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Optimization of Parameters for Semiempirical Methods II. Applications

JAMES J. P. STEWART, *Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, Colorado 80840*

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James J. P. Stewart

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

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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[1], MINDO/3[2], and AM1[3], 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-

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rivative, results from MNDO and AM1 calculations are presented for comparison. For the MNDO calculation, standard MNDO parameter sets were used for H^1, C^1, N^1, O^1, F^4, Al^5, Si^6, P^6, S^7, Cl^8, Br^9, and I^{10}, while for the AM1 calculation, only the AM1 parameter sets for H^3, C^3, N^3, O^3, F^{11}, Si^{12}, Cl^{11}, Br^{11}, and I^{11} 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.[13] 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_3H_8 will occur before C_4H_6, and CH_4S (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[1] and up to a few tens of molecules for the other elements[4-10], while for AM1 slightly over a hundred molecules were used in the parameterization of the C—H—N—O set.[3] 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 ΔH_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 ΔH_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 ΔH_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 ΔH_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[14] and JANAF[15] 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[16] and AM1[3]; 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.[17] Earlier calculated heats of formation were deemed unsuitable for two reasons. First, triangular conditions for the p–p two-electron one-center and π–π two-electron two-center integrals were not imposed. This was corrected[17] 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 ΔH_f of about 1 kcal/mol. Secondly, the Davidon-Fletcher-Powell optimization technique[18, 19] sometimes fails to locate stationary points on the potential energy hypersurface. To a large measure this has been corrected by the BFGS method.[20] The heat of association of water in forming the dimer was reported[3] 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.[21]

Ideally, in order for the standard deviation to be a useful guide to the probable difference between the experimental and calculated ΔH_f to be expected for a new molecule, the incidence of differences between calculated and experimental ΔH_f should fall on a normal distribution. This may be quantified by calculating the ratio of χ^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 that 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 ΔH_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 ±8 kcal/mol,[22] and −378 ± 6 kcal/mol,[23] 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[24] of −405 ±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,[25] 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 ΔH_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.

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

Empirical formula	Chemical name	Heat of formation Exp.	Calc.	Difference MNDO-PM3	MNDO	AM1	Footnote
H	Hydrogen (+)	365.7	353.6	−12.1	−39.0	−50.8	a
H_2	Hydrogen	0.0	−13.4	−13.4	0.7	−5.2	b
CH	Methylidyne	142.4	146.8	4.4	1.2	2.6	c
CH_2	Methylene, triplet	92.3	75.6	−16.7	−15.0	−11.5	d
CH_2	Methylene, singlet	99.8	113.2	13.4	7.6	11.1	d
CH_3	Methyl radical	34.8	29.8	−5.0	−9.0	−3.5	d
CH_3	Methyl (+)	261.0	256.5	−4.5	−17.1	−8.6	e
CH_4	Methane	−17.9	−13.0	4.9	5.9	9.1	f
C_2H_2	Acetylene	54.2	50.7	−3.5	3.7	0.6	d
C_2H_3	Vinyl	59.6	63.3	3.7	4.2	5.2	h
C_2H_3	Vinyl (+)	266.0	263.9	−2.1	−0.3	−4.5	h
C_2H_4	Ethylene	12.4	16.6	4.2	2.9	4.0	f
C_2H_4	Ethylene, radical cation	257.0	248.7	−8.3	−18.7	−13.1	i
C_2H_4	Methylmethylene	90.3	88.6	−1.7	−1.9	−2.6	j
C_2H_5	Ethyl radical	25.0	17.3	−7.7	−12.2	−6.9	k
C_2H_5	Ethyl (+) (classical)	216.0	222.5	6.5	3.7	0.8	l
C_2H_5	Ethyl (+) (nonclassical)	216.0	232.1	16.1	18.7	10.3	l
C_2H_6	Ethane	−20.2	−18.1	2.1	0.5	2.8	f
C_3	Carbon, trimer	196.0	206.6	10.6	24.3	16.4	d
C_3H_3	Propynyl (+)	281.0	275.3	−5.7	−15.6	−7.3	i
C_3H_3	Cyclopropenyl (+)	257.0	269.8	12.8	15.5	19.4	i
C_3H_4	Allene	45.6	47.1	1.5	−1.7	0.5	f
C_3H_4	Cyclopropene	66.2	68.2	2.0	2.1	8.6	m
C_3H_4	Propyne	44.4	40.2	−4.2	−3.0	−1.0	f
C_3H_5	Allyl (+)	226.0	232.7	6.7	−4.6	0.2	i
C_3H_5	Allyl	40.0	39.6	−0.4	−4.6	−1.4	h
C_3H_5	Propenyl (+)	237.0	238.2	1.2	3.1	−3.3	i
C_3H_5	Cyclopropyl (+)	235.0	261.8	26.8	23.2	25.6	i
C_3H_6	Cyclopropane	12.7	16.3	3.5	−1.5	5.0	f
C_3H_6	Propene	4.9	6.4	1.5	0.1	1.7	f
C_3H_7	Propyl (+)	208.0	214.4	6.4	4.4	−0.2	i
C_3H_7	2-Propyl (+)	192.0	197.3	5.3	8.7	−0.1	l
C_3H_7	i-Propyl radical	16.8	5.5	−11.3	−15.4	−10.0	k
C_3H_8	Propane	−24.8	−23.6	1.2	−0.1	0.5	f
C_4H_2	Diacetylene	113.0	102.5	−10.5	−9.8	−6.9	n
C_4H_4	Vinylacetylene	72.8	66.4	−6.4	−7.2	−4.9	n
C_4H_6	1-Methylcycloprop-1-ene	58.2	57.4	−0.8	−4.5	6.5	f
C_4H_6	Bicyclobutane	51.9	69.2	17.3	12.2	26.2	f
C_4H_6	1,2-Butadiene	38.8	38.0	−0.8	−5.3	−1.7	f
C_4H_6	1-Butyne	39.5	35.7	−3.8	−3.3	−2.0	f
C_4H_6	2-Butyne	34.7	29.8	−4.9	−9.8	−2.7	f
C_4H_6	Cyclobutene	37.5	37.7	0.2	−6.5	8.3	m
C_4H_6	Methylenecyclopropane	47.9	44.5	−3.4	−10.0	−0.2	f
C_4H_6	1,3-Butadiene	26.0	31.0	5.0	3.0	3.9	f
C_4H_7	2-Butenyl (+)	200.0	212.6	12.6	7.0	6.3	i
C_4H_7	Cyclobutyl (+)	213.0	225.6	12.6	8.4	13.2	i
C_4H_8	1-Butene	−0.2	1.8	2.0	0.6	0.6	f
C_4H_8	*cis*-2-Butene	−1.9	−2.5	−0.6	−2.4	−0.3	f
C_4H_8	Cyclobutane	6.8	−3.8	−10.6	−18.7	−7.8	f
C_4H_8	Isobutene	−4.3	−3.3	1.0	2.3	3.1	f
C_4H_8	*trans*-2-Butene	−3.0	−3.8	−0.8	−2.1	−0.3	f
C_4H_9	*n*-Butyl (+)	201.0	208.0	7.0	5.8	−1.1	i
C_4H_9	1-Methyl propyl (+)	183.0	190.8	7.8	11.0	1.0	i
C_4H_9	Isobutyl	4.5	−5.9	−10.4	−11.7	−7.4	k
C_4H_9	Isobutyl (+)	176.0	178.7	2.7	12.0	−1.2	i
C_4H_{10}	*n*-Butane	−30.4	−29.1	1.3	0.7	−0.8	f
C_4H_{10}	Isobutane	−32.4	−29.5	2.9	5.6	3.0	f
C_5H_5	Cyclopentadienyl (−)	21.3	15.9	−5.4	−2.4	3.9	o
C_5H_6	Cyclopentadiene	32.1	31.8	−0.3	0.0	5.0	m
C_5H_8	1,2-Dimethylcyclopropene	46.4	46.7	0.3	−7.2	8.2	p
C_5H_8	Methylene cyclobutane	29.1	19.7	−9.4	−18.2	−4.0	q
C_5H_8	1,*cis*-3-Pentadiene	19.1	21.1	2.0	0.6	1.8	f
C_5H_8	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_5H_8	Bicyclo(2.1.0)-pentane	37.3	37.8	0.5	−7.1	8.8	p
C_5H_8	1,4-Pentadiene	25.3	26.6	1.3	−0.7	−0.5	f
C_5H_8	Spiropentane	44.3	43.1	−1.2	−10.6	6.2	f
C_5H_8	1,*trans*-3-Pentadiene	18.1	21.3	3.2	1.0	2.5	f
C_5H_9	Cyclopentyl (+)	188.0	193.5	5.5	6.2	−2.1	r
C_5H_{10}	1-Pentene	−5.3	−4.0	1.3	0.3	−1.4	f
C_5H_{10}	2-Methyl-1-butene	−8.6	−7.9	0.7	2.1	1.8	f
C_5H_{10}	2-Methyl-2-butene	−10.1	−12.2	−2.1	−0.4	0.1	f
C_5H_{10}	3-Methyl-1-butene	−6.6	−3.9	2.7	4.3	2.2	f
C_5H_{10}	*cis*-2-Pentene	−7.0	−7.7	−0.7	−2.3	−1.9	f
C_5H_{10}	*cis*-Dimethylcyclopropane	1.3	1.4	0.1	−3.4	3.5	p
C_5H_{10}	Cyclopentane	−18.3	−23.9	−5.6	−12.2	−10.5	m
C_5H_{10}	*trans*-2-Pentene	−7.9	−8.7	−0.8	−2.4	−1.8	f
C_5H_{11}	1-Pentyl (+)	194.0	202.4	8.4	7.9	−1.2	i
C_5H_{11}	2-Pentyl (+)	173.0	184.6	11.6	15.5	3.4	i
C_5H_{11}	2-Ethylisopropyl (+)	156.0	171.9	15.9	25.6	10.5	i
C_5H_{11}	Neopentyl (+)	188.0	171.8	−16.2	−6.4	−21.5	t
C_5H_{12}	2-Methylbutane	−36.8	−34.4	2.4	6.8	1.4	f
C_5H_{12}	Neopentane	−40.3	−35.8	4.5	15.7	7.5	f
C_5H_{12}	*n*-Pentane	−35.1	−34.5	0.6	0.7	−2.9	f
C_6H_6	Benzene	19.8	23.5	3.6	1.5	2.2	f
C_6H_6	Fulvene	47.5	56.2	8.7	6.2	15.2	f
C_6H_8	1,3-Cyclohexadiene	25.4	20.4	−5.0	−10.9	−7.9	f
C_6H_{10}	2,3-Dimethyl-1,3-butadiene	10.8	14.0	3.2	4.3	6.6	f
C_6H_{10}	Cyclohexene	−1.1	−4.9	−3.8	−8.8	−9.0	f
C_6H_{10}	1,5-Hexadiene	20.1	21.1	1.0	−0.5	−2.3	f
C_6H_{10}	1,2-Dimethylcyclobutene	19.8	16.2	−3.6	−13.4	7.2	p
C_6H_{10}	Bicyclopropyl	30.9	36.1	5.2	−2.2	8.6	f
C_6H_{11}	1-Methylcyclopentyl (+)	165.0	174.5	9.5	13.6	2.4	i
C_6H_{11}	Cyclohexyl (+)	177.0	186.1	9.1	9.9	−2.8	r
C_6H_{12}	Cyclohexane	−29.5	−31.0	−1.5	−5.3	−9.0	m
C_6H_{14}	*n*-Hexane	−39.9	−39.9	0.0	0.8	−4.9	f
C_7H_7	Benzyl (+)	216.0	227.4	11.4	2.0	6.1	u
C_7H_7	Tropylium (+)	209.0	221.0	12.0	−1.3	1.4	v
C_7H_8	Cycloheptatriene	43.2	42.5	−0.7	−9.4	−4.9	m
C_7H_8	Norbornadiene	59.7	58.8	−0.9	3.2	8.0	p
C_7H_8	Toluene	12.0	14.1	2.1	1.6	2.4	f
C_7H_{11}	2-Norbornyl (+)	182.0	208.5	26.5	31.1	21.0	i
C_7H_{12}	Norbornane	−12.4	−13.7	−1.3	2.0	−2.0	w
C_7H_{16}	*n*-Heptane	−44.9	−45.3	−0.5	1.0	−6.8	f
C_8H_8	Cubane	148.7	113.8	−34.9	−49.6	2.5	f
C_8H_8	Styrene	35.3	39.2	3.9	2.3	3.4	f
C_8H_{10}	Ethylbenzene	7.2	9.5	2.3	1.6	1.5	f
C_8H_{14}	Bicyclo(2.2.2)-octane	−24.1	−27.8	−3.7	−2.2	−11.9	w
C_8H_{18}	*n*-Octane	−49.9	−50.8	−0.8	1.4	−8.6	f
C_9H_{20}	*n*-Nonane	−54.7	−56.2	−1.5	1.5	−10.7	f
$C_{10}H_8$	Azulene	73.5	81.3	7.8	−1.4	10.9	f
$C_{10}H_8$	Naphthalene	36.1	40.7	4.6	2.2	4.5	f
$C_{10}H_{16}$	Adamantane	−31.9	−34.6	−2.7	5.5	−11.3	x
$C_{14}H_{10}$	Anthracene	55.2	61.7	6.5	3.6	7.7	f
$C_{14}H_{10}$	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_2O	Water	−57.8	−53.4	4.4	−3.1	−1.4	d
H_3O	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_2O	Formaldehyde	−26.0	−34.1	−8.1	−6.9	−5.5	f
CH_2O	Hydroxymethylene (trans)	53.2	50.5	−2.8	−6.8	−5.0	j
CH_2O	Hydroxymethylene (cis)	58.5	50.1	−8.4	−12.2	−11.3	j
CH_3O	Methoxy (−)	−36.0	−37.9	−1.9	−3.7	−2.5	o
CH_3O	Methoxy	−0.5	−6.8	−6.3	0.3	−3.2	k

