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The molecular and electronic structures of ions and radicals derived from tetramethyllead, hexamethyldilead, dimethyllead, and tetramethyldilead: an SCF-MO study

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Abstract

Molecular geometries and energies have been calculated, using the semi-empirical MNDO method for closed shell species, and the UHF-MNDO method for neutral radicals and cation radicals for $PbMe_4$, Pb_2Me_6, $PbMe_2$, and three isomeric forms of Ph_2Me_4 and all of their cation radicals, together with fragment ions and radicals including $(PbMe_3)^+$, $PbMe_3$, and $(Pb_2Me_x)^+$ for $1 \leqslant x \leqslant 5$. The radical cation $(PbMe_4)^+$ is calculated to have C_{3v} skeletal symmetry, with a D_{2d} isomer some 26 kJ mol^{-1} higher in energy: the dinuclear cation radical $(Pb_2Me_6)^+$ is calculated to be a a(Pb-Pb) radical of D_{3d} skeletal symmetry. The mass spectral fragmentations of both $PbMe_4$ and Pb_2Me_6 are discussed.

Introduction

In two recent papers [1,2], we reported MNDO calculations in radical cations derived from $SnMe_4$ and Sn $_2Me_6$, and from $GeMe_4$ and Ge_2Me_6. A major point of difference between $(SnMe_4)^+$ and $(GeMe_4)^+$ is that the tin cation was calculated [1] to have C_{3v} symmetry, consistent with the interpretation of its electron spin resonance spectrum in frozen $CFCl_3$ matrices [3], whereas the germanium cation was calculated to have D_{2d} skeletal symmetry: experimentally $(GeMe_4)^+$ was found to have C_{2v} symmetry, suggested [4] to arise from D_{2d} by matrix perturbation effects.

As we have previously discussed cation radicals derived from CMe_4 and $SiMe_4$ [5,6], we present in this paper the results of a semi-empirical study of cations and radicals derived not only from $PbMe_4$ and Pb_2Me_6, but also from the as yet uncharacterised $PbMe_2$ and Pb_2 Me,.

Calculations

All calculations of molecular geometry and energy, and of electronic structure were made using the MNDO method [7], as implemented in Version 5.0 of the MOPAC system [8]. The published atomic parameters were used for H,C, and Pb [7,9]. UHF wavefunctions were employed for all open-shell species, and all geometric variables were independently and simultaneously optimised unless it is stated otherwise: the PRECISE option was used throughout. The accuracy and reliability of MNDO calculations on compounds containing lead have been discussed at length by Dewar [9].

Results and discussion

$PbMe_4$ and Pb_2Me_6, and their radical cations

The two neutral molecules $PbMe_4$ and Pb_2Me_6 optimise to geometries having T_d and D_{3d} skeletal symmetry precisely: in each case there is essentially free rotation about the Pb-C bonds. These geometries have been previously discussed by Dewar, and the results obtained here are in agreement with those reported earlier [9].

The HOMO of $PbMe_4$ is calculated to have t_2 symmetry in the point group T_d, as suggested from an early photoelectron study [10]. The ion $(PbMe_4)^+$ is thus, after vertical ionisation, sensitive to Jahn-Teller distortion. Two distortion pathways are open for skeletal perturbation from T_d symmetry: distortion along one component of the e vibrational mode leads to D_{2d} symmetry, while distortion along a t_2 vibration gives a structure of C_{3v} symmetry. Free optimisation of the geometry of $(PbMe_4)^+$ converged to a structure of precise C_{3v} symmetry, in which the unique Pb-C bond (Table 1) is considerably longer than the other three Pb-C bonds; this structure is thus very similar to those calculated [1] and observed [3] for the analogous cation $(SnMe_4)^+$. Within the C_{3v} geometry, the $PbMe_3$ fragment having three-fold rotational symmetry is very considerably flattened towards planarity: the C-Pb-C angle is 117.8°, considerably closer to the 120.0” calculated for $(PbMe_3)^+$ than to the 108.8” calculated for the neutral radical $PbMe_3$ (see below). Similarly the unique methyl group is considerably flattened, with an H-C-H angle of 117.8°, considerably closer to the 120 ° calculated, and observed [11], for the methyl radical than to the 110° expected in a normal methyl group bound to a heteroatom. These geometrical properties suggest that the C_{3v} isomer of $(PbMe_4)^+$ is tending towards dissociation to the cation $(PbMe_3)^+$ and the neutral methyl radical: the calculated energy for this dissociation is only + 13.9 $kJ\ mol^{-1}$.

