectively. The dipole moment in hydrocarbons is due mainly to the atomic charges: only a small fraction is due to lone-pairs. It

Table VIII. Comparison of experimental and calculated molecular geometries.

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
H <sub>2</sub>	Hydrogen	HH	0.741	0.699	-0.042	-0.078	-0.064	a
CH <sub>2</sub>	Methylene, singlet	CH	1.110	1.092	-0.018	-0.019	-0.007	a
		HCH	102.4	103.7	1.3	8.7	8.1	
CH <sub>2</sub>	Methylene, triplet	CH	1.029	1.064	0.035	0.024	0.034	a
		HCH	144.7	144.7	0.0	4.9	3.6	
CH <sub>4</sub>	Methane	CH	1.094	1.087	-0.007	0.010	0.018	b
C <sub>2</sub>	Carbon, dimer	CC	1.242	1.189	-0.053	-0.073	-0.078	a
C <sub>2</sub> H <sub>2</sub>	Acetylene	CC	1.203	1.190	-0.013	-0.008	-0.008	b
		CH	1.060	1.064	0.004	-0.009	0.001	
C <sub>2</sub> H <sub>4</sub>	Ethylene	CC	1.339	1.322	-0.017	-0.004	-0.013	b
		CH	1.086	1.086	0.000	0.003	0.012	
		HCC	121.2	123.1	1.9	2.0	1.5	
C <sub>2</sub> H <sub>6</sub>	Ethane	CC	1.536	1.504	-0.032	-0.015	-0.036	b
		CH	1.091	1.098	0.007	0.018	0.026	
		HCC	110.9	111.6	0.7	0.3	-0.2	
C <sub>3</sub> H <sub>4</sub>	Allene	CC	1.308	1.297	-0.011	-0.002	-0.010	c
		CH	1.087	1.086	-0.001	0.003	0.013	
		HCC	120.9	122.3	1.4	2.0	1.4	
C <sub>3</sub> H <sub>4</sub>	Cyclopropene	C <sub>2</sub> C <sub>3</sub>	1.509	1.484	-0.025	0.003	-0.020	d
		C <sub>1</sub> C <sub>2</sub>	1.296	1.314	0.018	0.032	0.022	
		C <sub>1</sub> H	1.072	1.073	0.001	-0.010	-0.003	
		HC <sub>1</sub> C <sub>2</sub>	149.9	151.5	1.6	1.7	2.0	
C <sub>3</sub> H <sub>4</sub>	Propyne	C <sub>2</sub> C <sub>1</sub>	1.206	1.191	-0.015	-0.009	-0.009	e
		C <sub>1</sub> H	1.056	1.064	0.008	-0.005	0.004	
		C <sub>3</sub> C <sub>3</sub>	1.459	1.433	-0.026	-0.014	-0.032	
		C <sub>3</sub> H	1.105	1.098	-0.007	0.006	0.016	
		HCC	111.0	110.7	-0.3	0.0	-0.5	
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	CC	1.510	1.499	-0.011	0.016	-0.009	f
		CH	1.089	1.095	0.006	0.007	0.015	
C <sub>3</sub> H <sub>6</sub>	Propene	C=C	1.336	1.328	-0.008	0.004	-0.005	g
		C-C	1.501	1.480	-0.021	-0.005	-0.025	
		CCC	124.3	123.4	-0.9	2.6	0.0	
		C <sub>3</sub> H	1.085	1.098	0.013	0.024	0.033	
		HC <sub>3</sub> C <sub>2</sub>	111.2	112.9	1.7	1.8	0.7	
		C <sub>2</sub> H	1.090	1.097	0.007	0.006	0.013	
		HC <sub>2</sub> C <sub>1</sub>	119.0	120.8	1.8	0.3	1.9	
		HC <sub>1</sub>	1.091	1.087	-0.004	-0.002	0.007	
		HC <sub>1</sub> C <sub>2</sub>	121.5	122.7	1.2	0.8	0.8	
		CC	1.526	1.512	-0.014	0.004	-0.019	g
C <sub>3</sub> H <sub>8</sub>	Propane	CCC	112.4	111.7	-0.7	3.0	-0.6	
		C <sub>2</sub> H	1.115	1.108	-0.007	0.000	0.007	
		HC <sub>2</sub> C <sub>1</sub>	109.5	109.9	0.4	-0.7	0.0	
		C <sub>1</sub> H	1.096	1.097	0.001	0.014	0.021	
		HC <sub>1</sub> C <sub>2</sub>	111.8	111.4	-0.4	-1.5	-1.4	
C <sub>4</sub> H <sub>2</sub>	Diacetylene	C <sub>1</sub> C <sub>2</sub>	1.205	1.193	-0.012	-0.006	-0.006	h
		C <sub>2</sub> C <sub>3</sub>	1.376	1.371	-0.005	-0.008	-0.020	
		CH	1.046	1.065	0.019	0.004	0.014	
C <sub>4</sub> H <sub>4</sub>	CH <sub>2</sub> =C=C=C =CH <sub>2</sub>	CH	1.083	1.087	0.004	0.007	0.017	i
		C <sub>1</sub> C <sub>2</sub>	1.318	1.301	-0.017	-0.007	-0.016	
		C <sub>2</sub> C <sub>3</sub>	1.283	1.267	-0.016	-0.013	-0.017	
C <sub>4</sub> H <sub>4</sub>	Vinylacetylene	C <sub>3</sub> C <sub>4</sub>	1.341	1.332	-0.009	0.004	-0.005	j
		C <sub>2</sub> C <sub>3</sub>	1.431	1.414	-0.017	-0.014	-0.026	
		C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	123.1	122.5	-0.6	2.3	1.0	
		C <sub>1</sub> C <sub>2</sub>	1.208	1.193	-0.015	-0.010	-0.010	
C <sub>4</sub> H <sub>6</sub>	Bicyclobutane	C <sub>1</sub> C <sub>2</sub>	1.498	1.507	0.009	0.029	0.012	k
		C <sub>1</sub> C <sub>3</sub>	1.497	1.481	-0.016	0.039	-0.002	
		C <sub>2</sub> C <sub>3</sub> C <sub>1</sub> C <sub>4</sub>	121.7	120.0	-1.7	0.9	0.3	
		C <sub>1</sub> H	1.071	1.083	0.012	0.003	0.008	
		C <sub>2</sub> H	1.093	1.095	0.002	0.005	0.012	
C <sub>4</sub> H <sub>6</sub>	2-Butyne	C <sub>2</sub> C <sub>3</sub>	1.213	1.193	-0.020	-0.013	-0.015	j
		C <sub>1</sub> C <sub>2</sub>	1.467	1.432	-0.035	-0.023	-0.042	
		CH	1.115	1.098	-0.017	-0.004	0.006	
		HCC	110.7	110.7	0.0	0.3	-0.1	



Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
C <sub>4</sub> H <sub>6</sub>	1,3-Butadiene	C <sub>1</sub> C <sub>2</sub>	1.344	1.331	-0.013	0.000	-0.009	l
		C <sub>2</sub> C <sub>3</sub>	1.467	1.456	-0.011	-0.002	-0.016	
C <sub>4</sub> H <sub>8</sub>	1-Butene	CCC	122.9	122.3	-0.6	2.8	0.5	m
		C <sub>2</sub> C <sub>3</sub>	1.347	1.328	-0.019	-0.006	-0.016	
		C <sub>1</sub> C <sub>2</sub>	1.508	1.489	-0.019	-0.003	-0.024	
C <sub>4</sub> H <sub>8</sub>	Cyclobutane	CCC	123.8	122.6	-1.2	1.6	-0.4	n
		CC	1.548	1.542	-0.006	0.001	-0.005	
C <sub>4</sub> H <sub>8</sub>	Isobutene	CH	1.105	1.100	-0.005	0.000	0.005	o
		C <sub>1</sub> C <sub>2</sub>	1.330	1.333	0.003	0.018	0.006	
C <sub>4</sub> H <sub>10</sub>	<i>n</i> -Butane	C <sub>2</sub> C <sub>3</sub>	1.507	1.487	-0.020	0.002	-0.023	e
		C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	122.4	122.1	-0.3	-0.5	0.0	
		C <sub>1</sub> C <sub>2</sub>	1.533	1.512	-0.021	-0.002	-0.026	
		C <sub>2</sub> C <sub>3</sub>	1.533	1.521	-0.012	0.007	-0.019	
C <sub>4</sub> H <sub>10</sub>	Isobutane	CCC	112.8	111.6	-1.2	2.0	-1.2	p
		CC	1.525	1.520	-0.005	0.016	-0.011	
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene C1	C=C	1.339	1.328	-0.011	0.001	-0.008	q
		C-C	1.511	1.489	-0.022	-0.005	-0.027	
		C-C=C	115.5	123.1	7.6	11.1	8.4	
		C-C-C	113.1	114.4	1.3	-0.5	1.2	
		C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-116.9	-127.5	-10.6	9.6	-13.8	
		C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	-4.3	14.2	18.5	110.0	16.2	
		C=C	1.339	1.328	-0.011	0.001	-0.008	
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene C2	C-C	1.511	1.490	-0.021	-0.005	-0.025	q
		C-C=C	115.5	123.1	7.6	11.2	8.3	
		C-C-C	108.9	110.8	1.9	3.8	2.9	
		C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-122.2	-129.3	-7.1	15.1	-11.9	
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene C3	C=C	1.339	1.328	-0.011	0.001	-0.008	q
		C-C	1.511	1.490	-0.021	-0.005	-0.025	
		C-C=C	115.5	123.0	7.5	11.1	8.3	
		C-C-C	108.9	111.1	2.2	3.7	3.0	
C <sub>5</sub> H <sub>12</sub>	Neopentane	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-128.6	-132.2	-3.6	22.1	-5.3	f
		CC	1.539	1.527	-0.012	0.015	-0.018	
		CH	1.120	1.098	-0.022	-0.011	-0.004	
		HCC	110.0	111.3	1.3	1.7	0.3	
C <sub>6</sub> H <sub>6</sub>	Benzene	CC	1.399	1.391	-0.008	0.008	-0.004	r
		CH	1.084	1.095	0.011	0.006	0.016	
C <sub>6</sub> H <sub>6</sub>	Fulvene	C <sub>3</sub> C <sub>4</sub>	1.476	1.471	-0.005	0.000	0.000	s
		C <sub>2</sub> C <sub>3</sub>	1.355	1.355	0.000	0.011	0.008	
		C <sub>1</sub> C <sub>2</sub>	1.470	1.478	0.008	0.021	0.013	
		C <sub>1</sub> C <sub>6</sub>	1.349	1.331	-0.018	-0.004	-0.017	
C <sub>6</sub> H <sub>10</sub>	Cyclohexene	C <sub>1</sub> C <sub>2</sub>	1.335	1.334	-0.001	0.011	0.002	t
		C <sub>2</sub> C <sub>3</sub>	1.504	1.487	-0.017	0.000	-0.021	
		C <sub>3</sub> C <sub>4</sub>	1.515	1.521	0.006	0.026	0.002	
		C <sub>4</sub> C <sub>5</sub>	1.550	1.519	-0.031	-0.011	-0.036	
		C <sub>5</sub> C <sub>4</sub> C <sub>2</sub> C <sub>1</sub>	21.8	27.8	6.0	-0.8	5.4	
C <sub>6</sub> H <sub>12</sub>	Cyclohexane	CC	1.536	1.521	-0.015	0.002	-0.021	u
		CCC	111.4	111.0	-0.4	2.7	-0.1	
		CCCC	46.3	56.0	9.7	0.0	8.9	
		CH	1.121	1.107	-0.014	-0.007	0.000	
H <sub>2</sub> O	Water	CH'	1.121	1.108	-0.013	-0.007	0.001	b
		OH	0.957	0.951	-0.006	-0.014	0.004	
CO	Carbon monoxide	HOH	104.5	107.7	3.2	2.3	-1.0	v
		CO	1.128	1.135	0.007	0.035	0.043	
CH <sub>2</sub> O	Formaldehyde	CO	1.208	1.202	-0.006	0.008	0.019	w
		CH	1.116	1.091	-0.025	-0.010	-0.006	
		HCO	121.8	121.8	0.0	1.7	0.4	
		CO	1.425	1.395	-0.030	-0.034	-0.015	
		CH	1.094	1.097	0.003	0.025	0.025	
CH <sub>4</sub> O	Methanol	HCO	108.5	112.2	3.7	3.8	2.4	x
		OH	0.945	0.949	0.004	0.002	0.019	
		COH	107.0	107.5	0.5	4.6	0.2	