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			Footnote
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	
CH_3O	CH_2OH (+)	168.0	166.3	−1.7	−12.4	−6.7	i
CH_4O	Methanol	−48.1	−51.9	−3.8	−9.3	−8.9	f
C_2H_2O	Ketene	−11.4	−9.2	2.2	4.6	5.7	f
C_2H_2O	HCCOH	36.0	23.2	−12.8	−16.7	−11.5	j
C_2H_4O	Acetaldehyde	−39.7	−44.2	−4.5	−2.5	−1.8	f
C_2H_4O	Ethylene oxide	−12.6	−8.1	4.5	−2.9	3.6	f
C_2H_5O	Ethoxy (−)	−47.5	−44.8	2.8	2.2	2.0	o
C_2H_6O	Ethanol	−56.2	−56.8	−0.6	−6.8	−6.5	f
C_2H_6O	Dimethyl ether	−44.0	−48.3	−4.3	−7.2	−9.2	f
C_3H_6O	Acetone	−51.9	−53.3	−1.4	2.5	2.7	f
C_3H_6O	Propanal	−45.5	−49.3	−3.8	−2.5	−2.8	f
C_3H_6O	Trimethylene oxide	−19.3	−26.7	−7.5	−17.9	−6.3	f
C_3H_8O	Isopropanol	−65.1	−64.0	1.1	−0.3	−2.9	f
C_3H_8O	Propanol	−61.2	−63.6	−2.4	−6.3	−9.4	f
C_4H_4O	Furan	−8.3	−4.0	4.3	−0.3	11.3	f
C_4H_6O	2-Butenal	−24.0	−27.1	−3.1	−3.4	−1.6	f
C_4H_6O	Divinyl ether	−3.3	−0.7	2.5	0.5	4.1	f
C_4H_8O	2-Butanone CH_3 eclipsed	−57.0	−57.4	−0.4	2.9	1.9	z
C_4H_8O	Butanal	−48.9	−54.7	−5.8	−3.9	−6.2	f
C_4H_8O	Tetrahydrofuran	−44.0	−51.3	−7.3	−15.3	−14.4	f
$C_4H_{10}O$	Diethyl ether	−60.3	−59.6	0.7	0.1	−4.7	f
$C_4H_{10}O$	*t*-Butanol	−74.7	−71.3	3.4	10.4	3.1	f
C_5H_8O	Cyclopentanone	−46.0	−37.2	8.8	9.6	9.9	f
$C_5H_{10}O$	Tetrahydropyran	−53.4	−57.4	−4.0	−8.6	−13.7	f
$C_5H_{12}O$	3-Pentanol	−75.2	−73.8	1.4	1.7	−5.5	f
C_6H_5O	Phenoxy (−)	−40.5	−44.1	−3.6	−1.7	−0.5	o
C_6H_6O	Phenol	−23.0	−21.7	1.4	−3.6	0.8	f
$C_6H_{10}O$	Cyclohexanone	−54.0	−60.2	−6.1	−6.1	−9.3	f
C_7H_6O	Benzaldehyde	−8.8	−10.6	−1.8	−0.8	−0.1	f
C_7H_8O	Anisole	−17.3	−14.6	2.7	−0.4	1.4	f
$C_{10}H_8O$	1-Naphthol	−5.1	−4.1	1.0	−1.7	2.9	f
$C_{10}H_8O$	2-Naphthol	−10.1	−4.6	5.5	0.4	6.3	f
O_2	Oxygen (singlet)	22.0	18.4	−3.6	−9.9	−21.3	aa
O_2	Oxygen (triplet)	0.0	−4.2	−4.2	−15.3	−27.0	b
H_2O_2	Hydrogen peroxide	−32.5	−40.8	−8.3	−5.7	−2.8	d
CO_2	Carbon dioxide	−94.1	−85.0	9.0	19.0	14.2	d
CHO_2	Formic acid anion	−106.6	−110.9	−4.3	5.0	−2.8	o
CH_2O_2	Formic acid	−90.5	−94.4	−3.9	−2.1	−6.9	c
$C_2H_2O_2$	*trans* Glyoxal	−50.7	−64.3	−13.6	−10.7	−8.0	f
$C_2H_3O_2$	Acetic acid anion	−122.5	−119.7	2.8	12.5	7.1	o
$C_2H_4O_2$	Acetic acid	−103.3	−102.0	1.3	2.2	0.3	f
$C_2H_4O_2$	Methyl formate	−83.6	−87.0	−3.4	−1.9	−7.5	n
$C_2H_6O_2$	Dimethyl peroxide	−30.1	−34.1	−4.0	1.8	3.1	f
$C_2H_6O_2$	Ethylene glycol	−93.9	−95.2	−1.3	−12.2	−13.6	f
C_3O_2	Carbon suboxide	−22.4	−24.0	−1.6	−1.1	7.8	f
$C_3H_4O_2$	*beta*-Propiolactone	−67.6	−70.6	−3.0	−3.3	−3.4	f
$C_3H_6O_2$	Propionic acid	−108.4	−106.4	2.0	2.1	−0.7	f
$C_3H_6O_2$	Methyl acetate	−97.9	−94.1	3.8	4.3	1.5	n
$C_3H_8O_2$	Dimethoxymethane	−83.3	−87.4	−4.1	−11.1	−20.0	f
$C_4H_6O_2$	Diacetyl	−78.2	−83.4	−5.2	−0.6	3.3	f
$C_4H_{10}O_2$	Diethyl peroxide	−46.1	−40.0	6.1	7.0	7.7	f
$C_5H_8O_2$	Acetylacetone	−90.5	−91.6	−1.1	6.3	4.8	f
$C_6H_4O_2$	*p*-Benzoquinone	−29.3	−31.5	−2.3	−3.5	4.2	f
$C_7H_6O_2$	Benzoic acid	−70.1	−66.2	3.9	2.4	2.1	f
O_3	Ozone	34.1	51.1	17.0	14.4	3.7	d
$C_4H_2O_3$	Malaic anhydride	−95.2	−90.1	5.1	6.7	18.8	f
$C_4H_6O_3$	Acetic anhydride	−137.1	−135.0	2.1	4.5	5.4	f
$C_2H_2O_4$	Oxalic acid	−175.0	−174.0	1.0	−0.1	2.6	f
H_2N	Amidogen	45.5	35.4	−10.1	−8.5	−7.1	d
H_3N	Ammonia	−11.0	−3.1	7.9	4.6	3.7	d
H_4N	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_4N	Methyl amine anion	30.5	21.7	-8.8	-7.0	2.6	o
CH_4N	CH_3-NH	37.0	27.3	-9.7	-4.3	-2.9	k
CH_4N	CH_2-NH_2 (+)	178.0	185.3	7.3	8.8	-1.7	k
CH_5N	Methylamine	-5.5	-5.2	0.3	-2.1	-1.9	f
C_2H_3N	Acetonitrile	20.9	23.3	2.4	-1.7	-1.6	cc
C_2H_3N	Methyl isocyanide	35.6	54.7	19.1	24.8	14.8	cc
C_2H_5N	Ethyleneimine (Azirane)	30.2	31.6	1.4	-5.1	2.9	f
C_2H_6N	Me_2N (-)	24.7	7.8	-16.9	-16.2	-2.3	o
C_2H_7N	Ethylamine	-11.4	-12.5	-1.1	-1.8	-3.8	f
C_2H_7N	Dimethylamine	-6.6	-7.9	-1.3	0.0	1.0	f
C_3H_3N	Acrylonitrile	44.1	50.2	6.1	-0.3	0.9	f
C_3H_5N	Ethyl cyanide	12.1	18.5	6.4	1.7	0.9	n
C_3H_9N	Isopropylamine	-20.0	-18.8	1.3	3.7	0.7	f
C_3H_9N	Trimethylamine	-6.6	-10.9	-4.3	3.8	4.9	f
C_3H_9N	*n*-Propylamine	-16.8	-17.9	-1.1	-1.4	-5.3	f
C_4H_5N	Pyrrole	25.9	27.1	1.2	6.6	14.0	f
C_4H_9N	Pyrrolidine	-0.8	-12.0	-11.2	-15.0	-9.6	f
$C_4H_{11}N$	*t*-Butylamine	-28.9	-25.2	3.7	13.4	7.7	f
C_5H_5N	Pyridine	34.6	30.4	-4.2	-5.8	-2.6	f
C_6H_7N	Aniline	20.8	21.3	0.5	0.9	-0.3	f
C_7H_5N	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_3NO	Formamide	-44.5	-41.8	2.7	4.3	-0.3	dd
C_3H_7NO	Dimethylformamide	-45.8	-44.6	1.2	8.4	8.9	f
NO_2	Nitrogen dioxide	7.9	-1.0	-8.9	-12.5	-22.9	d
NO_2	Nitrogen dioxide (+)	233.0	208.4	-24.6	7.6	-11.9	k
HNO_2	Nitrous acid, *trans*	-18.8	-14.9	3.9	-21.9	-20.6	d
CH_3NO_2	Nitromethane	-17.9	-15.9	2.0	21.2	8.0	f
CH_3NO_2	Methyl nitrite	-15.8	-9.1	6.7	-20.9	-16.0	f
$C_2H_5NO_2$	Nitroethane	-23.5	-20.9	2.6	20.2	6.6	f
$C_2H_5NO_2$	Glycine	-93.7	-96.0	-2.3	-2.0	-7.8	f
$C_3H_7NO_2$	1-Nitropropane	-30.0	-26.8	3.2	21.9	6.2	f
$C_3H_7NO_2$	2-Nitropropane	-33.2	-27.1	6.1	26.9	11.6	f
$C_3H_7NO_2$	Alanine	-111.4	-101.1	10.3	12.7	6.4	f
$C_4H_9NO_2$	1-Nitrobutane	-34.4	-32.1	2.3	21.6	4.0	f
$C_4H_9NO_2$	2-Nitrobutane	-39.1	-31.9	7.2	29.0	10.9	f
$C_6H_5NO_2$	Nitrobenzene	15.4	14.5	-0.9	20.4	9.9	n
$C_7H_7NO_2$	2-Nitrotoluene	9.3	4.7	-4.6	20.6	7.9	ee
NO_3	Nitrate anion	-74.7	-93.3	-18.6	7.7	-14.2	ff
NO_3	Nitrate radical	17.0	22.9	5.9	27.9	16.2	d
HNO_3	Nitric acid	-32.1	-38.0	-5.9	14.6	-5.4	d
CH_3NO_3	Methyl nitrate	-29.1	-32.4	-3.3	16.7	-2.2	f
$C_2H_5NO_3$	Ethyl nitrate	-36.8	-36.4	0.5	18.9	-0.4	f
$C_2H_5NO_3$	Nitroethanol	-75.1	-61.4	13.7	29.0	10.5	gg
N_2	Nitrogen	0.0	17.6	17.6	8.3	11.2	b
H_2N_2	Diazene	36.0	37.8	1.8	-4.1	-4.5	hh
H_4N_2	Hydrazine	22.8	20.6	-2.1	-8.6	-9.1	d
CH_2N_2	Diazomethane	71.0	61.0	-10.0	-3.7	-8.4	f
CH_2N_2	$N{=}N{-}CH_2$	79.0	91.7	12.7	-6.6	7.8	ii
CH_6N_2	Methylhydrazine	22.6	17.9	-4.7	-8.2	-5.3	f
C_2N_2	Cyanogen	73.8	77.5	3.7	-7.2	-5.9	f
$C_2H_8N_2$	1,1-Dimethylhydrazine	20.0	15.1	-4.9	-1.9	4.0	f
$C_2H_8N_2$	1,2-Dimethylhydrazine	22.0	15.6	-6.4	-7.0	-0.5	f
C_4N_2	Dicyanoacetylene	126.5	128.1	1.6	-15.1	-6.7	f
$C_4H_2N_2$	Fumaronitrile	81.3	86.0	4.7	-6.6	-5.3	f
$C_4H_4N_2$	Pyridazine	66.5	56.0	-10.5	-22.9	-11.2	f
$C_4H_4N_2$	Pyrimidine	47.0	38.0	-9.0	-12.0	-3.1	f
$C_4H_4N_2$	Pyrazine	46.9	39.3	-7.6	-9.1	-2.7	f
$C_6H_{14}N_2$	azo-*n*-Propane	8.6	5.8	-2.8	-6.0	4.3	jj
N_2O	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
$C_2H_6N_2O_2$	*n*-Nitrodimethylamine	−3.2	1.3	4.5	25.5	24.9	n
$C_6H_6N_2O_2$	Para nitroaniline	16.2	10.7	−5.5	19.4	5.3	f
N_2O_3	Dinitrogen trioxide	19.8	23.7	3.9	−6.1	2.1	d
N_2O_4	Dinitrogen tetroxide	2.2	8.3	6.2	27.8	22.9	d
$CH_2N_2O_4$	Dinitromethane	−13.3	−11.9	1.4	41.2	16.2	gg
$C_2H_4N_2O_4$	1,1-Dinitroethane	−24.1	−17.4	6.7	47.3	21.5	gg
$C_2H_4N_2O_4$	1,2-Dinitroethane	−22.9	−19.6	3.3	42.9	12.9	gg
$C_3H_6N_2O_4$	1,1-Dinitropropane	−25.9	−22.0	3.9	45.3	16.7	f
$C_3H_6N_2O_4$	1,3-Dinitropropane	−31.6	−26.6	5.0	44.5	12.8	gg
$C_3H_6N_2O_4$	2,2-Dinitropropane	−27.0	−23.0	4.0	50.2	21.5	gg
$C_4H_8N_2O_4$	1,1-Dinitrobutane	−34.1	−27.2	6.9	48.9	18.1	gg
$C_4H_8N_2O_4$	1,4-Dinitrobutane	−38.9	−32.7	6.2	45.8	11.2	gg
$C_6H_4N_2O_4$	*m*-Dinitrobenzene	11.3	9.2	−2.1	43.9	21.8	f
N_2O_5	Dinitrogen pentoxide	2.7	−19.0	−21.7	31.5	3.0	d
N_3	Azide	99.0	106.0	7.0	3.4	8.4	y
HN_3	Hydrazoic acid	70.3	75.3	5.0	2.8	5.5	cc
CHN_3O_6	Trinitromethane	−3.2	−4.7	−1.5	61.9	28.2	kk
$C_2H_3N_3O_6$	1,1,1-Trinitroethane	−12.4	−10.0	2.4	68.8	33.5	gg
$C_3H_5N_3O_6$	1,1,1-Trinitropropane	−18.4	−8.1	10.3	76.0	36.9	gg
$C_7H_5N_3O_6$	2,4,6-Trinitrotoluene	12.9	3.3	−9.6	61.8	28.4	f
$C_3H_5N_3O_9$	Glycerol trinitrate	−88.6	−76.6	12.0	80.2	17.4	f
CH_2N_4	[1 − H]Tetrazole	79.9	86.3	6.3	−26.1	29.7	f
CN_4O_8	Tetranitromethane	18.5	6.4	−12.1	76.5	34.6	gg
$C_5H_8N_4O_{12}$	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^-	Hydrogen sulfide	33.3	38.2	4.9	4.0	5.0	d
H_2S	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_4S	Thiomethanol	−5.4	−5.5	−0.1	−1.9	2.1	f
C_2H_4S	Thiirane	19.7	28.8	9.1	−0.9	12.6	f
C_2H_6S	Thioethanol	−11.0	−8.7	2.3	−2.4	2.4	f
C_2H_6S	Dimethyl thioether	−8.9	−11.0	−2.1	−8.1	−0.9	f
C_3H_6S	Thietane	14.6	7.5	−7.1	−19.7	−6.6	f
C_3H_8S	Isopropanthiol	−18.1	−13.3	4.8	1.9	5.2	d
C_3H_8S	1-Propanthiol	−16.2	−14.1	2.1	−1.9	0.8	f
C_4H_4S	Thiophene	27.6	30.7	3.1	−1.1	9.1	f
C_4H_8S	Tetrahydrothiophene	−8.1	−10.4	−2.3	−16.0	−7.9	f
$C_4H_{10}S$	Butanethiol	−21.1	−19.5	1.6	−1.8	−1.1	d
C_6H_6S	Thiophenol	26.9	27.7	0.8	−3.5	2.8	f
$C_6H_{12}S$	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_2H_4SO	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_2H_3NS	Methyl isothiocyanate	38.3	36.1	−2.2	−1.4	4.3	cc
C_2H_3NS	Methyl thiocyanate	27.1	28.3	1.2	−4.0	2.9	cc
S_2	Sulfur dimer	30.8	28.7	−2.1	4.0	4.0	d
H_2S_2	Hydrogen disulfide	3.7	8.6	4.9	2.8	1.2	cc
CS_2	Carbon disulfide	28.0	36.9	8.9	8.9	18.7	d
$C_2H_6S_2$	Ethanedithiol-1,2	−2.2	1.2	3.4	−4.1	2.9	d
$C_2H_6S_2$	2,3-Dithiabutane	−5.6	−4.8	0.8	−9.2	−1.7	f
$C_2N_2S_2$	$S_2(CN)_2$	82.3	78.5	−3.8	−11.7	−3.9	f
H_2S_3	Hydrogen trisulfide	7.3	26.4	19.1	1.1	−0.7	cc
$C_2H_6S_3$	2,3,4-Trithiapentane	0.0	−6.9	−6.9	−13.2	−6.0	mm
$C_3H_4S_3$	1,3-Dithiolan-2-thione	22.7	40.4	17.7	−11.3	15.8	d
S_4	Sulfur tetramer	34.8	55.2	20.4	11.0	11.0	d
H_2S_4	Hydrogen tetrasulfide	10.6	−0.3	−10.9	0.0	−1.7	cc
H_2S_5	Hydrogen pentasulfide	13.8	2.0	−11.9	66.2	−0.7	cc
S_8	S_8	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_2F	Fluoromethyl (+)	200.3	200.3	0.0	−17.5	−19.9	nn
CH_3F	Fluoromethane	−56.8	−53.8	3.0	−4.1	−4.2	oo
CH_3F	Trifluoromethane (+)............	233.3	228.2	−5.1	−10.1	−29.3	nn
C_2HF	Fluoroacetylene	*30.0*	*18.1*	−11.9	−14.3	−14.8	d
C_2H_3F	Fluoroethylene	−32.5	−28.6	3.9	−2.0	−1.5	pp
C_2H_4F	CH_3CHF (+)	166.0	172.9	6.9	−1.3	−8.9	qq
C_2H_5F	Fluoroethane	−62.9	−60.2	2.7	−2.2	−3.4	f
C_3H_7F	2-Fluoropropane	−69.4	−66.8	2.6	2.8	−0.4	f
C_6H_5F	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_2H_3OF	Acetyl fluoride......................	−106.4	−98.7	7.7	9.9	7.6	f
$C_7H_5O_2F$	*p*-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_2	Fluorine.............................	0.0	−21.7	−21.7	7.3	−22.5	b
CF_2	Difluoromethylene	−45.0	−49.1	−4.1	−20.2	−23.0	g
CHF_2	Difluoromethyl (+)	142.4	145.5	3.1	−10.0	−20.5	nn
CH_2F_2	Difluoromethane	−108.1	−103.8	4.4	−3.6	−8.0	f
CH_2F_2	Difluoromethane (+)	185.2	180.4	−4.8	−6.8	−33.6	nn
C_2F_2	Difluoroacetylene.................	5.0	−11.6	−16.6	−26.0	−24.6	d
$C_2H_2F_2$	gem-Difluoroethylene	−80.5	−73.0	7.5	−3.1	−2.2	f
$C_2H_3F_2$	CH_3CF_2 (+)	107.0	122.2	15.2	9.6	−1.7	qq
$C_2H_4F_2$	1,1-Difluoroethane	−118.8	−111.9	6.9	5.4	0.2	f
$C_6H_4F_2$	*o*-Difluorobenzene	−70.3	−63.1	7.2	−0.3	3.9	f
$C_6H_4F_2$	*m*-Difluorobenzene	−74.0	−63.3	10.7	3.1	6.1	f
$C_6H_4F_2$	*p*-Difluorobenzene	−73.3	−63.3	10.0	2.3	5.3	f
OF_2	Difluorine oxide	5.9	−4.8	−10.7	12.3	4.6	d
COF_2	Carbonyl fluoride	−152.7	−141.6	11.1	14.1	6.4	f
NF_2	NF_2 (−)	−29.5	−31.0	−1.5	−14.1	4.3	uu
NF_2	NF_2..................................	10.1	11.9	1.8	−24.9	−16.5	d
N_2F_2	*cis*-Difluorodiazene	16.4	28.0	11.6	−18.6	4.4	d
N_2F_2	*trans*-Difluorodiazene	19.4	29.2	9.8	−17.0	11.9	d
SF_2	Sulfur difluoride	−70.9	−91.9	−21.0	18.0	28.4	d
S_2F_2	FSSF	−80.4	−73.8	6.6	39.1	49.7	d
S_2F_2	SSF_2................................	−95.9	−56.1	39.8	111.4	110.0	d
CF_3	Trifluoromethyl (−)	−163.4	−178.8	−15.4	−15.4	−15.4	uu
CF_3	Trifluoromethyl	−112.4	−132.1	−19.7	−24.7	−30.4	d
CF_3	Trifluoromethyl (+)	99.3	99.6	0.3	1.6	−17.2	nn
CHF_3	Trifluoromethane	−166.3	−162.0	4.3	2.5	−6.2	f
CHF_3	Trifluoromethane (+)............	151.9	149.4	−2.5	6.8	−30.7	nn
C_2HF_3	Trifluoroethylene	−117.3	−121.5	−4.2	−13.8	−13.3	f
$C_2H_2F_3$	CF_3CH_2.	−123.6	−131.2	−7.6	−6.0	−7.8	vv
$C_2H_2F_3$	CF_3CH_2 (+)	114.0	122.3	8.3	7.2	0.4	qq
$C_2H_2F_3$	$CH_2F.CF_2$ (+)	81.0	92.7	11.7	1.4	−11.9	qq
$C_2H_3F_3$	1,1,1-Trifluoroethane	−178.0	−172.3	5.7	13.6	5.4	f
$C_7H_5F_3$	Trifluoromethylbenzene	−143.2	−134.9	8.3	15.7	8.8	f
$C_2HO_2F_3$	Trifluoroacetic acid	−255.0	−244.0	11.0	16.9	12.3	f
NF_3	Nitrogen trifluoride	−31.6	−24.4	7.2	−2.6	−8.4	d
C_2NF_3	Trifluoroacetonitrile	−118.4	−115.1	3.3	5.2	−1.1	d
H_4F_4	Hydrogen fluoride tetramer	−282.9	−280.2	2.7	38.6	−30.2	d
CF_4	Carbon tetrafluoride.............	−223.3	−225.1	−1.8	9.1	−2.4	f
C_2F_4	Tetrafluoroethylene	−157.9	−168.2	−10.3	−17.0	−16.9	f
COF_4	Trifluoromethyl hypofluorite	−182.8	−187.3	−4.5	19.5	5.1	d
N_2F_4	Tetrafluorohydrazine	−2.0	−0.5	1.5	−17.7	7.8	d
C_6HF_5	Pentafluorobenzene	−192.5	−188.6	3.9	−9.2	0.5	f
C_2F_6	Hexafluoroethane.................	−321.2	−317.8	3.4	21.6	8.0	d
C_6F_6	Hexafluorobenzene	−228.5	−229.3	−0.8	−14.9	−2.6	f
C_3OF_6	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_6	Sulfur hexafluoride	−291.4	−304.6	−13.2	320.7	294.0	d
C_4F_8	Perfluorocyclobutane	−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_3Cl	Methyl chloride	−20.0	−14.7	5.3	−2.5	1.0	d
C_2HCl	Chloroacetylene	51.1	46.6	−4.5	1.5	−3.3	d
C_2H_3Cl	Chloroethylene	8.6	9.7	1.1	−3.7	−2.7	d
C_2H_5Cl	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_7H_5OCl	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_2FCl	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_2Cl	Difluorochloromethane	−115.6	−109.7	5.9	1.2	1.4	f
CF_3Cl	Trifluorochloromethane	−169.2	−169.3	−0.1	9.6	6.6	d
Cl_2	Chlorine	0.0	−11.6	−11.6	−10.7	−14.2	b
HCl_2	Hydrogen dichloride (−)	−142.0	−111.0	31.0	47.2	47.6	xx
CCl_2	Dichloromethylene	57.0	57.5	0.5	0.6	−8.5	d
CH_2Cl_2	Dichloromethane	−23.0	−17.1	5.8	−5.1	−2.9	f
$C_2H_2Cl_2$	*gem*-Dichloroethylene	0.6	4.0	3.4	−3.2	−3.9	d
$C_2H_2Cl_2$	*cis*-Dichloroethylene	1.0	4.0	3.0	−3.6	−4.3	d
$C_2H_2Cl_2$	*trans*-Dichloroethylene	1.2	3.6	2.4	−4.9	−4.6	d
$C_2H_4Cl_2$	1,1-Dichloroethane	−30.9	−26.5	4.4	−1.6	−0.2	ff
$C_2H_4Cl_2$	1,2-Dichloroethane	−31.0	−24.7	6.3	−5.4	−2.8	ff
$C_6H_4Cl_2$	*o*-Dichlorobenzene	7.1	11.1	4.0	1.5	2.1	f
$C_6H_4Cl_2$	*m*-Dichlorobenzene	6.1	10.2	4.1	0.5	2.1	f
$C_6H_4Cl_2$	*p*-Dichlorobenzene	5.3	10.1	4.8	1.1	2.7	f
OCl_2	Chlorine monoxide	25.0	−16.2	−41.2	6.3	−5.5	d
$COCl_2$	Carbonyl chloride	−52.6	−49.1	3.5	0.0	5.3	d
SCl_2	Sulfur dichloride	−4.2	−10.9	−6.7	−19.7	−20.7	d
S_2Cl_2	ClSSCl	−4.0	−7.7	−3.7	−16.8	−17.6	d
$CHFCl_2$	Fluorodichloromethane	−67.7	−62.0	5.7	−1.5	2.5	dd
CF_2Cl_2	Difluorodichloromethane	−117.5	−116.1	1.4	7.3	10.5	d
CCl_3	Trichloromethyl	21.0	1.6	−19.4	−20.5	−25.7	g
$CHCl_3$	Chloroform	−24.7	−20.9	3.8	−4.3	−4.3	dd
C_2HCl_3	Trichloroethylene	−2.0	−2.3	−0.3	−4.4	−6.4	d
$C_2H_3Cl_3$	1,1,1-Trichloroethane	−35.5	−31.9	3.6	4.0	3.6	f
$CFCl_3$	Fluorotrichloromethane	−69.0	−67.3	1.7	3.8	8.1	d
CCl_4	Carbon tetrachloride	−22.9	−26.0	−3.1	−2.6	−5.2	d
C_2Cl_4	Tetrachloroethylene	−2.7	−8.1	−5.4	−5.3	−9.7	f
C_2Cl_6	Hexachloroethane	−34.5	−36.5	−2.0	7.1	−1.3	f
C_6Cl_6	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_3Br	Bromomethane	−9.1	−2.0	7.1	−1.3	2.9	f
C_2H_3Br	Bromoethylene	18.7	23.8	5.1	−2.9	−0.8	f
C_2H_5Br	Bromoethane	−15.2	−11.4	3.8	−1.8	2.1	f
C_3H_5Br	3-Bromopropene	10.9	15.3	4.4	−2.1	1.5	zz
C_3H_7Br	1-Bromopropane	−20.5	−16.7	3.8	−1.5	0.6	f
C_3H_7Br	2-Bromopropane	−23.5	−20.9	2.6	2.8	5.6	aaa
C_6H_5Br	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			
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
C_2H_3OBr	Acetyl bromide	−45.6	−43.5	2.1	2.4	11.3	f
C_7H_5OBr	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_3Br	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	d
ClBr	Bromine chloride (+)	261.0	247.6	−13.4	4.8	−14.6	ff
CCl_3Br	Trichlorobromomethane	−9.3	−14.1	−4.8	−5.8	−5.4	f
Br_2	Bromine	7.4	4.9	−2.5	−9.1	−12.7	d
Br_2	Bromine (+)	253.5	263.0	9.5	12.5	−7.7	yy
CBr_2	Dibromomethylene	84.3	104.9	20.6	7.8	5.7	g
CH_2Br_2	Dibromomethane	−3.5	7.9	11.4	−1.6	2.5	ccc
$COBr_2$	Carbonyl bromide	−20.1	−25.3	−5.2	−11.5	2.3	f
SBr_2	Sulfur dibromide	48.0	24.9	−23.1	−48.2	−48.5	g
S_2Br_2	S_2Br_2	25.1	21.8	−3.3	−23.6	−23.5	g
$C_2F_4Br_2$	1,2-Dibromotetrafluoroethane	−189.0	−191.3	−2.3	18.6	27.8	aaa
CBr_3	Tribromomethyl	64.7	64.2	−0.5	−35.8	−37.8	g
$CHBr_3$	Bromoform	4.4	17.5	13.1	−1.3	2.0	ccc
CBr_4	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	Iodomethylidyne	144.8	145.5	0.7	7.1	6.2	g
CH_3I	Methyl iodide	3.4	9.4	6.0	−1.5	2.3	f
C_2H_5I	Iodoethane	−2.0	2.1	4.1	−2.5	0.9	f
C_3H_5I	Allyl iodide	22.8	30.2	7.4	−3.3	−0.4	f
C_3H_5I	E-1-Iodo-1-propene	22.3	25.4	3.2	−7.8	−2.6	m
C_3H_5I	Z-1-Iodo-1-propene	20.7	29.2	8.6	−5.4	−0.2	m
C_3H_7I	1-Iodopropane	−7.1	−3.0	4.2	−2.2	−0.7	f
C_3H_7I	2-Iodopropane	−9.8	−5.3	4.5	2.3	4.1	f
C_4H_9I	1-Butyl iodide	−12.0	−8.3	3.7	−2.0	−2.7	f
C_4H_9I	2-Iodo-2-methylpropane	−17.2	−12.5	4.7	10.7	8.9	m
C_6H_5I	Iodobenzene	39.4	44.7	5.3	−6.9	−1.3	m
$C_6H_{11}I$	Iodocyclohexane	−11.9	−11.7	0.2	−5.0	−8.1	m
C_7H_7I	*o*-Iodotoluene	31.7	38.8	7.1	−4.7	0.1	m
C_7H_7I	*m*-Iodotoluene	31.9	35.3	3.4	−7.1	−1.4	m
C_7H_7I	*p*-Iodotoluene	29.1	35.3	6.2	−4.4	1.3	f
C_7H_7I	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_2H_3OI	Acetyl iodide	−30.2	−29.9	0.3	3.3	9.5	m
C_3H_5OI	1-Iodo-2-propanone	−31.2	−26.5	4.7	−1.6	0.2	m
C_7H_5OI	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_3I	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_2	Iodine	14.9	20.7	5.8	6.3	4.9	d
CI_2	Diiodomethylene	120.4	121.6	1.2	−15.5	1.2	g
CH_2I_2	Diiodomethane	27.0	33.5	6.5	−10.2	−5.5	yy
$C_2H_2I_2$	E-1,2-Diiodoethene	49.6	55.0	5.4	−14.3	−5.5	m
$C_2H_2I_2$	z-1,2-Diiodoethene	49.6	60.5	11.0	−14.5	−6.1	m
$C_2H_4I_2$	1,2-Diiodoethane	16.0	23.3	7.4	−4.4	−0.2	m
$C_3H_6I_2$	1,2-Diiodopropane	8.5	20.8	12.3	−1.2	1.2	f
$C_4H_8I_2$	1,2-Diiodobutane	2.7	16.1	13.4	3.7	3.5	f
$C_6H_4I_2$	*o*-Diiodobenzene	60.2	73.8	13.7	−15.4	−6.1	m
COI_2	Carbonyl iodide	9.6	−1.5	−11.1	−15.1	−3.0	g
SI_2	Sulfur diiodide	81.9	51.6	−30.3	−52.4	−55.9	g
S_2I_2	S_2I_2	59.0	46.3	−12.7	−26.7	−30.1	g
CI_3	Triiodomethyl	117.3	105.7	−11.6	−68.0	−52.7	g

