

## AM1 calculations for compounds containing mercury

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**Table IV. Average Errors in Geometries of Some Bond Lengths and Angles**

type of bond	no. of compds	AM1
Ge-H <sup>a</sup>	9	0.017
Ge-C	12	0.037
Ge-O	2	0.040
Ge-F	5	0.030
Ge-Cl	5	0.035
Ge-Br	2	0.042
CGeH	4	2.2
CGeCl	2	3.1

<sup>a</sup>All calculated bond lengths have positive errors (longer than the observed values).

later row elements. They have been attributed to the neglect of interactions between the inner-shell and valence-shell electrons, due to use of the core approximation in MNDO and AM1.

Table III compares the calculated geometries with experiment while Table IV analyses the average errors in the lengths of various kinds of bonds. The mean error for Ge-H bond lengths is much less in AM1 than MNDO. Since germanium forms long bonds, the average errors listed in Table IV are all small in percentage terms.

Figure 1 shows the AM1 geometries of some germanium compounds containing germanium double bonds. While no experimental values are available for comparison, results from a recent high level pseudopotential calculation are included (in parentheses) in Figure 1, for comparison. While both methods predict similar bond lengths, AM1 gives a larger H-Ge-H bond angle.

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## AM1 Calculations for Compounds Containing Mercury

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AM1 has been parametrized for mercury. Calculations are reported for a number of mercury-containing compounds. The results are generally better than those given by MNDO.

### Introduction

While the MNDO<sup>1</sup> and AM1<sup>2</sup> semiempirical SCF MO methods cannot be applied to transition metals because of the omission of d AOs, MNDO has been successfully extended to several main-group metals (lithium,<sup>3</sup> beryllium,<sup>4</sup> aluminum,<sup>5</sup> zinc,<sup>6</sup> tin,<sup>7</sup> lead,<sup>8</sup> and mercury<sup>9</sup>). Since AM1 has proved generally superior to MNDO, we are currently extending it to the "MNDO" elements. Here we report AM1 parameters for mercury.

### Procedure

The AM1 parameters for mercury were determined by a least-squares fit of the calculated (AM1) values of various properties of a selected set (basis set) of molecules to experiment, using a recently described<sup>7</sup> optimization procedure. This involves the minimization of an error function (SSQ) defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The best values for the weighting factors are found by trial-and-error, on the basis of the chemical acceptability of the final results. The minimization is carried out by a recently described procedure,<sup>7</sup> based on the Davidon-Fletcher-Powell (DFP) algorithm.<sup>10</sup> The first derivatives of the heats of formation and ionization energies with respect to the various parameters are calculated analytically. The derivative of the energy with respect to each geometrical variable is taken as a measure of the error in the latter.

The properties used in the parametrization included heats of formation, ionization energies, dipole moments, and geometries. The calculations were carried out by using

**Table I. Optimized AM1 Parameters for Mercury**

optimized parameters	value	MNDO
$U_{ss}$ , eV	-19.941 578	-19.809 574
$U_{pp}$ , eV	-11.110 870	-13.102 530
$\zeta_s$ , au	2.036 413	2.218 184
$\zeta_p$ , au	1.955 766	2.065 038
$\beta_s$ , eV	-0.908 657	-0.404 525
$\beta_p$ , eV	-4.909 384	-6.206 683
$\alpha$ , Å <sup>-1</sup>	1.484 734	1.335 641
$G_{ss}$	10.800 000	
$G_{pp}$	14.300 000	
$G_{sp}$	9.300 000	
$G_{p2}$	13.500 000	
$H_{sp}$	1.300 000	

the standard AM1 procedure and parameters, as implemented in the AMPAC program.<sup>11</sup> The only quantities

(1) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899, 4907.  
(2) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, 107, 3902.

(3) While parameters for lithium were developed some years ago by Professor W. Thiel and have been used with success in numerous studies of lithium compounds, notably by Professor Schleyer's group at Erlangen, they have never been formally published. They are, however, included in the MOPAC and AMPAC programs.