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
C <sub>2</sub> H <sub>2</sub> O	Ketene	CO	1.161	1.175	0.014	0.023	0.032	y
		CC	1.314	1.308	-0.006	0.005	-0.007	
		CH	1.083	1.084	0.001	0.002	0.012	
		HCC	118.7	122.0	3.3	3.0	2.7	
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	CC	1.410	1.406	-0.004	-0.014	0.007	z
		COC	111.3	114.1	2.8	8.7	1.6	
C <sub>3</sub> H <sub>4</sub> O	Acrolein	C <sub>3</sub> C <sub>2</sub>	1.335	1.330	-0.005	0.008	-0.001	aa
		C <sub>2</sub> C <sub>1</sub>	1.478	1.479	0.001	0.007	-0.010	
		CCC	121.0	123.6	2.6	6.3	2.2	
		CO	1.208	1.211	0.003	0.016	0.026	
C <sub>4</sub> H <sub>4</sub> O	Furan	OCC	124.0	124.0	0.0	1.5	0.0	bb
		CO	1.362	1.378	0.016	0.005	0.033	
		CCO	106.6	106.9	0.3	1.0	0.0	
		C <sub>3</sub> C <sub>2</sub>	1.361	1.373	0.012	0.029	0.019	
O <sub>2</sub>	Oxygen, triplet state	OO	1.216	1.169	-0.047	-0.082	-0.130	v
		H <sub>2</sub> O <sub>2</sub>	1.475	1.482	0.007	-0.179	-0.175	
		OH	0.950	0.945	-0.005	0.011	0.033	
		HOO	94.8	96.5	1.7	12.2	11.2	
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	HOOH	119.8	180.0	60.2	60.5	8.1	cc
		OO	3.000	2.769	-0.231	0.905	-0.383	
		CO	1.162	1.181	0.019	0.024	0.027	
		CH <sub>2</sub> O <sub>2</sub>	1.202	1.211	0.009	0.025	0.028	
H <sub>4</sub> O <sub>2</sub>	Water dimer	CO	1.202	1.211	0.009	0.025	0.028	b
		CH <sub>2</sub> O <sub>2</sub>	1.343	1.344	0.001	0.011	0.014	
		OCO	124.9	117.1	-7.8	-4.3	-7.3	
		OH	0.972	0.953	-0.019	-0.023	-0.001	
		HOC	106.3	111.6	5.3	9.9	4.3	
		CH	1.097	1.095	-0.002	0.008	0.006	
		HC—O	124.1	130.4	6.3	2.7	6.0	
		CO	1.207	1.207	0.000	0.013	0.022	
		CC	1.525	1.526	0.001	0.004	-0.017	
		CCO	121.2	120.5	-0.7	0.8	-0.2	
C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	<i>p</i> -Benzoquinone	C <sub>1</sub> C <sub>2</sub>	1.477	1.487	0.010	0.024	0.002	ee
		C <sub>2</sub> C <sub>3</sub>	1.322	1.335	0.013	0.027	0.016	
		CCC	121.1	121.6	0.5	1.0	0.8	
		CO	1.222	1.217	-0.005	0.004	0.014	
H <sub>3</sub> N	Ammonia	NH	1.012	0.999	-0.013	-0.005	-0.014	a
		HNH	106.7	108.1	1.4	-1.4	2.4	
		CN	1.175	1.157	-0.018	-0.022	-0.027	
CN	Cyanide	CN	1.290	1.355	0.065	-0.149	-0.164	a
		CHN	1.154	1.156	0.002	0.006	0.006	
CH <sub>5</sub> N	Methylamine	CH	1.063	1.070	0.007	-0.008	0.006	gg
		CN	1.474	1.469	-0.005	-0.014	-0.042	
		NH	1.011	0.999	-0.012	-0.003	-0.011	
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	HNC	112.0	109.8	-2.2	-2.2	-0.7	hh
		HNH	105.9	108.7	2.8	-0.4	3.1	
		CC	1.458	1.440	-0.018	-0.006	-0.019	
		CH	1.104	1.098	-0.006	0.006	0.016	
C <sub>2</sub> H <sub>3</sub> N	Methyl isocyanide	HCC	109.5	110.4	0.9	1.1	0.6	hh
		CN	1.157	1.159	0.002	0.005	0.006	
		CN—	1.424	1.433	0.009	0.000	-0.029	
		CH	1.101	1.097	-0.004	0.014	0.024	
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	HCN	109.1	109.7	0.6	1.1	1.0	ii
		—CN	1.166	1.181	0.015	0.025	0.015	
		CN	1.451	1.480	0.029	0.013	-0.006	
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	CNC	110.9	112.3	1.4	5.1	2.1	l
		CN	1.370	1.397	0.027	0.028	0.022	
		CNC	107.7	109.7	2.0	2.0	1.1	
		C <sub>3</sub> C <sub>2</sub>	1.382	1.390	0.008	0.013	0.020	
NO	Nitrogen oxide	CCC	109.8	107.0	-2.8	-2.4	-1.4	a
		C <sub>4</sub> C <sub>3</sub>	1.417	1.390	-0.027	-0.022	-0.015	
		NO	1.151	1.127	-0.024	-0.028	-0.036	

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
CHNO	Hydrogen isocyanate	NH	0.987	0.985	-0.002	0.011	-0.002	a
		CN	1.207	1.251	0.044	0.042	0.025	
		CNH	128.1	123.7	-4.4	-7.9	-0.9	
		CO	1.171	1.181	0.010	0.014	0.031	
		OCN	180.0	168.7	-11.3	-12.5	-13.3	
CH <sub>3</sub> NO	Formamide	CN	1.376	1.413	0.037	0.033	-0.009	ij
		NH	1.002	0.994	-0.008	-0.002	-0.016	
		CH	1.102	1.102	0.000	0.006	0.012	
		CO	1.193	1.217	0.024	0.032	0.050	
		OCN	123.8	118.5	-5.3	-2.7	-1.9	
NO <sub>2</sub>	Nitrogen dioxide	NO	1.197	1.181	-0.016	-0.023	-0.038	a
		ONO	136.0	137.8	1.8	-2.8	0.4	
HNO <sub>2</sub>	Nitrous acid ( <i>cis</i> )	N—O	1.460	1.339	-0.121	-0.163	-0.169	a
		N=O	1.200	1.175	-0.025	-0.031	-0.038	
		ONO	114.0	113.3	-0.7	3.1	2.6	
		OH	0.980	0.960	-0.020	-0.017	0.003	
HNO <sub>2</sub>	Nitrous acid ( <i>trans</i> )	HON	103.0	109.9	6.9	16.7	12.5	a
		N—O	1.460	1.383	-0.077	-0.148	-0.141	
		N=O	1.200	1.167	-0.033	-0.034	-0.042	
		ONO	118.0	109.1	-8.9	-4.7	-5.2	
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Salicylaldoxime	HON	0.980	0.950	-0.030	-0.022	-0.005	kk
		N(14)H(17)	1.834	1.847	0.013	0.940	0.302	
		O(10)N(14)	2.626	2.684	0.058	0.781	0.298	
HNO <sub>3</sub>	Nitric acid	N=O	1.206	1.203	-0.003	0.005	-0.011	a
		O=N=O	130.0	132.7	2.7	-3.5	-1.0	
		N—O	1.405	1.410	0.005	-0.065	-0.072	
		OH	0.960	0.953	-0.007	0.002	0.022	
		NOH	102.0	109.0	7.0	12.0	7.7	
N <sub>2</sub>	Nitrogen	NN	1.094	1.098	0.004	0.010	0.012	v
		H <sub>4</sub> N <sub>2</sub>	Hydrazine	NN	1.449	1.440	-0.009	
C <sub>2</sub> N <sub>2</sub>	Cyanogen	NH		1.022	1.001	-0.021	-0.001	-0.008
		HNN	112.0	106.5	-5.5	-4.8	-4.6	
		HNNH	90.0	180.3	90.3	90.2	90.2	
C <sub>2</sub> N <sub>2</sub>	Cyanogen	CN	1.154	1.159	0.005	0.008	0.008	b
		CC	1.389	1.382	-0.007	-0.011	-0.005	
C <sub>2</sub> H <sub>6</sub> N <sub>2</sub>	Dimethyldiazene	NN	1.254	1.228	-0.026	-0.032	-0.030	b
		CN	1.474	1.467	-0.007	0.000	-0.022	
		CNN	111.9	119.3	7.4	5.0	7.9	
N <sub>2</sub> O	Nitrous oxide	NN	1.128	1.124	-0.004	0.000	0.000	a
		NO	1.184	1.197	0.013	-0.003	-0.009	
H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	NH <sub>2</sub> —NO <sub>2</sub>	NN	1.427	1.431	0.004	-0.020	-0.060	ll
		NO	1.206	1.211	0.005	0.003	-0.002	
		NH	1.005	1.000	-0.005	0.013	-0.003	
		ONO	130.1	127.2	-2.9	-6.0	-6.1	
N <sub>2</sub> O <sub>3</sub>	Dinitrogen trioxide	NN	2.080	1.409	-0.671	-0.706	-0.728	a
		NO	1.100	1.172	0.072	0.063	0.061	
		NNO	110.0	118.2	8.2	11.0	12.8	
		NO'	1.180	1.268	0.088	0.079	0.101	
		O'NO'	134.0	150.4	16.4	14.8	13.5	
N <sub>2</sub> O <sub>4</sub>	Dinitrogen tetroxide	NN	1.750	1.759	0.009	-0.135	0.068	a
		NO	1.180	1.195	0.015	0.009	-0.008	
		ONN	113.2	114.6	1.4	2.1	1.0	
N <sub>3</sub>	Azide	NN	1.181	1.174	-0.007	-0.007	-0.004	a
		C <sub>3</sub> H <sub>3</sub> N <sub>3</sub>	<i>s</i> -Triazine	CN	1.338	1.358	0.020	
H <sub>2</sub> S	Hydrogen sulfide	NCN		126.8	121.6	-5.2	-3.4	-1.1
		HS	1.328	1.290	-0.038	-0.028	-0.011	
CS	Carbon sulfide	HSH	92.2	93.5	1.3	5.9	6.6	nn
		CS	1.534	1.447	-0.087	-0.050	-0.064	
CH <sub>2</sub> S	Thioformaldehyde	CS	1.611	1.539	-0.072	-0.074	-0.088	jj
		CH	1.093	1.095	0.002	-0.001	0.006	
		HCS	121.6	126.1	4.5	2.4	1.6	

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
CH <sub>3</sub> S	Thiomethanol	CS	1.818	1.801	-0.017	-0.101	-0.104	oo
		SH	1.329	1.306	-0.023	-0.027	-0.009	
		HSC	100.3	100.0	-0.3	2.1	1.0	
		HCSH	180.0	179.9	-0.1	-0.2	-0.1	
C <sub>4</sub> H <sub>4</sub> S	Thiophene	CS	1.714	1.725	0.011	-0.035	-0.037	qq
		CCS	92.2	91.4	-0.8	1.4	2.0	
		C <sub>3</sub> C <sub>2</sub>	1.370	1.366	-0.004	0.004	-0.003	
		CCC	111.5	112.1	0.6	0.4	-0.4	
CSO	Carbon oxysulfide	CO	1.159	1.176	0.017	0.022	0.034	rr
		CS	1.559	1.504	-0.055	-0.049	-0.065	
SO <sub>2</sub>	Sulfur dioxide	SO	1.432	1.442	0.010	0.044	0.094	a
		OSO	119.5	106.1	-13.4	-12.7	-16.6	
SO <sub>3</sub>	Sulfur trioxide	SO	1.430	1.384	-0.046	0.061	0.113	a
		S-O	1.550	1.668	0.118	0.078	0.157	
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	OH	0.970	0.947	-0.023	-0.023	-0.006	a
		SOH	105.0	117.7	12.7	12.2	1.5	
		S=O	1.420	1.668	0.248	0.209	0.287	
		SN	1.495	1.452	-0.043	-0.055	-0.054	
NS	Sulfur nitride	SN	1.495	1.452	-0.043	-0.055	-0.054	a
		CS	1.597	1.498	-0.099	-0.088	-0.095	
		C=N	1.192	1.231	0.039	0.027	0.025	
		C-N	1.479	1.440	-0.039	-0.042	-0.072	
C <sub>2</sub> H <sub>3</sub> NS	Methyl isothiocyanate	C-N=C	141.6	139.4	-2.2	-0.3	-1.0	ss
		CN	1.157	1.164	0.007	0.007	0.007	
		CS	1.701	1.664	-0.037	-0.071	-0.067	
		NCS	170.0	176.5	6.5	7.0	7.4	
C <sub>2</sub> N <sub>2</sub> S	Sulfur dicyanide	CSC	98.4	101.5	3.1	5.1	3.4	tt
		SS	1.889	1.857	-0.032	-0.114	-0.114	
		SS	2.055	2.034	-0.021	-0.131	-0.136	
		SH	1.327	1.311	-0.016	-0.023	-0.005	
S <sub>2</sub>	Sulfur dimer	HSS	91.3	103.2	11.9	11.2	9.9	uu
		HSSH	90.5	93.4	2.9	9.1	21.7	
		CS <sub>2</sub>	1.553	1.481	-0.072	-0.061	-0.070	
		C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	1.810	1.804	-0.006	-0.085	-0.089	
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	2,3-Dithiabutane	SS	2.038	2.021	-0.017	-0.103	-0.108	pp
		CSS	102.8	109.2	6.4	5.2	3.4	
		CSSC	84.7	88.0	3.3	19.8	10.0	
		SSC	102.8	109.2	6.4	5.1	3.4	
S <sub>6</sub>	S <sub>6</sub>	SS	2.057	2.048	-0.009	-0.110	-0.110	ww
		SSS	102.2	107.5	5.3	2.9	2.9	
		SSSS	74.5	64.6	-9.9	-5.1	-5.0	
		SS	2.048	1.973	-0.075	-0.113	-0.113	
S <sub>8</sub>	S <sub>8</sub>	SSS	107.9	116.0	8.1	0.4	0.4	xx
		SSSS	98.6	87.6	-11.0	-0.2	-0.2	
		HF	0.917	0.938	0.021	0.039	-0.091	
		CF	1.266	1.259	-0.007	-0.003	-0.007	
CHF	Fluoromethylidene	CH	1.121	1.100	-0.021	-0.001	0.006	yy
		CF	1.314	1.284	-0.030	-0.029	-0.023	
		FCH	101.6	105.6	4.0	9.5	9.0	
		CF	1.382	1.351	-0.031	-0.035	-0.007	
CH <sub>3</sub> F	Fluoromethane	CH	1.098	1.092	-0.006	0.020	0.023	zz
		CF	1.382	1.351	-0.031	-0.035	-0.007	
		FCH	108.5	108.6	0.1	2.1	1.0	
		CC	1.333	1.333	0.000	0.018	0.007	
C <sub>2</sub> H <sub>3</sub> F	Fluoroethylene	CH(g)	1.076	1.093	0.017	0.023	0.028	aaa
		CCH(g)	127.7	126.2	-1.5	-4.7	-3.8	
		CH(t)	1.085	1.085	0.000	0.002	0.011	
		CCH(t)	123.9	121.2	-2.7	-3.0	-3.1	
		CH(c)	1.090	1.086	-0.004	-0.003	0.006	
		CCH(c)	121.4	123.8	2.4	3.1	1.6	
		CF	1.348	1.338	-0.010	-0.024	0.003	
		FCC	121.0	122.0	1.0	2.3	2.2	