Table I. (continued)

Empirical formula	Chemical name	Heat of formation		Difference			
		Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
CHI_3	Iodoform	50.4	60.6	10.2	−18.4	−12.6	ccc
CI_4	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_3H_9Al	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_2	AlO_2 (−) ion	−116.0	−117.1	−1.1	25.5	59.3	d
AlO_2	AlO_2	−20.6	−37.4	−16.8	6.2	47.9	d
$HAlO_2$	AlO_2H	−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_2	AlF_2 (−) ion	−217.0	−229.6	−12.6	7.4	56.8	d
AlF_2	AlF_2	−166.0	−162.7	3.3	−5.1	42.6	d
AlF_2	AlF_2 (+)	22.0	29.0	7.0	−7.8	37.7	d
$AlOF_2$	AlF_2O (−) Ion	−311.6	−286.0	25.6	53.7	118.1	d
$AlOF_2$	AlF_2O	−265.0	−208.5	56.5	62.5	124.6	d
AlF_3	Aluminum trifluoride	−289.0	−291.5	−2.5	−2.3	71.3	d
AlF_4	AlF_4 (−) 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_2Cl	$AlClF_2$	−238.8	−234.6	4.2	−2.8	46.1	d
$AlCl_2$	$AlCl_2$ (−) ion	−115.0	−145.0	−30.0	−15.6	−5.0	d
$AlCl_2$	Aluminum dichloride	−67.0	−68.2	−1.2	−7.6	−6.1	d
$AlCl_2$	$AlCl_2$ (+)	115.0	124.3	9.3	3.9	−4.4	d
$AlFCl_2$	$AlCl_2F$	−189.0	−178.0	11.0	−2.4	21.8	d
$AlCl_3$	Aluminum trichloride	−139.7	−122.1	17.6	−0.6	−2.3	d
$AlBr_3$	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_3	Aluminum triiodide	−46.2	−39.9	6.3	57.8	51.1	d
Al_2	Al_2	116.4	79.6	−36.8	14.9	14.9	d
Al_2O	Al_2O	−34.7	−28.6	6.1	−37.0	16.1	d
Al_2O	Al_2O (+)	155.9	168.4	12.6	−46.8	2.3	d
Al_2O_2	Al_2O_2	−94.3	−87.6	6.8	−13.5	60.9	d
Al_2F_6	Al_2F_6	−629.5	−631.4	−1.9	−2.1	148.9	d
Al_2Cl_6	Al_2Cl_6	−309.7	−311.2	−1.5	14.4	7.9	d
Al_2Br_6	Al_2Br_6	−224.0	−224.9	−0.9	91.4	26.7	d
Al_2I_6	Al_2I_6	−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_2Si	Silylene (singlet)	61.1	72.8	11.7	3.2	6.7	ddd
H_2Si	Silylene (triplet)	6.5	−2.9	−9.4	−2.7	−30.7	eee
H_3Si	Silyl (−)	14.0	−2.8	−16.8	32.5	−15.8	fff
H_3Si	Silyl	46.4	42.9	−3.5	−9.5	−20.1	ggg
H_3Si	Silyl (+)	234.1	223.3	−10.8	−43.3	−11.2	fff
H_4Si	Silane	8.2	12.5	4.3	−7.0	−4.1	d
CH_5Si	Methylsilyl	30.5	23.3	−7.2	−11.5	−21.5	ggg
CH_6Si	Methylsilane	−7.8	−3.6	4.2	−5.8	−3.0	m
C_2H_6Si	Vinylsilane	−1.9	19.7	21.6	8.2	13.3	ff
C_2H_7Si	Dimethylsilyl	14.3	3.9	−10.4	−13.6	−21.8	ggg
C_2H_8Si	Ethylsilane	−15.0	−10.2	4.8	−6.7	−1.5	hhh
C_2H_8Si	Dimethylsilane	−20.0	−20.8	−0.8	−9.2	−5.6	m
C_3H_9Si	Trimethylsilyl	−0.8	−14.9	−14.1	−16.9	−22.1	ggg
$C_3H_{10}Si$	Trimethylsilane	−37.4	−37.3	0.1	−6.9	−1.9	m

Table I. (continued)

Empirical formula	Chemical name	Heat of formation Exp.	Heat of formation Calc.	Difference MNDO-PM3	Difference MNDO	Difference AM1	Footnote
$C_4H_{12}Si$	Diethylsilane	−43.6	−32.6	11.0	−0.5	7.3	iii
$C_4H_{12}Si$	Tetramethylsilane	−55.7	−53.7	2.0	−3.4	3.6	jjj
$C_5H_{12}Si$	1,1-Dimethylsilacyclobutane	−33.7	−35.6	−1.9	−14.7	−3.5	m
$C_6H_{16}Si$	Triethylsilane	−39.5	−55.4	−15.9	−24.5	−15.2	iii
$C_8H_{20}Si$	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
$C_3H_{10}SiO$	Trimethylsilicon hydroxide	−119.4	−115.4	4.0	−2.5	8.9	f
SiO_2	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_3SiF	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_2	Silicon difluoride	−141.2	−154.9	−13.7	−23.7	−13.4	kkk
H_2SiF_2	Difluorosilane	−189.0	−175.2	13.8	−3.5	7.5	kkk
$SiOF_2$	$SiOF_2$	−231.0	−229.4	1.6	42.4	10.3	d
SiF_3	Trifluorosilyl	−245.0	−260.3	−15.3	−3.9	−22.8	ggg
$HSiF_3$	Trifluorosilane	−287.0	−280.2	6.8	1.9	6.1	d
SiF_4	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_3SiCl	Chlorosilane	−32.4	−27.6	4.8	−11.5	−5.3	kkk
C_2H_7SiCl	Chlorodimethylsilane	−69.9	−63.7	6.2	−3.1	−0.1	iii
C_3H_9SiCl	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
$SiCl_2$	Silicon dichloride	−40.6	−49.4	−8.8	−5.7	−6.1	kkk
H_2SiCl_2	Dichlorosilane	−75.3	−69.5	5.8	−8.2	−5.4	kkk
CH_4SiCl_2	Dichloromethylsilane	−96.0	−88.9	7.1	−1.4	−2.5	f
$C_2H_6SiCl_2$	Dichlorodimethylsilane	−109.5	−108.1	1.4	−1.8	−5.8	m
$SiOCl_2$	$SiOCl_2$	−167.7	−121.2	46.5	73.6	49.4	g
$SiCl_3$	Trichlorosilyl	−76.0	−94.8	−18.8	−13.5	−40.0	ggg
$HSiCl_3$	Trichlorosilane	−119.3	−112.7	6.6	1.4	−5.8	kkk
CH_3SiCl_3	Trichloromethylsilane	−131.2	−132.9	−1.7	0.6	−12.4	m
$SiCl_4$	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_3SiBr	Bromosilane	−15.3	−16.0	−0.7	−2.7	−5.8	lll
C_3H_9SiBr	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
$SiBr_2$	Silicon dibromide	−9.6	−27.4	−17.8	20.8	3.6	kkk
H_2SiBr_2	Dibromosilane	−43.2	−47.2	−4.0	11.2	−2.6	kkk
$SiOBr_2$	$SiOBr_2$	−137.4	−94.1	43.3	86.0	60.0	g
$SiBr_3$	Silicon tribromide	−56.1	−60.8	−4.7	41.1	−9.6	g
$HSiBr_3$	Tribromosilane	−72.5	−79.6	−7.1	30.1	2.3	lll
$SiBr_4$	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_3SiI	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_2	Silicon diiodide	22.0	24.0	2.0	60.1	35.5	kkk
H_2SiI_2	Diiodosilane	−9.1	−12.4	−3.3	32.1	14.1	d
$SiOI_2$	$SiOI_2$	−99.4	−50.2	49.2	89.7	80.7	g
SiI_3	Silicon triiodide	0.5	4.7	4.2	44.9	11.9	g
$HSiI_3$	Triiodosilane	−17.8	−9.0	8.8	51.9	21.7	kkk
SiI_4	Silicon tetraiodide	−26.4	−14.2	12.2	68.8	28.0	d
Si_2	Silicon dimer	140.9	135.7	−5.2	74.4	−1.4	g
H_6Si_2	Disilane	17.1	17.9	0.8	5.3	−0.9	mmm
$C_6H_{18}Si_2$	Hexamethyldisilane	−85.8	−83.2	2.7	12.1	19.7	m
$C_6H_{18}Si_2O$	Hexamethyldisiloxane	−185.8	−182.8	3.0	−8.8	18.1	f
$C_6H_{19}Si_2N$	Hexamethyldisilazane	−113.9	−120.8	−6.9	−9.7	−4.1	f
Si_2Cl_6	Hexachlorodisilane	−243.5	−229.7	13.8	30.8	1.9	mmm
Si_2Br_6	Hexabromodisilane	−182.8	−164.7	18.1	116.9	38.9	g
Si_3	Silicon trimer	152.2	152.8	0.6	15.0	32.7	g
H_8Si_3	Si_3H_8	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_2P	Phosphino	30.1	29.3	−0.8	1.3	6.8	d

