Organometallics **1985**, *4*, 1973–1980

MNDO Calculations for Compounds Containing Lead[1]

Michael J. S. Dewar,* Mary K. Holloway, Gilbert L. Grady,[2] and James J. P. Stewart[3]

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received February 22, 1985

MNDO has been parametrized for lead. Calculations are reported for a number of compounds of lead.

Introduction

Previous articles of this series have described the MNDO method[4] and introduced parameters for hydrogen,[5] for the second-period elements beryllium,[6] boron,[7] carbon,[5] nitrogen,[5] oxygen,[5] and fluorine,[8] for the third-period elements aluminum,[9] silicon,[10] phosphorus,[10] sulfur,[10,11] and chlorine,[10,11] and for bromine,[13] iodine,[14] and tin.[15] Since d AOs are not currently included in MNDO, calculations for lead are limited to compounds of Pb(II) and Pb(IV).

Procedure

Parameters were determined by a least-squares optimization procedure which involved minimizing the sum of the squares (SSQ) of the weighted errors in the heats of formation (ΔH_f), ionisation potentials (IP), dipole moments (μ), and geometries for the molecules in the parametrization basis set. The search direction vector was determined using the first and second derivatives of SSQ with respect to the parameters. First derivatives of SSQ were obtained from first derivatives of ΔH_f IP, μ, and geometry with respect to the parameters. First derivatives of ΔH_f and IP were determined analytically, while those for μ were evaluated by finite difference. Derivatives of the energy with respect to geometry were used as a measure of the difference between calculated and experimental geometries. Approximate second derivatives of SSQ were obtained from a knowledge of the first derivatives of SSQ for two points in parametric space.

All calculations were carried out by using the MNDO method,[4] as implemented in the MOPAC package of computer programs.[16] Geometries were fully optimized with no assumptions, other than symmetry where appropriate. Transition states were located by the reaction coordinate method and refined by minimizing the norm of the gradient.[17] All stationary points were characterized by calculating force constants.[17] Triplet states were calculated by using both RHF (half-electron[18]) and UHF procedures.

Table I. MNDO Parameters for Lead

optimized parameters	value	derived parameters	value
U_{ss}, eV	−47.319 692	E_{heat}, kcal/mol	46.62
U_{pp}, eV	−28.847 560	E_{el}, eV	−105.834 504 0
ζ_s, au	2.498 286	D_1, au	1.552 662 4
ζ_p, au	2.082 071	D_2, au	1.448 855 8
β_s, eV	−8.042 387	A_M, au	0.360 161 7
β_p, eV	−3.000 000	A_D, au	0.323 930 9
α, cm^{-1}	1.728 333	A_Q, au	0.350 205 7
G_{ss}, eV	9.800 000		
G_{pp}, eV	7.300 000		
G_{sp}, eV	8.300 000		
G_{p2}, eV	6.500 000		
H_{sp}, eV	1.300 000		

Results and Discussion

Table I shows the final parameters for lead, in the usual notation.[4–15] Table II shows the heats of formation (ΔH_f), first ionization energies (I_1) obtained using Koopman's theorem, and dipole moments (μ), for 32 lead compounds, including both Pb(II) and Pb(IV) species. Molecules included in the basis set for parametrization are indicated by asterisks. Experimental values, where available, are given for comparison.

The mean absolute error in ΔH_f is 11.2 kcal/mol, almost the same as that (11.4 kcal/mol) for tin.[15] It should, however, be noted that the thermochemical data for lead compounds are not in general of high accuracy, the average uncertainty for the 16 measured values for which error limits are listed being 4.8 kcal/mol. The largest error in the calculated values is that for $PbCl_2$, this alone being greater than 20 kcal/mol. It should be remembered that errors of this magnitude can occur in calculations using good ab initio methods, even in the case of simple organic molecules.[19]

The calculated ionization energies are systematically too large, with a mean error of 1.37 eV for the 15 molecules in Table II for which experimental values are available. A similar error was found in MNDO calculations for compounds of the third-period elements and for those containing bromine (0.92-eV error), iodine (1.31-eV error), and tin (1.30-eV error). These errors were attributed to neglect of interactions between the inner-shell electrons and valence electrons, due to use of the core approximation in MNDO. However, attempts to correct the calculated values for lead in the way used successfully for chlorine[12] (and subsequently for bromine[13] and iodine[14]) were unsuccessful.

Dipole moments are well reproduced, with an average absolute error of 0.41 D for the six molecules in Table II for which experimental values are available. This compares favorably with an average absolute error of 0.30 D

---

[1] Part 79 of the series "Ground States of Molecules". For part 78 see: Dewar, M. J. S.; Merz, K. M., Jr. *Organometallics*, second of three papers in this issue.

[2] Permanent address: St. Michael's College, Winooski, VT 05404.

[3] Currently at the Air Force Academy, Colorado Springs, CO, on leave from the University of Strathclyde, Glasgow, Scotland.

[4] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[5] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

[6] Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 777.

[7] Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

[8] Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 58.

[9] Davis, L. P.; Guidry, R. M.; Williams, J. R.; Dewar, M. J. S. *J. Comput. Chem.* **1981**, *2*, 433.

[10] Dewar, M. J. S.; Rzepa, H. S.; McKee, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 3607.

[11] Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84.

[12] Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1983**, *4*, 158.

[13] Dewar, M. J. S.; Healy, E. *J. Comput. Chem.* **1983**, *4*, 542.

[14] Dewar, M. J. S.; Healy, E. *J. Comput. Chem.* **1984**, *5*, 358.

[15] Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771.

[16] QCPE Bulletin, University of Indiana, No. 455.

[17] McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[18] Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

[19] Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.