(4) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* 1978, 100, 777.

(5) Davis, L. P.; Guidry, R. M.; Williams, J. R.; Dewar, M. J. S. *J. Comput. Chem.* 1984, 11, 443.

(6) Dewar, M. J. S.; Merz, K. M., Jr. *Organometallics* 1984, 5, 1494.

(7) (a) Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* 1984, 106, 6771. (b) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *Ibid.* 1984, 106, 6773.

(8) Dewar, M. J. S.; Holloway, M. K.; Grady, G. L.; Stewart, J. J. P. *Organometallics* 1985, 4, 1973.

(9) Dewar, M. J. S.; Grady, G. L.; Merz, K. M., Jr.; Stewart, J. J. P. *Organometallics* 1985, 4, 1964.

(10) Davidon, W. C. *Comput. J.* 1958, 1, 406. Fletcher, R.; Powell, M. J. D. *Ibid.* 1963, 6, 163.

(11) Available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405 (Program No. 506).

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**Table II. Calculated Heats of Formation ( $\Delta H_f$ ), Ionization Potentials (IP), and Dipole Moments for Molecules Containing Mercury<sup>a</sup>**

compd	$\Delta H_f$ , kcal/mol			dipole moment, D			ionization energy, eV		
	AM1	obsd	error	AM1	obsd	error	AM1	obsd	error
Hg(CH <sub>3</sub> ) <sub>2</sub>	27.3	22.5 <sup>b</sup>	4.8				9.35	9.33	0.02
Hg(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	19.7	18.0 <sup>b</sup>	1.7	0.09			8.77	8.45	0.32
Hg( <i>i</i> -Pr) <sub>2</sub>	15.8	9.7	6.1				8.45		
Hg( <i>n</i> -Pr) <sub>2</sub>	7.8	8.2	-0.4	0.08			8.87	8.29	0.58
Hg( <i>n</i> -Bu) <sub>2</sub>	-3.9	-7.7 <sup>c</sup>	3.8	0.16			8.85		
Hg( <i>i</i> -Bu) <sub>2</sub>	7.6	-9.2 <sup>c</sup>	16.8	0.10			8.44		
Hg( <i>i</i> -Am) <sub>2</sub>	-12.4	-19.8 <sup>c</sup>	7.4	0.15			8.81		
<i>n</i> -PrHgCl	-22.2			3.65			10.26	10.15	0.11
<i>i</i> -PrHgCl	-18.2			3.78			9.76	9.80	-0.04
Hg(CN) <sub>2</sub>	84.3	91.0	-6.7				12.64		
HgF <sub>2</sub>	-54.2	-70.2	16.0				12.68		
HgCl <sub>2</sub>	-44.8	-35.0	-9.8				11.93	11.37	0.56
HgBr <sub>2</sub>	-43.9	-20.4	-23.5				11.16	10.62	0.54
HgI <sub>2</sub>	19.1	-4.1 <sup>b</sup>	23.2				10.38	9.5	0.88
CH <sub>3</sub> HgCl	-12.5	-12.5 <sup>b</sup>	0.0	3.50	3.36	0.14	10.88	10.84 <sup>d</sup>	0.04
CH <sub>3</sub> HgBr	-11.0	-4.4 <sup>b</sup>	-6.6	3.15	3.10	0.05	10.59	10.16 <sup>d</sup>	0.43
CH <sub>3</sub> HgI	21.2	5.2	16.0	3.10	2.90	0.20	9.90	9.25	0.65
C <sub>2</sub> H <sub>5</sub> HgCl	-16.4	-15.0 <sup>b</sup>	-1.4	3.65	2.99	0.66	10.16	10.22	-0.06
C <sub>2</sub> H <sub>5</sub> HgBr	-14.9	-7.2 <sup>b</sup>	-7.7	3.27	2.80	0.47	9.94		
C <sub>2</sub> H <sub>5</sub> HgI	17.1	3.3	13.8	3.20	3.04	0.16	9.66		
HgPh <sub>2</sub>	101.2	93.8	7.4				9.36		
PhHgCl	26.4	24.8	1.6	2.87	2.99	-0.12	9.76	9.40 <sup>d</sup>	0.36
HgCH <sub>3</sub>	38.2	40.0 <sup>b</sup>	-1.8	1.04			8.22		
HgF	-10.7	1.0 <sup>b</sup>	-11.7	3.83			10.59		
HgCl	-2.7	20.1 <sup>b</sup>	-22.8	4.84			10.20		
HgBr	-3.5	24.9	-28.4	4.57			9.81		
HgI	25.7	31.6 <sup>b</sup>	-5.9	4.44			9.44		
HgH	55.9	57.2	-1.3	2.06			8.67		
Hg <sub>2</sub>	28.0	26.0	2.0				8.69		
HgO(singlet)	102.7	10.0	92.7	5.32			10.64		
HgO(triplet)	65.3			4.13			5.69		
Hg	14.7	14.7	0.0				9.14	10.44	-1.30
Hg <sup>1+</sup>	225.5	256.8	-31.3				19.94		
Hg <sup>2+</sup>	685.4	690.4	-5.0						
Hg <sub>2</sub> <sup>+</sup>	220.7	244.1	-23.4				15.59		
HgMe <sub>2</sub> <sup>+</sup>	229.4	233.7 <sup>b</sup>	-4.3				15.19		
HgMe <sup>+</sup>	220.8	222.0 <sup>b</sup>	-1.2				15.59		