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
C <sub>3</sub> H <sub>3</sub> F	Fluoroallene	C <sub>1</sub> C <sub>2</sub>	1.301	1.310	0.009	0.019	0.012	bbb
		C <sub>1</sub> H	1.083	1.094	0.011	0.016	0.022	
		HC <sub>1</sub> C <sub>2</sub>	124.3	124.8	0.5	-1.4	-1.4	
		C <sub>1</sub> F	1.360	1.340	-0.020	-0.035	-0.008	
		FC <sub>1</sub> C <sub>2</sub>	121.9	122.2	0.3	1.0	1.8	
		C <sub>2</sub> C <sub>3</sub>	1.309	1.294	-0.015	-0.006	-0.014	
		C <sub>3</sub> H	1.086	1.087	0.001	0.005	0.015	
		HC <sub>3</sub> C <sub>2</sub>	120.8	122.3	1.5	2.1	1.5	
CNF	Cyanogen fluoride	CN	1.159	1.159	0.000	0.001	0.006	ccc
NOF	Nitrosyl fluoride	CF	1.262	1.297	0.035	0.011	0.045	a
		NF	1.520	1.367	-0.153	-0.215	-0.153	
F <sub>2</sub>	Fluorine	NO	1.130	1.162	0.032	0.031	0.018	a
		FNO	110.2	111.6	1.4	3.7	2.1	
H <sub>2</sub> F <sub>2</sub>	Hydrogen fluoride dimer	FF	1.412	1.350	-0.062	-0.146	0.015	a
CF <sub>2</sub>	Difluoromethylene	HF	0.920	0.939	0.019	0.036	-0.093	a
		H'F	1.870	1.743	-0.127	1.093	0.417	
		H'FH	108.0	147.0	39.0	71.5	-18.1	
OF <sub>2</sub>	F <sub>2</sub> O	CF	1.300	1.298	-0.002	0.004	0.012	a
		FCF	104.9	106.3	1.4	3.4	1.1	
COF <sub>2</sub>	Carbonyl difluoride	OF	1.412	1.378	-0.034	-0.131	-0.058	a
		FOF	103.2	100.9	-2.3	5.9	-0.7	
SF <sub>2</sub>	Sulfur difluoride	CO	1.174	1.199	0.025	0.045	0.046	a
		CF	1.312	1.322	0.010	0.004	0.016	
		FCO	126.0	124.6	-1.4	-1.9	-1.5	
CSF <sub>2</sub>	Thiocarbonyl difluoride	SF	1.592	1.560	-0.032	-0.020	0.031	a
		FSF	98.2	96.5	-1.7	1.3	-1.3	
		CS	1.589	1.600	0.011	-0.014	-0.030	
SOF <sub>2</sub>	Thionyl fluoride	CF	1.315	1.338	0.023	0.006	0.027	pp
		FCS	126.5	128.9	2.4	-0.5	1.1	
		SO	1.412	1.467	0.055	0.068	0.132	
		SF	1.585	1.574	-0.011	0.023	0.058	
		FSO	106.8	101.0	-5.8	-3.9	-7.0	
SO <sub>2</sub> F <sub>2</sub>	Sulfuryl fluoride	FSF	92.8	93.9	1.1	4.2	2.0	a
		SF	1.530	1.547	0.017	0.080	0.111	
		FSF	96.1	95.3	-0.8	1.7	1.1	
		SO	1.405	1.400	-0.005	0.103	0.171	
S <sub>2</sub> F <sub>2</sub>	FSSF	OSO	124.0	126.4	2.4	0.8	3.5	a
		SF	1.635	1.584	-0.051	-0.063	-0.006	
		SS	1.888	2.008	0.120	0.078	0.060	
		FSS	108.3	112.0	3.7	-1.8	-2.1	
S <sub>2</sub> F <sub>2</sub>	SSF <sub>2</sub>	FSSF	87.9	87.4	-0.5	-1.3	-0.8	a
		SS	1.860	1.919	0.059	0.035	0.019	
		SF	1.598	1.592	-0.006	0.003	0.054	
		FSS	107.5	114.5	7.0	1.4	1.3	
CHF <sub>3</sub>	Trifluoromethane	FSF	92.5	90.8	-1.7	3.9	0.2	a
		CH	1.098	1.110	0.012	0.038	0.032	
		CF	1.333	1.346	0.013	0.020	0.035	
NF <sub>3</sub>	Nitrogen trifluoride	FCH	110.3	113.1	2.8	1.2	2.7	a
		NF	1.371	1.354	-0.017	-0.056	-0.011	
C <sub>2</sub> NF <sub>3</sub>	Trifluoroacetonitrile	FNF	102.2	105.0	2.8	4.0	0.4	a
		CC	1.461	1.487	0.026	0.037	0.025	
		CF	1.335	1.350	0.015	0.020	0.036	
		CCF	111.4	113.4	2.0	0.5	2.1	
CF <sub>4</sub>	Carbon tetrafluoride	CN	1.153	1.155	0.002	0.006	0.006	ddd
		CF	1.321	1.337	0.016	0.026	0.037	
		CC	1.311	1.355	0.044	0.070	0.057	
SF <sub>4</sub>	Sulfur tetrafluoride	C <sub>2</sub> F <sub>4</sub>	1.319	1.326	0.007	-0.001	0.021	aaa
		FCC	123.8	125.1	1.3	0.4	1.6	
		SF	1.545	1.633	0.088	0.061	0.112	
		FSF	101.6	81.0	-20.6	-13.0	-18.6	
		SF'	1.646	1.591	-0.055	-0.005	0.022	
FSF'	87.8	81.0	-6.8	0.9	-4.8			

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	CC	1.560	1.608	0.048	0.114	0.061	a
		CF	1.320	1.341	0.021	0.026	0.043	
		FCC	109.5	111.4	1.9	1.2	2.6	
SF <sub>6</sub>	Sulfur hexafluoride	SF	1.564	1.560	-0.004	0.091	0.110	a
HCl	Hydrogen chloride	HCl	1.275	1.268	-0.007	0.073	0.009	a
CHCl	Chloromethylene	CH	1.120	1.100	-0.020	-0.020	-0.010	a
		CCl	1.689	1.554	-0.135	0.050	-0.042	
		CiCH	103.4	115.5	12.1	6.0	7.7	
CH <sub>3</sub> Cl	Chloromethane	CCl	1.781	1.764	-0.017	0.014	-0.040	a
		CH	1.096	1.094	-0.002	0.006	0.016	
		HCCl	110.9	109.9	-1.0	-2.8	-2.6	
OCl	Chlorine monoxide	ClO	1.546	1.548	0.002	0.073	0.090	a
NOCl	NOCl	CiN	1.950	1.764	-0.186	-0.167	-0.219	a
		NO	1.170	1.156	-0.014	-0.033	-0.033	
		CNCl	114.0	118.9	4.9	3.5	5.4	
NO <sub>2</sub> Cl	NO <sub>2</sub> Cl	CiN	1.830	1.818	-0.012	-0.020	-0.059	a
		NOCl	1.210	1.197	-0.013	-0.019	-0.024	
		ClF	1.628	1.582	-0.046	0.022	0.019	
FCl	Chlorine fluoride	ClF	1.630	1.690	0.060	0.105	0.051	a
		O <sub>3</sub> FCl	1.460	1.453	-0.007	0.270	0.328	
		OCiF	95.2	102.8	7.6	11.0	3.0	
CHF <sub>2</sub> Cl	Chlorodifluoromethane	CH	1.090	1.108	0.018	0.036	0.037	eee
		CCl	1.740	1.822	0.082	0.099	0.069	
		CiCH	107.0	109.9	2.9	-2.2	-1.8	
		CF	1.350	1.346	-0.004	-0.008	0.019	
		FCCl	110.5	110.1	-0.4	-0.4	1.9	
		FCCiH	120.0	122.6	2.6	1.0	2.0	
F <sub>3</sub> Cl	Chlorine trifluoride C2v	ClF	1.598	1.671	0.073	0.101	0.085	a
		ClF'	1.698	1.671	-0.027	0.001	-0.015	
		FCiF'	87.5	120.0	32.5	32.5	32.5	
		Cl <sub>2</sub>	1.986	2.035	0.049	0.010	-0.068	
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	CCl	1.772	1.758	-0.014	0.014	-0.031	ddd
		CiCCl	111.8	107.9	-3.9	-0.6	1.2	
		CH	1.103	1.102	-0.001	0.000	0.010	
OCl <sub>2</sub>	Cl <sub>2</sub> O	ClO	1.701	1.700	-0.001	-0.018	0.032	a
		ClOCl	110.8	109.2	-1.6	2.1	0.3	
COCl <sub>2</sub>	Carbonyl chloride	CO	1.166	1.198	0.032	0.034	0.056	a
		CCl	1.746	1.737	-0.009	0.014	-0.027	
		CiCO	124.4	124.2	-0.2	-0.5	-1.1	
SCl <sub>2</sub>	Sulfur dichloride	SCl	2.015	2.031	0.016	-0.043	-0.090	a
		CiSCl	102.7	101.6	-1.1	3.6	3.1	
SOCl <sub>2</sub>	Thionyl chloride	SO	1.443	1.479	0.036	0.026	0.110	fff
		SCl	2.076	2.080	0.004	-0.038	-0.102	
		CiSO	106.3	104.7	-1.6	0.3	-0.2	
S <sub>2</sub> Cl <sub>2</sub>	ClSSCl	SCl	2.057	2.044	-0.013	-0.081	-0.131	a
		SS	1.931	1.965	0.034	-0.011	-0.004	
		CiSSCl	108.2	113.1	4.9	0.0	-0.3	
CF <sub>2</sub> Cl <sub>2</sub>	Dichlorodifluoromethane	CCl	1.770	1.808	0.038	0.055	0.037	a
		CiCCl	108.5	106.6	-1.9	-1.7	-1.8	
		CF	1.330	1.345	0.015	0.007	0.040	
		FCCl	109.8	111.4	1.6	0.8	2.1	
CHCl <sub>3</sub>	Chloroform	CCl	1.782	1.753	-0.029	0.000	-0.034	ddd
		CiCH	107.5	110.4	2.9	1.1	0.2	
CFCl <sub>3</sub>	Trichlorofluoro- methane	CF	1.330	1.349	0.019	-0.003	0.046	a
		CCl	1.760	1.779	0.019	0.046	0.026	
CCl <sub>4</sub>	Carbon tetrachloride	CCl	1.760	1.747	-0.013	0.022	0.000	ddd
		C <sub>2</sub> Cl <sub>6</sub>	1.550	1.512	-0.038	0.016	0.007	
		CCl	1.740	1.754	0.014	0.050	0.020	
C <sub>2</sub> Cl <sub>6</sub>	Hexachloroethane	CiCC	109.0	110.2	1.2	2.4	0.7	a
		CCl	1.740	1.754	0.014	0.050	0.020	
HBr	Hydrogen bromide	HBr	1.415	1.471	0.056	0.025	0.006	ggg