Some 25 $kJ\ mol^{-1}$ higher in energy is an isomeric cation of D_{2d} symmetry: when only C_{2v} symmetry was imposed on the skeleton (cf the second isomer of $(SnMe_4)^+$ [1]), D_{2d} *symmetry* nevertheless resulted.

These two isomeric forms for $(PbMe_4)^+$ should be readily distinguishable using the hyperfine coupling due to hydrogen atoms in the ESR spectrum. In the C_{3v} isomer, the calculated spin density at the hydrogen atoms in the unique methyl group is – 0.0238, while that for the remaining hydrogen atoms is +0.0020: adopting the scale factor of 850 G suggested [1] for tin-centred radicals, the C_{3v} isomer of $(PbMe_4)^+$ may be expected to show hyperfine coupling to three equivalent hydrogen atoms with $A(^1H)$ of ca. 20 G, and to a further nine equivalent hydrogen atoms with $A(^1H)$ of ca. 1.7 G. For the D_{2d} isomer, on the other hand, the spin density on the twelve hydrogen atoms, rendered equivalent by a combination of skeletal symmetry and free rotation about the Pb-C bonds, is -0.0013, suggesting hyperfine coupling to twelve equivalent hydrogen atoms with $A(^1H)$ of ca. 1.1 G.

In neutral Pb_2Me_6, the HOMO has a_{1g} symmetry, and is strongly **localised** in the Pb-Pb bond, as a bonding orbital. Vertical ionisation from this level to give $(Pb_2Me_6)^+$ is thus expected to yield a molecular ion not sensitive to Jahn-Teller distortion, but with a much weakened Pb-Pb bond. Full optimisation of this structure gave a geometry retaining D_{3d} skeletal symmetry, in which the Pb-Pb distance has increased from 2.771 Å calculated for neutral Pb_2Me_6 to 3.072 A calculated in the cation $(Pb_2Me_6)^+$. At the same time the individual $PbMe_3$ fragments have become rather flatter: the C-Pb-C angle increased upon ionisation from 107.0” in the neutral to 113.8” in the cation, intermediate between the values calculated for the radical $PbMe_3$ and the corresponding cation $(PbMe_3)^+$ (see below, and Table 1). This cation is thus very similar in structure to the analogous tin cation $(Sn_2Me_6)^+$ [1]: neither of these species exhibits the almost planar coordination of the metal atoms deduced [12] from the ESR spectrum. As for the tin system also, ionisation of Pb_2Me_6 significantly weakens the Pb-Pb bond, as expected from the **localisation** of the HOMO in this bond: the calculated value of $D(Me_3Pb-PbMe_3)$ in the neutral compound is 82.0 $kJ\,mol^{-1}$, while that of $D(Me_3Pb^+-PbMe_3)$ in $(Pb_2Me_6)^+$ is only 27.0 $kJ\,mol^{-1}$.

$PbMe_3$ and $(PbMe_3)^+$

The neutral radical $PbMe_3$ is calculated to have C_{3v} skeletal symmetry with a sharply pyramidal structure: the calculated angle C-Pb-C is **108.8°**, similar to the angles calculated for the related radicals $SiMe_3$ (113.5° [5]), $GeMe_3$ (112.6° [2]) and $SnMe_3$ (110.0° [1]): these radicals, which are all found experimentally to be pyramidal [13–15], may be contrasted with CMe_3, calculated [5,16] and observed [17] to have a planar skeleton. There is thus a monotonic change in the C-M-C angle in radicals MMe_3 as M changes from carbon through to lead. The distinction between CMe_3 and its heavier analogues has been discussed [1] in terms [18] of the relative electronegativities of the central atom and the ligating methyl groups.

The cation $(PbMe_3)^+$ is calculated to have a planar PbC_3 skeleton, as expected: the LUMO is largely concentrated on the central atom, as a **6p** orbital normal to the skeletal plane.