0276-7333/85/2304-1973$01.50/0

Table II. Calculated Heats of Formation, Ionization Potentials, and Dipole Moments for Molecules Containing Lead

	ΔH_f, kcal/mol		IP, eV		dipole moment, μ(D)		
compd	calcd	obsd	calcd	obsd	calcd	obsd	charge on lead calcd
PbF	−22.58	−19.18[a]	7.45		3.20		0.48
PbF_2*	−94.16	−104.00[a]	12.69	11.84[h]	4.92		1.02
PbCl*	−15.26	3.60[a]	7.68		3.54		0.40
$PbCl_2$*	−76.99	−41.60[a]	11.89	10.34[i]	4.62		0.84
PbBr	6.01	16.95[a]	7.73		3.29		0.36
$PbBr_2$	−33.84	−24.95[a]	11.04	9.85[i]	4.12		0.73
PbI	26.10	25.75[a]	7.83		2.68		0.24
PbI_2	8.75	−0.76[a]	10.02	8.90[i]	2.92		0.45
PbH	40.76	56.50[b]	7.33		0.53		0.27
PbH_4*	63.10	59.70[c]	12.13		0.00		0.004
PbO*	29.12	16.80[d]	10.47	9.08[j]	3.62		0.56
PbO_2	123.59		10.50	8.87[j]	2.83		0.64
PbS	18.63	31.50[a]	10.05		4.37		0.52
PbS_2	88.47		10.07		0.00		0.45
Pb_2	72.56	79.50[b]	6.91		0.00		0.00
$Pb(CH_3)_4$*	26.12	32.60[e]	10.29	8.90[k]	0.00		−0.11
$Pb(C_2H_5)_4$*	10.57	26.00[e]	9.80	8.13[k]	0.08	0.00[m]	−0.06
$Pb(CH_3)_3$-*t*-Bu*	26.28	6.92[f]	9.62	7.99[f]	0.04		−0.08
$Pb_2(CH_3)_6$*	45.59	38.71[f]	9.17	7.41[f]	0.00		−0.03
$Pb(CH_3)_3C_2H_5$	22.20		10.00	8.65[k]	0.11		−0.10
$Pb(CH_3)_2(C_2H_5)_2$	18.22		9.93	8.45[k]	0.06		−0.09
$Pb(C_2H_5)_3CH_3$	14.82		9.90	8.26[k]	0.09		−0.07
$Pb(CH_3)_3\cdot$	34.58	46.66[f]	8.71	7.60[f]	0.82		0.16
$Pb(CH_3)_3^+$	211.95	200.07[f]	15.41				0.36
$PbCl^+$	159.77	178.20[a]	17.99				1.25
$PbCl_2^+$	188.93	195.10[a]	17.34				1.11
Pb^+	218.37	219.00[g]	13.55				1.00
$PbCl(CH_3)_3$*	−13.93		10.50		4.53	4.50[m]	0.08
$PbCl(C_2H_5)_3$*	−16.57		10.08		4.46	4.42[m]	0.12
$PbCl_2(C_2H_5)_2$*	−39.98		10.38		6.19	4.74[m]	0.26
$PbBr(C_2H_5)_3$	1.56		9.98		3.97	4.49[m]	0.05
$PbCp_2$	133.69		8.24	7.55[l]	0.99	1.29[n]	0.65

[a] Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, 1. [b] Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37*. [c] Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 46. [d] Chase, M. N.; Curnutt, J. L.; Hu, H. T.; Prophet, H.; Syverud, A. N.; Walker, L. C. *J. Phys. Chem. Ref. Data* **1974**, *3*, 311. [e] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970. [f] Lappert, M. F.; Pedley, J. B.; Simpson, J.; Spalding, T. R. *J. Organomet. Chem.* **1971**, *29*, 195. [g] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982**, *11*. [h] Novak, I.; Potts, A. W. *J. Chem. Soc., Dalton Trans.* **1983**, 2211. [i] Novak, I.; Potts, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1984**, *33*, 1. [j] Zmbov, K. F.; Miletic, M. *Adv. Mass Spectrom.* **1978**, *7A*, 573. [k] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p 454. [l] Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064. [m] McClellan, A. L. "Tables of Experimental Dipole Moments", W. H. Freeman and Co.: San Francisco, 1963; Vol. 1. [n] Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1959**, *92*, 938.

for compounds containing only the "organic" elements (C, H, O, N).

Table III shows calculated and experimental geometries. Calculated bond lengths involving lead are systematically too small, by ca. 0.1 Å, except for PbCl, where the PbCl bond is calculated to be too long by 0.2 Å. The experimental value for this seems, however, anomalously small. MNDO predicts little, if any, difference in bond length between PbX_2 and PbX (X = F, Cl, Br, I), a conclusion supported by experiment in the case of F, Br, and I. It is difficult to see any reason why the same should not also be true for the chlorides.

While the average error in the lengths of bonds to lead is much larger than those for the second- or third-period elements, the error is in fact only 4.3%, bonds formed by lead being relatively long. The chemical effects of such errors should be small.

Bond angles involving lead are systematically overestimated by 4°. This is little more than the average error (2.8°) for organic molecules. MNDO predicts a bent geometry for O–Pb–O (bond angle, 101.6°) and a linear one for $PbCl_2^+$, a conclusion contrary to that expected on the basis of the Walsh rules.[20] According to MNDO, linear PbO_2 corresponds to a hilltop on the potential surface. No structural studies of either PbO_2 or $PbCl_2^+$ seem as yet to have been reported.

The calculated charge on lead varies from −0.11 in $Pb(CH_3)_4$ to +1.25 in $PbCl^+$, with a signed average value of +0.28 for 27 molecules (excluding radicals and cations) in Table II. Only the organolead molecules in Table II have a slight negative charge on lead (average of −0.09), with the exception of bis(cyclopentadienyl)lead ($PbCp_2$) which has a charge of +0.65.

Table IV compares calculated and observed higher ionization energies of lead compounds. Although the calculated values are systematically too large, for reasons discussed previously, the orbital ordering is in good agreement for PbX_2 species (X = F, Cl, Br, I). The same is also true of bis(cyclopentadienyl)lead ($PbCp_2$).

However, orbital assignments for $Pb(CH_3)_4$ are in substantial disagreement. The MNDO orbital ordering for $Pb(CH_3)_4$ is identical with that observed for neopentane.[21] Although Jonas et al.[21] (quoted in Table IV) found that the $2t_2$ and $2a_1$ orbitals were significantly destabilized for both $Si(CH_3)_4$ and $Pb(CH_3)_4$, another study[22] assigned a

---

(20) Walsh, A. D. *J. Chem. Soc.* **1953**, 2266.

(21) See Table IV, footnote c.

(22) Evans, S.; Green, J. C.; Joachim, P. J.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 905.