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
CH <sub>3</sub> Br	Bromomethane	CBr	1.933	1.951	0.018	-0.055	-0.028	pp
		CH	1.086	1.090	0.004	0.016	0.024	
		HCB	107.7	108.4	0.7	0.8	1.1	
C <sub>2</sub> H <sub>3</sub> OBr	Acetyl bromide	CC	1.516	1.477	-0.039	-0.001	-0.026	pp
		CBr	1.973	1.966	-0.007	-0.086	-0.026	
		BrCC	111.0	106.3	-4.7	2.0	2.3	
		CO	1.183	1.185	0.002	0.026	0.042	
		CCO	127.1	134.3	7.2	0.2	-3.0	
		BrC	1.789	1.796	0.007	-0.046	-0.029	
CNBr	Cyanogen bromide	CN	1.158	1.155	-0.003	0.003	0.006	a
NOBr	BrNO	BrN	2.140	1.888	-0.252	-0.271	-0.218	pp
		NO	1.146	1.147	0.001	-0.007	-0.011	
		BrNO	114.5	120.8	6.3	4.4	8.0	
FBr	BrF	BrF	1.755	1.774	0.019	-0.029	0.022	a
F <sub>3</sub> Br	Bromine trifluoride	BrF	1.721	1.786	0.065	0.036	0.087	a
		BrF'	1.806	1.786	-0.020	-0.049	0.010	
		FBrF'	86.2	120.0	33.8	33.8	-4.8	
CF <sub>3</sub> Br	Trifluorobromo- methane	CBr	1.909	1.960	0.051	0.029	0.134	a
		CF	1.328	1.335	0.007	0.019	0.039	
		FCBr	110.3	110.8	0.5	0.8	3.4	
F <sub>5</sub> Br	Bromine pentafluoride	BrF(ax)	1.680	1.755	0.075	0.086	0.134	a
		BrF(eq)	1.790	1.774	-0.016	-0.019	0.014	
ClBr	Bromine chloride	BrCl	2.136	2.176	0.040	-0.056	-0.072	a
Br <sub>2</sub>	Bromine	BrBr	2.283	2.443	0.160	-0.115	-0.099	a
CH <sub>2</sub> Br <sub>2</sub>	Dibromomethane	CH	1.079	1.095	0.016	0.023	0.031	pp
		HCH	113.6	111.4	-2.2	-2.7	-3.3	
		CBr	1.927	1.912	-0.015	-0.059	-0.025	
		BrCH	106.5	112.5	6.0	2.0	1.7	
C <sub>2</sub> Br <sub>4</sub>	Tetrabromoethylene	CC	1.362	1.450	0.088	-0.020	-0.018	pp
		CBr	1.881	1.865	-0.016	-0.060	-0.024	
		BrCC	122.4	111.9	-10.5	1.3	0.0	
HI	Hydrogen iodide	HI	1.609	1.677	0.068	-0.042	-0.022	ggg
CH <sub>3</sub> I	Iodomethane	CH	1.084	1.093	0.009	0.020	0.025	pp
		CI	2.132	2.028	-0.104	-0.117	-0.082	
		HCH	111.2	109.9	-1.3	-2.8	-1.4	
CNI	Cyanogen iodide	CN	1.159	1.155	-0.004	0.005	0.003	a
		CI	1.994	1.908	-0.086	-0.103	-0.067	
FI	Iodine fluoride	IF	1.906	1.889	-0.017	-0.004	-0.025	a
CF <sub>3</sub> I	Trifluoroiodomethane	CI	2.130	2.052	-0.078	-0.005	0.045	a
		CF	1.332	1.340	0.008	0.022	0.037	
		FCI	110.6	112.1	1.5	1.9	3.5	
F <sub>5</sub> I	Iodine pentafluoride	IF(ax)	1.844	1.867	0.023	0.139	0.087	hhh
		IF(eq)	1.869	1.882	0.013	0.088	0.029	
		F(ax)IF(eq)	81.9	102.6	20.7	-3.8	-4.6	
F <sub>7</sub> I	Iodine heptafluoride	IF(ax)	1.760	2.698	0.938	0.731	0.866	iii
		IF(eq)	1.860	1.913	0.053	0.218	0.114	
ClI	Iodine chloride	ICl	2.327	2.192	-0.135	-0.065	-0.109	a
BrI	Iodine bromide	IBr	2.485	2.561	0.076	-0.135	-0.131	a
I <sub>2</sub>	Iodine	II	2.666	2.668	0.002	-0.151	-0.128	a
HAi	AlH	AlH	1.648	1.663	0.015	-0.222	-0.180	a
AlO	AlO	AlO	1.618	1.533	-0.085	-0.143	-0.053	a
AlF	Aluminum fluoride	AlF	1.654	1.652	-0.002	-0.094	-0.077	a
AlF <sub>3</sub>	Aluminum trifluoride	AlF	1.630	1.644	0.014	-0.038	-0.014	a
AlF <sub>4</sub>	AlF <sub>4</sub> (-)	AlF	1.690	1.688	-0.002	-0.041	-0.023	a
AlCl	Aluminum chloride	AlCl	2.130	1.947	-0.183	-0.055	-0.145	a
AlCl <sub>3</sub>	Aluminum trichloride	AlCl	2.060	1.966	-0.094	0.005	-0.064	a
AlBr	Aluminum bromide	AlBr	2.295	2.292	-0.003	-0.093	-0.201	a
AlBr <sub>3</sub>	Aluminum tribromide	AlBr	2.270	1.875	-0.395	-0.095	-0.161	a
AlI <sub>3</sub>	Aluminum triiodide	AlI	2.499	2.487	-0.012	-0.174	-0.190	a
Al <sub>2</sub>	Al <sub>2</sub>	AlAl	2.467	2.554	0.087	-0.175	-0.175	a
Al <sub>2</sub> O	Al <sub>2</sub> O	AlO	1.730	1.677	-0.053	-0.124	-0.012	a
H <sub>2</sub> Si	Silylene (singlet)	SiH	1.519	1.513	-0.006	-0.139	-0.062	ijj
		HSiH	92.1	94.9	2.8	5.2	8.9	

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors			Footnote
					PM3	MNDO	AM1	
H <sub>4</sub> Si	Silane	SiH	1.481	1.488	0.007	-0.105	-0.020	a
C <sub>4</sub> H <sub>12</sub> Si	Tetramethylsilane	SiC	1.879	1.890	0.011	-0.064	-0.050	pp
SiN	Silicon nitride	SiN	1.572	1.464	-0.108	-0.021	-0.087	a
SiF <sub>2</sub>	Difluorosilylene	SiF	1.591	1.575	-0.016	-0.013	0.021	a
HSiF <sub>3</sub>	Trifluorosilane	FSiF	101.0	95.3	-5.7	-4.1	-3.9	
		SiH	1.447	1.507	0.060	-0.072	-0.007	a
		SiF	1.562	1.590	0.028	0.031	0.047	
SiF <sub>4</sub>	Tetrafluorosilane	FSiH	110.6	112.6	2.0	3.0	1.2	
		SiF	1.552	1.580	0.028	0.032	0.052	a
		SiCl	2.063	1.946	-0.117	0.009	-0.077	a
SiCl <sub>2</sub>	Dichlorosilylene	ClSiCl	109.7	101.9	-7.8	-4.2	-5.3	kkk
SiCl <sub>4</sub>	Silicon tetrachloride	SiCl	2.017	2.041	0.024	0.063	0.022	a
H <sub>3</sub> SiBr	Bromosilane	SiBr	2.210	1.901	-0.309	0.018	0.030	pp
		SiH	1.481	1.491	0.010	-0.113	-0.016	
		HSiBr	107.9	108.3	0.4	-1.0	2.4	
SiBr <sub>4</sub>	Silicon tetrabromide	SiBr	2.150	1.796	-0.354	0.040	0.093	a
H <sub>3</sub> SiI	Iodosilane	SiI	2.437	2.012	-0.425	-0.051	-0.003	a
		SiF	1.486	1.492	0.006	-0.116	-0.020	
		HSiI	108.5	108.0	-0.5	-0.1	1.3	
SiI <sub>4</sub>	Silicon tetraiodide	SiI	2.430	2.467	0.037	-0.097	-0.005	a
Si <sub>2</sub>	Silicon dimer	SiSi	2.246	2.297	0.051	-0.259	-0.019	a
H <sub>6</sub> Si <sub>2</sub>	Disilane	SiSi	2.331	2.396	0.065	-0.158	0.086	lll
		SiH	1.492	1.487	-0.005	-0.113	-0.026	
		HSiSi	110.3	109.7	-0.6	0.9	-0.7	
H <sub>3</sub> P	Phosphine	PH	1.420	1.324	-0.096	-0.080	-0.054	a
		HPH	93.8	97.1	3.3	2.3	2.8	
CP	Carbon phosphide	CP	1.562	1.389	-0.173	-0.145	-0.151	a
CHP	Methinophosphide	CP	1.542	1.409	-0.133	-0.114	-0.123	a
		HC	1.067	1.068	0.001	-0.010	-0.003	
C <sub>3</sub> H <sub>9</sub> P	Trimethylphosphine	CP	1.843	1.872	0.029	-0.081	-0.079	pp
		CPC	98.9	100.6	1.7	7.9	2.2	
PO	Phosphorus oxide	PO	1.476	1.459	-0.017	-0.053	-0.004	a
NP	Phosphorus nitride	PN	1.491	1.414	-0.077	-0.093	-0.091	a
PF <sub>3</sub>	Phosphorus trifluoride	PF	1.570	1.558	-0.012	-0.014	0.024	a
		FPF	97.8	95.8	-2.0	1.1	-1.3	
POF <sub>3</sub>	Phosphoryl fluoride	PF	1.520	1.529	0.009	0.034	0.071	a
		FPF	102.5	99.8	-2.7	-0.6	-0.9	
		PO	1.450	1.452	0.002	0.036	0.096	
PSF <sub>3</sub>	Thiophosphoryl fluoride	PF	1.530	1.539	0.009	0.027	0.071	a
		FPF	100.3	95.1	-5.2	-1.0	-3.0	
		PS	1.870	1.934	0.064	0.105	0.063	
PF <sub>5</sub>	Phosphorus pentafluoride	PF(ax)	1.577	1.553	-0.024	0.025	0.044	a
		PF(eq)	1.534	1.528	-0.006	0.039	0.071	
PCl <sub>3</sub>	Phosphorus trichloride	PCl	2.039	2.064	0.025	-0.050	-0.100	a
		CIPCl	100.3	99.7	-0.6	4.9	4.4	
PCl <sub>5</sub>	Phosphorus pentachloride	PCl(ax)	2.190	2.093	-0.097	-0.078	-0.101	a
		PCl(eq)	2.040	2.052	0.012	-0.007	-0.054	
PBr <sub>3</sub>	Phosphorus tribromide	PBR	2.220	2.150	-0.070	-0.131	-0.134	pp
		BrPBR	101.0	101.3	0.3	4.7	6.2	
P <sub>2</sub>	Phosphorus dimer	PP	1.894	1.715	-0.179	-0.200	-0.200	a
P <sub>4</sub>	Phosphorus tetramer	PP	2.210	2.197	-0.013	-0.158	-0.158	a
P <sub>4</sub> O <sub>6</sub>	Phosphorus trioxide	PO	1.650	1.708	0.058	-0.046	0.031	a
		OPO	99.0	96.5	-2.5	-3.0	-1.9	

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is curious that in order to reproduce the observed dipole for propyne (0.78D) the atomic charges would have to be markedly larger than that predicted by current semiempiri-

cal methods. Whether the charges should in fact be larger, or some limitation of semiempirical methods is resulting in an incorrect calculation of the dipole based on the charge

Table IX. Unsigned average errors in bond lengths in angstroms.

	H	C	N	O	F	Al	Si	P	S	Cl	Br	I
H	1											
(PM3)	0.042											
(MNDO)	0.078											
(AM1)	0.064											
C	51	72										
(PM3)	0.009	0.017										
(MNDO)	0.010	0.014										
(AM1)	0.014	0.017										
N	7	21	8									
(PM3)	0.011	0.018	0.092									
(MNDO)	0.139	0.022	0.120									
(AM1)	0.051	0.025	0.122									
O	8	18	18	3								
(PM3)	0.014	0.012	0.034	0.095								
(MNDO)	0.014	0.021	0.085	0.389								
(AM1)	0.012	0.030	0.062	0.229								
F	3	19	2	1	1							
(PM3)	0.056	0.015	0.085	0.034	0.062							
(MNDO)	0.389	0.016	0.135	0.131	0.146							
(AM1)	0.200	0.026	0.082	0.058	0.015							
Al	1					1						
(PM3)	0.015			0.069	0.006	0.087						
(MNDO)	0.222			0.133	0.058	0.175						
(AM1)	0.180			0.033	0.038	0.175						
Si	6	1	1				2					
(PM3)	0.016	0.011	0.108		0.024		0.058					
(MNDO)	0.110	0.064	0.021		0.025		0.209					
(AM1)	0.025	0.050	0.087		0.040		0.052					
P	1	3	1	3	5			2				
(PM3)	0.096	0.112	0.077	0.026	0.012			0.096				
(MNDO)	0.080	0.113	0.093	0.045	0.028			0.179				
(AM1)	0.054	0.118	0.091	0.044	0.056			0.179				
S	3	10	1	7	8			1	8			
(PM3)	0.026	0.047	0.043	0.074	0.033			0.064	0.046			
(MNDO)	0.026	0.063	0.055	0.084	0.043			0.105	0.087			
(AM1)	0.008	0.071	0.054	0.152	0.063			0.063	0.083			
Cl	1	10	2	3	4	2	2	3	3	1		
(PM3)	0.007	0.037	0.099	0.003	0.052	0.138	0.070	0.045	0.011	0.049		
(MNDO)	0.073	0.036	0.093	0.120	0.057	0.030	0.036	0.045	0.054	0.010		
(AM1)	0.009	0.033	0.139	0.150	0.042	0.105	0.049	0.085	0.108	0.068		
Br	1	6	1		5	2	2	1		1	1	
(PM3)	0.056	0.019	0.252		0.039	0.199	0.332	0.070		0.040	0.160	
(MNDO)	0.025	0.056	0.271		0.044	0.094	0.029	0.131		0.056	0.115	
(AM1)	0.006	0.044	0.218		0.053	0.181	0.061	0.134		0.072	0.099	
I	1	3			5	1	2			1	1	1
(PM3)	0.068	0.089			0.209	0.012	0.231			0.135	0.076	0.002
(MNDO)	0.042	0.075			0.236	0.174	0.074			0.065	0.135	0.151
(AM1)	0.022	0.065			0.224	0.190	0.004			0.109	0.131	0.128

distribution is not clear. Whatever the reason, it appears that any charge distribution which would give rise to the experimentally observed dipole would be unacceptable, and more "realistic" charges would be preferable to those which would accurately reproduce the observed dipole moment. In consequence, the dipoles of nonconjugated hydrocarbons are too low, on average.

### IONIZATION POTENTIALS

Table XIV lists the calculated and observed first ionization potentials for 256 compounds. In this report, only first ionization

potentials will be considered. The average differences in IPs between experimental and calculated values are 0.57, 0.78, and 0.61 eV for PM3, MNDO, and AM1, respectively. IPs for doublet and other open shell systems are not reported, but differences for these systems are likely to be of the same order as for closed-shell systems.

### DISCUSSION

#### Bonding in Hypervalent Compounds

A more complete optimization of the parameters involved in MNDO/AM1 has re-

Table X. Signed average errors in bond lengths in angstroms.

