Organometallics 1988, 7, 522–524

# AM1 Parameters for Zinc

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*Received August 24, 1987*

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

## Introduction

In our continuing effort to improve semiempirical molecular models we have developed a new "third generation" method, AM1.[2] AM1 parameters for the "organic" elements (CHON) and silicon have already been reported[2,3] while those for the halogens[4] and boron[5] are in course of publication. Here we present optimized AM1 parameters for zinc.

We decided to parametrize AM1 for zinc for several reasons: first, because organozinc chemistry is not only interesting and varied but has also played an important role in synthetic and mechanistic organic chemistry;[6] second, because zinc is a metal and, at the time we began this work, AM1 parameters were not available for any metals; third, because zinc is important in a number of biological systems.[7]

Since thermochemical data for zinc compounds are scanty, we drew on our experience in parametrizing MNDO for zinc[8] and mercury[9] in hope of overcoming this deficiency. The lack of such data for zinc is especially deplorable in light of the importance of zinc in biochemistry.

## Procedure

The AM1 parameters for zinc were determined by a least-squares fit of the values calculated for various properties of a selected set (basis set) of molecules to experiment, using standard AM1 parameters for other elements and a recently described optimization procedure.[10] 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 properties used in the parametrization included heats of formation, ionization energies, dipole moments, and geometries. The minimization of SSQ is effected by a derivative optimization method, based on the Davidon Fletcher Powell (DFP) algorithm.[11] The first derivatives of the heat of formation and ionization energies with respect to the various parameters were calculated analytically. The derivatives of the dipole moments were evaluated by finite difference, and the derivative of the energy with respect to geometry was used as a measure of the deviation of the calculated geometry from the experimental.

**Table I. AM1 Parameters for Zinc**

| optimized parameters | value | derived parameters | value |
|---|---|---|---|
| $U_{ss}$ | −21.040 008[a] | $E$(heat) | 31.17[b] |
| $U_{pp}$ | −17.655 574[a] | $E_{el}$ | −30.280 016[a] |
| $\zeta_s$ | 1.954 299[c] | D1 | 1.358 111 3[d] |
| $\zeta_p$ | 1.372 365[c] | D2 | 1.545 740 6[d] |
| $\beta_s$ | −1.997 429[a] | AM | 0.433 664 1[d] |
| $\beta_p$ | −4.758 119[a] | AD | 0.231 742 3[d] |
| $\alpha$ | −1.484 563[e] | AQ | 0.262 116 5[d] |
| $G_{ss}$ | 11.800 000[a] | | |
| $G_{pp}$ | 13.300 000[a] | | |
| $G_{sp}$ | 11.182 018[a] | | |
| $G_{p2}$ | 12.930 520[a] | | |
| $H_{sp}$ | 0.484 606[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$^{-1}$.

The calculations were carried out by using the standard AM1 procedure and parameters, as implemented in the AMPAC[12] package of computer programs. The only quantities 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

Within the AM1 formalism there is an opportunity to modify the core repulsion terms (CRT) with the use of Gaussian type functions.[2] However during the course of our parametrization we discovered this to be unnecessary for zinc. Inclusion of such terms led to no improvement.

Table I shows the final parameters for zinc, in the notation used previously.[2]

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

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**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 |
| $ZnMe_2$ | 19.84 | 12.67,[a] 13.1[b] | 0.0 | 0.4[e] | 9.74 | 9.4[f] |
| $ZnEt_2$ | 14.34 | 12.1,[a] 13.6[b] | 0.0 | 0.0[e] | 9.17 | 8.6[f] |
| $ZnnPr_2$ | 2.55 | -2.9[b] | 0.38 | 0.1[e] | 9.26 | |
| $ZnnBu_2$ | -11.09 | -11.9[b] | 0.0 | 0.0[e] | 9.24 | |
| $ZnF_2$ | -50.61 | | 0.0 | | 13.33 | 13.91[g] |
| $ZnCl_2$ | -54.57 | -63.6[a] | 0.0 | | 12.20 | 11.87[h] |
| $ZnBr_2$ | -63.14 | | 0.0 | | 11.36 | 10.89[h] |
| $ZnI_2$ | 4.67 | | 0.0 | | 10.49 | 9.73[h] |
| ZnMeF | -18.50 | | 2.25 | | 11.04 | |
| ZnMeCl | -20.37 | | 2.56 | | 11.19 | |
| ZnMeBr | -23.86 | | 2.40 | | 10.91 | |
| ZnMeI | 10.13 | | 3.06 | | 10.11 | |
| ZnF | -6.54 | | 2.49 | | 10.51 | |
| ZnCl | -4.49 | 1[c] | 3.49 | | 10.42 | |
| ZnBr | -9.44 | | 3.26 | | 10.01 | |
| ZnI | 26.96 | 15[c] | 3.92 | | 9.75 | |
| ZnH | 50.96 | 54.4[c] | 1.87 | | 9.34 | |
| $ZnMe^+$ | 213.04 | 215.1[a] | | | 17.82 | |
| $Zn^0$ | 31.17 | 31.17[d] | | | 9.24 | 9.39[f], 9.57[f] |
| $Zn^+$ | 244.25 | 249.35[a] | | | 21.04 | |
| $Zn^{2+}$ | 729.46 | 665.09[a] | | | | |
| $ZnCl_2^+$ | 219.50 | 207.7[a] | | | 20.39 | |
| $ZnMe_2^+$ | 229.89 | 221.7[a] | | | 15.81 | |
| ZnO ($S_0$) | 89.17 | | 5.66 | | 10.83 | |
| ZnO ($T_1$) | 75.14 | | 3.22 | | 5.4 | |
| ZnCpEt (classical) | 68.24 | | 1.68 | 0.6[e] | 8.65 | |
| ZnCpEt (nonclassical) | 65.26 | | 1.85 | | 8.98 | |
| ZnCpPh (classical) | 108.55 | | 1.18 | 0.4[e] | 8.79 | |
| ZnCpPh (nonclassical) | 107.55 | | 1.27 | | 9.03 | |