Table III. Calculated (Observed) Geometrical Parameters

molecule	bond lengths, Å		bond angles, deg		ref
PbF	PbF	2.00 (2.06)			*a*
PbF_2	PbF	2.00 (2.03)	FPbF	97.8 (97.8)	*b*
PbCl	PbCl	2.38 (2.18)			*a*
$PbCl_2$	PbCl	2.38 (2.46)	ClPbCl	101.4 (96)	*a*
$PbCl_4$	PbCl	2.38 (2.43)	ClPbCl	109.5	*a*
PbBr	PbBr	2.47 (2.55)			*a*
$PbBr_2$	PbBr	2.47 (2.60)	BrPbBr	102.7 (98.8)	*b*
PbI	PbI	2.58 (2.74)			*a*
PbI_2	PbI	2.60 (2.80)	IPbI	104.9 (99.7)	*b*
PbO	PbO	1.88 (1.92)			*c*
PbS	PbS	2.12 (2.29)			*c*
$Pb(CH_3)_4$	PbC	2.17 (2.24)	CPbC	109.5 (109.5)	*d*
	CH	1.10 (1.08)	HCPb	109.3 (104.6)	
			HCH	109.8	
$Pb_2(CH_3)_6$	PbPb	2.78 (2.88)	PbPbC	111.7 (109.5)	*e*
	PbC	2.17 (2.25)	HCPb	108.8	
	CH	1.10	HCH	109.9	
$PbCp_2$	PbC	2.57 (2.78)	CCC	107.9	*f*
	CC	1.44 (1.43)	HCC	125.7	
	CH	1.08 (1.11)	θ^g	150.7 (135 ± 15)	

[a] Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, 1. [b] Demidov, A. V.; Gershikov, A. G.; Zasorin, E. Z.; Spiridonov, V. P.; Ivanov, A. A. *Zh. Struct. Khim.* **1983**, *24*, 7. [c] Lovas, F. J.; Tiemann, E. *J. Phys. Chem. Ref. Data* **1974**, *3*, 609. [d] Oyamada, T.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2638. [e] Skinner, H. A.; Sutton, L. E. *Trans. Faraday Soc.* **1940**, *36*, 1209. [f] Almenningen, A.; Haaland, A.; Motzfeldt, T. *J. Organomet. Chem.* **1967**, *7*, 97. [g] θ is the angle made by lead with the centers of the two cyclopentadiene rings.

band at 15.3 eV to the $2a_1$ orbital, in agreement with our results. In the latter photoelectron spectrum, the t_1, e, and $2t_2$ ionizations were not resolved.

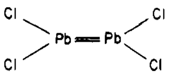
Table V compares calculated and observed vibrational frequencies for four small lead compounds: PbF_2, $PbCl_2$, $PbBr_2$, and PbO. Calculated vibrational frequencies for bent PbO_2 are also included. The average error in the calculated values is approximately 14%, similar to previous MINDO/3 results.[23]

It is of interest to note that the calculated symmetric stretch is lower than the antisymmetric one for PbF_2, unlike $PbCl_2$ and $PbBr_2$. Since the reported assignment for PbF_2 was based solely on similar assignments for CF_2, SiF_2, and GeF_2 spectra, the MNDO aasignment is entirely possible.

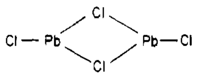
Lead Dichloride Dimer Formation. The gaseous heats of dimerization of several dichlorides, including $PbCl_2$, have been determined by using mass spectrometry.[24] Although there are two possible modes of dimerization, i.e., 1 and 2, Schäfer and Binnewies suggested the latter structure for $(PbCl_2)_2$. Indeed, the calculated heat of formation of 1 rose sharply as the Pb–Pb bond distance was decreased, its minimum value, at distances up to 11 Å, being simply twice the heat of formation of $PbCl_2$.

However, a stable dimer corresponding to structure 2 is an energy minimum on the MNDO potential surface. The terminal chlorines have Cl–Pb–Pb angles less than 180°, such that isomeric cis and trans forms, 3 and 4, are possible. These differ little in energy and are interconverted via a transition state (5) in which one terminal chlorine has a Cl–Pb–Pb angle of 180°.

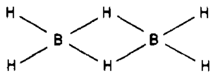
The calculated geometries and heats of formation of 3–5 are shown in Figure 1. Thus, the calculated heats of dimerization for production of 3 and 4 are −28.1 and −29.0 kcal/mol, respectively, in excellent agreement with the experimental value of −30.5 kcal/mol.



1



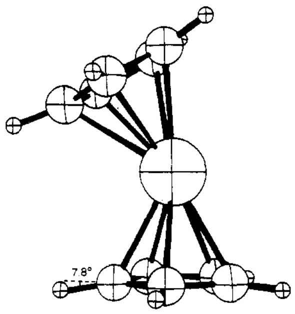
2



6

Despite the obvious analogy to the three-center two-electron bonding in diborane (6), 3 and 4 exhibit no three-center bonding but instead contain strongly polarized Pb–Cl bonds and are highly ionic in character.

(Cyclopentadienyl)lead Compounds. As mentioned above, both the gas-phase structure[25] and photoelectron spectrum[26] of plumbocene, bis(cyclopentadienyl)lead (7), have been determined. Although the MNDO results for the observed bent sandwich structure of 7 (θ = 150.7°) agree well with experiment, this structure is actually a transition state on the MNDO potential energy surface, while the linear (eclipsed) sandwich structure 8 is a hilltop (two negative force constants). There was no energy difference between staggered and eclipsed forms of 8, although the staggered geometry was found to have three negative force constants, rather than two.



7

The classical isomer 9 was the only species found to be a true minimum on the potential surface, lying some 34 kcal/mol lower in energy than 7. The heat of formation and calculated geometry for 7 were given in Tables II and III, while those for 8 and 9 are shown in Figure 2.

Similar results for stannocene[15] illustrated the tendency[27] of MNDO to underestimate the stabilities of nonclassical species relative to classical isomers.

It is thus somewhat surprising that, as with (cyclopentadienyl)tin, the nido structure 10 of (cyclopentadienyl)lead was found to be the global minimum on the $C_5H_5Pb^+$ potential surface. The phenyl (11) and fulvenyl (12) analogues were 12.5 and 19.4 kcal/mol higher in energy, respectively. All three were characterized as minima. See Figure 3 for their calculated geometries and heats of formation.

Although a mass spectral peak corresponding to C_5H_5Pb has been observed, the reported nido structure of this species was assigned solely on calculated atomization en-

---

(23) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1685.
(24) Schäfer, V. H.; Binnewies, M. *Z. Anorg. Allg. Chem.* **1974**, *410*, 251.