	H	C	N	O	F	Al	Si	P	S	Cl	Br	I
H	1											
(PM3)	-0.04											
(MNDO)	-0.08											
(AM1)	-0.06											
C	51	72										
(PM3)	0.00	-0.01										
(MNDO)	0.01	0.00										
(AM1)	0.01	-0.01										
N	7	21	8									
(PM3)	-0.01	0.01	-0.09									
(MNDO)	0.14	0.00	-0.12									
(AM1)	0.04	-0.01	-0.10									
O	8	18	18	3								
(PM3)	-0.01	0.01	0.00	-0.09								
(MNDO)	-0.01	0.02	0.02	0.21								
(AM1)	0.01	0.03	-0.01	-0.23								
F	3	19	2	1	1							
(PM3)	-0.03	0.00	-0.08	-0.03	-0.06							
(MNDO)	0.39	0.00	-0.14	-0.13	-0.15							
(AM1)	0.08	0.02	-0.08	-0.06	0.01							
Al	1			2	3	1						
(PM3)	0.02			-0.07	0.00	0.09						
(MNDO)	-0.22			-0.13	-0.06	-0.18						
(AM1)	-0.18			-0.03	-0.04	-0.18						
Si	6	1	1		3		2					
(PM3)	0.01	0.01	-0.11		0.01		0.06					
(MNDO)	-0.11	-0.06	-0.02		0.02		-0.21					
(AM1)	-0.03	-0.05	-0.09		0.04		0.03					
P	1	3	1	3	5			2				
(PM3)	-0.10	-0.09	-0.08	0.01	0.00			-0.10				
(MNDO)	-0.08	-0.11	-0.09	-0.02	0.02			-0.18				
(AM1)	-0.05	-0.12	-0.09	0.04	0.06			-0.18				
S	3	10	1	7	8			1	8			
(PM3)	-0.03	-0.04	-0.04	0.06	-0.01			0.06	0.01			
(MNDO)	-0.03	-0.06	-0.05	0.08	0.02			0.11	-0.06			
(AM1)	-0.01	-0.07	-0.05	0.15	0.06			0.06	-0.06			
Cl	1	10	2	3	4	2	2	3	3	1		
(PM3)	-0.01	-0.01	-0.10	0.00	0.01	-0.14	-0.05	-0.02	0.00	0.05		
(MNDO)	0.07	0.04	-0.09	0.11	0.06	-0.02	0.04	-0.05	-0.05	0.01		
(AM1)	0.01	0.00	-0.14	0.15	0.03	-0.10	-0.03	-0.08	-0.11	-0.07		
Br	1	6	1		5	2	2	1		1	1	
(PM3)	0.06	0.01	-0.25		0.02	-0.20	-0.33	-0.07		0.04	0.16	
(MNDO)	0.02	-0.05	-0.27		0.00	-0.09	0.03	-0.13		-0.06	-0.11	
(AM1)	0.01	0.00	-0.22		0.05	-0.18	0.06	-0.13		-0.07	-0.10	
I	1	3			5	1	2			1	1	1
(PM3)	0.07	-0.09			0.20	-0.01	-0.19			-0.14	0.08	0.00
(MNDO)	-0.04	-0.08			0.23	-0.17	-0.07			-0.07	-0.14	-0.15
(AM1)	-0.02	-0.03			0.21	-0.19	0.00			-0.11	-0.13	-0.13

sulted in a greater than 50% reduction in the differences between experimental and calculated values of  $\Delta H_f$ . Most of the improvement is due to better prediction of hypervalent compounds, for example,  $\text{SF}_6$  and  $\text{H}_2\text{SO}_4$ . No hypervalent compounds were used in the parameterization of MNDO and only a few were used in parameterizing AM1. Hitherto, no purely 's-p' basis set model has proven successful in describing the bonding in hypervalent systems; "d" orbitals are normally considered essen-

tial.<sup>6,25,33</sup> Using the new parameter set,  $\Delta H_f$  and geometries are reproduced with chemically useful accuracy. Thus we conclude that d orbitals are not essential for a description of the bonding in hypervalent compounds. This conclusion cannot be used to refute the assertion that d-orbital participation is important, only that within the MNDO framework s and p atomic orbitals are sufficient.

For the hypervalent compounds surveyed, no geometric quantities can be identified as resulting from the angular properties of d

**Table XI.** Average errors in calculated bond lengths.

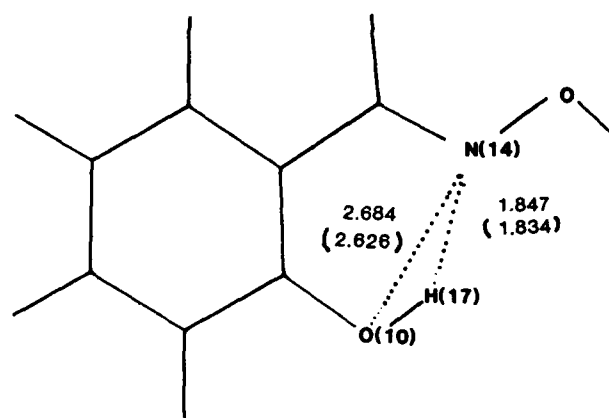
In bonds involving	No.	Average error (Å)		
		PM3	MNDO	AM1
Hydrogen	84	0.005	0.014	0.008
Carbon	214	0.002	0.002	0.002
Nitrogen	62	0.013	0.017	0.015
Oxygen	63	0.006	0.016	0.012
Fluorine	59	0.011	0.022	0.015
Aluminum	12	0.044	0.074	0.075
Silicon	19	0.045	0.030	0.019
Phosphorus	20	0.030	0.041	0.041
Sulfur	41	0.008	0.013	0.015
Chlorine	33	0.021	0.020	0.029
Bromine	21	0.059	0.046	0.048
Iodine	15	0.055	0.063	0.058

orbitals; the only reason for invoking them is to explain the increased valency. The parameters for the *s* and *p* atomic orbitals in MNDO are adjusted to optimally reproduce experimental results. As a result, the *s* and *p* orbitals cannot be simply identified with a given principal quantum number (although an integer PQN is used as part of the definition of the Slater atomic orbitals). Rather, the *s* and *p* orbitals represent not only the assumed atomic orbitals but also all higher atomic orbitals including those of different angular quantum number right up to the continuum. In this respect, semiempirical methods differ from *ab initio*. Using *ab initio* methods *d* orbitals would be essential for describing the hypervalents; the *s-p* basis functions, being *ab initio*, could not perform the double duty of representing *d* orbitals.

Very few data are available for gas-phase organophosphorus V compounds, so the validity of the new parameters for the study of such compounds cannot be confirmed. In addition, all systems studied are gas phase, whereas reactions of biochemical interest occur mainly in the aqueous phase, although it has been postulated<sup>34</sup> that during the course of a biochemical reaction the reactive site may behave as if it were in the gas phase. Nevertheless, the available data are reproduced with sufficient accuracy to warrant consideration of using these parameters for the study of biochemically important systems.

**Table XII.** Average errors in molecular geometries.

Geometric parameter	No.	PM3	MNDO	AM1
Bond lengths (angstroms)	372	0.036	0.054	0.050
Angles (degrees)	158	3.932	4.342	3.281
Torsion angles (degrees)	16	14.875	21.619	12.494

**Figure 3.** Intermolecular distances in salicylaldehyde. All distances in Angstroms. Observed distance in parentheses.

## CONCLUSION

The parameter set here has three limitations: in the limit, it is only as good as the reference data used; it cannot overcome any limitations in the algebraic form of the Hamiltonian (here MNDO/AM1); and it should be used with caution when applied to the prediction of any properties not used either in the parameterization or in subsequent surveys. In particular, when venturing into a new field of application, frequent comparison of calculated and experimental results is imperative.

Using the new optimization procedure described in the previous report, the task of optimizing parameters is relatively straight-

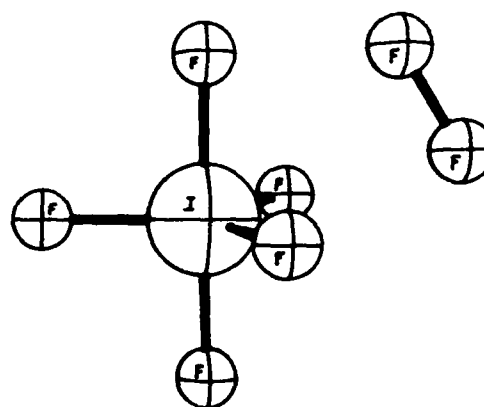
**Figure 4.** Calculated geometry for IF<sub>7</sub>.

Table XIII. Comparison of experimental and calculated dipole moments.

Empirical formula	Chemical name	Dipole moment		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
C <sub>3</sub> H <sub>4</sub>	Cyclopropene	0.45	0.39	-0.06	0.03	-0.09	a
C <sub>3</sub> H <sub>4</sub>	Propyne	0.78	0.36	-0.42	-0.66	-0.38	a
C <sub>3</sub> H <sub>6</sub>	Propene	0.37	0.23	-0.14	-0.33	-0.14	a
C <sub>3</sub> H <sub>8</sub>	Propane	0.08	0.01	-0.07	-0.08	-0.08	a
C <sub>4</sub> H <sub>6</sub>	Bicyclobutane	0.68	0.43	-0.25	-0.27	-0.26	a
C <sub>4</sub> H <sub>7</sub>	Cyclobutene	0.13	0.15	0.02	-0.05	0.04	a
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	0.42	0.53	0.11	-0.24	0.11	a
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	0.20	0.15	-0.05	-0.15	-0.03	a
C <sub>6</sub> H <sub>6</sub>	Fulvene	0.42	0.66	0.24	0.27	0.27	b
C <sub>7</sub> H <sub>8</sub>	Toluene	0.36	0.26	-0.10	-0.30	-0.10	a
H <sub>2</sub> O	Water	1.85	1.74	-0.11	-0.07	0.01	a
CO	Carbon monoxide	0.11	0.18	0.07	0.09	-0.05	a
CH <sub>2</sub> O	Formaldehyde	2.33	2.16	-0.17	-0.17	-0.01	a
CH <sub>4</sub> O	Methanol	1.70	1.49	-0.21	-0.22	-0.08	a
C <sub>2</sub> H <sub>2</sub> O	Ketene	1.42	1.06	-0.36	-0.38	-0.07	a
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	2.69	2.54	-0.15	-0.31	0.00	a
C <sub>2</sub> H <sub>4</sub> O	Ethylene oxide	1.89	1.77	-0.12	0.03	0.02	a
C <sub>2</sub> H <sub>6</sub> O	Ethanol	1.69	1.45	-0.24	-0.29	-0.14	a
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	1.30	1.25	-0.05	-0.03	0.13	a
C <sub>3</sub> H <sub>6</sub> O	Acetone	2.88	2.78	-0.10	-0.37	0.04	a
C <sub>4</sub> H <sub>4</sub> O	Furan	0.66	0.22	-0.44	-0.24	-0.17	a
C <sub>4</sub> H <sub>10</sub> O	Diethyl ether	1.15	1.33	0.18	0.21	0.30	a
C <sub>6</sub> H <sub>6</sub> O	Phenol	1.45	1.14	-0.31	-0.29	-0.22	a
C <sub>7</sub> H <sub>8</sub> O	Anisole	1.38	1.08	-0.30	-0.31	-0.13	a
CH <sub>2</sub> O <sub>2</sub>	Formic acid	1.41	1.51	0.10	0.08	0.07	a
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	1.74	1.83	0.09	-0.06	0.12	a
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	1.77	1.59	-0.18	-0.15	-0.26	a
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propionic acid	1.75	1.81	0.06	-0.04	0.08	a
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	1.72	1.82	0.10	0.03	0.02	a
O <sub>3</sub>	Ozone	0.53	1.71	1.18	0.65	0.67	a
H <sub>3</sub> N	Ammonia	1.47	1.55	0.08	0.28	0.38	a
CHN	Hydrogen cyanide	2.98	2.70	-0.28	-0.48	-0.62	a
CH <sub>5</sub> N	Methylamine	1.31	1.40	0.09	0.17	0.18	a
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	3.92	3.21	-0.71	-1.29	-1.03	a
C <sub>2</sub> H <sub>3</sub> N	Methyl isocyanide	3.85	3.69	-0.16	-1.68	-1.02	a
C <sub>2</sub> H <sub>3</sub> N	Ethyleneimine (Azirane)	1.90	1.69	-0.21	-0.15	-0.15	a
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	1.22	1.43	0.21	0.30	0.33	a
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	1.03	1.27	0.24	0.14	0.20	a
C <sub>3</sub> H <sub>3</sub> N	Acrylonitrile	3.87	3.25	-0.62	-0.90	-0.87	a
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	0.61	1.15	0.54	0.14	0.41	a
C <sub>4</sub> H <sub>5</sub> N	Pyrrrole	1.74	2.18	0.44	0.07	0.21	c
C <sub>5</sub> H <sub>5</sub> N	Pyridine	2.22	1.94	-0.28	-0.26	-0.25	d
C <sub>6</sub> H <sub>7</sub> N	Aniline	1.53	1.30	-0.23	-0.07	0.01	a
CH <sub>3</sub> NO	Formamide	3.73	3.12	-0.61	-0.62	-0.03	a
C <sub>3</sub> H <sub>7</sub> NO	Dimethylformamide	3.82	3.06	-0.76	-0.65	-0.27	a
HNO <sub>2</sub>	Nitrous acid, trans	1.86	2.08	0.22	0.42	0.45	e
HNO <sub>3</sub>	Nitric acid	2.17	2.32	0.15	0.61	0.40	a
CH <sub>2</sub> N <sub>2</sub>	Diazomethane	1.50	1.92	0.42	-0.25	-0.17	a
CH <sub>2</sub> N <sub>2</sub>	N=N-CH <sub>2</sub> -	1.59	1.87	0.28	-0.04	0.04	a
CH <sub>6</sub> N <sub>2</sub>	Methylhydrazine	1.66	0.32	-1.34	-1.42	-0.89	f
N <sub>2</sub> O	Nitrous oxide	0.17	0.26	0.09	0.59	0.47	a
CH <sub>4</sub> S	Thiomethanol	1.52	1.95	0.43	0.15	0.44	g
C <sub>2</sub> H <sub>6</sub> S	Thioethanol	1.52	1.98	0.46	0.11	0.44	g
C <sub>2</sub> H <sub>6</sub> S	Dimethyl thioether	1.50	1.96	0.46	0.22	0.32	h
C <sub>6</sub> H <sub>6</sub> S	Thiophene	0.53	0.67	0.14	0.36	0.32	g
CSO	Carbon oxysulfide	0.71	0.38	-0.33	0.21	-0.18	h
SO <sub>2</sub>	Sulfur dioxide	1.57	3.63	2.06	1.90	2.06	g
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	2,3-Dithiabutane	1.98	2.57	0.59	-0.02	0.26	g
HF	Hydrogen fluoride	1.83	1.40	-0.43	0.16	-0.09	i
CH <sub>3</sub> F	Fluoromethane	1.86	1.44	-0.42	-0.10	-0.24	j
C <sub>2</sub> HF	Fluoroacetylene	0.70	1.11	0.41	0.88	0.36	k
C <sub>2</sub> H <sub>3</sub> F	Fluoroethylene	1.43	1.37	-0.06	0.27	-0.05	h
C <sub>2</sub> H <sub>5</sub> F	Fluoroethane	1.96	1.58	-0.38	-0.09	-0.27	h
C <sub>6</sub> H <sub>5</sub> F	Fluorobenzene	1.66	1.60	-0.06	0.30	-0.08	h

