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Ground states of molecules. Part 84. MNDO calculations for compounds containing zinc

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the recent work of Martin, Farnham, and co-workers[5] on **5**. They have demonstrated a linear free energy correlation between the rate of ligand permutation and the electronegativity of Y.

The ^{13}C NMR spectrum of **8** at room temperature deserves special comment since it shows no methyl carbon, probably because of line broadening. However, at −77 °C, the methyl carbon is seen as a doublet of triplets due to the unequal coupling of this carbon to one equatorial F and two axial F's.

Tetrafluorophenylsiliconate (2A) and Difluorotriphenylsiliconate (9). These ions are prepared by the method outlined in eq 1. Compound **2A** was prepared both to further test the synthetic method and to determine whether our monosubstituted pentacoordiante 18-crown-6 derivative would behave differently than that of K–M. We find no differences, with $PhSiF_4^-$ giving only one ^{19}F signal through a wide temperature range although our sample is slightly impure (see Experimental Section). Such behavior is consistent with a rapidly exchanging ion whose exchange cannot be slowed for NMR analysis. K–M reached a similar conclusion while drawing attention to the similar behavior of analogous phosphorus compounds.[3]

$Ph_3SiF_2^-$ (**9**) is the first acyclic, tricarbon-substituted siliconate reported, although a related bipyridyl ion was reported some years ago by Corey and West.[18,19] It has physical properties like its counterparts but shows no temperature-dependent NMR behavior. Over a wide temperature range, only a single ^{19}F signal is observed. These observations suggest that three phenyls occupy equatorial positions and do not exchange.

The 18-crown-6 pentacoordinate silicon compounds described herein have properties which have allowed detailed temperature-dependent NMR study. In compounds **1** and **8** activation free energy barriers of 11.7 and 9.9 kcal/mol were obtained. Although these barriers are quite a bit lower than that for Ph_2PF_3 (18.7 kcal/mol),[20] the qualitative NMR behavior of our pentacoordinate silicon compounds is similar to that of analogous phosphorus compounds, a conclusion similar to that reached by Holmes.[11] Since only a few pentacoordinate silicon compounds have yet been studied by dynamic NMR techniques, it is premature to generalize about the relationship between structure and activation barriers. Nevertheless and, perhaps, coincidentially, compounds **1** and **8** have $\Delta G^{\ddagger}$'s close to the other trifluoropentacoordinate species whose $\Delta G^{\ddagger}$'s have been reported: namely, **4** (7–9 kcal/mol) and **6B** (approximately 12 kcal/mol). Additional comment will await the completion of studies designed to probe these structural relationships in acyclic silicon compounds.

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Registry No. **1**·18-crown-6-K^+, 102307-90-4; **2A**·18-crown-6-K^+, 102307-91-5; **8**·18-crown-6-K^+, 102307-93-7; **9**·18-crown-6-K^+, 102418-62-2; $PhMeSiF_2$, 328-57-4; SbF_3, 7783-56-4; $PhMeSiCl_2$, 149-74-6; Ph_2SiF_2, 312-40-3; $PhSiF_3$, 368-47-8; Ph_3SiF, 379-50-0.

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MNDO Calculations for Compounds Containing Zinc[1]

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

Introduction

The MNDO method[3,4] is now established[5] as a practical procedure for studying chemical behavior, giving results comparable[6,7] with those from good ab initio models (e.g., 6-31G*) while requiring less than one-thousandth as much computer time. Parameters have been reported for hydrogen,[3] for the second period elements beryllium,[9] boron,[10] carbon,[3] nitrogen,[3] oxygen,[3] and fluorine,[11] for the third-

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[1] Part 84 of the series "Ground States of Molecules". For Part 83 see: Dewar, M. J. S.; Dieter, K. M., in progress.

[2] Welch Predoctoral Fellow 1985.

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[5] For example, CA SEARCH list 148 citations of MNDO in the period since January, 1982, to be compared with 1073 for ab initio.

[6] Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**; *101*, 5558. Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898. These comparisons were restricted to a relatively small number of molecules composed only of second period elements by the availability of geometry-optimized 6-31G* calculations. Extension of such tests to additional molecules would clearly be very useful, allowing further comparisons with the very extensive tests we have carried out, and published, of our own procedures. Such systematic tests of ab initio methods should indeed have been carried out many years ago by those using them. It should not have been left to us to do this.