Table I. (continued)

		Heat of formation		Difference			
Empirical formula	Chemical name	Exp.	Calc.	MNDO-PM3	MNDO	AM1	Footnote
H_3P	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_5P	Methylphosphine	−7.0	−9.5	−2.5	−7.7	2.0	nnn
C_2H_7P	Ethylphosphine	−12.0	−11.7	0.3	−9.1	−0.2	nnn
C_2H_7P	Dimethylphosphine	−15.0	−19.6	−4.6	−17.1	−3.2	nnn
C_3H_9P	Trimethylphosphine	−22.5	−29.8	−7.3	−25.7	−8.1	f
$C_4H_{11}P$	Diethylphosphine	−25.0	−23.3	1.7	−20.0	−6.5	nnn
$C_6H_{15}P$	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_2	Phosphorus difluoride	−119.0	−144.4	−25.4	−19.0	11.2	g
PF_3	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
POC_1	POCl	−64.7	−76.4	−11.7	−10.1	14.2	g
PCl_2	Phosphorus dichloride	−21.3	−40.1	−18.8	−28.1	−31.5	g
PCl_3	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_2	Phosphorus dibromide	6.7	0.4	−6.3	−16.0	−20.4	g
PBr_3	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_2	Phosphorus diiodide	41.3	36.6	−4.7	−4.8	−8.6	g
PI_3	Phosphorus triiodide	25.1	31.3	6.2	−0.3	−7.4	g
P_2	Phosphorus dimer	42.8	32.0	−10.8	−1.7	−1.7	g
H_4P_2	P_2H_4	5.0	−3.7	−8.7	−7.9	−5.3	ff
P_4	Phosphorus tetramer	31.1	42.9	11.8	5.1	5.1	g
P_4O_6	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[26] or new experimental measurements.

As we have seen, in a few instances very large differences between experimental and calculated ΔH_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_2H_6SO	Dimethyl sulfoxide	−36.1	−38.8	−2.7	40.0	41.2	a
$C_4H_{10}SO$	Diethyl sulfoxide	−49.1	−46.6	2.5	41.5	42.1	a
SO_2	Sulfur dioxide	−71.0	−50.8	20.2	75.4	98.0	b
$C_2H_6SO_2$	Dimethyl sulfone	−89.1	−76.3	12.8	142.8	142.1	a
$C_4H_{10}SO_2$	Diethyl sulfone	−102.5	−80.8	21.7	143.1	142.0	a
SO_3	Sulfur trioxide	−94.6	−104.8	−10.2	153.1	177.7	b
$C_2H_6SO_3$	Dimethyl sulfite	−115.5	−130.0	−14.5	50.4	56.4	a
H_2SO_4	Sulfuric acid	−175.7	−181.4	−5.8	172.2	177.7	b
$C_2H_6SO_4$	Dimethyl sulfate	−164.1	−172.1	−8.0	158.6	162.7	a
O_2F	Fluorine dioxide	3.0	12.9	9.9	21.1	6.0	b
NO_2F	Fluorine nitrite	−26.0	−25.6	0.4	26.7	4.7	b
NO_3F	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_2F	SO_2F	−113.2	−102.5	10.7	127.2	143.8	c
SOF_2	Thionyl fluoride	−130.0	−138.2	−8.2	84.3	96.1	b
SO_2F_2	Sulfuryl fluoride	−181.3	−184.3	−3.0	203.3	211.4	b
NOF_3	F_3NO	−39.0	−26.6	12.4	61.8	24.4	b
SF_3	Sulfur trifluoride	−130.0	−134.3	−4.3	89.9	97.1	c
SOF_3	SOF_3	−185.1	−176.5	8.6	180.2	183.5	c
SF_4	Sulfur tetrafluoride	−182.4	−185.3	−2.9	135.9	138.9	b
SOF_4	SOF_4	−235.5	−236.3	−0.8	269.1	255.4	c
SF_5	Sulfur pentafluoride (−)	−291.0	−303.0	−12.0	159.4	169.0	d
SF_5	Sulfur pentafluoride	−217.1	−232.5	−15.4	208.2	198.7	b
O_2Cl	Chlorine dioxide	25.0	1.5	−23.5	111.0	80.9	b
NO_2Cl	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_2Cl	SO_2Cl	−66.4	−57.3	9.1	92.3	111.4	c
O_3FCl	Perchloryl fluoride	−5.1	14.6	19.7	328.4	251.6	b
F_3Cl	Chlorine trifluoride	−38.0	−22.1	15.9	116.7	58.2	b
F_5Cl	Chlorine pentafluoride	−54.0	−54.0	0.0	258.8	144.5	b
$SOCl_2$	Thionyl chloride	−50.8	−47.6	3.2	28.6	43.1	e
SO_2Cl_2	Sulfuryl chloride	−86.2	−62.3	23.9	79.9	99.0	b
SCl_3	Sulfur trichloride	8.8	−19.1	−27.9	−41.3	−37.5	c
$SOCl_3$	$SOCl_3$	−47.5	−46.5	1.0	49.9	60.8	c
SCl_4	Sulfur tetrachloride	−0.7	−19.8	−19.1	−32.6	−25.5	c
$SOCl_4$	$SOCl_4$	−55.7	−59.3	−3.6	22.7	33.6	c
SCl_5	Sulfur pentachloride	−8.6	9.2	17.8	4.3	11.4	c
SCl_6	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_2Br	SO_2Br	−52.8	−42.9	9.9	89.5	112.7	c
F_3Br	Bromine trifluoride	−61.1	−47.1	14.0	84.0	82.6	b
F_5Br	Bromine pentafluoride	−102.5	−75.8	26.7	207.4	183.7	b
$SOBr_2$	Thionyl bromide	−11.5	−18.6	−7.1	16.1	37.7	c
SO_2Br_2	Sulfuryl bromide	−59.5	−46.2	13.3	127.9	149.5	c
SBr_3	Sulfur tribromide	50.2	16.4	−33.8	−51.3	−48.4	c
$SOBr_3$	$SOBr_3$	−8.6	−10.0	−1.4	41.4	59.5	c
SBr_4	Sulfur tetrabromide	53.0	18.8	−34.2	−42.9	−34.1	c
$SOBr_4$	$SOBr_4$	−3.3	−20.7	−17.4	26.6	38.3	c
SBr_5	Sulfur pentabromide	55.9	44.0	−11.9	23.5	28.1	c
SBr_6	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_2I	SO_2I	−34.9	−32.0	2.9	64.5	86.7	c
F_5I	Iodine pentafluoride	−200.8	−202.9	−2.1	298.8	267.9	b
F_7I	Iodine heptafluoride	−229.7	−225.4	4.3	334.9	274.1	b
SOI_2	Thionyl iodide	21.5	11.1	−10.4	26.6	34.9	c
SO_2I_2	Sulfuryl iodide	−26.0	−30.0	−4.0	51.7	72.8	c
SI_3	Sulfur triiodide	100.3	54.7	−45.6	−60.0	−64.9	c
SOI_3	SOI_3	40.4	23.8	−16.6	1.7	0.1	c
SI_4	Sulfur tetraiodide	120.2	83.8	−36.4	−38.0	−42.0	c
SOI_4	SOI_4	60.0	27.6	−32.4	−17.0	−17.8	c
SI_5	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_6	Sulfur hexaiodide	158.9	167.0	8.1	48.7	32.2	c
$C_4H_{12}SiF$	$SiMe_4F$ (−) C_{3v} symmetry	−147.5	−122.4	25.1	33.5	23.5	d
SiF_5	SiF_5 (−)	−507.1	−504.4	2.7	17.7	3.6	d
SiF_4Cl	SiF_4Cl (−)	−465.3	−465.2	0.1	17.5	8.0	d
$SiCl_5$	$SiCl_5$ (−)	−237.2	−254.6	−17.4	−19.3	−30.4	d
C_3H_9PO	Trimethylphosphine oxide	−102.2	−82.7	19.5	59.3	78.9	a
PO_2	Phosphorus dioxide	−71.0	−76.7	−5.7	24.0	61.8	c
CH_5PO_3	Methylphosphonic acid	−240.5	−213.3	27.2	25.2	51.5	a
$C_2H_7PO_3$	Ethylphosphonic acid	−239.4	−218.5	20.9	19.9	43.4	a
$C_3H_9PO_3$	Trimethyl phosphite	−168.3	−192.2	−23.9	−38.0	−3.5	a
$C_6H_{15}PO_3$	Triethyl phosphite	−195.9	−208.5	−12.6	−27.5	3.3	a
$C_6H_{15}PO_4$	Triethyl phosphate	−284.5	−252.9	31.6	75.0	104.8	a
$C_2H_6PO_2F$	Methyl methylphosphonofluoridate	−197.3	−207.6	−10.3	51.4	80.5	g
$C_3H_8PO_2F$	Ethyl methylphosphonofluoridate	−205.8	−212.3	−6.5	53.9	82.6	g
$C_4H_{10}PO_2F$	*n*-Propyl methylphosphonofluoridate	−210.2	−217.4	−7.2	53.9	80.7	g
$C_4H_{10}PO_2F$	*i*-Propyl methylphosphonofluoridate	−214.6	−216.7	−2.1	60.8	87.2	g
$C_5H_{12}PO_2F$	*i*-Propyl ethylphosphonofluoridate	−219.8	−217.5	2.2	59.4	85.2	g
$C_5H_{12}PO_2F$	*s*-Butyl methylphosphonofluoridate	−220.1	−221.2	−1.1	63.2	86.8	g
$C_5H_{12}PO_2F$	*n*-Butyl methylphosphonofluoridate	−215.1	−222.9	−7.8	53.8	78.4	g
$C_6H_{14}PO_2F$	Neopentyl methylphosphonofluoridate	−224.2	−226.6	−2.4	70.4	87.8	g
POF_2	POF_2	−213.6	−188.9	24.7	61.7	99.0	c
CH_3POF_2	Methylphosphonodifluoride	−233.2	−225.3	7.9	86.1	119.8	g
POF_3	Phosphorus oxyfluoride	−289.5	−297.7	−8.2	90.0	132.2	h
PF_4	Phosphorus tetrafluoride (−)	−325.0	−332.1	−7.1	22.8	66.2	d
PF_4	Phosphorus tetrafluoride	−287.9	−303.9	−16.0	53.3	93.9	c
PF_5	Phosphorus pentafluoride	−381.1	−386.9	−5.8	132.3	166.3	b
PF_6	Phosphorus hexafluoride (−)	−522.0	−508.5	13.5	152.4	194.3	d
$POCl_2$	$POCl_2$	−109.9	−94.8	15.1	33.9	51.2	c
CH_3POCl_2	Methylphosphonodichloride	−124.1	−128.9	−4.8	48.7	62.9	g
$POCl_3$	Phosphorus oxychloride	−132.8	−140.2	−7.4	53.2	58.7	h
$PSCl_3$	Phosphorus thiochloride	−91.0	−60.2	30.8	62.6	53.6	b
PCl_4	Phosphorus tetrachloride	−80.5	−102.8	−22.3	−22.7	−30.8	c
PCl_5	Phosphorus pentachloride	−89.6	−111.6	−22.0	47.7	36.1	h
$POBr_2$	$POBr_2$	−78.3	−50.8	27.5	26.4	70.1	c
$POBr_3$	Phosphorus oxybromide	−97.0	−80.2	16.8	68.3	84.6	b
$PSBr_3$	Phosphorus thiobromide	−67.2	−7.8	59.4	85.7	83.3	b
PBr_4	Phosphorus tetrabromide	−17.4	−17.4	0.0	−11.9	−10.7	c
PBr_5	Phosphorus pentabromide	−11.0	−27.1	−16.1	42.8	73.3	c
POI_2	POI_2	−40.1	−35.2	4.9	19.5	42.8	c
POI_3	Phosphorus oxyiodide	−39.7	−8.3	31.4	71.3	79.3	c
PI_4	Phosphorus tetraiodide	60.2	44.7	−15.5	−36.1	−47.1	c
PI_5	Phosphorus pentaiodide	97.7	88.5	−9.2	−16.0	−36.1	c
P_4O_{10}	Phosphorus pentoxide	−694.1	−712.6	−18.5	262.4	444.7	b

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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 ΔH_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 ΔH_f of CO and heat of atomization of the halogens[27] (F: 18.9, Cl: 29.0, Br: 26.7, I: 25.5 kcal/mol) are known, the heats of the reactions

$$\mathrm{CO + X = COX} \quad \text{and} \quad \mathrm{COX + X = COX_2}$$

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 P_4O_6, further work will be required to resolve this conflict.

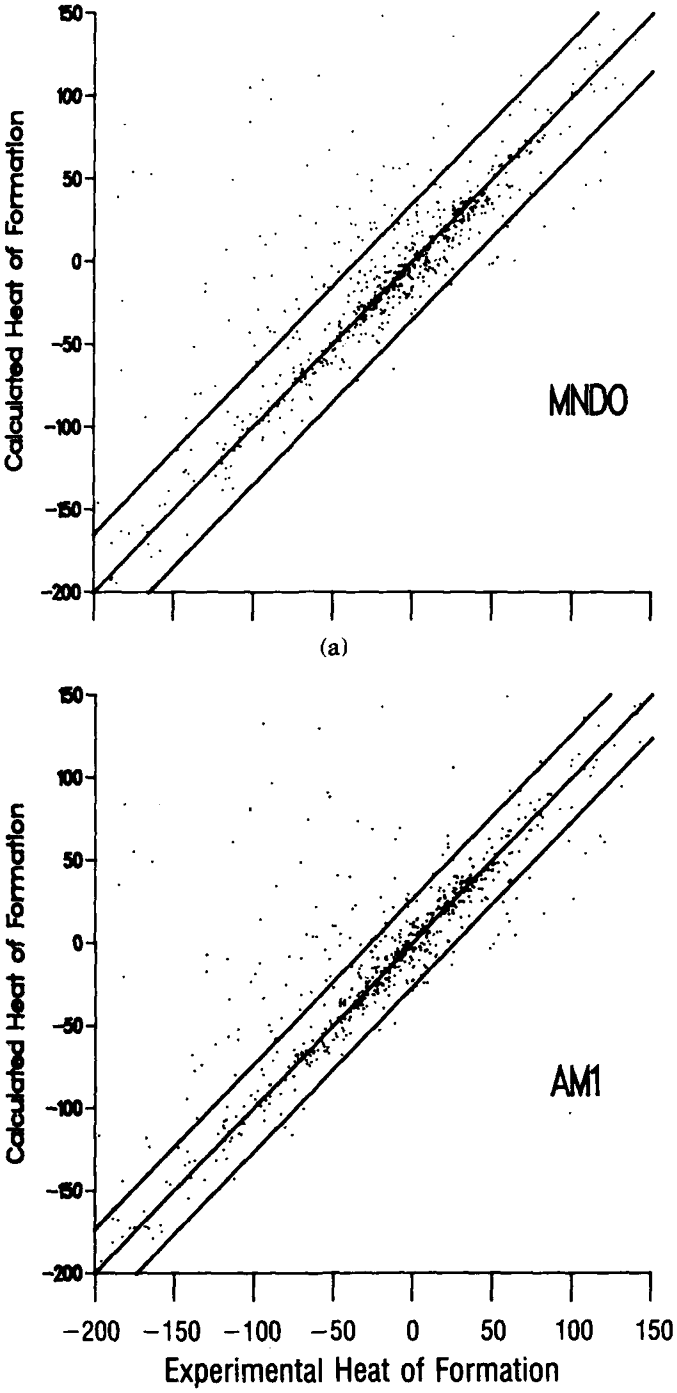
The differences between the experimental and calculated values of ΔH_f for three of the oxyhalides of silicon are large and positive. This difference is vividly illustrated by investigating the metathetical reaction

$$\mathrm{SiX_4 + SiO_2 = SiOX_2 + SiOX_2}$$

for which the calculated and experimental ΔH_f and ΔH_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 ΔH_r, and the small predicted ΔH_r, we postulate that the experimental ΔH_f for $SiOCl_2$, $SiOBr_2$, and $SiOI_2$ 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 ΔH_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 ΔH_f of nitro and polynitro organics.[28] For 26 nitro-organic compounds and three organic nitrates, the average calculated differences in ΔH_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.