Table XIII. (continued)

Empirical formula	Chemical name	Dipole moment		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
HOF	Hypofluorous acid	2.23	1.68	-0.55	-0.42	-0.63	l
CHOF	HCOF	2.02	2.46	0.44	0.48	0.55	h
CNF	Cyanogen fluoride	2.17	1.63	-0.54	-1.28	-0.96	k
NOF	Nitrosyl fluoride	1.81	0.26	-1.55	-1.30	-1.43	h
NO <sub>2</sub> F	Fluorine nitrite	0.47	0.89	0.42	0.19	0.35	g
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	1.96	1.81	-0.15	0.26	0.08	h
C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	1,1-Difluoroethane	2.30	2.12	-0.18	0.20	-0.03	h
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	<i>o</i> -Difluorobenzene	2.59	2.74	0.15	0.77	0.09	m
OF <sub>2</sub>	Difluorine oxide	0.30	0.38	0.08	0.02	-0.19	h
COF <sub>2</sub>	Carbonyl fluoride	0.95	1.08	0.13	-0.14	0.33	g
N <sub>2</sub> F <sub>2</sub>	<i>cis</i> -Difluorodiazene	0.16	0.63	0.47	-0.14	0.50	g
CHF <sub>3</sub>	Trifluoromethane	1.65	1.88	0.23	0.58	0.43	j
C <sub>2</sub> HF <sub>3</sub>	Trifluoroethylene	1.30	1.49	0.19	0.52	0.13	n
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1-Trifluoroethane	2.32	2.40	0.08	0.55	0.27	h
C <sub>2</sub> HO <sub>2</sub> F <sub>3</sub>	Trifluoroacetic acid	2.28	1.96	-0.32	0.17	-0.42	h
NF <sub>3</sub>	Nitrogen trifluoride	0.24	0.26	0.02	-0.04	-0.20	h
C <sub>2</sub> NF <sub>3</sub>	Trifluoroacetonitrile	1.26	0.32	-0.94	-0.90	-1.23	o
COF <sub>4</sub>	Trifluoromethyl hypofluorite	0.33	0.28	-0.05	-0.24	0.02	p
HCl	Hydrogen chloride	1.12	1.38	0.26	0.36	0.26	q
C <sub>2</sub> HCl	Chloroacetylene	0.44	0.14	-0.30	0.34	-0.17	r
FCl	Chlorine fluoride	0.88	1.42	0.54	0.59	0.03	s
SCl <sub>2</sub>	Sulfur dichloride	0.36	0.59	0.23	0.40	-0.30	g
HBr	Hydrogen bromide	0.83	1.27	0.44	0.24	0.55	a
CH <sub>3</sub> Br	Bromomethane	1.82	1.55	-0.27	-0.26	-0.34	a
C <sub>2</sub> H <sub>3</sub> Br	Bromoethylene	1.42	1.33	-0.09	-0.11	-0.12	s
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	2.03	1.85	-0.18	-0.37	-0.37	a
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	2.18	1.81	-0.37	-0.47	-0.48	a
C <sub>6</sub> H <sub>5</sub> Br	Bromobenzene	1.70	1.18	-0.52	-0.28	-0.25	a
OBr	BrO	1.61	3.32	1.71	0.38	0.75	t
C <sub>2</sub> H <sub>3</sub> OBr	Acetyl bromide	2.43	2.95	0.52	0.02	0.16	s
FBr	Bromine fluoride	1.42	2.25	0.83	0.68	0.04	s
CF <sub>3</sub> Br	Bromotrifluoromethane	0.65	0.90	0.25	0.53	0.37	u
ClBr	Bromine chloride	0.52	0.06	-0.46	0.23	-0.07	v
CH <sub>2</sub> Br <sub>2</sub>	Dibromomethane	1.43	1.45	0.02	-0.06	-0.11	s
CHBr <sub>3</sub>	Bromoform	0.99	0.96	-0.03	-0.08	-0.08	s
HI	Hydrogen iodide	0.44	0.97	0.53	0.57	0.83	a
CH <sub>3</sub> I	Methyl iodide	1.65	1.44	-0.21	-0.28	-0.30	a
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	1.91	1.83	-0.08	-0.50	-0.41	a
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane	2.04	1.78	-0.26	-0.57	-0.50	a
C <sub>6</sub> H <sub>5</sub> I	Iodobenzene	1.70	0.81	-0.89	-0.10	-0.27	a
CF <sub>3</sub> I	Trifluoroiodomethane	1.00	1.55	0.55	1.13	0.67	w
BrI	Iodine bromide	0.74	0.53	-0.21	-0.02	-0.11	v
CH <sub>2</sub> I <sub>2</sub>	Diiodomethane	1.62	1.20	-0.42	-0.47	-0.50	a
AlF	Aluminum fluoride	1.53	3.29	1.76	-1.22	-1.09	x
C <sub>2</sub> H <sub>5</sub> Si	Vinylsilane	0.66	0.24	-0.42	-0.12	-0.11	a
C <sub>2</sub> H <sub>6</sub> Si	Ethylsilane	0.81	0.37	0.44	-0.71	-0.45	g
C <sub>2</sub> H <sub>8</sub> Si	Dimethylsilane	0.75	0.46	-0.29	-0.57	-0.30	a
C <sub>3</sub> H <sub>10</sub> Si	Trimethylsilane	0.52	0.37	-0.15	-0.35	-0.13	a
H <sub>2</sub> SiF <sub>2</sub>	Difluorosilane	1.54	1.41	-0.13	0.69	0.03	a
HSiF <sub>3</sub>	Trifluorosilane	1.27	1.51	0.24	1.53	0.28	a
H <sub>2</sub> SiCl <sub>2</sub>	Dichlorosilane	1.18	2.68	1.50	2.29	0.58	a
HSiCl <sub>3</sub>	Trichlorosilane	0.86	2.38	1.52	1.87	0.56	a
H <sub>2</sub> SiBr <sub>2</sub>	Dibromosilane	1.43	3.09	1.66	1.90	0.38	s
C <sub>6</sub> H <sub>19</sub> Si <sub>2</sub> N	Hexamethyldisilazane	0.37	0.35	-0.02	-0.10	0.24	a
H <sub>3</sub> P	Phosphine	0.58	1.18	0.60	0.77	1.61	a
CH <sub>5</sub> P	Methylphosphine	1.10	1.15	0.05	0.51	0.93	h
C <sub>2</sub> H <sub>7</sub> P	Dimethylphosphine	1.23	1.16	-0.07	0.58	0.67	h
C <sub>3</sub> H <sub>9</sub> P	Trimethylphosphine	1.19	1.08	-0.11	0.74	0.56	h
PF <sub>3</sub>	Phosphorus trifluoride	1.03	2.25	1.22	1.41	1.06	a
POF <sub>3</sub>	Phosphorus oxyfluoride	1.76	2.04	0.28	-0.56	0.18	a
H <sub>4</sub> P <sub>2</sub>	P <sub>2</sub> H <sub>4</sub>	0.92	2.19	1.27	-0.92	-0.92	y

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forward. Once the onerous task of assembling a database of experimental results has been done, a full optimization of all parameters for an element requires only about 2–10 h on a VAX 11-780.

For many of the properties studied, the new parameter sets are significantly better than the original MNDO/AM1. In particular, differences between experimental and calculated  $\Delta H_f$  for P(V), S(IV), S(VI), I(V), and I(VII) are considerably reduced. The energy of the hydrogen bond in water dimer is less than that obtained using AM1, but the geometry is more realistic.

Calculations made using these parameters should be useful in identifying potentially incorrect thermochemical data. Thus the reported experimental  $\Delta H_f$ ,  $-11.8$  kcal/mol, of triethylphosphine is predicted to be inconsistent with the heats of formation of related systems. For this system the predicted  $\Delta H_f$  is  $-36.7$  kcal/mol.

In other instances related homologues are absent. Nonetheless, the high internal consistency of the computational model can be used to identify potentially incorrect experimental data. For several systems, such as SiOX<sub>2</sub> and COX, X = Cl, Br, or I, the experimental  $\Delta H_f$  reported is predicted to be incorrect by a few tens of kcal/mol. Although the new parameters were derived from ex-

perimental data, and consequently are subject to inaccuracies in those data, they are internally consistent, and thus the prediction is made that the experimental  $\Delta H_f$  of COI is too positive and that of three of the oxyhalides of silicon too negative.

As limitations in the generality of the method become apparent—limitations not revealed by the surveys presented here—the parameters can more readily be reoptimized in an attempt to remove these limitations. The parameters may be reoptimized as significant amounts of new or improved experimental data become available or if significant improvements to the algebraic form of the Hamiltonian are developed. Although, as we have seen, optimization is now a more straightforward task, it should not be attempted lightly—a proliferation of parameter sets differing only slightly one from another would be undesirable. Rather, only when a significant increase in accuracy could be obtained, such as a drop in the average error of more than 30%, should a new parameter set be released for general use.

It is unlikely that any computational method will be able to reduce the average error to below about 4 kcal/mol for the set of compounds surveyed here; current experimental data are simply not accurate enough. Unfortunately, determination of the accu-

Table XIV. Comparison of experimental and calculated ionization potentials.