(25) See Table III, footnote *f*.
(26) See Table IV, footnote *d*.
(27) (a) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569. (b) *Ibid.* **1980**, *19*, 2662. (c) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

Table IV. MNDO Higher Ionization Potentials

molecule	point group	MNDO	exptl	assignt
PbF_2[a]	C_{2v}	13.13, 13.19	12.89	$1a_2 + 3b_2$
		13.89, 13.94, 14.12	13.58	$1b_1 + 3a_1 + 2b_2$
		23.15		$2a_1$
$PbCl_2$[b]	C_{2v}	12.18, 12.30	10.86	$3b_2 + 1a_2$
		12.92, 13.37	11.58	$1b_1 + 3a_1$
		14.21	12.19	$2b_2$
		23.09	16.47	$2a_1$
$PbBr_2$[b]	C_{2v}	11.23, 11.36	10.29	$3b_2 + 1a_2$
		11.93, 12.42	11.07	$1b_1 + 3a_1$
		13.21	11.71	$2b_2$
		23.61	16.19	$2a_1$
PbI_2[b]	C_{2v}	10.25, 10.37	9.20, 9.49	$3b_2 + 1a_2$
		10.97, 11.39	10.20, 10.32	$1b_1 + 3a_1$
		11.93	10.91	$2b_2$
		22.30	16.32	$2a_1$
$Pb(CH_3)_4$[c]	T_d	13.87	13.0	$1t_1$
		13.95	15.1	1e
		14.30	13.7	$2t_2$
		20.32	11.5	$2a_1$
		29.88		$1t_2$
		33.20	16.4	$1a_1$
$PbCp_2$[d]	C_{2v}	8.31	7.85	$9b_2$
		9.41	8.54	$11a_1$
		9.61	8.88	$6b_1$
		11.15	10.10	$10a_1$
		13.52	10.6	$8b_2$
		13.19		
		13.19		
		13.20		
		13.21	12.0	
		13.60	to	
		13.61	14.5	
		13.64		
		13.65		

[a] Novak, I.; Potts, A. W. *J. Chem. Soc., Dalton Trans.* **1983**, 2211. [b] Novak, I.; Potts, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1984**, *33*, 1. [c] Jonas, A. E.; Schweitzer, G. K.; Grimm, F. A.; Carlson, T. A. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 29. [d] Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064.

Table V. Vibrational Frequencies

compd	symmetry	descript	MNDO	exptl
PbF_2[a]	a_1	sym stretch	621.6	531
	a_1	bend	188.2	165
	b_1	antisym stretch	642.7	507
$PbCl_2$[b]	a_1	sym stretch	371.2	314
	a_1	bend	103.0	99
	b_1	antisym stretch	365.4	299
$PbBr_2$[c]	a_1	sym stretch	249.1	200
	a_1	bend	67.3	64
	b_1	antisym stretch	243.9	189
PbO[d]	a_1	stretch	821.4	718.4
PbO_2	a_1	sym stretch	500.6	
	a_1	bend	88.7	
	b_1	antisym stretch	672.6	

[a] Hauge, R. H.; Hastie, J. W.; Margrave, J. L. *J. Mol. Spectrosc.* **1973**, *45*, 420. [b] Andrews, L.; Frederick, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 755. [c] Demidov, A. V.; Gershikov, A. G.; Zasorin, E. Z.; Spiridonov, V. P.; Ivanov, A. A. *Zh. Struct. Khim.* **1983**, *24*, 7. [d] Ogden, J. S.; Ricks, M. J. *J. Chem. Phys.* **1972**, *56*, 1658.

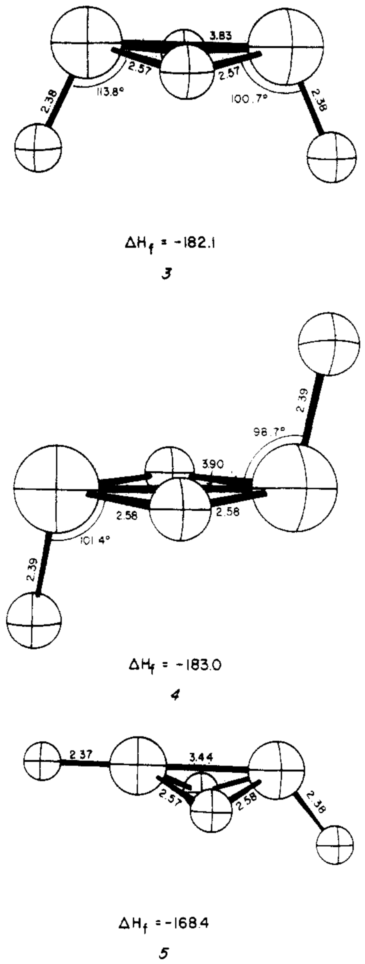


Figure 1. Calculated geometries (bond lengths in Å, angles in deg) and heats of formation (kcal/mol) of **3**–**5**.

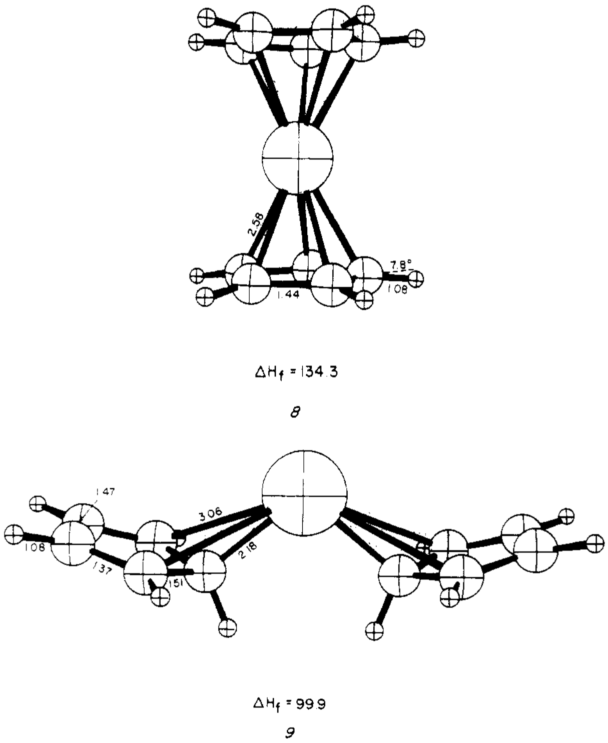


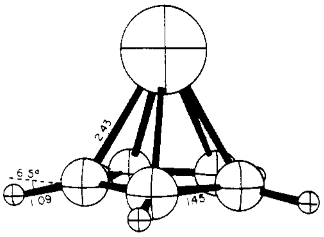
Figure 2. Calculated geometries (bond lengths in Å, angles in deg) and heats of formation (kcal/mol) of **8** and **9**.