(a)

(b)

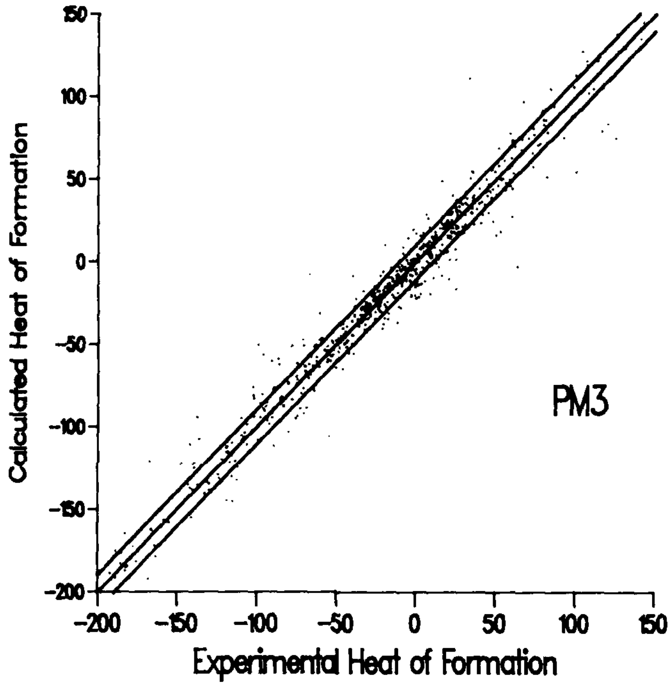
Figure 1. Calculated and experimental heats of formation for all compounds surveyed.

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.[29] 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 MNDO or PM3.

HEATS OF ASSOCIATION AND HYDROGEN BONDING

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



(c)

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[21] 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.

	ΔH_f(Exp)[a]			ΔH_r(Exp)	ΔH_f(Calc)			ΔH_r(Calc)
X	SiX_4	SiO_2	$SiOX_2$		SiX_4	SiO_2	$SiOX_2$	
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

[a] For references, see Table I.

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

Compound	ΔH_f(Exp)[a]	ΔH_f(Calc)	Difference
PH_3	1.3	0.2	−1.1
CH_3PH_2	−7.0	−9.5	−2.5
$(CH_3)_2PH$	−15.0	−19.6	−4.6
$(CH_3)_3P$	−22.5	−29.8	−7.3
$C_2H_5PH_2$	−12.0	−11.7	+0.3
$(C_2H_5)_2PH$	−25.0	−23.3	+1.7
$(C_2H_5)_3P$	−11.8	−36.7	−24.9

[a] 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 salicylaldoximes (Fig. 3), are poorly reproduced[30] 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_2 and NH_2 groups may be estimated by reference to the metathetic reaction

Table VII. Heats of association.

Associating molecules	Heat of association (kcal)		
	PM3	MNDO	AM1
CO_2—CO_2	0.0	0.0	0.0
NH_3—H_2	0.0	0.0	0.0
O_2—O_2	0.0	0.0	0.0
H_2—N_2	0.0	0.0	0.0
H_2—CO_2	0.0	0.0	0.0
H_2O—H_2O	−3.5	−1.0	−5.5
NH_3—NH_3	−0.9	−0.8	−2.4
H_2O—H_2O (C_2v)	−2.0	−1.0	−5.0
Benzene—Benzene	−3.8	0.0	−0.4
H_2O—H_2	−0.9	0.0	−1.1
H_2O—CH_4	−1.2	0.0	−1.2
CH_2O—H_2O	−1.6	−0.7	−3.7
H_2O—CH_2O	−1.6	−1.0	−4.0
H_2O—CH_3OH	−1.9	−0.9	−4.8
CH_3OH—H_2O	−1.5	−0.7	−2.7
CH_2O—CH_2O	−1.0	−0.8	−2.4
HCOOH—CH_4	−2.3	0.1	−0.8
H_2O—CO_2	−0.9	−0.8	−2.7
H_2O—HCOOH	−5.3	−1.0	−7.4
H_2O—O_3	−1.8	−1.1	−6.8
HCOOH—HCOOH	−8.6	−1.7	−6.4
H_2O—NH_3	−1.1	−0.5	−2.7
H_2O—C_5H_5N	−1.7	−1.1	−3.1
NH_3—CO_2	−0.5	−0.4	−1.8
HCOOH—NH_3	−5.3	−0.9	−4.1
NH_2CHO—NH_2CHO	−4.7	−2.1	−8.1
NH_2COOH—NH_2COOH	−1.9	−3.3	−9.0

	Aniline +	Nitro-benzene =	Benzene +	Para-nitroaniline	ΔH_r
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_2 and C_6H_5N planes, is 37.5° ±2°.[31] This, together with the fact that the calculated barrier to inversion of an —NH_2 group in ammonia and methylamine is 5.4 and 5.7 kcal/mol at the MP3/6-31G*//3-21G* level[32], and the very small experimental ΔH_r 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

Table VI. Heats of hydration of ammonium ion.[a]

Hydration reaction	Heat of hydration		Error		
	Exp.	Calc.	PM3	MNDO	AM1
$NH_4(+) + H_2O = NH_4(+)H_2O$	−17.3	−13.5	3.8	8.8	2.0
$NH_4(+)H_2O + H_2O = NH_4(+)(H_2O)_2$	−14.7	−9.3	5.4	6.8	1.6
$NH_4(+)(H_2O)_2 + H_2O = NH_4(+)(H_2O)_3$	−13.4	−9.3	4.1	6.0	−1.5

[a] Source: P. Kebarle, *Environmental Effects on Molecular Structure and Properties,* B. Pullman, (Ed.), D. Reidel, Dodrecht, The Netherlands, 1976, p. 81.

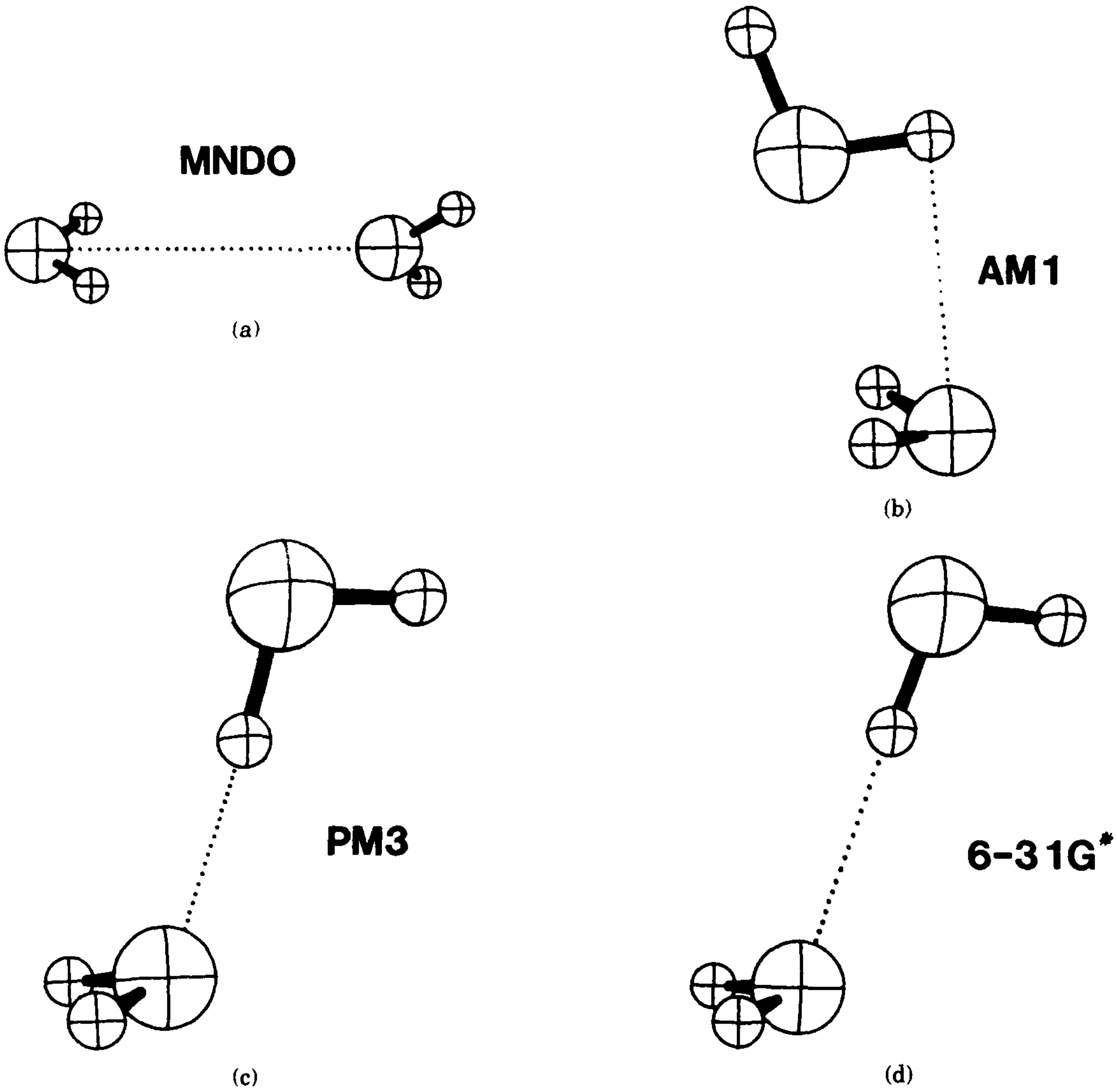


Figure 2. Calculated structures for water dimers.

calculated. However, in gas-phase PNA the $-NH_2$ group is predicted to be pyramidal.

STRUCTURE OF IODINE HEPTAFLUORIDE

The geometry of IF_7 is currently not known. It has been assumed, however, to be a bicapped pentagonal pyramid[15]. 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 IF_7 is a distorted trigonal bipyramid in which a 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 IF_5 and the heats of formation of IF_5 and IF_7 (but not F_2) are all reproduced accurately, we predict that the geometry of 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_2	Hydrogen	HH	0.741	0.699	−0.042	−0.078	−0.064	a
CH_2	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_2	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_4	Methane	CH	1.094	1.087	−0.007	0.010	0.018	b
C_2	Carbon, dimer	CC	1.242	1.189	−0.053	−0.073	−0.078	a
C_2H_2	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_2H_4	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_2H_6	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_3H_4	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_3H_4	Cyclopropene	C_2C_3	1.509	1.484	−0.025	0.003	−0.020	d
		C_1C_2	1.296	1.314	0.018	0.032	0.022	
		C_1H	1.072	1.073	0.001	−0.010	−0.003	
		HC_1C_2	149.9	151.5	1.6	1.7	2.0	
C_3H_4	Propyne	C_2C_1	1.206	1.191	−0.015	−0.009	−0.009	e
		C_1H	1.056	1.064	0.008	−0.005	0.004	
		C_3C_3	1.459	1.433	−0.026	−0.014	−0.032	
		C_3H	1.105	1.098	−0.007	0.006	0.016	
		HCC	111.0	110.7	−0.3	0.0	−0.5	
C_3H_6	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_3H_6	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_3H	1.085	1.098	0.013	0.024	0.033	
		HC_3C_2	111.2	112.9	1.7	1.8	0.7	
		C_2H	1.090	1.097	0.007	0.006	0.013	
		HC_2C_1	119.0	120.8	1.8	0.3	1.9	
		HC_1	1.091	1.087	−0.004	−0.002	0.007	
		HC_1C_2	121.5	122.7	1.2	0.8	0.8	
C_3H_8	Propane	CC	1.526	1.512	−0.014	0.004	−0.019	g
		CCC	112.4	111.7	−0.7	3.0	−0.6	
		C_2H	1.115	1.108	−0.007	0.000	0.007	
		HC_2C_1	109.5	109.9	0.4	−0.7	0.0	
		C_1H	1.096	1.097	0.001	0.014	0.021	
		HC_1C_2	111.8	111.4	−0.4	−1.5	−1.4	
C_4H_2	Diacetylene	C_1C_2	1.205	1.193	−0.012	−0.006	−0.006	h
		C_2C_3	1.376	1.371	−0.005	−0.008	−0.020	
		CH	1.046	1.065	0.019	0.004	0.014	
C_4H_4	$CH_2{=}C{=}C{=}C{=}CH_2$	CH	1.083	1.087	0.004	0.007	0.017	i
		C_1C_2	1.318	1.301	−0.017	−0.007	−0.016	
		C_2C_3	1.283	1.267	−0.016	−0.013	−0.017	
C_4H_4	Vinylacetylene	C_3C_4	1.341	1.332	−0.009	0.004	−0.005	j
		C_2C_3	1.431	1.414	−0.017	−0.014	−0.026	
		$C_2C_3C_4$	123.1	122.5	−0.6	2.3	1.0	
		C_1C_2	1.208	1.193	−0.015	−0.010	−0.010	
C_4H_6	Bicyclobutane	C_1C_2	1.498	1.507	0.009	0.029	0.012	k
		C_1C_3	1.497	1.481	−0.016	0.039	−0.002	
		$C_2C_3C_1C_4$	121.7	120.0	−1.7	0.9	0.3	
		C_1H	1.071	1.083	0.012	0.003	0.008	
		C_2H	1.093	1.095	0.002	0.005	0.012	
C_4H_6	2-Butyne	C_2C_3	1.213	1.193	−0.020	−0.013	−0.015	j
		C_1C_2	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_4H_6	1,3-Butadiene	C_1C_2	1.344	1.331	−0.013	0.000	−0.009	l
		C_2C_3	1.467	1.456	−0.011	−0.002	−0.016	
		CCC	122.9	122.3	−0.6	2.8	0.5	
C_4H_8	1-Butene	C_2C_3	1.347	1.328	−0.019	−0.006	−0.016	m
		C_1C_2	1.508	1.489	−0.019	−0.003	−0.024	
		CCC	123.8	122.6	−1.2	1.6	−0.4	
C_4H_8	Cyclobutane	CC	1.548	1.542	−0.006	0.001	−0.005	n
		CH	1.105	1.100	−0.005	0.000	0.005	
C_4H_8	Isobutene	C_1C_2	1.330	1.333	0.003	0.018	0.006	o
		C_2C_3	1.507	1.487	−0.020	0.002	−0.023	
		$C_1C_2C_3$	122.4	122.1	−0.3	−0.5	0.0	
C_4H_{10}	*n*-Butane	C_1C_2	1.533	1.512	−0.021	−0.002	−0.026	e
		C_2C_3	1.533	1.521	−0.012	0.007	−0.019	
		CCC	112.8	111.6	−1.2	2.0	−1.2	
C_4H_{10}	Isobutane	CC	1.525	1.520	−0.005	0.016	−0.011	p
C_5H_8	1,4-Pentadiene Cl	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	
		$C_1—C_2—C_3—C_4$	−116.9	−127.5	−10.6	9.6	−13.8	
		$C_2—C_3—C_4—C_5$	−4.3	14.2	18.5	110.0	16.2	
C_5H_8	1,4-Pentadiene C2	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	123.1	7.6	11.2	8.3	
		C—C—C	108.9	110.8	1.9	3.8	2.9	
		$C_1—C_2—C_3—C_4$	−122.2	−129.3	−7.1	15.1	−11.9	
C_5H_8	1,4-Pentadiene Cs	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	
		$C_1—C_2—C_3—C_4$	−128.6	−132.2	−3.6	22.1	−5.3	
C_5H_{12}	Neopentane	CC	1.539	1.527	−0.012	0.015	−0.018	f
		CH	1.120	1.098	−0.022	−0.011	−0.004	
		HCC	110.0	111.3	1.3	1.7	0.3	
C_6H_6	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_6H_6	Fulvene	C_3C_4	1.476	1.471	−0.005	0.000	0.000	s
		C_2C_3	1.355	1.355	0.000	0.011	0.008	
		C_1C_2	1.470	1.478	0.008	0.021	0.013	
		C_1C_6	1.349	1.331	−0.018	−0.004	−0.017	
C_6H_{10}	Cyclohexene	C_1C_2	1.335	1.334	−0.001	0.011	0.002	t
		C_2C_3	1.504	1.487	−0.017	0.000	−0.021	
		C_3C_4	1.515	1.521	0.006	0.026	0.002	
		C_4C_5	1.550	1.519	−0.031	−0.011	−0.036	
		$C_5C_4C_2C_1$	21.8	27.8	6.0	−0.8	5.4	
C_6H_{12}	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	
		CH′	1.121	1.108	−0.013	−0.007	0.001	
H_2O	Water	OH	0.957	0.951	−0.006	−0.014	0.004	b
		HOH	104.5	107.7	3.2	2.3	−1.0	
CO	Carbon monoxide	CO	1.128	1.135	0.007	0.035	0.043	v
CH_2O	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	
CH_4O	Methanol	CO	1.425	1.395	−0.030	−0.034	−0.015	x
		CH	1.094	1.097	0.003	0.025	0.025	
		HCO	108.5	112.2	3.7	3.8	2.4	
		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_2H_2O	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_2H_6O	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_3H_4O	Acrolein	C_3C_2	1.335	1.330	−0.005	0.008	−0.001	aa
		C_2C_1	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	
		OCC	124.0	124.0	0.0	1.5	0.0	
C_4H_4O	Furan	CO	1.362	1.378	0.016	0.005	0.033	bb
		CCO	106.6	106.9	0.3	1.0	0.0	
		C_3C_2	1.361	1.373	0.012	0.029	0.019	
		CCC	110.7	110.2	−0.5	−0.4	−0.6	
O_2	Oxygen, triplet state	OO	1.216	1.169	−0.047	−0.082	−0.130	v
H_2O_2	Hydrogen peroxide	OO	1.475	1.482	0.007	−0.179	−0.175	cc
		OH	0.950	0.945	−0.005	0.011	0.033	
		HOO	94.8	96.5	1.7	12.2	11.2	
		HOOH	119.8	180.0	60.2	60.5	8.1	
H_4O_2	Water dimer	OO	3.000	2.769	−0.231	0.905	−0.383	
CO_2	Carbon dioxide	CO	1.162	1.181	0.019	0.024	0.027	b
CH_2O_2	Formic acid	C=O	1.202	1.211	0.009	0.025	0.028	dd
		C—O	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	
$C_2H_2O_2$	*trans* Glyoxal	CO	1.207	1.207	0.000	0.013	0.022	aa
		CC	1.525	1.526	0.001	0.004	−0.017	
		CCO	121.2	120.5	−0.7	0.8	−0.2	
$C_6H_4O_2$	*p*-Benzoquinone	C_1C_2	1.477	1.487	0.010	0.024	0.002	ee
		C_2C_3	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_3N	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	Cyanide	CN	1.175	1.157	−0.018	−0.022	−0.027	a
CN	Cyanide (+)	CN	1.290	1.355	0.065	−0.149	−0.164	a
CHN	Hydrogen cyanide	CN	1.154	1.156	0.002	0.006	0.006	ff
		CH	1.063	1.070	0.007	−0.008	0.006	
CH_5N	Methylamine	CN	1.474	1.469	−0.005	−0.014	−0.042	gg
		NH	1.011	0.999	−0.012	−0.003	−0.011	
		HNC	112.0	109.8	−2.2	−2.2	−0.7	
		HNH	105.9	108.7	2.8	−0.4	3.1	
C_2H_3N	Acetonitrile	CC	1.458	1.440	−0.018	−0.006	−0.019	hh
		CH	1.104	1.098	−0.006	0.006	0.016	
		HCC	109.5	110.4	0.9	1.1	0.6	
		CN	1.157	1.159	0.002	0.005	0.006	
C_2H_3N	Methyl isocyanide	CN—	1.424	1.433	0.009	0.000	−0.029	hh
		CH	1.101	1.097	−0.004	0.014	0.024	
		HCN	109.1	109.7	0.6	1.1	1.0	
		—CN	1.166	1.181	0.015	0.025	0.015	
C_3H_9N	Trimethylamine	CN	1.451	1.480	0.029	0.013	−0.006	ii
		CNC	110.9	112.3	1.4	5.1	2.1	
C_4H_5N	Pyrrole	CN	1.370	1.397	0.027	0.028	0.022	l
		CNC	107.7	109.7	2 0	2.0	1.1	
		C_3C_2	1.382	1.390	0.008	0.013	0.020	
		CCC	109.8	107.0	−2.8	−2.4	−1.4	
		C_4C_3	1.417	1.390	−0.027	−0.022	−0.015	
NO	Nitrogen oxide	NO	1.151	1.127	−0.024	−0.028	−0.036	a