<sup>a</sup> Except where noted, for references to experimental values, see: Dewar, M. J. S.; Grady, G. L.; Merz, K. M., Jr.; Stewart, J. J. P. *Organometallics* 1985, 4, 1964. <sup>b</sup> Wagman, D. D., et al. *J. Phys. Chem. Ref. Data* 1982, 11, Suppl. 2. <sup>c</sup> Pedley, J. B.; Rylance, J. Sussex—N.P.L. Computer Analyzed Thermochemical Data; University of Sussex, Sussex 1977. <sup>d</sup> Baidin, V. N.; Timoshenko, M. M.; Chizhov, Yu. V., et al. *J. Organomet. Chem.* 1985, 292, 55.

in AM1 that depend on the period to which an atom belongs are the relevant overlap integrals. AMPAC provides for their calculation for all elements.

### Results and Discussion

AM1 differs from MNDO primarily in the use of a different core repulsion function, the MNDO function being augmented by additional Gaussian terms. These terms were, however, omitted in the case of mercury because their inclusion led to no significant improvement. As in the case of MNDO, different values of the parameters  $\zeta$  and  $\beta$  had to be used for s and p AOs.

Table I shows the final values of the AM1 parameters for mercury, in the usual<sup>2</sup> notation. The one-center two-electron parameters ( $g$  and  $h$ ) were set equal to the MNDO values.<sup>9</sup>

Table II shows the heats of formation ( $\Delta H_f$ ), dipole moments ( $\mu$ ), and first ionization potentials (IP), calculated for a number of molecules containing mercury, together with available experimental values. The IPs were estimated from orbital energies, using Koopmans' theorem.

The calculated heats of formation (Table II) agree reasonably well with experiment, particularly since there is considerable uncertainty concerning the accuracy of the experimental values.<sup>12</sup> The only enormous error is for

**Table III. Comparison of Errors**

property	no. of compds	mean absolute error	
		AM1	MNDO
heat of formation, kcal/mol	27	8.88	11.50
dipole moment, D	7	0.23	0.18
ionization energy, eV	13	0.44	1.03

HgO, where MNDO fared almost equally badly. Unfortunately HgO seems to be the only compound containing both mercury and oxygen for which an experimental heat of formation is available and even this is dubious.<sup>13</sup> Nevertheless it does seem likely that the AM1 value is much too positive.