[7] Wiberg[8] has shown that good estimates of heats of formation can be derived from 6-31G* energies by applying empirical corrections based on group additivity relationships. Similar improvements could no doubt be effected in the same way in the case of MNDO. Such a treatment is, however, inherently limited to stable molecules. It cannot be used to study reactions because there is no way to apply such corrections to intervening segments of potential energy surfaces in general or to transition states in particular. Since the potentially most important application of theoretical calculations to chemistry lies in the study of reactions and reaction mechanisms and since our procedures have been developed primarily for such use, the only relevant way to compare ours with ab initio ones is to compare the corresponding uncorrected energies. The only comparisons of this kind hitherto reported are those of Dewar and Storch.[6]

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period elements aluminum,[12] silicon,[13] phosphorus,[13] sulfur,[14] and chlorine,[15] and for bromine,[16] iodine,[17] tin,[18] mercury,[19] and lead.[20] Since d AOs are not currently included in MNDO, calculations are confined to compounds involving only normal group valencies. Schleyer et al.[21] have reported extensive 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, zinc seemed an obvious target, 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;[22] secondly, because zinc is a metal and, at the time we began this work, MNDO parameters were available for only five metals (Be, Al, Sn, Pb, Hg); thirdly, because zinc is important in a number of biological systems.[23]

While thermochemical data for zinc compounds are unfortunately scanty, we hoped that the experience gained during our parametrization of mercury would mitigate this shortcoming. The lack of such data for zinc is especially deplorable in light of the importance of zinc in biochemistry.

Procedure

The MNDO 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 MNDO parameters for other elements and a recently described optimization procedure.[18] 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.[24] 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. MNDO Parameters for Zinc

optimized parameters	value	derived parameters	value
U_{ss}	−20.839 716[a]	E(heat)	31.17[b]
U_{pp}	−19.625 224[a]	E_{el}	−29.879 432[a]
ζ_s	2.047 359[c]	D1	1.303 782 6[d]
ζ_p	1.460 946[c]	D2	1.452 018 3[d]
β_s	−1.000 000[a]	AM	0.433 664 1[d]
β_p	−2.000 000[a]	AD	0.237 591 2[d]
α	1.506 457[e]	AQ	0.273 885 8[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}

Table II. Calculated Heats of Formation (ΔH_f), First Ionization Energies (I_1), and and Dipole Moment (μ)

	ΔH_f, kcal/mol		μ, D		I_1, eV	
compd	calcd	obsd	calcd	obsd	calcd	obsd
$ZnMe_2$	19.88	12.67,[a] 13.1[b]	0.0	0.4[e]	10.54	9.4[f]
$ZnEt_2$	13.08	12.1,[a] 13.6[b]	0.08	0.0[e]	10.21	8.6[f]
Zn(Pr-*n*)$_2$	4.58	−2.9[b]	0.04	0.1[e]	10.19	
Zn(Bu-*n*)$_2$	−4.64	−11.9[b]	0.1	0.0[e]	10.19	
ZnF_2	−116.34		0.0		14.37	13.91[g]
$ZnCl_2$	−48.7	−63.6[a]	0.0		12.80	11.87[h]
$ZnBr_2$	2.71		0.0		11.76	10.89[h]
ZnI_2	42.35		0.0		10.62	9.73[h]
ZnMeF	−52.10		1.77		11.54	
ZnMeCl	−18.1		2.53		11.84	
ZnMeBr	8.22		2.58		11.32	
ZnMeI	29.54		2.50		10.25	
ZnF	−52.15		2.07		11.13	
ZnCl	−13.76	1[c]	3.34		11.41	
ZnBr	14.85		3.62		11.06	
ZnI	40.34	15[c]	3.88		10.09	
ZnH	43.16	54.4[c]	1.43		10.21	
$ZnMe^+$	227.7	215.1[a]			17.72	
Zn^0	31.17	31.17[d]			9.04	9.39,[f] 9.57[f]
Zn^+	239.63	249.35[a]			5.9	
Zn^{2+}	720.22	665.09[a]				
$ZnCl_2^+$	236.29	207.7[a]	1.38		21.08	
$ZnMe_2^+$	242.36	221.7[a]	1.38		8.66	
ZnO (S_0)	41.81		5.04		11.16	
ZnO (T_1)	42.75		1.86		5.06	
ZnS (S_1)	79.02		6.09		9.24	
ZnS (T_0)	69.5	−14[c]	2.52		4.90	
ZnCpEt	66.04		0.73	0.6[e]	8.72	
ZnCpPh	104.14		0.65	0.4[e]	8.76	

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The calculations were carried out by using the standard MNDO procedure and parameters, as implemented in the MOPAC[25] package of computer programs. The only quantities in MNDO that depend on the period to which