Table VIII. (continued)

Empirical formula	Chemical name	Geometric variable	Exp.	Calc.	Errors PM3	Errors MNDO	Errors AM1	Footnote
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_3NO	Formamide	CN	1.376	1.413	0.037	0.033	−0.009	jj
		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_2	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_2	Nitrous acid (*cis*)	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	
		HON	103.0	109.9	6.9	16.7	12.5	
HNO_2	Nitrous acid (*trans*)	N—O	1.460	1.383	−0.077	−0.148	−0.141	a
		N=O	1.200	1.167	−0.033	−0.034	−0.042	
		ONO	118.0	109.1	−8.9	−4.7	−5.2	
		OH	0.980	0.950	−0.030	−0.022	−0.005	
		HON	105.0	104.6	−0.4	5.0	2.0	
$C_7H_7NO_2$	Salicylaldoxime	N(14)H(17)	1.834	1.847	0.013	0.940	0.302	kk
		O(10)N(14)	2.626	2.684	0.058	0.781	0.298	
HNO_3	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_2	Nitrogen	NN	1.094	1.098	0.004	0.010	0.012	v
H_4N_2	Hydrazine	NN	1.449	1.440	−0.009	−0.052	−0.071	a
		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_2N_2	Cyanogen	CN	1.154	1.159	0.005	0.008	0.008	b
		CC	1.389	1.382	−0.007	−0.011	−0.005	
$C_2H_6N_2$	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_2O	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	
$H_2N_2O_2$	$NH_2—NO_2$	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_2O_3	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_2O_4	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_3	Azide	NN	1.181	1.174	−0.007	−0.007	−0.004	a
$C_3H_3N_3$	*s*-Triazine	CN	1.338	1.358	0.020	0.019	0.026	mm
		NCN	126.8	121.6	−5.2	−3.4	−1.1	
H_2S	Hydrogen sulfide	HS	1.328	1.290	−0.038	−0.028	−0.011	a
		HSH	92.2	93.5	1.3	5.9	6.6	
CS	Carbon sulfide	CS	1.534	1.447	−0.087	−0.050	−0.064	nn
CH_2S	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_4S	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_4H_4S	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_3C_2	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_2	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_3	Sulfur trioxide	SO	1.430	1.384	−0.046	0.061	0.113	a
H_2SO_4	Sulfuric acid	S—O	1.550	1.668	0.118	0.078	0.157	a
		OH	0.970	0.947	−0.023	−0.023	−0.006	
		SOH	105.0	117.7	12.7	12.2	1.5	
		S=O	1.420	1.668	0.248	0.209	0.287	
NS	Sulfur nitride	SN	1.495	1.452	−0.043	−0.055	−0.054	a
C_2H_3NS	Methyl isothiocyanate	CS	1.597	1.498	−0.099	−0.088	−0.095	ss
		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—N=C	141.6	139.4	−2.2	−0.3	−1.0	
C_2N_2S	Sulfur dicyanide	CN	1.157	1.164	0.007	0.007	0.007	tt
		CS	1.701	1.664	−0.037	−0.071	−0.067	
		NCS	170.0	176.5	6.5	7.0	7.4	
		CSC	98.4	101.5	3.1	5.1	3.4	
S_2	Sulfur dimer	SS	1.889	1.857	−0.032	−0.114	−0.114	a
H_2S_2	H_2S_2	SS	2.055	2.034	−0.021	−0.131	−0.136	uu
		SH	1.327	1.311	−0.016	−0.023	−0.005	
		HSS	91.3	103.2	11.9	11.2	9.9	
		HSSH	90.5	93.4	2.9	9.1	21.7	
CS_2	Carbon disulfide	CS	1.553	1.481	−0.072	−0.061	−0.070	pp
$C_2H_6S_2$	2,3-Dithiabutane	CS	1.810	1.804	−0.006	−0.085	−0.089	vv
		SS	2.038	2.021	−0.017	−0.103	−0.108	
		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_6	S_6	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	
S_8	S_8	SS	2.048	1.973	−0.075	−0.113	−0.113	xx
		SSS	107.9	116.0	8.1	0.4	0.4	
		SSSS	98.6	87.6	−11.0	−0.2	−0.2	
HF	Hydrogen fluoride	HF	0.917	0.938	0.021	0.039	−0.091	yy
CF	Fluoromethylidyne	CF	1.266	1.259	−0.007	−0.003	−0.007	a
CHF	Fluoromethylene	CH	1.121	1.100	−0.021	−0.001	0.006	a
		CF	1.314	1.284	−0.030	−0.029	−0.023	
		FCH	101.6	105.6	4.0	9.5	9.0	
CH_3F	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	
C_2H_3F	Fluoroethylene	CC	1.333	1.333	0.000	0.018	0.007	aaa
		CH(g)	1.076	1.093	0.017	0.023	0.028	
		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_3H_3F	Fluoroallene	C_1C_2	1.301	1.310	0.009	0.019	0.012	bbb
		C_1H	1.083	1.094	0.011	0.016	0.022	
		HC_1C_2	124.3	124.8	0.5	-1.4	-1.4	
		C_1F	1.360	1.340	-0.020	-0.035	-0.008	
		FC_1C_2	121.9	122.2	0.3	1.0	1.8	
		C_2C_3	1.309	1.294	-0.015	-0.006	-0.014	
		C_3H	1.086	1.087	0.001	0.005	0.015	
		HC_3C_2	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
		CF	1.262	1.297	0.035	0.011	0.045	
NOF	Nitrosyl fluoride	NF	1.520	1.367	-0.153	-0.215	-0.153	a
		NO	1.130	1.162	0.032	0.031	0.018	
		FNO	110.2	111.6	1.4	3.7	2.1	
F_2	Fluorine	FF	1.412	1.350	-0.062	-0.146	0.015	a
H_2F_2	Hydrogen fluoride dimer	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	
CF_2	Difluoromethylene	CF	1.300	1.298	-0.002	0.004	0.012	a
		FCF	104.9	106.3	1.4	3.4	1.1	
OF_2	F_2O	OF	1.412	1.378	-0.034	-0.131	-0.058	a
		FOF	103.2	100.9	-2.3	5.9	-0.7	
COF_2	Carbonyl 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	
SF_2	Sulfur difluoride	SF	1.592	1.560	-0.032	-0.020	0.031	a
		FSF	98.2	96.5	-1.7	1.3	-1.3	
CSF_2	Thiocarbonyl difluoride	CS	1.589	1.600	0.011	-0.014	-0.030	pp
		CF	1.315	1.338	0.023	0.006	0.027	
		FCS	126.5	128.9	2.4	-0.5	1.1	
SOF_2	Thionyl fluoride	SO	1.412	1.467	0.055	0.068	0.132	a
		SF	1.585	1.574	-0.011	0.023	0.058	
		FSO	106.8	101.0	-5.8	-3.9	-7.0	
		FSF	92.8	93.9	1.1	4.2	2.0	
SO_2F_2	Sulfuryl fluoride	SF	1.530	1.547	0.017	0.080	0.111	a
		FSF	96.1	95.3	-0.8	1.7	1.1	
		SO	1.405	1.400	-0.005	0.103	0.171	
		OSO	124.0	126.4	2.4	0.8	3.5	
S_2F_2	FSSF	SF	1.635	1.584	-0.051	-0.063	-0.006	a
		SS	1.888	2.008	0.120	0.078	0.060	
		FSS	108.3	112.0	3.7	-1.8	-2.1	
		FSSF	87.9	87.4	-0.5	-1.3	-0.8	
S_2F_2	SSF_2	SS	1.860	1.919	0.059	0.035	0.019	a
		SF	1.598	1.592	-0.006	0.003	0.054	
		FSS	107.5	114.5	7.0	1.4	1.3	
		FSF	92.5	90.8	-1.7	3.9	0.2	
CHF_3	Trifluoromethane	CH	1.098	1.110	0.012	0.038	0.032	a
		CF	1.333	1.346	0.013	0.020	0.035	
		FCH	110.3	113.1	2.8	1.2	2.7	
NF_3	Nitrogen trifluoride	NF	1.371	1.354	-0.017	-0.056	-0.011	a
		FNF	102.2	105.0	2.8	4.0	0.4	
C_2NF_3	Trifluoroacetonitrile	CC	1.461	1.487	0.026	0.037	0.025	a
		CF	1.335	1.350	0.015	0.020	0.036	
		CCF	111.4	113.4	2.0	0.5	2.1	
		CN	1.153	1.155	0.002	0.006	0.006	
CF_4	Carbon tetrafluoride	CF	1.321	1.337	0.016	0.026	0.037	ddd
C_2F_4	Tetrafluoroethylene	CC	1.311	1.355	0.044	0.070	0.057	aaa
		CF	1.319	1.326	0.007	-0.001	0.021	
		FCC	123.8	125.1	1.3	0.4	1.6	
SF_4	Sulfur tetrafluoride	SF	1.545	1.633	0.088	0.061	0.112	a
		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_2F_6	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_6	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	
		ClCH	103.4	115.5	12.1	6.0	7.7	
CH_3Cl	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	ClN	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_2Cl	NO_2Cl	ClN	1.830	1.818	−0.012	−0.020	−0.059	a
		NOCl	1.210	1.197	−0.013	−0.019	−0.024	
FCl	Chlorine fluoride	ClF	1.628	1.582	−0.046	0.022	0.019	a
O_3FCl	ClO_3F	ClF	1.630	1.690	0.060	0.105	0.051	a
		ClO	1.460	1.453	−0.007	0.270	0.328	
		OClF	95.2	102.8	7.6	11.0	3.0	
CHF_2Cl	Chlorodifluoromethane	CH	1.090	1.108	0.018	0.036	0.037	eee
		CCl	1.740	1.822	0.082	0.099	0.069	
		ClCH	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	
		FCClH	120.0	122.6	2.6	1.0	2.0	
F_3Cl	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	
		FClF′	87.5	120.0	32.5	32.5	32.5	
Cl_2	Chlorine	ClCl	1.986	2.035	0.049	0.010	−0.068	a
CH_2Cl_2	Dichloromethane	CCl	1.772	1.758	−0.014	0.014	−0.031	ddd
		ClCCl	111.8	107.9	−3.9	−0.6	1.2	
		CH	1.103	1.102	−0.001	0.000	0.010	
OCl_2	Cl_2O	ClO	1.701	1.700	−0.001	−0.018	0.032	a
		ClOCl	110.8	109.2	−1.6	2.1	0.3	
$COCl_2$	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	
		ClCO	124.4	124.2	−0.2	−0.5	−1.1	
SCl_2	Sulfur dichloride	SCl	2.015	2.031	0.016	−0.043	−0.090	a
		ClSCl	102.7	101.6	−1.1	3.6	3.1	
$SOCl_2$	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	
		ClSO	106.3	104.7	−1.6	0.3	−0.2	
S_2Cl_2	ClSSCl	SCl	2.057	2.044	−0.013	−0.081	−0.131	a
		SS	1.931	1.965	0.034	−0.011	−0.004	
		ClSSCl	108.2	113.1	4.9	0.0	−0.3	
CF_2Cl_2	Dichlorofluoromethane	CCl	1.770	1.808	0.038	0.055	0.037	a
		ClCCl	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	
$CHCl_3$	Chloroform	CCl	1.782	1.753	−0.029	0.000	−0.034	ddd
		ClCH	107.5	110.4	2.9	1.1	0.2	
$CFCl_3$	Trichlorofluoromethane	CF	1.330	1.349	0.019	−0.003	0.046	a
		CCl	1.760	1.779	0.019	0.046	0.026	
CCl_4	Carbon tetrachloride	CCl	1.760	1.747	−0.013	0.022	0.000	ddd
C_2Cl_6	Hexachloroethane	CC	1.550	1.512	−0.038	0.016	0.007	a
		CCl	1.740	1.754	0.014	0.050	0.020	
		ClCC	109.0	110.2	1.2	2.4	0.7	
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_3Br	Bromomethane	CBr	1.933	1.951	0.018	−0.055	−0.028	pp
		CH	1.086	1.090	0.004	0.016	0.024	
		HCBr	107.7	108.4	0.7	0.8	1.1	
C_2H_3OBr	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	
CNBr	Cyanogen bromide	BrC	1.789	1.796	0.007	−0.046	−0.029	a
		CN	1.158	1.155	−0.003	0.003	0.006	
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_3Br	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_3Br	Trifluorobromomethane	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_5Br	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_2	Bromine	BrBr	2.283	2.443	0.160	−0.115	−0.099	a
CH_2Br_2	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_2Br_4	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_3I	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_3I	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_5I	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_7I	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_2	Iodine	II	2.666	2.668	0.002	−0.151	−0.128	a
HAl	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_3	Aluminum trifluoride	AlF	1.630	1.644	0.014	−0.038	−0.014	a
AlF_4	$AlF_4(-)$	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
$AlCl_3$	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
$AlBr_3$	Aluminum tribromide	AlBr	2.270	1.875	−0.395	−0.095	−0.161	a
AlI_3	Aluminum triiodide	AlI	2.499	2.487	−0.012	−0.174	−0.190	a
Al_2	Al_2	AlAl	2.467	2.554	0.087	−0.175	−0.175	a
Al_2O	Al_2O	AlO	1.730	1.677	−0.053	−0.124	−0.012	a
H_2Si	Silylene (singlet)	SiH	1.519	1.513	−0.006	−0.139	−0.062	jjj
		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_4Si	Silane	SiH	1.481	1.488	0.007	−0.105	−0.020	a
$C_4H_{12}Si$	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_2	Difluorosilylene	SiF	1.591	1.575	−0.016	−0.013	0.021	a
		FSiF	101.0	95.3	−5.7	−4.1	−3.9	
$HSiF_3$	Trifluorosilane	SiH	1.447	1.507	0.060	−0.072	−0.007	a
		SiF	1.562	1.590	0.028	0.031	0.047	
		FSiH	110.6	112.6	2.0	3.0	1.2	
SiF_4	Tetrafluorosilane	SiF	1.552	1.580	0.028	0.032	0.052	a
SiCl	Chlorosilylidyne	SiCl	2.063	1.946	−0.117	0.009	−0.077	a
$SiCl_2$	Dichlorosilylene	ClSiCl	109.7	101.9	−7.8	−4.2	−5.3	kkk
$SiCl_4$	Silicon tetrachloride	SiCl	2.017	2.041	0.024	0.063	0.022	a
H_3SiBr	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	
$SiBr_4$	Silicon tetrabromide	SiBr	2.150	1.796	−0.354	0.040	0.093	a
H_3SiI	Iodosilane	SiI	2.437	2.012	−0.425	−0.051	−0.003	a
		SiH	1.486	1.492	0.006	−0.116	−0.020	
		HSiI	108.5	108.0	−0.5	−0.1	1.3	
SiI_4	Silicon tetraiodide	SiI	2.430	2.467	0.037	−0.097	−0.005	a
Si_2	Silicon dimer	SiSi	2.246	2.297	0.051	−0.259	−0.019	a
H_6Si_2	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_3P	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_3H_9P	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_3	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_3	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_3	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_5	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_3	Phosphorus trichloride	PCl	2.039	2.064	0.025	−0.050	−0.100	a
		ClPCl	100.3	99.7	−0.6	4.9	4.4	
PCl_5	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_3	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_2	Phosphorus dimer	PP	1.894	1.715	−0.179	−0.200	−0.200	a
P_4	Phosphorus tetramer	PP	2.210	2.197	−0.013	−0.158	−0.158	a
P_4O_6	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 semiempirical 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			2	3	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		3		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 ΔH_f. Most of the improvement is due to better prediction of hypervalent compounds, for example, SF_6 and H_2SO_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 essential.[6,25,33] Using the new parameter set, ΔH_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 (A) 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^{34} 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.