ergies,[28] unlike the tin and germanium analogues which were synthesized and characterized by Jutzi et al.[29] On the basis of calculated atomization energies, **10** was considerably more stable than either **11** or **12**, which were similar in energy, the latter being slightly more stable. Except for the reversal in stability of **11** and **12**, our results are similar. It is probable that the previous calculations,

---

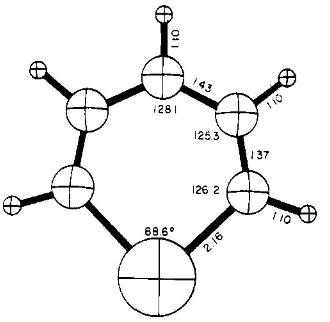
[28] Nekrasov, Yu. S.; Sizoi, V. F.; Zagorevskii, D. V.; Borisov, Yu. A. *J. Organomet. Chem.* **1981**, *205*, 157.

[29] (a) Jutzi, P.; Kohl, F.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 59. (b) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.



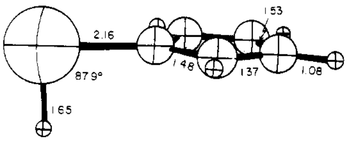
ΔH$_f$ = 229.9

10



ΔH$_f$ = 242.4

11



ΔH$_f$ = 269.3

12

Figure 3. Calculated geometries (bond lengths in Å, angles in deg) and heats of formation (kcal/mol) of **10–12**.

which were carried out on assumed geometries, overestimated the stability of **10**, since the nido structure of $C_6H_5^+$ was also found to be considerably more stable (100 kcal/mol difference in atomization energies) than the phenyl cation, which seems unlikely.

As with the MNDO results for $C_5H_5Sn^+$,[15] the positive charge in **11**, although mostly centered on Pb (+0.85), polarizes the π system, causing positive charge to develop at the position para to lead (+0.32) and strengthening the C_1–C_2 and C_4–C_5 bonds. The MNDO geometry of **12** is also similar to that found for its tin analogue, for which a detailed rationalization was given previously.

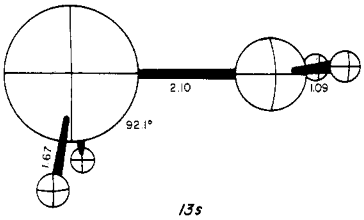
Multiple Bonding by Lead. Although multiple bonding by silicon,[30] germanium,[31] and tin[15,32] has recently been of considerable interest, it appears that no work has been reported on multiple bonding by lead.

We were therefore interested in examining: (a) the lowest singlet and triplet states of plumbene (**13**) and diplumbene (**14**); and (b) plumbabenzene (**15**) and its isomers 1-plumbacyclohexadienylidene (**16**), 2-plumbacyclohexadienylidene (**17**), 4-plumbacyclohexadienylidene (**18**), and Dewar plumbabenzene (**19**). Heats of formation of **13–19** are listed in Table VI. Geometries for singlet and triplet **13** and **14**, as well as **15**, are shown in Figure 4, while those for **16–19** are given in Table VII.

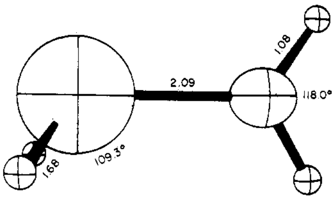
Table VI. Calculated Heats of Formation of 13–19

compd	RHF S	UHF S	RHF T	UHF T
13	83.7	83.7	90.1	84.9
13 (planar)	111.8^a			
14	54.6	54.6	105.7	96.5
14 (planar)	61.0^a			
15	84.3	84.3		
15 (planar)	128.1^a			
16	48.3			
17	47.4			
18	186.2	156.7	164.8	144.5
19	149.0			

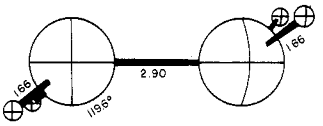
^{a} Transition state.



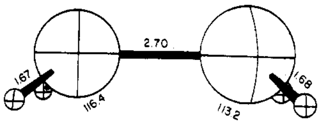
13s



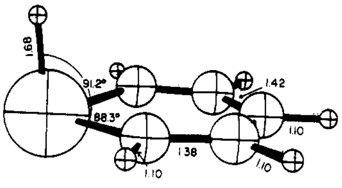
13T



14S

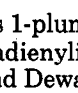


14T

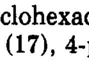


15

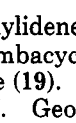
Figure 4. Calculated geometries (bond lengths in Å, angles in deg) of **13S**, **13T**, **14S**, **14T**, and **15**. MNDO UHF geometries are shown for **13T** and **14T**.



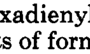
16



17



18



19

---

(30) Silene, for reviews, see: (a) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. *Acc. Chem. Res.* **1975**, *8*, 18, and (b) Sakurai, H. *Kagaku (Kyoto)* **1982**, *37*, 925. Silabenzene, see: Chandresekhar, J.; Schleyer, P. v. R.; Baumgartner, R. O. W.; Reetz, M. T. *J. Org. Chem.* **1983**, *48*, 3453 and references cited therein.

(31) (a) Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 324. (b) Bleckmann, P.; Minkwitz, R.; Neumann, W. P.; Schriewer, M.; Thibud, M.; Watta, B. *Tetrahedron Lett.* **1984**, *25*, 2467. (c) Nagase, S.; Kudo, T. *THEOCHEM* **1983**, *103*, 35.

(32) (a) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329. (b) Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Comm.* **1982**, 1407. (c) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871.