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

| | bond lengths (Å) | | bond angles (deg) | |
|---|---|---|---|---|
| molecule | | calcd (obsd) | | calcd (obsd) |
| $ZnMe_2$ | ZnC | 1.90 (1.930)[a] | CZnC | 180.0 (180.0)[a] |
| $ZnEt_2$ | ZnC | 1.93 (1.950)[a] | CZnC | 178.0 (180.0)[a] |
| | | | ZnCC | 113.5 (114.5)[a] |
| $ZnnPr_2$ | ZnC | 1.93 (1.952)[a] | CZnC | 180.0 (180.0)[a] |
| | | | ZnCC | 114.0 (114.5)[a] |
| | | | CCC | 112.0 (113.6)[a] |
| $ZnF_2$ | ZnF | 1.75 (1.810)[b] | FZnF | 180.0 (180.0)[b] |
| $ZnCl_2$ | ZnCl | 2.07 (2.050)[b] | ClZnCl | 180.0 (180.0)[b] |
| $ZnBr_2$ | ZnBr | 2.11 (2.210)[b] | BrZnBr | 180.0 (180.0)[b] |
| $ZnI_2$ | ZnI | 2.35 (2.38, 2.42)[b] | IZnI | 180.0 (180.0)[b] |

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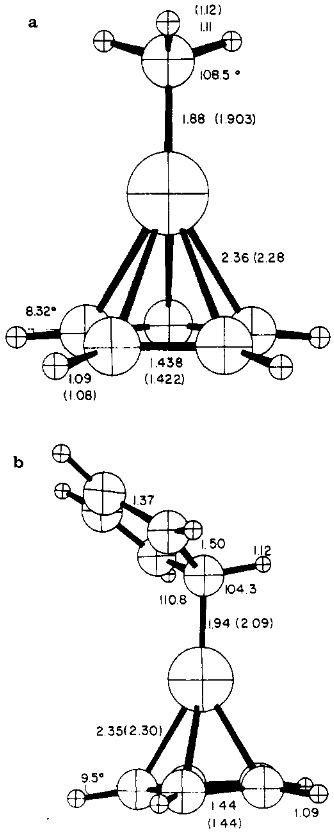

**Figure 1.**

The calculated heats of formation all compare well with the experimental values with the exception of the zinc dication, which is off by 64 kcal/mol. All of the calculated ionization potentials compare well with the experimental values, being in error by only a few tenths of an electronvolt.

While the dipole moments seem to be too large, the experimental values refer to measurements in solution, not in the gas phase. No gas-phase data are available to provide an indication of the magnitude of possible solvent effects.

The calculated geometries (Table III) compare well with experiment, the only significant error being the shortness of the ZnBr bond (calcd 2.11 Å; obsd 2.21 Å). While MNDO predicts cyclopentadienylmethylzinc (CpZnMe) to have the classical $\eta^1$ structure, AM1 and gas-phase studies[13] have indicated it to be a half-sandwich with a $\eta^5$-cyclopentadienyl group. The calculated (observed) geometry of $\eta^5$-CpZnMe is given in Figure 1a; the agreement between calculation and experiment is satisfactory. The same is true for bis(pentamethylcyclopentadienyl)zinc, which has one $\eta^5$-bonded and one $\eta^1$-bonded (or $\sigma$-bonded) Cp ring;[14] AM1 predicts this structure to be the most stable, and the calculated (observed) geometry is given in Figure 1b. Again the agreement is satisfactory.