Empirical formula	Chemical name	Ionization potential		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
H <sub>2</sub>	Hydrogen	15.40	16.11	0.71	0.35	-0.48	a
CH <sub>4</sub>	Methane	13.60	13.64	0.04	0.27	-0.29	b
C <sub>2</sub> H <sub>2</sub>	Acetylene	11.40	11.61	0.21	-0.39	0.10	a
C <sub>2</sub> H <sub>4</sub>	Ethylene	10.51	10.64	0.13	-0.34	0.04	a
C <sub>2</sub> H <sub>6</sub>	Ethane.....	12.00	11.98	-0.02	0.70	-0.23	a
C <sub>3</sub>	Carbon, trimer	11.10	11.75	0.65	-0.06	0.23	a
C <sub>3</sub> H <sub>4</sub>	Allene	10.07	10.18	0.11	-0.05	0.07	a
C <sub>3</sub> H <sub>4</sub>	Cyclopropene	9.86	9.88	0.02	0.02	-0.04	c
C <sub>3</sub> H <sub>4</sub>	Propyne	10.37	10.89	0.52	0.35	0.37	b
C <sub>3</sub> H <sub>6</sub>	Cyclopropane.....	11.00	11.78	0.78	0.43	0.48	b
C <sub>3</sub> H <sub>6</sub>	Propene	9.88	10.10	0.22	0.08	0.11	d
C <sub>3</sub> H <sub>8</sub>	Propane	11.50	11.51	0.01	0.84	-0.18	e
C <sub>4</sub> H <sub>2</sub>	Diacetylene	10.17	10.47	0.30	-0.18	0.20	a
C <sub>4</sub> H <sub>6</sub>	1,2-Butadiene	9.15	9.72	0.57	0.69	0.52	a
C <sub>4</sub> H <sub>6</sub>	1-Butyne.....	10.20	10.77	0.57	0.48	0.42	a
C <sub>4</sub> H <sub>6</sub>	2-Butyne	9.60	10.34	0.74	0.87	0.57	a
C <sub>4</sub> H <sub>6</sub>	Cyclobutene	9.43	9.82	0.39	0.34	0.29	a
C <sub>4</sub> H <sub>6</sub>	1,3-Butadiene	9.08	9.47	0.39	0.06	0.25	b
C <sub>4</sub> H <sub>8</sub>	1-Butene	9.70	10.03	0.33	0.24	0.23	a
C <sub>4</sub> H <sub>8</sub>	Cyclobutane.....	10.70	11.02	0.32	1.11	0.29	a
C <sub>4</sub> H <sub>10</sub>	n-Butane	11.20	11.35	0.15	1.01	-0.03	a
C <sub>4</sub> H <sub>10</sub>	Isobutane	11.40	11.59	0.19	0.72	-0.11	e
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	8.57	9.23	0.66	0.47	0.51	a
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	9.18	9.52	0.34	0.54	0.26	a
C <sub>5</sub> H <sub>10</sub>	1-Pentene.....	7.90	10.15	2.25	2.07	2.09	a
C <sub>5</sub> H <sub>10</sub>	2-Methyl-1-butene	7.40	9.85	2.45	2.41	2.30	a
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	8.70	9.39	0.69	0.94	0.55	a
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	9.60	10.26	0.66	0.38	0.49	a
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	10.50	11.07	0.57	1.56	0.47	a
C <sub>5</sub> H <sub>12</sub>	2-Methylbutane.....	10.30	11.44	1.14	1.70	0.90	a
C <sub>5</sub> H <sub>12</sub>	Neopentane	11.30	12.06	0.76	0.82	0.23	e
C <sub>5</sub> H <sub>12</sub>	n-Pentane	10.30	11.30	1.00	1.86	0.81	a
C <sub>6</sub> H <sub>6</sub>	Benzene	9.25	9.75	0.50	0.14	0.40	a
C <sub>6</sub> H <sub>10</sub>	Cyclohexene	10.30	9.59	-0.71	-0.55	-0.81	a
C <sub>6</sub> H <sub>12</sub>	Cyclohexane.....	10.30	11.29	0.99	1.44	0.64	a
C <sub>7</sub> H <sub>8</sub>	Cycloheptatriene	8.50	8.95	0.45	0.22	0.25	a
C <sub>7</sub> H <sub>8</sub>	Toluene	8.82	9.44	0.62	0.46	0.51	b
C <sub>8</sub> H <sub>10</sub>	Ethylbenzene	8.80	9.52	0.72	0.48	0.58	a
C <sub>8</sub> H <sub>14</sub>	Bicyclo(2.2.2)-octane	9.45	10.94	1.49	1.95	1.11	a
C <sub>10</sub> H <sub>8</sub>	Naphthalene.....	8.15	8.84	0.69	0.42	0.56	a
C <sub>10</sub> H <sub>16</sub>	Adamantane	9.60	10.85	1.25	1.67	0.83	a
C <sub>14</sub> H <sub>10</sub>	Anthracene	8.16	8.25	0.09	-0.11	-0.04	a
H <sub>2</sub> O	Water	12.62	12.32	-0.30	-0.43	-0.16	b
CO	Carbon monoxide	14.01	13.03	-0.98	-0.58	-0.70	a
CH <sub>2</sub> O	Formaldehyde.....	10.10	10.63	0.53	0.94	0.68	a
CH <sub>4</sub> O	Methanol	10.96	11.14	0.18	0.46	0.17	a
C <sub>2</sub> H <sub>2</sub> O	Ketene	9.64	9.46	-0.18	-0.35	-0.04	a
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	10.21	10.71	0.50	0.67	0.51	a
C <sub>2</sub> H <sub>4</sub> O	Ethylene oxide	10.57	11.34	0.77	0.92	0.76	b
C <sub>2</sub> H <sub>6</sub> O	Ethanol	10.60	10.90	0.30	0.70	0.28	a
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether.....	10.04	10.69	0.65	1.00	0.57	a
C <sub>3</sub> H <sub>6</sub> O	Acetone	9.72	10.77	1.05	1.04	0.95	a
C <sub>3</sub> H <sub>8</sub> O	Propanol	10.00	10.62	0.62	0.81	0.59	a
C <sub>4</sub> H <sub>4</sub> O	Furan	8.88	9.38	0.50	0.26	0.44	a
C <sub>4</sub> H <sub>6</sub> O	2-Butenal	9.90	10.50	0.60	0.49	0.57	a
C <sub>4</sub> H <sub>6</sub> O	Butanal.....	9.83	10.63	0.80	0.97	0.76	a
C <sub>4</sub> H <sub>10</sub> O	Diethyl ether	9.60	10.79	1.19	1.18	0.96	a
C <sub>5</sub> H <sub>12</sub> O	3-Pentanol	10.16	10.92	0.76	0.93	0.65	a
C <sub>7</sub> H <sub>6</sub> O	Benzaldehyde	9.70	10.05	0.35	0.04	0.30	a
C <sub>7</sub> H <sub>8</sub> O	Anisole	8.40	9.11	0.71	0.44	0.60	a
C <sub>10</sub> H <sub>8</sub> O	1-Naphthol.....	7.80	8.59	0.79	0.54	0.69	a
C <sub>10</sub> H <sub>8</sub> O	2-Naphthol	7.90	8.72	0.82	0.58	0.74	a
CO <sub>2</sub>	Carbon dioxide	13.78	12.73	-1.05	-0.99	-0.57	b
CH <sub>2</sub> O <sub>2</sub>	Formic acid	11.51	11.56	0.05	0.23	0.31	a



Table XIV. (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	trans Glyoxal	10.59	10.57	-0.02	0.16	0.07	a
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid .....	10.80	11.44	0.64	0.77	0.82	a
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	11.02	11.35	0.33	0.59	0.55	f
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Dimethyl peroxide	10.60	10.77	0.17	0.09	0.29	a
C <sub>3</sub> O <sub>2</sub>	Carbon suboxide	10.60	10.22	-0.38	-0.53	-0.10	a
C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	beta-Propiolactone	10.60	9.96	-0.64	-0.73	-0.54	a
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propionic acid .....	10.50	11.34	0.84	1.00	0.99	a
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	10.60	11.27	0.67	0.86	0.80	a
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	Acetylacetone	8.38	10.89	2.51	2.40	2.36	a
C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	Benzoic acid	9.80	10.13	0.33	-0.03	0.28	a
O <sub>3</sub>	Ozone	12.75	12.69	-0.06	-0.05	0.35	g
C <sub>4</sub> H <sub>2</sub> O <sub>3</sub>	Malaic anhydride .....	10.84	11.71	0.87	0.86	1.18	a
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Oxalic acid	11.20	11.67	0.47	0.59	0.76	a
H <sub>3</sub> N	Ammonia	10.85	9.70	-1.15	0.34	-0.43	b
CHN	Hydrogen cyanide	13.60	12.60	-1.00	-0.19	0.08	b
CH <sub>5</sub> N	Methylamine	9.60	9.40	-0.20	0.96	0.15	a
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile .....	12.21	12.33	0.12	0.58	0.25	a
C <sub>2</sub> H <sub>3</sub> N	Methyl isocyanide	11.32	11.70	0.38	0.92	0.67	a
C <sub>2</sub> H <sub>5</sub> N	Ethyleneimine (Azirane)	9.90	9.92	0.02	0.78	0.41	a
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	9.50	9.50	0.00	1.01	0.39	a
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	8.93	9.22	0.29	1.11	0.46	h
C <sub>3</sub> H <sub>3</sub> N	Acrylonitrile .....	10.91	10.89	-0.02	-0.30	-0.05	a
C <sub>3</sub> H <sub>5</sub> N	Ethyl cyanide	11.90	12.01	0.11	0.69	0.09	a
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	8.54	9.07	0.53	1.05	0.58	h
C <sub>4</sub> H <sub>5</sub> N	Pyrrrole	8.21	8.93	0.72	0.35	0.45	a
C <sub>5</sub> H <sub>5</sub> N	Pyridine	9.67	10.10	0.43	0.02	0.26	a
C <sub>6</sub> H <sub>7</sub> N	Aniline .....	7.70	8.61	0.91	1.05	0.82	a
C <sub>7</sub> H <sub>5</sub> N	Phenyl cyanide	9.70	10.10	0.40	0.11	0.32	a
CHNO	Hydrogen isocyanate	11.60	10.59	-1.01	-0.50	-0.36	a
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	11.30	12.17	0.87	0.24	0.68	a
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	11.00	10.64	-0.36	0.42	0.19	a
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	Alanine	8.10	9.88	1.78	2.71	2.27	a
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene .....	9.90	10.60	0.70	0.41	0.66	a
N <sub>2</sub>	Nitrogen	15.60	13.80	-1.80	-0.73	-1.28	a
CH <sub>2</sub> N <sub>2</sub>	Diazomethane	9.00	9.22	0.22	-0.33	-0.18	a
CH <sub>6</sub> N <sub>2</sub>	Methylhydrazine	9.30	8.92	-0.38	0.36	-0.34	a
C <sub>2</sub> N <sub>2</sub>	Cyanogen	13.36	12.87	-0.49	-0.16	-0.05	a
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyridazine .....	9.30	9.94	0.64	1.19	1.37	a
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrimidine	9.73	10.29	0.56	0.65	0.85	a
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	9.90	10.16	0.26	0.12	0.35	a
N <sub>2</sub> O <sub>4</sub>	Dinitrogen tetroxide	11.40	11.61	0.21	0.65	-0.19	a
N <sub>2</sub> O <sub>5</sub>	Dinitrogen pentoxide	12.30	12.38	0.08	0.88	1.32	a
HS	Hydrogen sulfide .....	10.40	9.79	-0.61	0.20	0.16	i
H <sub>2</sub> S	Hydrogen sulfide	10.43	9.63	-0.80	0.21	0.13	j
CS	Carbon sulfide	11.30	10.60	-0.70	0.26	0.48	a
CH <sub>4</sub> S	Thiomethanol	9.44	9.21	-0.23	0.88	0.56	j
C <sub>2</sub> H <sub>4</sub> S	Thiirane	8.87	9.23	0.36	1.29	1.01	j
C <sub>2</sub> H <sub>6</sub> S	Thioethanol .....	9.21	9.19	-0.02	1.07	0.72	k
C <sub>2</sub> H <sub>6</sub> S	Dimethyl thioether	8.65	8.88	0.23	1.42	0.94	j
C <sub>3</sub> H <sub>6</sub> S	Thiethane	8.65	8.95	0.30	1.36	0.93	l
C <sub>3</sub> H <sub>8</sub> S	Isopropanthiol	9.14	9.22	0.08	1.12	0.78	a
C <sub>3</sub> H <sub>8</sub> S	1-Propanthiol	9.19	9.19	0.00	1.08	0.74	a
C <sub>4</sub> H <sub>4</sub> S	Thiophene .....	8.95	9.54	0.59	0.56	0.72	j
C <sub>4</sub> H <sub>6</sub> S	Tetrahydrothiophene	8.60	8.79	0.19	1.32	0.80	a
C <sub>4</sub> H <sub>10</sub> S	Butanethiol	9.15	9.19	0.04	1.12	0.78	a
C <sub>4</sub> H <sub>6</sub> S	Thiophenol	8.47	8.78	0.31	0.59	0.65	l
CSO	Carbon oxysulfide	11.20	10.71	-0.49	-0.14	0.03	a
C <sub>2</sub> H <sub>4</sub> SO	Thiolacetic acid .....	9.70	10.05	0.35	1.32	1.20	a
C <sub>2</sub> H <sub>6</sub> SO	Dimethyl sulfoxide	9.01	9.35	0.34	0.82	0.94	a
SO <sub>2</sub>	Sulfur dioxide	12.30	10.55	-1.75	-0.51	-0.32	j
SO <sub>3</sub>	Sulfur trioxide	11.00	12.91	1.91	2.06	2.25	j
CHNS	Hydrogen isothiocyanate	9.94	9.38	-0.56	0.25	0.09	a
C <sub>2</sub> H <sub>3</sub> NS	Methyl isothiocyanate .....	9.37	9.17	-0.20	0.51	0.34	a
C <sub>2</sub> H <sub>3</sub> NS	Methyl thiocyanate	9.96	9.68	-0.28	0.81	0.52	a