Table VII. Calculated Geometries (Bond Lengths in Å; Angles in deg) of Singlet 16–19

compd	parameter
16	$PbC_1 = 2.10$; $C_1C_2 = 1.35$; $C_2C_3 = 1.51$ $C_1H = 1.09$; $C_2H = 1.10$; $C_3H = 1.12$ $C_5PbC_1 = 90.8$; $PbC_1C_2 = 126.4$ $C_1C_2C_3 = 128.3$; $C_2C_3C_4 = 119.6$ $C_1C_2H = 117.6$; $C_2C_3H = 112.0$ $HC_3H = 106.0$
17	$PbC_1 = 2.16$; $C_1C_2 = 1.49$; $C_2C_3 = 1.35$ $C_3C_4 = 1.46$; $C_4C_5 = 1.35$; $C_5Pb = 2.09$ $C_1H = 1.11$; $C_2H = 1.10$; $C_3H = 1.10$ $C_4H = 1.10$; $C_5H = 1.09$; $PbC_1C_2 = 119.6$ $C_1C_2C_3 = 127.8$; $C_2C_3C_4 = 127.7$ $C_3C_4C_5 = 126.5$; $HC_1C_2 = 108.8$ $HC_2C_3 = 118.1$; $HC_3C_4 = 114.1$ $HC_4C_5 = 119.6$; $HC_5Pb = 116.4$
18 (UHF)	$PbC_1 = 2.13$; $C_1C_2 = 1.40$; $C_2C_3 = 1.38$ $PbH = 1.66$; $C_1H = 1.08$; $C_2H = 1.09$ $PbC_1C_2 = 118.5$; $C_1C_2C_3 = 119.8$ $C_2C_3C_4 = 145.1$; $HPbC_1 = 111.3$ $HC_1C_2 = 122.4$; $HC_2C_3 = 119.4$
19	$PbC_1 = 2.15$; $C_1C_2 = 1.35$; $C_2C_3 = 1.51$ $C_3Pb = 2.24$; $PbH = 1.66$; $C_1H = 1.08$ $C_2H = 1.09$; $C_3H = 1.09$; $PbC_1C_2 = 93.6$ $C_1C_2C_3 = 114.2$; $C_2C_3Pb = 85.8$ $C_2C_3C_4 = 115.0$; $C_1PbC_5 = 99.4$ $HPbC_1 = 127.0$; $HC_1C_2 = 130.7$ $HC_2C_3 = 119.3$; $HC_4Pb = 129.6$ $PbC_1C_2C_3 = -2.1$; $C_1PbC_3C_4 = 114.2$ $HC_1C_2C_3 = 177.3$; $HC_2C_1Pb = 178.6$

The structures of singlet **13** and **15** and the relative energies of **15**, **16**, and **17** illustrate the tendency for lead to prefer divalency whenever possible. Thus, singlets **13** and **15** correspond to union of PbH_2 and PbH anions with CH_2 and C_5H_5 cations, respectively, such that lead has two electrons in an s orbital (inert pair) and one in each of three orthogonal p orbitals which are used in PbH and PbC bonding. On the basis of this analysis, planar geometries for **13** and **15** would be expected to be much higher in energy, as is the case. In addition, the barrier to 1,2-hydrogen migration, from **15** to **17**, is only 6.5 kcal/mol, and since MNDO tends to overestimate[33] activation barriers for shifts of this kind, this process may actually be activationless. It seems unlikely, then, that **15** can be observed experimentally.

The absence of any π bonding in **13** is further confirmed by the small singlet–triplet gap (1.2 kcal/mol MNDO UHF), although **13T** has perpendicular PbH_2 and CH_2 residues analogous to triplet ethylene (see Figure 4). **14**, by comparison, has a large singlet–triplet gap (41.9 kcal/mol MNDO UHF) but is also nonplanar with both lead atoms being roughly pyramidal. A planar geometry for **14** is 6.4 kcal/mol higher in energy and a transition state of the potential surface. This behavior is identical with that of the tin analogue, which was explained[15] in terms of a σ conjugative interaction between metal sp^3 orbitals, producing a second bond between metal atoms (thus a closed-shell structure with a large singlet–triplet gap) and a C_{2v} geometry in which the sp^3 orbitals are trans to one another. A small bond order (0.2) between Pb atoms in trans **14S** is also understandable in light of the formally negative π bond order, which, when added to the σ bond order, gives an apparently small value.

The corresponding triplet **14T** has an analogous structure with both lead atoms pyramidal. Here, however, the cis configuration is the lower in energy. The reason for this is evident from the form of the MOs in the two isomers; see Figure 5. The LUMO of the singlet, which is singly occupied in the triplet, is higher in energy in the trans isomer because it has an extra node.

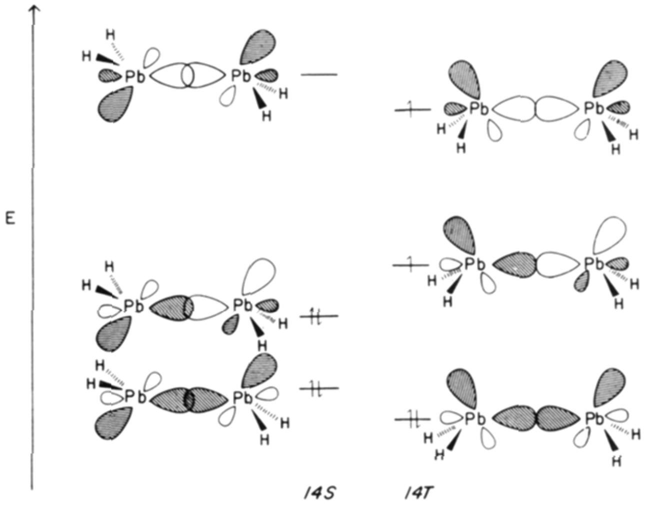


Figure 5. Orbitals of *trans*-**14S** and *cis*-**14T**.

Table VIII. Calculated Heats of Formation (kcal/mol) of 20–23

compd	unbridged	bridged
20	−213.8	
21[a]	−191.7 (−200.8)	−194.8 (−198.1)
22		13.2
23	−170.2	−186.4

[a] MNDO UHF values in parentheses.

Although **14S** and **14T** are respectiely 5.6 and 14.5 kcal/mol stable to dissociation to two molecules of PbH_2, there is no barrier to either process.