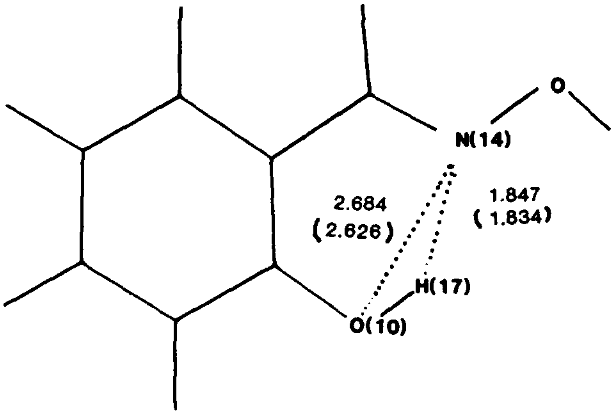

Figure 3. Intermolecular distances in salicylaldoxime. All distances in Angstroms. Observed distance in parentheses.

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-

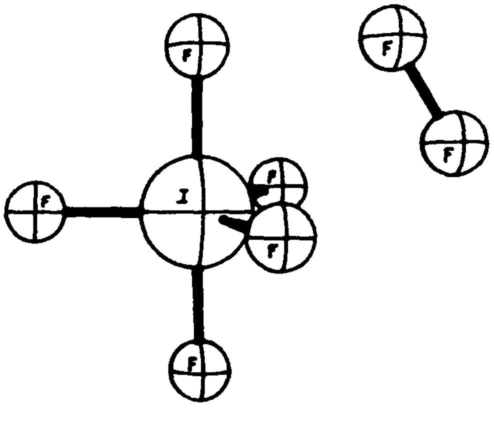

Figure 4. Calculated geometry for IF_7.

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

Table XIII. Comparison of experimental and calculated dipole moments.