Table XIV. (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
H <sub>2</sub> S <sub>2</sub>	Hydrogen disulfide	10.01	9.86	-0.15	0.72	0.34	m
CS <sub>2</sub>	Carbon disulfide	10.08	9.83	-0.25	0.50	0.44	j
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	1,2-Ethanedithiol	9.00	9.32	0.32	1.43	1.13	a
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	Ethanedithiol-1,2	9.30	9.32	0.02	1.13	0.83	l
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	2,3-Dithiabutane	8.71	9.40	0.69	1.50	1.28	j
C <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	S2(CN)2	11.05	10.56	-0.49	0.66	0.43	a
C <sub>3</sub> H <sub>4</sub> S <sub>3</sub>	1,3-Dithiolan-2-thione	8.40	9.25	0.85	1.59	1.42	a
S <sub>8</sub>	S8	9.04	9.09	0.05	1.98	1.98	j
HF	Hydrogen fluoride	16.06	16.14	0.08	-1.24	-1.97	n
CH <sub>3</sub> F	Fluoromethane	13.31	12.92	-0.39	-0.26	-1.21	o
C <sub>2</sub> HF	Fluoroacetylene	11.30	11.56	0.26	-0.24	-0.15	a
C <sub>2</sub> H <sub>3</sub> F	Fluoroethylene	10.58	10.60	0.02	-0.41	-0.34	a
C <sub>2</sub> H <sub>5</sub> F	Fluoroethane	12.43	12.07	-0.36	0.18	-0.85	a
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	11.08	12.10	1.02	1.25	0.44	a
C <sub>6</sub> H <sub>5</sub> F	Fluorobenzene	9.19	9.81	0.62	0.28	0.35	a
C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> F	p-Fluorobenzoic acid	9.90	10.16	0.26	-0.07	0.05	a
NOF	Nitrosyl fluoride	12.94	11.54	-1.40	-0.01	-0.42	p
NO <sub>2</sub> F	Fluorine nitrite	13.51	13.37	-0.14	-0.52	-0.12	p
SF	SF	10.00	9.75	-0.25	0.79	0.62	a
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	13.17	12.86	-0.31	-0.08	-1.15	o
C <sub>2</sub> F <sub>2</sub>	Difluoroacetylene	11.20	11.54	0.34	-0.03	-0.27	a
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	gem-Difluoroethylene	10.72	10.54	-0.18	-0.54	-0.73	a
C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	1,1-Difluoroethane	12.80	12.82	0.02	-0.07	-0.87	a
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	o-Difluorobenzene	9.68	9.98	0.30	0.01	-0.05	a
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	m-Difluorobenzene	9.68	10.02	0.34	0.05	0.04	a
C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	p-Difluorobenzene	9.30	9.87	0.57	0.26	0.19	a
OF <sub>2</sub>	Difluorine oxide	13.26	13.47	0.21	0.26	-0.36	q
N <sub>2</sub> F <sub>2</sub>	trans-Difluorodiazene	13.40	11.91	-1.49	-0.40	-1.15	q
SF <sub>2</sub>	Sulfur difluoride	10.20	9.81	-0.39	1.07	0.72	a
SOF <sub>2</sub>	Thionyl fluoride	12.58	11.03	-1.55	0.09	-0.36	a
SO <sub>2</sub> F <sub>2</sub>	Sulfuryl fluoride	13.04	13.10	0.06	0.77	0.40	a
S <sub>2</sub> F <sub>2</sub>	FSSF	10.68	10.47	-0.21	1.03	0.73	a
CHF <sub>3</sub>	Trifluoromethane	14.80	14.36	-0.44	-0.23	-1.49	a
C <sub>2</sub> HF <sub>3</sub>	Trifluoroethylene	10.54	10.68	0.14	-0.08	-0.45	a
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1-Trifluoroethane	13.80	14.38	0.58	0.21	-0.68	a
C <sub>7</sub> H <sub>5</sub> F <sub>3</sub>	Trifluoromethylbenzene	9.68	10.34	0.66	0.39	0.57	a
C <sub>2</sub> HO <sub>2</sub> F <sub>3</sub>	Trifluoroacetic acid	12.00	12.47	0.47	0.73	0.49	a
NF <sub>3</sub>	Nitrogen trifluoride	13.73	12.24	-1.49	0.20	-0.55	a
CF <sub>4</sub>	Carbon tetrafluoride	16.23	16.79	0.56	0.58	-0.91	a
C <sub>2</sub> F <sub>4</sub>	Tetrafluoroethylene	10.50	10.84	0.34	0.42	-0.22	a
COF <sub>4</sub>	Trifluoromethyl hypofluorite	13.60	14.18	0.58	0.63	0.07	a
N <sub>2</sub> F <sub>4</sub>	Tetrafluorohydrazine	12.00	12.46	0.46	1.04	0.47	a
SF <sub>4</sub>	Sulfur tetrafluoride	12.05	10.41	-1.64	1.01	0.00	a
C <sub>6</sub> HF <sub>5</sub>	Pentafluorobenzene	9.75	10.55	0.80	0.65	0.32	a
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	14.60	14.48	-0.12	-0.10	-1.37	a
C <sub>6</sub> F <sub>6</sub>	Hexafluorobenzene	10.90	10.85	-0.05	-0.13	-0.53	a
C <sub>3</sub> OF <sub>6</sub>	Perfluoroacetone	12.10	12.71	0.61	0.90	0.24	a
SF <sub>6</sub>	Sulfur hexafluoride	15.70	16.39	0.69	0.19	-1.39	a
HCl	Hydrogen chloride	12.75	11.06	-1.69	0.25	-0.42	n
CH <sub>3</sub> Cl	Methyl chloride	11.30	10.48	-0.82	0.94	0.04	a
C <sub>7</sub> H <sub>5</sub> OCl	Benzoyl chloride	9.90	10.29	0.39	0.12	0.34	a
NOCl	Nitrosyl chloride	10.90	10.59	-0.31	1.07	0.66	a
NO <sub>2</sub> Cl	Nitryl chloride	11.40	12.42	1.02	1.61	1.54	a
FCl	Chlorine fluoride	12.02	11.13	-0.89	1.35	0.37	r
CH <sub>2</sub> FCl	Fluorochloromethane	11.74	10.85	-0.89	0.80	-0.16	a
CHF <sub>2</sub> Cl	Difluorochloromethane	12.60	11.36	-1.24	0.63	-0.32	a
CF <sub>3</sub> Cl	Trifluorochloromethane	10.30	11.88	1.58	3.83	2.94	a
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	11.30	10.58	-0.72	1.19	0.09	a
COCl <sub>2</sub>	Carbonyl chloride	11.84	11.23	-0.61	0.86	0.53	a
SCl <sub>2</sub>	Sulfur dichloride	9.70	9.60	-0.10	1.34	0.88	a
SOCl <sub>2</sub>	Thionyl chloride	11.10	10.65	-0.45	1.45	0.91	a
SO <sub>2</sub> Cl <sub>2</sub>	Sulfuryl chloride	12.40	10.55	-1.85	-0.62	-0.64	a
S <sub>2</sub> Cl <sub>2</sub>	ClSSCl	9.40	9.96	0.56	2.04	1.63	a
CHFCl <sub>2</sub>	Fluorodichloromethane	12.00	10.99	-1.01	0.96	0.03	a
CF <sub>2</sub> Cl <sub>2</sub>	Difluorodichloromethane	12.30	11.33	-0.97	1.06	0.21	a

Table XIV. (continued)

Empirical formula	Chemical name	Ionization potential		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
CHCl <sub>3</sub>	Chloroform .....	11.48	10.84	-0.64	1.43	0.29	a
CFCl <sub>3</sub>	Fluorotrichloromethane	11.90	11.16	-0.74	1.39	0.55	a
C <sub>2</sub> Cl <sub>6</sub>	Hexachloroethane	11.20	10.84	-0.36	1.88	0.98	a
HBr	Hydrogen bromide	11.71	12.13	0.42	0.39	-0.25	n
CH <sub>3</sub> Br	Bromomethane	10.53	11.01	0.48	1.03	0.27	a
C <sub>2</sub> H <sub>3</sub> Br	Bromoethylene .....	9.90	10.44	0.54	0.35	0.25	a
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	10.28	10.91	0.63	1.20	0.41	a
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	10.18	10.93	0.75	1.29	0.51	a
C <sub>6</sub> H <sub>5</sub> Br	Bromobenzene	9.25	9.81	0.56	0.30	0.35	a
C <sub>2</sub> H <sub>3</sub> OBr	Acetyl bromide	10.55	11.20	0.65	0.88	0.63	s
CF <sub>3</sub> Br	Bromotrifluoromethane .....	12.10	12.23	0.13	1.15	0.23	a
Br <sub>2</sub>	Bromine	10.70	11.24	0.54	0.96	0.24	a
CH <sub>2</sub> Br <sub>2</sub>	Dibromomethane	10.50	10.59	0.09	1.20	0.46	a
C <sub>2</sub> F <sub>4</sub> Br <sub>2</sub>	1,2-Dibromotetrafluoroethane	14.44	12.00	-2.44	-1.65	-2.53	a
CHBr <sub>3</sub>	Bromoform	10.50	10.84	0.34	1.37	0.57	a
CBr <sub>4</sub>	Carbon tetrabromide .....	10.30	11.22	0.92	1.73	0.92	a
HI	Hydrogen iodide	10.39	9.97	-0.42	0.82	0.52	t
CH <sub>3</sub> I	Methyl iodide	9.50	9.47	-0.03	1.35	1.01	a
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	9.34	9.44	0.10	1.48	1.09	a
C <sub>3</sub> H <sub>5</sub> I	3-Iodo-propene	9.30	9.44	0.14	0.99	0.93	a
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane .....	9.27	9.45	0.18	1.53	1.16	a
C <sub>3</sub> H <sub>7</sub> I	2-Iodopropane	9.40	9.43	0.03	1.39	1.00	a
C <sub>4</sub> H <sub>9</sub> I	1-Butyl iodide	9.20	9.45	0.25	1.60	1.23	a
C <sub>6</sub> H <sub>5</sub> I	Iodobenzene	8.70	9.05	0.35	0.85	0.95	a
C <sub>6</sub> H <sub>11</sub> I	Iodocyclohexane	8.91	9.42	0.51	1.86	1.47	a
C <sub>7</sub> H <sub>7</sub> I	<i>o</i> -Iodotoluene .....	8.53	9.02	0.49	0.98	0.99	a
C <sub>7</sub> H <sub>7</sub> I	<i>m</i> -Iodotoluene	8.55	9.01	0.46	0.96	0.97	a
C <sub>7</sub> H <sub>7</sub> I	<i>p</i> -Iodotoluene	8.38	8.94	0.56	1.07	1.03	a
C <sub>7</sub> H <sub>7</sub> I	Benzyl iodide	8.91	9.35	0.44	0.55	0.60	a
CF <sub>3</sub> I	Trifluoroiodomethane	10.45	10.28	-0.17	2.03	1.52	a
ClI	Iodine chloride .....	10.10	9.74	-0.36	1.48	1.02	u
BrI	Iodine bromide	9.85	9.84	-0.01	1.43	0.99	u
I <sub>2</sub>	Iodine	9.34	9.53	0.19	1.53	1.33	v
CH <sub>2</sub> I <sub>2</sub>	Diiodomethane	9.46	8.98	-0.48	1.41	1.10	a
C <sub>2</sub> H <sub>4</sub> I <sub>2</sub>	1,2-Diiodoethane	9.50	9.66	0.16	1.52	1.21	a
C <sub>3</sub> H <sub>9</sub> Al	Trimethylaluminum .....	9.76	10.12	0.36	0.92	0.43	w
C <sub>2</sub> H <sub>6</sub> Si	Vinylsilane	10.40	10.01	-0.39	-0.17	-0.01	a
C <sub>2</sub> H <sub>8</sub> Si	Ethylsilane	10.95	10.64	-0.31	0.19	0.12	j
C <sub>2</sub> H <sub>8</sub> Si	Dimethylsilane	11.20	10.65	-0.55	0.27	-0.03	a
C <sub>3</sub> H <sub>10</sub> Si	Trimethylsilane	10.80	10.51	-0.29	0.60	0.15	a
C <sub>4</sub> H <sub>12</sub> Si	Tetramethylsilane	10.40	10.42	0.02	0.94	0.52	a
H <sub>2</sub> SiF <sub>2</sub>	Difluorosilane .....	12.85	10.82	-2.03	-0.63	-1.24	x
SiF <sub>4</sub>	Silicon tetrafluoride	15.81	15.19	-0.62	0.02	-1.09	y
H <sub>2</sub> SiCl <sub>2</sub>	Dichlorosilane	11.70	10.27	-1.43	0.82	-0.14	x
C <sub>2</sub> H <sub>6</sub> SiCl <sub>2</sub>	Dichlorodimethylsilane	10.79	10.27	-0.52	1.43	0.70	a
SiCl <sub>4</sub>	Silicon tetrachloride	11.79	11.23	-0.56	2.02	1.19	s
C <sub>6</sub> H <sub>19</sub> Si <sub>2</sub> N	Hexamethyldisilazane .....	8.66	8.38	-0.28	1.03	0.83	z
H <sub>3</sub> P	Phosphine	9.98	8.67	-1.31	1.36	0.92	t
CP	Carbon phosphide	10.50	10.90	0.40	1.06	1.31	a
CHP	Methinophosphine	10.79	10.74	-0.05	0.44	0.63	a
CH <sub>3</sub> P	Methylphosphine	9.72	8.66	-1.06	1.07	0.68	a
C <sub>2</sub> H <sub>7</sub> P	Dimethylphosphine .....	9.10	8.68	-0.42	1.14	0.91	a
C <sub>3</sub> H <sub>9</sub> P	Trimethylphosphine	8.60	8.81	0.21	1.25	1.16	j
C <sub>3</sub> H <sub>9</sub> PO <sub>3</sub>	Trimethyl phosphite	9.22	9.69	0.47	1.69	1.88	aa
PF <sub>3</sub>	Phosphorus trifluoride	9.71	10.70	0.99	3.42	2.75	t
POF <sub>3</sub>	Phosphorus oxyfluoride	12.77	12.05	-0.72	0.40	-0.05	a
PCl <sub>3</sub>	Phosphorus trichloride .....	10.50	10.42	-0.08	1.67	0.92	a
POCl <sub>3</sub>	Phosphorus oxychloride	11.85	12.29	0.44	0.93	0.18	a
PCl <sub>5</sub>	Phosphorus pentachloride	10.80	11.86	1.06	1.49	0.61	a
PBr <sub>3</sub>	Phosphorus tribromide	10.00	10.84	0.84	1.44	0.76	a
PI <sub>3</sub>	Phosphorus triiodide	9.15	9.97	0.82	1.29	1.02	a
P <sub>2</sub>	Phosphorus dimer .....	10.62	8.91	-1.71	0.82	0.82	a
P <sub>4</sub>	Phosphorus tetramer	9.54	10.17	0.63	1.96	1.96	a

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racy of any given computational method, requires accurate thermochemical data as standards. Even more unfortunate, little effort appears to be committed to increasing the accuracy of existing thermochemical data, as is indicated by the dates of the latest determinations reported in recent thermochemical tables.<sup>15,16</sup> With the steady advance in the accuracy of *ab initio* methods, there is a significant probability that within a few years the heats of formation calculated using such methods will become more accurate than experimental, and that semiempirical methods will be parameterized against high-level *ab initio* calculations rather than experimental values. Even now good *ab initio* calculations of molecular geometries are of an accuracy comparable with microwave data and significantly better than many single molecule geometries obtained from x-ray determinations.

Several deficiencies in the prediction of geometric variables have been corrected.

Even so, some problems still remain intractable. Cyclobutane, for example, is still persistently  $D_{4h}$ , in variance with experiment. However, as the purpose of this work has been to develop and demonstrate a rapid optimization procedure for semiempirical methods, sporadic deficiencies in the results are not too serious. It is possible that modification of the Hamiltonian, a relatively easy operation now that reparameterization is rapid, will allow correction of these faults.

Note added in proof. A recent article by K. Szalewicz, S. J. Cole, W. Kolos, and R. J. Bartlett, *J. Chem. Phys.* **89**, 3662 (1988) on "Supermolecular Many-Body Perturbation Theory and Coupled-Cluster Calculations Including Triple Excitations" indicates that for the water dimer, the total interaction energy is  $-4.7 \pm 0.35$  kcal/mol.

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