Lead Tetraacetate. Both the crystal structure[34] and IR spectrum[35] of lead tetraacetate (**20**) indicate a distorted cubic geometry, in which both oxygen atoms of each acetate group are coordinated with lead. This is supported by the increased carbonyl character of the acetate groups in coordinating solvents, which are proposed to displace one of the chelated acetate oxygen atoms.[35a]

We were unable to locate this distorted cubic geometry for **20**, although the cis form (C=O bonds cis to Pb—O bonds) was more stable than its trans isomer by 28.7 kcal/mol. Since eight oxygen atoms are in rather close contact in the bridged geometry for **20**, the inability of MNDO to reproduce this structure is probably due to its known overestimation of repulsions between atoms at their van der Waals distance.[5,33]

However, the triacetyllead radical (**21**), triacetyllead cation (**22**), and lead diacetate (**23**) all had minimum energy geometries with bridging acetate groups. The stability of this geometry relative to an unbridged one was (a) 2.7 kcal/mol less stable for **21**, (b) 6.2 kcal/mol more stable for **23**, and (c) the only structure found for **22**. The heats of formation of **20–23** are given in Table VIII while the geometries for **20**, unbridged **21**, and bridged **22** and **23** are shown in Figure 6.

Although **20** is an extremely versatile oxidizing reagent, we were primarily interested in its reaction with olefins, due to the unexpected prediction[36] that the analogous mercuric acetate oxidation proceeded via a charge-induced

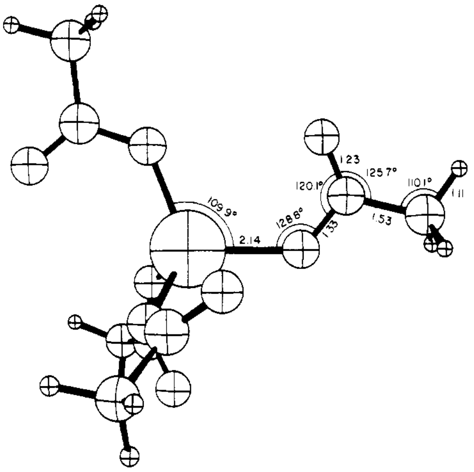
---

[33] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. H.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

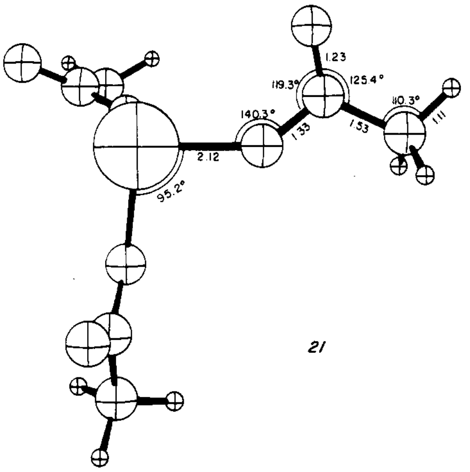
[34] Kamenar, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 321.

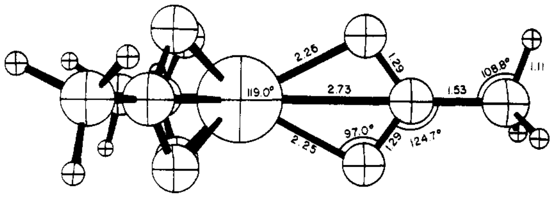
[35] (a) Partch, R.; Monthony, J. *Tetrahedron Lett.* **1967**, 4427. (b) Huesler, K.; Loeliger, H. *Helv. Chim. Acta* **1969**, *52*, 1495.

[36] Dewar, M. J. S.; Merz, K. M., Jr. *Organometallics*, second of three papers in this issue.

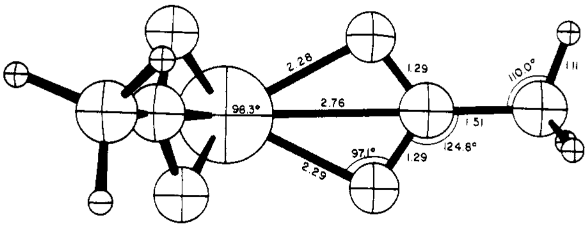


20





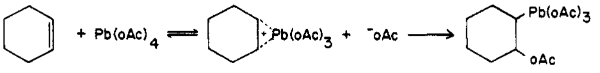
22



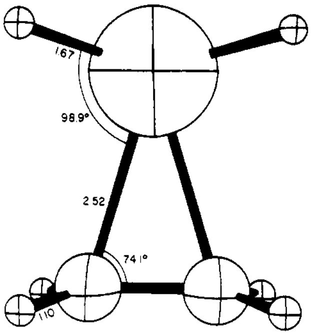
23

Figure 6. Calculated geometries (bond lengths in Å, angles in deg) of **20**, unbridged **21**, and bridged **22** and **23**.

dipole (CID) complex rather than the previously suggested symmetrical π complex. The initial step in lead tetraacetate oxidation of olefins has also been represented as the formation of a symmetrical π complex, which is then attacked by an acetate anion (eq 1).[37]

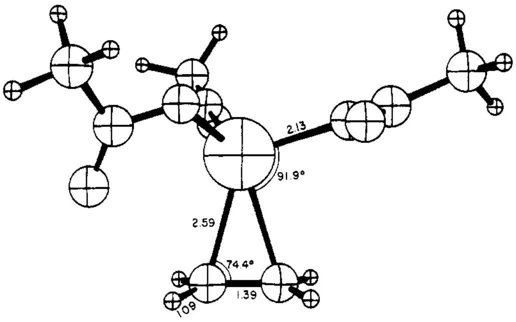


(1)



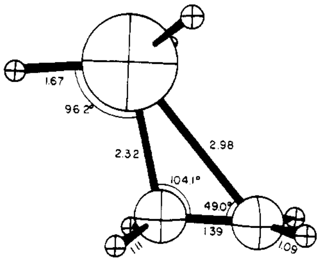
ΔH_f = 261.3

24



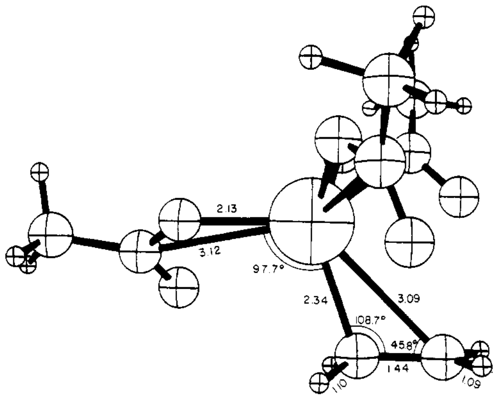
ΔH_f = 56.1

25



ΔH_f = 259.9

26



ΔH_f = 51.9

27

Figure 7. Calculated energies (kcal/mol) and geometries (bond lengths in Å, angles in deg) of **24**–**27**.