A likely source of such an error is the failure of MNDO and AM1 to allow for changes in orbitals with atomic charge, particularly when a large negative charge is concentrated on one atom; cf. the large positive errors<sup>14</sup> in the AM1 heats of formation for HO<sup>-</sup> or NH<sub>2</sub><sup>-</sup>. Since the calculated (AM1) dipole moment of HgO (5.32) corresponds to a formal charge of ca. -0.6e on oxygen and since the neglect of orbital expansion will make this value too

(13) The heat of formation reported for HgO was estimated indirectly. See: Pedley, J. B.; Marshall, E. M. *J. Phys. Chem. Ref. Data* 1983, 12, 967.

(14) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* 1986, 108, 8075.

(12) Pilcher, G. *Int. Rev. Sci.: Phys. Chem., Ser Two* 1975, 10, 45.

Table IV. Calculated and Observed Geometrical Parameters<sup>a</sup>

molecule	point group	geometries calcd (obsd)			
HgMe <sub>2</sub>	C <sub>3d</sub>	HgC	2.052 (2.083) <sup>b</sup>		
HgPh <sub>2</sub>	C <sub>2h</sub>	HgC	2.052 (2.085)		
HgMeCl <sup>b</sup>	C <sub>3v</sub>	HgC	2.050 (2.052), HgCl	2.254 (2.285), CHgCl	180.0 (180.0)
HgMeBr <sup>b</sup>	C <sub>3v</sub>	HgC	2.050 (2.061), HgBr	2.257 (2.405), CHgBr	180.0 (180.0)
HgMeI	C <sub>3v</sub>	HgC	2.053 (2.087), HgI	2.494 (2.528), CHgI	180.0 (180.0)
HgMeCN	C <sub>3v</sub>	HgC	2.046 (2.082), HgC(N)	2.012 (2.051), HgCN	180.0 (180.0)
		CN	1.168 (1.141)		
Hg(CF <sub>3</sub> ) <sub>2</sub>	D <sub>3h</sub>	HgC	2.210 (2.101), CF	1.376 (1.345), FCF	103.5 (106.8)
cis-ClHgCH=CHCl	C <sub>s</sub>	HgCl	2.250 (2.27), HgC	2.059 (2.14), ClHgC	170.8 (169.0)
HgCl <sub>2</sub>	D <sub>∞h</sub>	HgCl	2.239 (2.252), ClHgCl		180.0 (180.0)
HgBr <sub>2</sub>	D <sub>∞h</sub>	HgBr	2.249 (2.44), BrHgBr		180.0 (180.0)
HgI <sub>2</sub>	D <sub>∞h</sub>	HgI	2.496 (2.554), IHgI		180.0 (180.0)
HgF <sub>2</sub>	D <sub>∞h</sub>	HgF	1.908 (1.96), FHgF		180.0 (180.0)
HgCl	C <sub>∞v</sub>	HgCl	2.239 (2.23)		
HgF	C <sub>∞v</sub>	HgF	1.870 (1.89)		
HgBr	C <sub>∞v</sub>	HgBr	2.229 (2.33)		
HgI	C <sub>∞v</sub>	HgI	2.526 (2.49)		
PhHgBr	C <sub>2v</sub>	HgBr	2.251 (2.435), HgC	2.051 (2.071)	
HgO(singlet)	C <sub>∞v</sub>	HgO	2.062 (1.841)		
HgO(triplet)		HgO	2.130		

<sup>a</sup> Except where noted, for references, see: Dewar, M. J. S.; Grady, G. L.; Merz, K. M., Jr.; Stewart, J. J. P. *Organometallics* 1985, 4, 1964.

<sup>b</sup> Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A., et al. *J. Phys. Chem. Ref. Data* 1979, 8(3), 619.