Use of MNDO in studies of reaction mechanisms and in biochemistry was restricted by its tendency to overestimate interatomic repulsions at separations greater than ca. 1.5 times the corresponding covalent distance.[2] MNDO consequently fails to reproduce hydrogen bonds adequately, and it leads to activation energies that are too large for reactions where the transition states contain unusually long bonds. Since these problems have been overcome in AM1 and since the AM1 results for zinc compounds are significantly better than those given by MNDO,[8] AM1 should prove a useful aid in studies of the chemistry and biochemistry of zinc.

**Acknowledgment.** This work was supported by the Air Force Office of Scientific Research (Contract No. AF86-0022), and the Robert A. Welch Foundation (Grant No. F-126).

**Registry No.** $\eta^5$-CpZnMe, 67291-89-8; $ZnMe_2$, 544-97-8; $ZnEt_2$, 557-20-0; Zn $n$-$Pr_2$, 628-91-1; Zn $n$-$Bu_2$, 1119-90-0; $ZnF_2$, 7783-49-5; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; $ZnI_2$, 10139-47-6; ZnMeF, 102436-61-3; ZnMeCl, 5158-46-3; ZnMeBr, 18815-74-2; ZnMeI, 18815-73-1; ZnF, 20654-98-2; ZnCl, 18623-80-8; ZnBr, 13550-22-6; ZnI, 31246-29-4; ZnH, 13981-87-8; $ZnMe^+$, 47936-33-4; $ZnCl_2^+$, 102436-59-9; $ZnMe_2^+$, 102436-60-2; ZnO, 1314-13-2; $\eta^1$-ZnCpEt, 38282-37-0; $\eta^5$-ZnCpEt, 111689-06-6; $\eta^1$-ZnCpPh, 111616-47-8; $\eta^5$-ZnCpPh, 94980-39-9; Zn, 7440-66-6; $Zn^+$, 15176-26-8; $Zn^{2+}$, 23713-49-7; $(\eta^1,\eta^5)$bis(pentamethylcyclopentadienyl)zinc, 97286-54-9.

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# Synthesis and Characterization of $(\mu\text{-}R^1C{=}NPh)(\mu\text{-}RS)Fe_2(CO)_6$ Complexes

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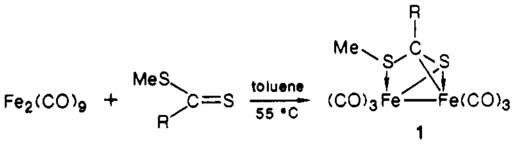
*Received August 7, 1987*

New $\mu$-iminoacyl complexes of the type $(\mu\text{-}R^1C{=}NPh)(\mu\text{-}RS)Fe_2(CO)_6$ were prepared by the reactions of triiron dodecacarbonyl with thioimidates $(R^1C(SR){=}NPh)$. The geometry of the bridging iminoacyl and thiolate ligands was determined primarily from IR and $^{13}C$ NMR spectral correlations to related acyl and thioacyl systems. In related work, reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2CO)_6]$ with $N$-phenylbenzimidoyl chloride was found to be an alternate and superior route to complexes of this class.

## Introduction

The reactions of iron carbonyls with organic thiocarbonyl compounds have received considerable attention in the literature. These include the reactions of $O$-alkyl thioesters,[1,2] dithioesters,[3] $O$-alkyl $S$-alkyl dithiocarbonates,[4] trithiocarbonates,[5] $O$-alkyl thioformates,[2,4b] dithioformates,[2] thioketones,[6] thioureas,[7] and thioamides.[7] Diiron hexacarbonyl complexes are typically isolated in these instances with the organic thiocarbonyl substrate retaining its structural integrity and bonding to the diiron centers as a formal six-electron donor (e.g. eq 1).[3] In some cases, however, diiron hexacarbonyl complexes are isolated

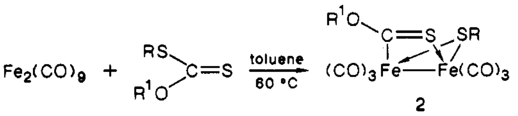


1

(1)

R = alkyl, aryl

where cleavage of an additional C–S bond has occurred with subsequent formation of bridging, three-electron thiolate and thioacyl ligands (e.g. eq 2).[4a] This type of



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(2)

R = $R^1$ = alkyl, aryl

cleavage reaction also has been observed in the synthesis of other thiolate-bridged diiron hexacarbonyl complexes as well (eq 3–5).[8]

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