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Table III. Calculated (Observed) Geometrical Parameters

molecule	bond lengths (Å), calcd (obsd)	bond angles (deg), calcd (obsd)
$ZnMe_2$	ZnC, 1.89 (1.930)[a]	CZnC, 179.4 (180.0)[a]
$ZnEt_2$	ZnC, 1.91 (1.950)[a]	CZnC, 177.0 (180.0)[a]
		ZnCC, 118.7 (114.5)[a]
		CCC, 115.3 (113.6)[a]
Zn(Pr-*n*)$_2$	ZnC, 1.91 (1.952)[a]	CZnC, 179.0 (180.0)[a]
		ZnCC, 118.0 (114.5)[a]
ZnF_2	ZnF, 1.68 (1.810)[b]	FZnF, 180.0 (180.0)[b]
$ZnCl_2$	ZnCl, 2.12 (2.050)[b]	ClZnCl, 180.0 (180.0)[b]
$ZnBr_2$	ZnBr, 2.23 (2.210)[b]	BrZnBr, 180.0 (180.0)[b]
ZnI_2	ZnI, 2.38 (2.38, 2.42)[b]	IZnI, 180.0 (180.0)[b]

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an atom belongs are the relevant overlap integrals. MOPAC provides for their calculation for all elements.

Results and Discussion

Table I shows the final parameters for zinc, in the notation used previously.[3,4]

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

The errors in the heats of formation calculated for ZnS and Zn^{2+} are both large: 83 and 55 kcal/mol, respectively. MNDO is known[4] to perform poorly for diatomic molecules, and the formalism of MNDO is not sufficiently flexible to include multiply charged atoms. Omitting these two species, the average error in the calculated ΔH_f's is 13 kcal/mol, comparable with those for other metals.[18-20] While the average error in the dipole moments is small (0.1 D), this relates to experimental values determined in solution, usually in *n*-heptane. The average error in the ionization potentials is 1 eV, similar again to that for other metals.[18-20]

The calculated geometries compare well with experiment, the only significant errors being the shortness of the ZnF bond (calculated 1.68 Å; observed 1.81 Å) and the inability to handle sandwich compounds. Thus while MNDO predicts cyclopentadienylmethylzinc (CpZnMe) to have the classical η^1 structure, gas-phase studies[26] have indicated it to be a half-sandwich with a η^5-cyclopentadienyl group. This weakness (i.e., the inability to handle nonclassical bonding) has been noted previously in the case of boron,[27] tin,[18] and lead.[20] The geometry of η^5-CpZnMe is therefore not included in Table III. The same is true for bis(pentamethylcyclopentadienyl)zinc, which has one η^5-bonded and one η^1-bonded (or σ-bonded) Cp ring.[28] MNDO again predicts a classical structure.

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Registry No. $ZnMe_2$, 544-97-8; $ZnEt_2$, 557-20-0; Zn(Pr-*n*)$_2$, 628-91-1; Zn(Bu-*n*)$_2$, 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; Zn, 7440-66-6; Zn^+, 15176-26-8; Zn^{2+}, 23713-49-7; $ZnCl_2^+$, 102436-59-9; $ZnMe_2^+$, 102436-60-2; ZnO, 1314-13-2; ZnS, 1314-98-3; ZnCpEt, 38097-43-7; ZnCpPh, 94980-39-9.

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Structure of a Lithiated Phosphoylide, $\{[Li(CH_2)P(C_6H_5)_2(CH_2)]_2(dioxane)_3\}_2\cdot(dioxane)$

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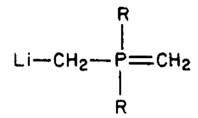
Pale yellow, air-sensitive crystals of $[Li(CH_2)(CH_2)P(C_6H_5)_2]_4\cdot(C_4H_8O_2)_7$ belong to space group $P\bar{1}$ with cell constants of a = 13.529 (3) Å, b = 14.472 (1) Å, c = 11.771 (1) Å, α = 109.017 (8)°, β = 90.05 (1)°, and γ = 94.009 (9)°. The structure was solved by a combination of direct methods and difference Fourier maps and refined by least-squares methods to final error indices of R = 10.9% and R_w = 10.4% by using the 3552 unique reflections with $I > 3\sigma(I)$ from the data set containing 5954 unique reflections. The molecular structure consists of two eight-membered rings in the saddle conformation, each composed of two $[(CH_2)(CH_2)P(C_6H_5)_2]^-$ ligands bridging two lithiums. The two rings are joined by a disordered bridging dioxane molecule which is coordinated to a Li in each ring. The coordination about the lithiums is completed by additional dioxanes which are also disordered.

Lithiated phosphoylides, $[Li(CH_2)(CH_2)PR_2]$, have been known $[Li(CH_2)(CH_2)P(C_6H_5)_2]_4\cdot(C_4H_8O_2)_7$ the mid 1960s and have been used as starting materials for the synthesis of organometallic compounds.[1-4] NMR studies demonstrated[1] that does not exist in solution and suggested that



$$Li{-}CH_2{-}\overset{\displaystyle R}{\underset{\displaystyle R}{P}}{=}CH_2$$

are the most probable structures for this class of molecules.

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