Empirical formula	Chemical name	Dipole moment		Errors			Footnote
		Exp.	Calc.	PM3	MNDO	AM1	
C_3H_4	Cyclopropene	0.45	0.39	−0.06	0.03	−0.09	a
C_3H_4	Propyne	0.78	0.36	−0.42	−0.66	−0.38	a
C_3H_6	Propene	0.37	0.23	−0.14	−0.33	−0.14	a
C_3H_8	Propane	0.08	0.01	−0.07	−0.08	−0.08	a
C_4H_6	Bicyclobutane	0.68	0.43	−0.25	−0.27	−0.26	a
C_4H_6	Cyclobutene	0.13	0.15	0.02	−0.05	0.04	a
C_5H_6	Cyclopentadiene	0.42	0.53	0.11	−0.24	0.11	a
C_5H_8	Cyclopentene	0.20	0.15	−0.05	−0.15	−0.03	a
C_6H_6	Fulvene	0.42	0.66	0.24	0.27	0.27	b
C_7H_8	Toluene	0.36	0.26	−0.10	−0.30	−0.10	a
H_2O	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_2O	Formaldehyde	2.33	2.16	−0.17	−0.17	−0.01	a
CH_4O	Methanol	1.70	1.49	−0.21	−0.22	−0.08	a
C_2H_2O	Ketene	1.42	1.06	−0.36	−0.38	−0.07	a
C_2H_4O	Acetaldehyde	2.69	2.54	−0.15	−0.31	0.00	a
C_2H_4O	Ethylene oxide	1.89	1.77	−0.12	0.03	0.02	a
C_2H_6O	Ethanol	1.69	1.45	−0.24	−0.29	−0.14	a
C_2H_6O	Dimethyl ether	1.30	1.25	−0.05	−0.03	0.13	a
C_3H_6O	Acetone	2.88	2.78	−0.10	−0.37	0.04	a
C_4H_4O	Furan	0.66	0.22	−0.44	−0.24	−0.17	a
$C_4H_{10}O$	Diethyl ether	1.15	1.33	0.18	0.21	0.30	a
C_6H_6O	Phenol	1.45	1.14	−0.31	−0.29	−0.22	a
C_7H_8O	Anisole	1.38	1.08	−0.30	−0.31	−0.13	a
CH_2O_2	Formic acid	1.41	1.51	0.10	0.08	0.07	a
$C_2H_4O_2$	Acetic acid	1.74	1.83	0.09	−0.06	0.12	a
$C_2H_4O_2$	Methyl formate	1.77	1.59	−0.18	−0.15	−0.26	a
$C_3H_6O_2$	Propionic acid	1.75	1.81	0.06	−0.04	0.08	a
$C_3H_6O_2$	Methyl acetate	1.72	1.82	0.10	0.03	0.02	a
O_3	Ozone	0.53	1.71	1.18	0.65	0.67	a
H_3N	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_5N	Methylamine	1.31	1.40	0.09	0.17	0.18	a
C_2H_3N	Acetonitrile	3.92	3.21	−0.71	−1.29	−1.03	a
C_2H_3N	Methyl isocyanide	3.85	3.69	−0.16	−1.68	−1.02	a
C_2H_5N	Ethyleneimine (Azirane)	1.90	1.69	−0.21	−0.15	−0.15	a
C_2H_7N	Ethylamine	1.22	1.43	0.21	0.30	0.33	a
C_2H_7N	Dimethylamine	1.03	1.27	0.24	0.14	0.20	a
C_3H_3N	Acrylonitrile	3.87	3.25	−0.62	−0.90	−0.87	a
C_3H_9N	Trimethylamine	0.61	1.15	0.54	0.14	0.41	a
C_4H_5N	Pyrrole	1.74	2.18	0.44	0.07	0.21	c
C_5H_5N	Pyridine	2.22	1.94	−0.28	−0.26	−0.25	d
C_6H_7N	Aniline	1.53	1.30	−0.23	−0.07	0.01	a
CH_3NO	Formamide	3.73	3.12	−0.61	−0.62	−0.03	a
C_3H_7NO	Dimethylformamide	3.82	3.06	−0.76	−0.65	−0.27	a
HNO_2	Nitrous acid, trans	1.86	2.08	0.22	0.42	0.45	e
HNO_3	Nitric acid	2.17	2.32	0.15	0.61	0.40	a
CH_2N_2	Diazomethane	1.50	1.92	0.42	−0.25	−0.17	a
CH_2N_2	$N{=}N{-}CH_2{-}$	1.59	1.87	0.28	−0.04	0.04	a
CH_6N_2	Methylhydrazine	1.66	0.32	−1.34	−1.42	−0.89	f
N_2O	Nitrous oxide	0.17	0.26	0.09	0.59	0.47	a
CH_4S	Thiomethanol	1.52	1.95	0.43	0.15	0.44	g
C_2H_6S	Thioethanol	1.52	1.98	0.46	0.11	0.44	g
C_2H_6S	Dimethyl thioether	1.50	1.96	0.46	0.22	0.32	h
C_4H_4S	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_2	Sulfur dioxide	1.57	3.63	2.06	1.90	2.06	g
$C_2H_6S_2$	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_3F	Fluoromethane	1.86	1.44	−0.42	−0.10	−0.24	j
C_2HF	Fluoroacetylene	0.70	1.11	0.41	0.88	0.36	k
C_2H_3F	Fluoroethylene	1.43	1.37	−0.06	0.27	−0.05	h
C_2H_5F	Fluoroethane	1.96	1.58	−0.38	−0.09	−0.27	h
C_6H_5F	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_2F	Fluorine nitrite	0.47	0.89	0.42	0.19	0.35	g
CH_2F_2	Difluoromethane	1.96	1.81	−0.15	0.26	0.08	h
$C_2H_4F_2$	1,1-Difluoroethane	2.30	2.12	−0.18	0.20	−0.03	h
$C_6H_4F_2$	*o*-Difluorobenzene	2.59	2.74	0.15	0.77	0.09	m
OF_2	Difluorine oxide	0.30	0.38	0.08	0.02	−0.19	h
COF_2	Carbonyl fluoride	0.95	1.08	0.13	−0.14	0.33	g
N_2F_2	*cis*-Difluorodiazene	0.16	0.63	0.47	−0.14	0.50	g
CHF_3	Trifluoromethane	1.65	1.88	0.23	0.58	0.43	j
C_2HF_3	Trifluoroethylene	1.30	1.49	0.19	0.52	0.13	n
$C_2H_3F_3$	1,1,1-Trifluoroethane	2.32	2.40	0.08	0.55	0.27	h
$C_2HO_2F_3$	Trifluoroacetic acid	2.28	1.96	−0.32	0.17	−0.42	h
NF_3	Nitrogen trifluoride	0.24	0.26	0.02	−0.04	−0.20	h
C_2NF_3	Trifluoroacetonitrile	1.26	0.32	−0.94	−0.90	−1.23	o
COF_4	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_2HCl	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_2	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_3Br	Bromomethane	1.82	1.55	−0.27	−0.26	−0.34	a
C_2H_3Br	Bromoethylene	1.42	1.33	−0.09	−0.11	−0.12	s
C_2H_5Br	Bromoethane	2.03	1.85	−0.18	−0.37	−0.37	a
C_3H_7Br	1-Bromopropane	2.18	1.81	−0.37	−0.47	−0.48	a
C_6H_5Br	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_2H_3OBr	*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_3Br	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_2Br_2	Dibromomethane	1.43	1.45	0.02	−0.06	−0.11	s
$CHBr_3$	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_3I	Methyl iodide	1.65	1.44	−0.21	−0.28	−0.30	a
C_2H_5I	Iodoethane	1.91	1.83	−0.08	−0.50	−0.41	a
C_3H_7I	1-Iodopropane	2.04	1.78	−0.26	−0.57	−0.50	a
C_6H_5I	Iodobenzene	1.70	0.81	−0.89	−0.10	−0.27	a
CF_3I	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_2I_2	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_2H_6Si	Vinylsilane	0.66	0.24	−0.42	−0.12	−0.11	a
C_2H_8Si	Ethylsilane	0.81	0.37	0.44	−0.71	−0.45	g
C_2H_8Si	Dimethylsilane	0.75	0.46	−0.29	−0.57	−0.30	a
$C_3H_{10}Si$	Trimethylsilane	0.52	0.37	−0.15	−0.35	−0.13	a
H_2SiF_2	Difluorosilane	1.54	1.41	−0.13	0.69	0.03	a
$HSiF_3$	Trifluorosilane	1.27	1.51	0.24	1.53	0.28	a
H_2SiCl_2	Dichlorosilane	1.18	2.68	1.50	2.29	0.58	a
$HSiCl_3$	Trichlorosilane	0.86	2.38	1.52	1.87	0.56	a
H_2SiBr_2	*Dibromosilane*	1.43	3.09	1.66	1.90	0.38	s
$C_6H_{19}Si_2N$	Hexamethyldisilazane	0.37	0.35	−0.02	−0.10	0.24	a
H_3P	Phosphine	0.58	1.18	0.60	0.77	1.61	a
CH_5P	Methylphosphine	1.10	1.15	0.05	0.51	0.93	h
C_2H_7P	Dimethylphosphine	1.23	1.16	−0.07	0.58	0.67	h
C_3H_9P	Trimethylphosphine	1.19	1.08	−0.11	0.74	0.56	h
PF_3	Phosphorus trifluoride	1.03	2.25	1.22	1.41	1.06	a
POF_3	Phosphorus oxyfluoride	1.76	2.04	0.28	−0.56	0.18	a
H_4P_2	P_2H_4	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 ΔH_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 ΔH_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 ΔH_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 $SiOX_2$ and COX, X = Cl, Br, or I, the experimental ΔH_f reported is predicted to be incorrect by a few tens of kcals/mol. Although the new parameters were derived from experimental data, and consequently are subject to inaccuracies in those data, they are internally consistent, and thus the prediction is made that the experimental ΔH_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_2	Hydrogen	15.40	16.11	0.71	0.35	−0.48	a
CH_4	Methane	13.60	13.64	0.04	0.27	−0.29	b
C_2H_2	Acetylene	11.40	11.61	0.21	−0.39	0.10	a
C_2H_4	Ethylene	10.51	10.64	0.13	−0.34	0.04	a
C_2H_6	Ethane	12.00	11.98	−0.02	0.70	−0.23	a
C_3	Carbon, trimer	11.10	11.75	0.65	−0.06	0.23	a
C_3H_4	Allene	10.07	10.18	0.11	−0.05	0.07	a
C_3H_4	Cyclopropene	9.86	9.88	0.02	0.02	−0.04	c
C_3H_4	Propyne	10.37	10.89	0.52	0.35	0.37	b
C_3H_6	Cyclopropane	11.00	11.78	0.78	0.43	0.48	b
C_3H_6	Propene	9.88	10.10	0.22	0.08	0.11	d
C_3H_8	Propane	11.50	11.51	0.01	0.84	−0.18	e
C_4H_2	Diacetylene	10.17	10.47	0.30	−0.18	0.20	a
C_4H_6	1,2-Butadiene	9.15	9.72	0.57	0.69	0.52	a
C_4H_6	1-Butyne	10.20	10.77	0.57	0.48	0.42	a
C_4H_6	2-Butyne	9.60	10.34	0.74	0.87	0.57	a
C_4H_6	Cyclobutene	9.43	9.82	0.39	0.34	0.29	a
C_4H_6	1,3-Butadiene	9.08	9.47	0.39	0.06	0.25	b
C_4H_8	1-Butene	9.70	10.03	0.33	0.24	0.23	a
C_4H_8	Cyclobutane	10.70	11.02	0.32	1.11	0.29	a
C_4H_{10}	*n*-Butane	11.20	11.35	0.15	1.01	−0.03	a
C_4H_{10}	Isobutane	11.40	11.59	0.19	0.72	−0.11	e
C_5H_6	Cyclopentadiene	8.57	9.23	0.66	0.47	0.51	a
C_5H_8	Cyclopentene	9.18	9.52	0.34	0.54	0.26	a
C_5H_{10}	1-Pentene	7.90	10.15	2.25	2.07	2.09	a
C_5H_{10}	2-Methyl-1-butene	7.40	9.85	2.45	2.41	2.30	a
C_5H_{10}	2-Methyl-2-butene	8.70	9.39	0.69	0.94	0.55	a
C_5H_{10}	3-Methyl-1-butene	9.60	10.26	0.66	0.38	0.49	a
C_5H_{10}	Cyclopentane	10.50	11.07	0.57	1.56	0.47	a
C_5H_{12}	2-Methylbutane	10.30	11.44	1.14	1.70	0.90	a
C_5H_{12}	Neopentane	11.30	12.06	0.76	0.82	0.23	e
C_5H_{12}	*n*-Pentane	10.30	11.30	1.00	1.86	0.81	a
C_6H_6	Benzene	9.25	9.75	0.50	0.14	0.40	a
C_6H_{10}	Cyclohexene	10.30	9.59	−0.71	−0.55	−0.81	a
C_6H_{12}	Cyclohexane	10.30	11.29	0.99	1.44	0.64	a
C_7H_8	Cycloheptatriene	8.50	8.95	0.45	0.22	0.25	a
C_7H_8	Toluene	8.82	9.44	0.62	0.46	0.51	b
C_8H_{10}	Ethylbenzene	8.80	9.52	0.72	0.48	0.58	a
C_8H_{14}	Bicyclo(2.2.2)-octane	9.45	10.94	1.49	1.95	1.11	a
$C_{10}H_8$	Naphthalene	8.15	8.84	0.69	0.42	0.56	a
$C_{10}H_{16}$	Adamantane	9.60	10.85	1.25	1.67	0.83	a
$C_{14}H_{10}$	Anthracene	8.16	8.25	0.09	−0.11	−0.04	a
H_2O	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_2O	Formaldehyde	10.10	10.63	0.53	0.94	0.68	a
CH_4O	Methanol	10.96	11.14	0.18	0.46	0.17	a
C_2H_2O	Ketene	9.64	9.46	−0.18	−0.35	−0.04	a
C_2H_4O	Acetaldehyde	10.21	10.71	0.50	0.67	0.51	a
C_2H_4O	Ethylene oxide	10.57	11.34	0.77	0.92	0.76	b
C_2H_6O	Ethanol	10.60	10.90	0.30	0.70	0.28	a
C_2H_6O	Dimethyl ether	10.04	10.69	0.65	1.00	0.57	a
C_3H_6O	Acetone	9.72	10.77	1.05	1.04	0.95	a
C_3H_8O	Propanol	10.00	10.62	0.62	0.81	0.59	a
C_4H_4O	Furan	8.88	9.38	0.50	0.26	0.44	a
C_4H_6O	2-Butenal	9.90	10.50	0.60	0.49	0.57	a
C_4H_8O	Butanal	9.83	10.63	0.80	0.97	0.76	a
$C_4H_{10}O$	Diethyl ether	9.60	10.79	1.19	1.18	0.96	a
$C_5H_{12}O$	3-Pentanol	10.16	10.92	0.76	0.93	0.65	a
C_7H_6O	Benzaldehyde	9.70	10.05	0.35	0.04	0.30	a
C_7H_8O	Anisole	8.40	9.11	0.71	0.44	0.60	a
$C_{10}H_8O$	1-Napthol	7.80	8.59	0.79	0.54	0.69	a
$C_{10}H_8O$	2-Napthol	7.90	8.72	0.82	0.58	0.74	a
CO_2	Carbon dioxide	13.78	12.73	−1.05	−0.99	−0.57	b
CH_2O_2	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	
$C_2H_2O_2$	trans Glyoxal	10.59	10.57	−0.02	0.16	0.07	a
$C_2H_4O_2$	Acetic acid	10.80	11.44	0.64	0.77	0.82	a
$C_2H_4O_2$	Methyl formate	11.02	11.35	0.33	0.59	0.55	f
$C_2H_6O_2$	Dimethyl peroxide	10.60	10.77	0.17	0.09	0.29	a
C_3O_2	Carbon suboxide	10.60	10.22	−0.38	−0.53	−0.10	a
$C_3H_4O_2$	beta-Propiolactone	10.60	9.96	−0.64	−0.73	−0.54	a
$C_3H_6O_2$	Propionic acid	10.50	11.34	0.84	1.00	0.99	a
$C_3H_6O_2$	Methyl acetate	10.60	11.27	0.67	0.86	0.80	a
$C_5H_8O_2$	Acetylacetone	8.38	10.89	2.51	2.40	2.36	a
$C_7H_6O_2$	Benzoic acid	9.80	10.13	0.33	−0.03	0.28	a
O_3	Ozone	12.75	12.69	−0.06	−0.05	0.35	g
$C_4H_2O_3$	Malaic anhydride	10.84	11.71	0.87	0.86	1.18	a
$C_2H_2O_4$	Oxalic acid	11.20	11.67	0.47	0.59	0.76	a
H_3N	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_5N	Methylamine	9.60	9.40	−0.20	0.96	0.15	a
C_2H_3N	Acetonitrile	12.21	12.33	0.12	0.58	0.25	a
C_2H_3N	Methyl isocyanide	11.32	11.70	0.38	0.92	0.67	a
C_2H_5N	Ethyleneimine (Azirane)	9.90	9.92	0.02	0.78	0.41	a
C_2H_7N	Ethylamine	9.50	9.50	0.00	1.01	0.39	a
C_2H_7N	Dimethylamine	8.93	9.22	0.29	1.11	0.46	h
C_3H_3N	Acrylonitrile	10.91	10.89	−0.02	−0.30	−0.05	a
C_3H_5N	Ethyl cyanide	11.90	12.01	0.11	0.69	0.09	a
C_3H_9N	Trimethylamine	8.54	9.07	0.53	1.05	0.58	h
C_4H_5N	Pyrrole	8.21	8.93	0.72	0.35	0.45	a
C_5H_5N	Pyridine	9.67	10.10	0.43	0.02	0.26	a
C_6H_7N	Aniline	7.70	8.61	0.91	1.05	0.82	a
C_7H_5N	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_3NO_2	Nitromethane	11.30	12.17	0.87	0.24	0.68	a
CH_3NO_2	Methyl nitrite	11.00	10.64	−0.36	0.42	0.19	a
$C_3H_7NO_2$	Alanine	8.10	9.88	1.78	2.71	2.27	a
$C_6H_5NO_2$	Nitrobenzene	9.90	10.60	0.70	0.41	0.66	a
N_2	Nitrogen	15.60	13.80	−1.80	−0.73	−1.28	a
CH_2N_2	Diazomethane	9.00	9.22	0.22	−0.33	−0.18	a
CH_6N_2	Methylhydrazine	9.30	8.92	−0.38	0.36	−0.34	a
C_2N_2	Cyanogen	13.36	12.87	−0.49	−0.16	−0.05	a
$C_4H_4N_2$	Pyridazine	9.30	9.94	0.64	1.19	1.37	a
$C_4H_4N_2$	Pyrimidine	9.73	10.29	0.56	0.65	0.85	a
$C_4H_4N_2$	Pyrazine	9.90	10.16	0.26	0.12	0.35	a
N_2O_4	Dinitrogen tetroxide	11.40	11.61	0.21	0.65	−0.19	a
N_2O_5	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_2S	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_4S	Thiomethanol	9.44	9.21	−0.23	0.88	0.56	j
C_2H_4S	Thiirane	8.87	9.23	0.36	1.29	1.01	j
C_2H_6S	Thioethanol	9.21	9.19	−0.02	1.07	0.72	k
C_2H_6S	Dimethyl thioether	8.65	8.88	0.23	1.42	0.94	j
C_3H_6S	Thiethane	8.65	8.95	0.30	1.36	0.93	l
C_3H_8S	Isopropanthiol	9.14	9.22	0.08	1.12	0.78	a
C_3H_8S	1-Propanthiol	9.19	9.19	0.00	1.08	0.74	a
C_4H_4S	Thiophene	8.95	9.54	0.59	0.56	0.72	j
C_4H_8S	Tetrahydrothiophene	8.60	8.79	0.19	1.32	0.80	a
$C_4H_{10}S$	Butanethiol	9.15	9.19	0.04	1.12	0.78	a
C_6H_6S	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_2H_4SO	Thiolacetic acid	9.70	10.05	0.35	1.32	1.20	a
C_2H_6SO	Dimethyl sulfoxide	9.01	9.35	0.34	0.82	0.94	a
SO_2	Sulfur dioxide	12.30	10.55	−1.75	−0.51	−0.32	j
SO_3	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_2H_3NS	Methyl isothiocyanate	9.37	9.17	−0.20	0.51	0.34	a
C_2H_3NS	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_2S_2	Hydrogen disulfide	10.01	9.86	−0.15	0.72	0.34	m
CS_2	Carbon disulfide	10.08	9.83	−0.25	0.50	0.44	j
$C_2H_6S_2$	1,2-Ethanedithiol	9.00	9.32	0.32	1.43	1.13	a
$C_2H_6S_2$	Ethanedithiol-1,2	9.30	9.32	0.02	1.13	0.83	l
$C_2H_6S_2$	2,3-Dithiabutane	8.71	9.40	0.69	1.50	1.28	j
$C_2N_2S_2$	S2(CN)2	11.05	10.56	−0.49	0.66	0.43	a
$C_3H_4S_3$	1,3-Dithiolan-2-thione	8.40	9.25	0.85	1.59	1.42	a
S_8	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_3F	Fluoromethane	13.31	12.92	−0.39	−0.26	−1.21	o
C_2HF	Fluoroacetylene	11.30	11.56	0.26	−0.24	−0.15	a
C_2H_3F	Fluoroethylene	10.58	10.60	0.02	−0.41	−0.34	a
C_2H_5F	Fluoroethane	12.43	12.07	−0.36	0.18	−0.85	a
C_3H_7F	2-Fluoropropane	11.08	12.10	1.02	1.25	0.44	a
C_6H_5F	Fluorobenzene	9.19	9.81	0.62	0.28	0.35	a
$C_7H_5O_2F$	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_2F	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_2F_2	Difluoromethane	13.17	12.86	−0.31	−0.08	−1.15	o
C_2F_2	Difluoroacetylene	11.20	11.54	0.34	−0.03	−0.27	a
$C_2H_2F_2$	gem-Difluoroethylene	10.72	10.54	−0.18	−0.54	−0.73	a
$C_2H_4F_2$	1,1-Difluoroethane	12.80	12.82	0.02	−0.07	−0.87	a
$C_6H_4F_2$	*o*-Difluorobenzene	9.68	9.98	0.30	0.01	−0.05	a
$C_6H_4F_2$	*m*-Difluorobenzene	9.68	10.02	0.34	0.05	0.04	a
$C_6H_4F_2$	*p*-Difluorobenzene	9.30	9.87	0.57	0.26	0.19	a
OF_2	Difluorine oxide	13.26	13.47	0.21	0.26	−0.36	q
N_2F_2	trans-Difluorodiazene	13.40	11.91	−1.49	−0.40	−1.15	q
SF_2	Sulfur difluoride	10.20	9.81	−0.39	1.07	0.72	a
SOF_2	Thionyl fluoride	12.58	11.03	−1.55	0.09	−0.36	a
SO_2F_2	Sulfuryl fluoride	13.04	13.10	0.06	0.77	0.40	a
S_2F_2	FSSF	10.68	10.47	−0.21	1.03	0.73	a
CHF_3	Trifluoromethane	14.80	14.36	−0.44	−0.23	−1.49	a
C_2HF_3	Trifluoroethylene	10.54	10.68	0.14	−0.08	−0.45	a
$C_2H_3F_3$	1,1,1-Trifluoroethane	13.80	14.38	0.58	0.21	−0.68	a
$C_7H_5F_3$	Trifluoromethylbenzene	9.68	10.34	0.66	0.39	0.57	a
$C_2HO_2F_3$	Trifluoroacetic acid	12.00	12.47	0.47	0.73	0.49	a
NF_3	Nitrogen trifluoride	13.73	12.24	−1.49	0.20	−0.55	a
CF_4	Carbon tetrafluoride	16.23	16.79	0.56	0.58	−0.91	a
C_2F_4	Tetrafluoroethylene	10.50	10.84	0.34	0.42	−0.22	a
COF_4	Trifluoromethyl hypofluorite	13.60	14.18	0.58	0.63	0.07	a
N_2F_4	Tetrafluorohydrazine	12.00	12.46	0.46	1.04	0.47	a
SF_4	Sulfur tetrafluoride	12.05	10.41	−1.64	1.01	0.00	a
C_6HF_5	Pentafluorobenzene	9.75	10.55	0.80	0.65	0.32	a
C_2F_6	Hexafluoroethane	14.60	14.48	−0.12	−0.10	−1.37	a
C_6F_6	Hexafluorobenzene	10.90	10.85	−0.05	−0.13	−0.53	a
C_3OF_6	Perfluoroacetone	12.10	12.71	0.61	0.90	0.24	a
SF_6	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_3Cl	Methyl chloride	11.30	10.48	−0.82	0.94	0.04	a
C_7H_5OCl	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_2Cl	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_2FCl	Fluorochloromethane	11.74	10.85	−0.89	0.80	−0.16	a
CHF_2Cl	Difluorochloromethane	12.60	11.36	−1.24	0.63	−0.32	a
CF_3Cl	Trifluorochloromethane	10.30	11.88	1.58	3.83	2.94	a
CH_2Cl_2	Dichloromethane	11.30	10.58	−0.72	1.19	0.09	a
$COCl_2$	Carbonyl chloride	11.84	11.23	−0.61	0.86	0.53	a
SCl_2	Sulfur dichloride	9.70	9.60	−0.10	1.34	0.88	a
$SOCl_2$	Thionyl chloride	11.10	10.65	−0.45	1.45	0.91	a
SO_2Cl_2	Sulfuryl chloride	12.40	10.55	−1.85	−0.62	−0.64	a
S_2Cl_2	ClSSCl	9.40	9.96	0.56	2.04	1.63	a
$CHFCl_2$	Fluorodichloromethane	12.00	10.99	−1.01	0.96	0.03	a
CF_2Cl_2	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	
$CHCl_3$	Chloroform	11.48	10.84	−0.64	1.43	0.29	a
$CFCl_3$	Fluorotrichloromethane	11.90	11.16	−0.74	1.39	0.55	a
C_2Cl_6	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_3Br	Bromomethane	10.53	11.01	0.48	1.03	0.27	a
C_2H_3Br	Bromoethylene	9.90	10.44	0.54	0.35	0.25	a
C_2H_5Br	Bromoethane	10.28	10.91	0.63	1.20	0.41	a
C_3H_7Br	1-Bromopropane	10.18	10.93	0.75	1.29	0.51	a
C_6H_5Br	Bromobenzene	9.25	9.81	0.56	0.30	0.35	a
C_2H_3OBr	Acetyl bromide	10.55	11.20	0.65	0.88	0.63	s
CF_3Br	Bromotrifluoromethane	12.10	12.23	0.13	1.15	0.23	a
Br_2	Bromine	10.70	11.24	0.54	0.96	0.24	a
CH_2Br_2	Dibromomethane	10.50	10.59	0.09	1.20	0.46	a
$C_2F_4Br_2$	1,2-Dibromotetrafluoroethane	14.44	12.00	−2.44	−1.65	−2.53	a
$CHBr_3$	Bromoform	10.50	10.84	0.34	1.37	0.57	a
CBr_4	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_3I	Methyl iodide	9.50	9.47	−0.03	1.35	1.01	a
C_2H_5I	Iodoethane	9.34	9.44	0.10	1.48	1.09	a
C_3H_5I	3-Iodo-propene	9.30	9.44	0.14	0.99	0.93	a
C_3H_7I	1-Iodopropane	9.27	9.45	0.18	1.53	1.16	a
C_3H_7I	2-Iodopropane	9.40	9.43	0.03	1.39	1.00	a
C_4H_9I	1-Butyl iodide	9.20	9.45	0.25	1.60	1.23	a
C_6H_5I	Iodobenzene	8.70	9.05	0.35	0.85	0.95	a
$C_6H_{11}I$	Iodocyclohexane	8.91	9.42	0.51	1.86	1.47	a
C_7H_7I	*o*-Iodotoluene	8.53	9.02	0.49	0.98	0.99	a
C_7H_7I	*m*-Iodotoluene	8.55	9.01	0.46	0.96	0.97	a
C_7H_7I	*p*-Iodotoluene	8.38	8.94	0.56	1.07	1.03	a
C_7H_7I	Benzyl iodide	8.91	9.35	0.44	0.55	0.60	a
CF_3I	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_2	Iodine	9.34	9.53	0.19	1.53	1.33	v
CH_2I_2	Diiodomethane	9.46	8.98	−0.48	1.41	1.10	a
$C_2H_4I_2$	1,2-Diiodoethane	9.50	9.66	0.16	1.52	1.21	a
C_3H_9Al	Trimethylaluminum	9.76	10.12	0.36	0.92	0.43	w
C_2H_6Si	Vinylsilane	10.40	10.01	−0.39	−0.17	−0.01	a
C_2H_8Si	Ethylsilane	10.95	10.64	−0.31	0.19	0.12	j
C_2H_8Si	Dimethylsilane	11.20	10.65	−0.55	0.27	−0.03	a
$C_3H_{10}Si$	Trimethylsilane	10.80	10.51	−0.29	0.60	0.15	a
$C_4H_{12}Si$	Tetramethylsilane	10.40	10.42	0.02	0.94	0.52	a
H_2SiF_2	Difluorosilane	12.85	10.82	−2.03	−0.63	−1.24	x
SiF_4	Silicon tetrafluoride	15.81	15.19	−0.62	0.02	−1.09	y
H_2SiCl_2	Dichlorosilane	11.70	10.27	−1.43	0.82	−0.14	x
$C_2H_6SiCl_2$	Dichlorodimethylsilane	10.79	10.27	−0.52	1.43	0.70	a
$SiCl_4$	Silicon tetrachloride	11.79	11.23	−0.56	2.02	1.19	s
$C_6H_{19}Si_2N$	Hexamethyldisilazane	8.66	8.38	−0.28	1.03	0.83	z
H_3P	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_5P	Methylphosphine	9.72	8.66	−1.06	1.07	0.68	a
C_2H_7P	Dimethylphosphine	9.10	8.68	−0.42	1.14	0.91	a
C_3H_9P	Trimethylphosphine	8.60	8.81	0.21	1.25	1.16	j
$C_3H_9PO_3$	Trimethyl phosphite	9.22	9.69	0.47	1.69	1.88	aa
PF_3	Phosphorus trifluoride	9.71	10.70	0.99	3.42	2.75	t
POF_3	Phosphorus oxyfluoride	12.77	12.05	−0.72	0.40	−0.05	a
PCl_3	Phosphorus trichloride	10.50	10.42	−0.08	1.67	0.92	a
$POCl_3$	Phosphorus oxychloride	11.85	12.29	0.44	0.93	0.18	a
PCl_5	Phosphorus pentachloride	10.80	11.86	1.06	1.49	0.61	a
PBr_3	Phosphorus tribromide	10.00	10.84	0.84	1.44	0.76	a
PI_3	Phosphorus triiodide	9.15	9.97	0.82	1.29	1.02	a
P_2	Phosphorus dimer	10.62	8.91	−1.71	0.82	0.82	a
P_4	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.[15,16] 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 ±0.35 kcal/mol.

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