under argon and the tetrahydrofuran removed in vacuo to leave a black tar. This was then redissolved in degassed hexane and refiltered to give a clear, deep red solution. The hexane solution was transferred to a sublimation vessel, where the solvent was first removed in vacuo and then the excess **4b** removed by sublimation at $10^{-6}$ torr. UV-visible (THF): 353, 408, and 475 nm.

**Cr + Poly[(dimethylsiloxane)-*co*-(naphthoxymethylsiloxane)], 5.** Chromium (1.5 g, 28.5 mmol) was evaporated over a period of 90 min into 120 mL of **5** [$C_{10}H_7OSiMe:Si(Me)_2$ ratio = 1:13] within a rotary solution reactor.[29] The flask was cooled to ~270 K so as to maintain a pressure of less than $10^{-3}$ torr during the metal evaporation. After the crucible was allowed to cool at the end of the reaction, the flask was backfilled with argon and the resulting deep red liquid extracted into a Schlenk tube. The extremely air-sensitive liquid was then filtered through a glass frit to remove excess metal particles. From the UV-visible spectrum of the product it was possible to determine that 10-12% of the naphthalene groups present were complexed, corresponding to a 20% yield of product based on metal evaporated. UV-visible ($C_6H_{12}$): 354, 408, and 470 nm.

**Ligand Substitution Reactions.** In the reaction of the bis(naphthalene)chromium complexes of **4b** and **5** with carbon monoxide two methods were employed: (i) A saturated solution of the complex was prepared in degassed hexane (30 mL) in a Schlenk tube fitted with a rubber septum and magnetic stir bar. Carbon monoxide was bubbled through the stirred solution, and aliquots of the reaction mixture were taken for infrared spectroscopic examination. (ii) A saturated solution was placed in an ampule with a magnetic stir bar. One atmosphere of carbon monoxide was added and the mixture stirred overnight. The solvent was removed in vacuo leaving an orange oil.

In all cases two products were formed. $Cr(CO)_6$ was identified by its $\nu_{CO}$ stretching frequency at 1990 $cm^{-1}$ and could be sublimed from the product oil. The (naphthalene)$Cr(CO)_3$ complexes for **4b** and **5** were identified by $^1H$ and $^{13}C$ NMR and IR spectroscopy for the former and IR spectroscopy for the latter. IR spectra (hexane) of the (naphthalene)$Cr(CO)_3$ complexes: for **4b**, $\nu(CO)$ = 1976, 1913, 1898 $cm^{-1}$; for **5**, $\nu(CO)$ = 1978, 1910, 1895 $cm^{-1}$. Reaction of the (naphthalene)$_2$Cr complexes with RNC (R = *t*-Bu, c-Hex) was performed by adding the isocyanide to a hexane solution of the complex under an argon atmosphere and stirring for approximately 3 h. The IR spectra of the products in all cases contained an extremely broad band due to $\nu(CN)$ with maximum absorption in the 1900 $cm^{-1}$ region. The products were identified as the corresponding $Cr(CNR)_6$ complexes from their IR data.[13]

**Acknowledgment.** We wish to acknowledge the support of the 3-M Co., and partial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.** 1, 17882-66-5; **2**, 17882-88-1; **4a**, 98194-75-3; **4b**, 98216-99-0; I (M = Cr), 98194-72-0; I (M = V), 98194-73-1; II (M = Cr), 98300-87-9; II (M = V), 98300-88-0; $D_4$, 556-67-2; $Cr(CO)_6$, 13007-92-6; ($\eta^6$-$C_{10}H_7O$-$D_4$*)$Cr(CO)_3$, 98194-74-2; $Cr(CN\text{-}t\text{-}Bu)_6$, 61817-78-5; $Cr(CN\text{-}c\text{-}Hc)_6$, 68829-55-0; Cr, 7440-47-3; V, 7440-62-2; Ti, 7440-32-6; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; *tert*-butyl isocyanide, 7188-38-7; cyclohexyl isocyanide, 931-53-3.

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# MNDO Calculations for Compounds Containing Mercury[1]

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*Received February 14, 1985*

MNDO has been parametrized for mercury. Calculations are reported for a number of compounds of mercury. The results are comparable with those for other metals.