Symmetrically bridged and open "classical" cation structures for the complex between **22** and an olefin were modeled by using (a) PbH_3^+ and ethylene and (b) **22** and ethylene. In both instances, the symmetrically bridged

---

[37] See, for example: Moriarty, R. M. In "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. II, p 183.

Table IX. Calculated Heats of Formation, Ionization Potentials, and Dipole Moments for Molecules Containing Lead

compd	ΔH_f, kcal/mol	IP, eV	dipole moment μ, D	charge on lead
$PbH_3\cdot$	66.3	9.45	0.17	0.28
PbF_4	-32.1	14.80	0.01	1.09
$PbCl_4$	-50.0	13.24	0.01	0.54
$PbVr_4$	5.3	12.19	0.00	0.30
PbI_4	40.6	11.04	0.00	-0.29
$Pb(CH_3)_3F$	-6.0	10.49	4.59	0.21
$Pb(CH_3)_3Br$	14.0	10.31	4.05	0.01
$Pb(CH_3)_3I$	27.7	10.11	2.65	-0.15
HPb(O)OH	64.2	10.87	2.31	0.58
$CH_3Pb(O)OH$	52.1	10.35	3.65	0.49
HPb(O)H	105.8	10.55	3.77	0.40
$CH_3Pb(O)H$	94.6	10.19	4.22	0.33
H_3PbNH_2	71.7	10.17	1.64	0.08
H_3PbSH	55.3	10.20	2.35	0.06
H_3PbOH	28.5	10.94	2.65	0.19
$H_2Pb(OH)_2$	-4.9	11.11	3.41	0.35
$Pb(OH)_4$	-61.1	11.61	1.02	0.60
28	47.6	9.98	0.28	-0.03
29	106.9	9.16	0.28	0.05
30	19.4	3.92		0.03

structures **24** and **25** were transition states between mirror-image open geometries **26** and **27**. The energies and geometries of these species are shown in Figure 7.

In addition to slightly longer than normal Pb–C bond lengths (2.32 and 2.34 Å) and shorter than normal C–C bond lengths (1.39 and 1.44 Å) in **26** and **27**, the Pb–C bond order in each (0.47 and 0.38) is rather small, while the C–C bond order (1.52 and 1.40) is rather large. Thus, **26** and **27** correspond more closely to CID complexes, similar to those formed by the acetylmercury cation with ethylene. A 21 kcal/mol barrier to rotation about the terminal carbon seems to confirm this analysis.

The syn or anti attack of acetate anion was mimicked by using NH_3, since the reaction of two charged species in the gas phase is generally an activationless process. The activation barriers to syn and anti addition to **26** were 10.1 and 2.2 kcal/mol, respectively, although the syn product was characterized as a rotational transition state to the anti product. This difference in activation barriers might be expected to be even greater for **27**, because of the bulkiness of the three acetate groups.

Other Compounds of Lead. Table IX gives heats of formation, ionization energies, and dipoles of some additional lead(IV) compounds, most of which are analogues of simple carbon derivatives.

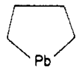
(a) The lead atoms in plumbanones (R_2PbO), like those in **14**, are pyramidal.

(b) The plumbyl radical is also predicted to be pyramidal, unlike methyl radical[38] but like silyl[39] and germyl.[40] The bond angles predicted by MNDO in PbH_3 (110.2°) are close to tetrahedral, like those in stannyl (109.5°) and germyl (109.8°), while methyl is predicted to be planar (120°) and silyl to have an intermediate geometry (115.8°). The reasons for this have been discussed elsewhere.[41]

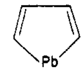
Table X. Calculated Geometries (Bond Lengths in Å; Angles in deg) of 28–30

parameter	28	29	30
PbC_1	2.18	2.14	2.16
C_1C_2	1.53	1.35	1.35
C_2C_3	1.55	1.48	1.47
PbH	1.66	1.66	1.69
C_1H	1.10	1.08	1.09
C_2H	1.12	1.09	1.09
PbC_1C_2	105.2	108.3	111.9
$C_1C_2C_3$	116.1	120.2	118.4
C_1PbC_4	87.9	83.2	79.4
$HPbC_1$	114.1	114.2	94.2
HC_1C_2	112.0	126.8	121.4
HC_2C_3	108.2	117.1	117.7
$PbC_1C_2C_3$	26.2	0.0	2.4
$C_1C_2C_3C_4$	-37.6	0.0	-0.8
$C_2C_1PbC_4$	-8.9	0.0	-2.3

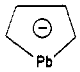
(c) While plumbacyclopentane (**28**) and 5-plumbacyclopentadiene (**29**) have geometries similar to their carbon analogues, the former puckered and the latter planar, the Pb–C and Pb–H bonds in the plumbacyclopentadienate anion (**30**) are orthogonal, as in **15**; see Table X.



28



29



30

(d) Of the lead tetrahalides (PbX_4, X = F, Cl, Br, I), only $PbCl_4$ is predicted to be stable in the gas phase relative to dissociation into PbX_2 and X_2. Although gas-phase heats of formation have been reported for the lead tetrahalides,[42] these seem unreliable for several reasons: (1) they were estimated by comparison with dihalides and tetrahalides of titanium and zirconium; (2) there are two different sets of values which differ by as much as 85 kcal/mol; (3) PbF_4 (crystalline), $PbCl_4$ (liquid), and $PbBr_4$ are reported[43] to be unstable to dissociation, and PbI_4 has yet to be observed in solid, liquid, or gas phase; and (4) PbF_4 seems likely to be ionic, rather than covalent, given its high melting point (600 °C[43]).

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. F49620-83-C-0024), the Robert A. Welch Foundation (Grant F-126), and the National Science Foundation (Grant CHE82-17948).

Registry No. Pb, 7439-92-1.

---

(38) (a) Dyke, J.; Jonathan, N.; Lee, E.; Morris, A. *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1385. (b) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(39) Morehouse, R. L.; Christiansen, J. J.; Gordy, W. *J. Chem. Phys.* **1966**, *45*, 1751.

(40) Jackel, G. S.; Christiansen, J. J.; Gordy, W. *J. Chem. Phys.* **1967**, *47*, 4274.

(41) Dewar, M. J. S. *J. Am. Chem. Soc.*, submitted for publication.

(42) (a) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37.* (b) Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, 1.

(43) Standen, A., Executive Ed. "Kirk-Othmer Encyclopedia of Chemical Technology", 2nd ed.; Interscience: New York, 1967; Vol. 12.