Table V. Calculated Formal Charges

compds	charge on	
	Hg	others
HgPh <sub>2</sub>	+0.624	(C) -0.287
Hg(CF <sub>3</sub> ) <sub>2</sub>	+0.692	(C) +0.204
Hg(CN) <sub>2</sub>	+0.718	(C) -0.310
HgF <sub>2</sub>	+0.889	(F) -0.444
HgCl <sub>2</sub>	+0.645	(Cl) -0.323
HgBr <sub>2</sub>	+0.540	(Br) -0.270
HgI <sub>2</sub>	+0.374	(I) -0.187
HgH <sub>2</sub>	+0.395	(H) -0.197
HgFMe	+0.633	(F) -0.531, (C) -0.363
HgClMe	+0.546	(Cl) -0.418, (C) -0.389
HgBrMe	+0.504	(Br) -0.340, (C) -0.418
HgI Me	+0.434	(I) -0.248, (C) -0.436
HgHMe	+0.454	(H) -0.188, (C) -0.476
HgMe <sub>2</sub>	+0.511	(C) -0.467
HgEt <sub>2</sub>	+0.501	(C) -0.404
HgMeCN	+0.616	(C) -0.390, (CN) -0.375

small, the real negative charge on oxygen must be much larger.

As Table II shows, AM1 predicts HgO to have a triplet ground state with a large singlet-triplet splitting (37 kcal/mol). It seems most unlikely that this can be the case, given that formation of the triplet from the singlet involves loss of an HgO bond. It seems likely that both predictions are further erroneous consequences of the neglect of orbital expansion in AM1.

The two unpaired "triplet" electrons are necessarily segregated in AOs of oxygen and mercury and should therefore make no significant contribution to the polarity of HgO. The dipole moment calculated for the triplet is indeed less than that for the singlet (Table I). Since the errors in the AM1 heats of formation of anions decrease rapidly with even a small decrease in the "localized" negative charge,<sup>14</sup> the error in the AM1 heat of formation for triplet HgO should be much less than that for singlet HgO. Indeed, the AM1 value for the triplet, combined with the experimental value for the singlet, leads to a triplet excitation energy of 55 kcal/mol, which is not unreasonable.

If HgO is neglected, the average absolute error in the heats of formation of the remaining 27 molecules in Table

II is 9.2 kcal/mol, significantly less than the corresponding MNDO error (13.3 kcal/mol).

Table II also lists results for the few ionic compounds of mercury for which gas-phase heats of formation have been reported. The agreement is satisfactory.

Calculated (AM1) dipole moments are compared with experiment in Table II, the experimental values being for measurements in solution (benzene). The average unsigned error for seven molecules is 0.23 D, close to the MNDO value. In the case of methylmercuric iodide, the dipole moment in benzene (2.90 D) is much less than the value (1.30 D) derived from a microwave study in the gas phase.<sup>8</sup> This discrepancy is surprising because gas-phase dipole moments usually agree closely with those measured in benzene<sup>9</sup> and because the AM1 values agree closely with those measured in solution for all four methylmercury halides.

The AM1 ionization potentials, derived from Koopmans' theorem, agree well with experiment (Table II), the mean absolute error being 0.44 eV. This is much less than the corresponding error in MNDO (1.03 eV).

Table IV compares with experiment the geometries calculated for a number of mercury-containing molecules. The agreement is satisfactory. Both AM1 and MNDO predict compounds of divalent mercury to be linear, in agreement with experiment. The errors in bond lengths are uniformly less in AM1 than in MNDO, particularly for Hg-C bonds where the average unsigned error is much less (AM1, 0.039 Å; MNDO, 0.102 Å).

Table V shows the formal charges calculated by AM1 for Hg, and the atoms attached to Hg, in a number of mercury compounds. While no reliable estimates are available for comparison, the values seem reasonable in relation to the relative electronegativities of the atoms concerned.

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