## Introduction

The MNDO method[4,5] is now established[6] as a practical procedure for studying chemical behavior, giving results comparable[7] with those from quite good ab initio models (e.g., 4-31G) while requiring only one-thousandth as much computer time. Parameters have been reported for hydrogen,[4] for the second-period elements beryllium,[8] boron,[9] carbon,[4] nitrogen,[4] oxygen,[4] and fluorine,[10] for the third-period elements aluminum,[11] silicon,[12] phosphorus,[12] sulfur,[13] and chlorine,[14] and for bromine,[15] iodine,[16] and tin.[17]

**Table I. MNDO Parameters for Mercury**

| optimized parameters | value | derived parameters | value |
|---|---|---|---|
| $U_{ss}$ | $-19.809\,574^a$ | $E_{heat}$ | $14.69^b$ |
| $U_{pp}$ | $-13.102\,530^a$ | $E_{el}$ | $-28.819\,148^a$ |
| $\zeta_s$ | $2.218\,184^c$ | $D_1$ | $1.737\,804\,8^d$ |
| $\zeta_p$ | $2.065\,038^c$ | $D_2$ | $1.460\,806\,4^d$ |
| $\beta_s$ | $-0.404\,525^a$ | $A_M$ | $0.396\,912\,9^d$ |
| $\beta_p$ | $-6.206\,683^a$ | $A_D$ | $0.304\,769\,4^d$ |
| $A_{1p}$ | $1.335\,641^e$ | $A_Q$ | $0.348\,310\,2^d$ |
| $G_{ss}$ | $10.800\,000^a$ | | |
| $G_{pp}$ | $14.300\,000^a$ | | |
| $G_{sp}$ | $9.300\,000^a$ | | |
| $G_{p2}$ | $13.500\,000^a$ | | |
| $H_{sp}$ | $1.300\,000^a$ | | |

[a] In eV. [b] In kcal/mol at 298 K (heat of atomization). [c] Atomic units (Bohrs). [d] In atomic units. [e] In $Å^{-1}$.

Since d AOs are not currently included[17] in MNDO, calculations are confined to compounds involving only normal group valencies. Schleyer et al.[18] have reported extensive

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[1] Part 74 of the series "Ground States of Molecules". For part 73 see Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P., to be submitted for publication.

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0276-7333/85/2304-1964$01.50/0 © 1985 American Chemical Society

**Table II. Calculated Heats of Formation ($\Delta H_f$), First Ionization Energies ($I_1$), and Dipole Moments ($\mu$)**

| | $\Delta H_f$, kcal/mol | | $\mu$, D | | $I_1$, eV | |
|---|---|---|---|---|---|---|
| compd | calcd | obsd | calcd | obsd | calcd | obsd |
| $HgMe_2$ | 10.12 | 22.3[a] | 0.0 | | 10.16 | 9.33[b] |
| $HgEt_2$ | 11.74 | 17.8[a] | 0.08 | | 9.80 | 8.45[b] |
| $HgPh_2$ | 101.72 | 93.8[a] | 0.0 | | 11.94 | |
| Hg-*i*-$Pr_2$ | 22.75 | 9.7[a] | 0.202 | | 9.61 | |
| Hg-*n*-$Pr_2$ | 5.30 | 8.2[a] | 0.584 | | 9.79 | 8.29[b] |
| $HgCN_2$ | 69.06 | 91.0[f] | 0.0 | | 13.02 | |
| $HgF_2$ | −66.86 | −70.20[c] | 0.0 | | 13.64 | |
| $HgCl_2$ | −36.96 | −34.97[c] | 0.0 | | 12.59 | 11.37[d] |
| $HgBr_2$ | 3.71 | −20.4[c] | 0.0 | | 11.63 | 10.62[d] |
| $HgI_2$ | 21.14 | −3.85[c] | 0.0 | | 10.62 | 9.5[d] |
| HgMeCl | −18.02 | −12.3[a] | 3.42 | 3.36[e] | 11.68 | 10.88[d] |
| HgMeBr | 2.77 | 5.2[a] | 3.20 | 3.10[e] | 11.07 | 9.25[d] |
| HgMeI | 13.47 | 5.2[a] | 2.88 | 2.9[e] | 10.20 | 9.25[d] |
| HgEtCl | −16.77 | −12.30[a] | 3.37 | 2.99[e] | 11.13 | 10.22[g] |
| HgEtBr | 3.92 | −4.40[a] | 3.13 | 2.8[e] | 11.00 | |
| HgEtI | 14.41 | 3.3[a] | 2.79 | 3.04[e] | 10.23 | |
| Hg-*n*-PrCl | −20.09 | | 3.41 | | 11.11 | 10.15[g] |
| Hg-*i*-PrCl | −10.82 | | 3.32 | | 10.84 | 9.80[g] |
| HgPhCl | 29.75 | 24.8[a] | 2.996 | 2.99[e] | 9.50 | |
| HgF | −24.50 | 0.7[c] | 3.81 | | 11.05 | |
| HgCl | −6.33 | 18.75[c] | 4.99 | | 10.84 | |
| HgBr | 14.75 | 24.9[c] | 4.9 | | 10.49 | |
| HgI | 24.38 | 31.9,[c] 47.94[f] | 4.53 | | 9.84 | |
| HgH | 37.74 | 57.2[f] | 1.98 | | 9.54 | |
| HgMe | 28.89 | 40.0[f] | 1.38 | | 8.66 | |
| $Hg^0$ | 14.69 | 14.69[h] | | | 9.01 | 10.437[h] |
| $Hg^{1+}$ | 222.46 | 256.82[f] | | | 5.40 | |
| $Hg^{2+}$ | 679.29 | 690.83[f] | | | | |
| $Hg_2$ | 30.22 | 26.0[f] | | | 8.48 | |
| HgO (singlet) | 101.58 | 10.0[c] | 3.74 | | 10.26 | |
| HgO (triplet) | 60.15 | | 3.76 | | 5.54 | |

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MNDO calculations for compounds containing lithium, but the parameters for lithium have not yet been published.

In our continuing program of improving and extending the scope of MNDO, mercury seemed an obvious target, for several reasons. First, because organomercury chemistry is not only interesting and varied but has also played an important role in synthetic and mechanistic organic chemistry. Secondly, because mercury is a metal and, at the time we began this work, MNDO parameters were available for only three metals (Be, Al, Sn). Thirdly, because MNDO parameters are not as yet available for *any* of the elements in group 2.[22] We would have preferred, in this connection, to parametrize zinc, but the dearth of thermochemical data for compounds of zinc presented problems. We hoped that experience gained from parametrizing mercury would later help to overcome this obstacle.

## Procedure

The calculations were carried out by using the standard MNDO procedure and parameters, as implemented in the MOPAC[19] package of computer programs. The only quantities in MNDO that depend on the period to which an atom belongs are the relevant overlap integrals. MOPAC provides for their calculation for all elements. The parameters were determined in the usual way, by minimizing the sum ($Y$) of the weighted squares of errors in various properties of a *basis set* of molecules, the properties including heats of formation, dipole moments, geometries, and ionization energies. A new procedure was used to optimize the parameters, involving their first and second derivatives with respect to $Y$. The derivatives were calculated analytically, with the exception of those for dipole moments, which were evaluated by finite difference. This procedure was 300–2000 times faster than the original nonderivative method.[4]

## Results and Discussion

Table I shows the final parameters for mercury, in the notation used previously.[4-17] They present no unexpected features.

Table II shows the heats of formation ($\Delta H_f$), first ionization energies, and dipole moments ($\mu$) calculated for 30 molecules containing mercury, together with available experimental values for comparison. The ionization energies were estimated from orbital energies, using Koopmans' theorem.

With the exception of mercuric oxide (HgO), the calculated heats of formation agree reasonably well with experiment, particularly since there is considerable uncertainty[20] concerning the accuracy of the experimental values. Excluding HgO, the average absolute error is 12.1

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**Table III. Calculated (Observed) Geometrical Parameters**

| molecule | bond lengths (Å), calcd (obsd) | bond angles (deg), calcd (obsd) |
|---|---|---|
| $HgMe_2$ | HgC, 1.990 (2.083[a]) | CHgC, 180.0 (180.0[b]) |
| $HgPh_2$ | HgC, 2.020 (2.085[c]) | |
| HgMeCl | HgC, 1.983 (2.061[d])<br>HgCl, 2.290 (2.282[d]) | CHgCl, 180.0 (180.0[d]) |
| HgMeBr | HgC, 1.985 (2.074[d])<br>HgBr, 2.390 (2.406[d]) | CHgBr, 180.0 (180.0[d]) |
| HgMeI | HgC, 1.990 (2.087[e])<br>HgI, 2.480 (2.528[e]) | CHgI, 180.0 (180.0[e,b]) |
| HgMeCN | HgC, 1.980 (2.082[e])<br>HgCN, 1.934 (2.051[e])<br>CN, 1.170 (1.141[e]) | HgCN, 180.0 (180.0[e,b]) |
| $HgCl_2$ | HgCl, 2.274 (2.27,[f] 2.252[g]) | ClHgCl, 180.0 (180.0[g,b]) |
| $HgBr_2$ | HgBr, 2.380 (2.44[f]) | BrHgBr, 180.0 (180.0[b]) |
| $HgI_2$ | HgI, 2.491 (2.61,[f] 2.554[h]) | IHgI, 180.0 (180.0[b]) |
| $HgF_2$ | HgF, 1.885 (1.96[i]) | FHgF, 180.0 (180.0[b]) |
| HgCl | HgCl, 2.280 (2.23[i]) | |
| HgF | HgF, 1.870 (1.89[i]) | |
| HgBr | HgBr, 2.370 (2.33[i]) | |
| HgI | HgI, 2.470 (2.49[i]) | |
| $Hg(CF_3)_2$ | HgC, 2.260 (2.101[j])<br>CF, 1.367 (1.345[j]) | <br>FCF, 104.3 (106.8[j]) |
| *cis*-ClHgCH=CHCl | HgCl, 2.280 (2.27[k])<br>HgC, 1.966 (2.14[k]) | ClHgC, 176.4 (169.0[k]) |
| HgPhBr | HgBr, 2.380 (2.4351)<br>HgC, 2.000 (2.071) | |
| HgO (singlet) | HgO, 1.880 (1.84i) | |
| HgO (triplet) | HgO, 2.000 | |

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kcal/mol. The discrepancy in the case of HgO is difficult to assess since the "experimental" value was estimated indirectly and on the assumption that it has a singlet ground state. MNDO in fact predicts it to have a *triplet* ground state and the calculated singlet–triplet splitting is large enough to make this a very strong prediction. Here, as elsewhere, the lack of accurate thermochemical data is not only deplorable in itself but also a serious obstacle to any kind of theoretical calculation, given that the only way to assess the value of *any* current procedure, ab initio or semiempirical, is by comparisons with experiment.

MNDO reproduces ionization potentials fairly well. The average error for the seven molecules in Table II, for which data are available, is 1.13 eV. This result is consistent with results reported previously, the errors in ionization energies of later period elements (e.g., tin,[17] chlorine[14]) being ca. 1 eV.

Table II compares our calculated dipole moments with value measured in benzene solution. The agreement is excellent. There is, however, a curious discrepancy in the case of methylmercuric iodide for which Freige and Hartmann[21] have reported a gas-phase (microwave, Stark effect) value of 1.30 D, in complete disagreement with that measured in solution (2.90 D). This discrepancy is difficult to explain, given that gas-phase values for dipole moment usually agree closely with those measured in nonpolar solvents in general and in benzene in particular (see footnote *e* in Table II). Our calculated value (2.88 D) for $CH_3H_5I$ agrees exactly with that measured in solution. Furthermore, we were unable to find any satisfactory set of parameters for mercury that reproduced the smaller value reported by Feige and Hartmann.[21]

Table III compares the calculated geometries with experiment. Compounds of divalent mercury have invariably been found to be linear, as our calculations predict. The lengths of Hg–C and Hg–halogen bonds are well reproduced.

**Acknowledgment.** This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 49620-83-C-0024), the Robert A. Welch Foundation (Grant No. F-126), and the National Science Foundation (Grant CHE82-17948).

**Registry No.** Hg, 7439-97-6.

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(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)