ESR spectroscopy should provide a ready distinction between $(Pb_2Me_6)^+$ and its likely open-shell dissociation product $PbMe_3$. The mean spin densities calculated at hydrogen are **+0.0016** and -0.0073 respectively: hence, using the same factor, 850 G, as earlier, the ESR spectrum of $(Pb_2Me_6)^+$ should be **characterised** by hyperfine coupling to eighteen equivalent hydrogen atoms with $A(^1H)$ of ca. 1.4. G, while that of $PbMe_3$ should be **characterised** by hyperfine coupling to only nine equivalent hydrogen atoms, but with $A(^1H)$ of ca. 6.2 G. Moreover the 6s spin density calculated at lead (^{207}Pb has natural abundance 22.1% and nuclear spin $I = 1/2$) is **+0.0568** in the mononuclear radical $PbMe_3$ but only – 0.0068 in binuclear $(Pb_2Me_6)^+$: hence the patterns of ^{207}Pb satellites will also be entirely different.

$PbMe_2$ and $(PbMe_2)^+$

The lead(II)alkyl $PbMe_2$ is calculated to have a bond angle C-Pb-C of only 97.3”: this is typical not only of the bond angles in **lead(II)** halides [19], but of other

Table 1

Optimised molecular parameters

	Skeletal point **group**	$A H_f^\circ$ **(kJ mol^{-1})**	**Distances (Å)** Pb-C	Pb-Pb	**Angles (°)** C-Pb-C	C-Pb-Pb	**ρ[H(1s)]**	**ρ[Pb(6s)]**
(a) ***$PbMe_4$ and Pb_2 Me, and*** their ***radical*** cations								
$PbMe_4$	T_d	**+111.2**	2.172		109.5		–	
$(PbMe_4)^+$	C_{3v}	+ 975.7	**2.472**(× 1) 2.199(x 3)		**98.6**(x 3) **117.8**(× 3)		− **0.0238**(x 3) + **0.0020**(x 9)	− 0.0052
	$D_{2d\ a}$	+ 1001.5	2.243		**113.8**(x 2) **107.3**(x 4)		-0.0013	− 0.0164
Pb_2Me_6	D_{3d}	+ 190.2	2.177	2.771	107.0	111.8	–	–
$(Pb_2Me_6)^+$	D_{3d}	+ 995.7	2.189	3.072	113.8	104.6	+ 0.0018	− 0.0068
(b) $PbMe_3$ and $(PbMe_3)^+$								
$PbMe_3$	$c_{3''}$	+136.1	2.176		108.0		− 0.0073	+ 0.0568
$(PbMe_3)^+$	D_{3h}	+886.6	2.1%		120.0	–		
(c) ***$PbMe_2$ and $(PbMe_2)^+$***								
$PbMe_2$	$c_{2''}$	+42.0	2.140		97.3	–	–	
$(PbMe_2)^+$	$C_{2''}$	+897.9	2.1%		118.6	–	-0.0096	+ 0.0261

(d) Isomeric forms of *Pb_2Me_4 and of $(Pb_2Me_4)^+$*								
Pb_2Me_4, (1)	C_{2h}	*+67.5*	2.147	2.975	97.6	119.4		–
$(Pb_2Me_4)^+$	C_{2h}	*+871.7*	2.171	2.929	107.3	125.7	– 0.0081	+ 0.0417
Pb_2Me_4 (2)	C_{2v}	*+ 129.9*	2.345(×4,C_b) 2.156(x 2,C_t)	2.876	98.9(C_b–Pb–C_b) 95.8(C_t–Pb–C_b)	118.3(C_t)		
$(Pb_2Me_4)^+$	$C_{2''}$	*+926.5*	2.209(x 2,Pb_1–C_b) 2.517(×2,Pb_2–C_b) 2.441(X 1,Pb_1–C_t) 2.135(x 1,Pb_2–C_t)	3.081	107.6(C_b–Pb_1–C_b) 90.2(C_b–Pb_2–C_b) 107.7(C_t–Pb_1–C_b) 99.7(C_t–Pb_2–C_b)	121.0(C_t–Pb_1–Pb_2) 103.8(C_t–Pb_2–Pb_1)	+0.0011(x6) +0.0001(x 3) – 0.0267(x 3)	+0.0143(Pb_1) – 0.0002(Pb_2)
$Me_3PbPbMe$ (3)	C_s	+ 102.5	2.174(x 3) 2.127(x 1)	2.750	101.4(x 3)	116.7(x 3) 167.6(x 1)		
$(Me_3PbPbMe)^+$	C_s	+ 885.6	2.507(×1,Pb_1) 2.163(×2,Pb_1) 2.106(×1,Pb_2)	2.919	95.q x 2) 102.0(x 1)	99.q x 1,Pb_1) 126.7(x 2,Pb_1) 169.3(x 1,Pb_2)	–0.0278(× 3) +0.0031(×6) + 0.0003(x 3)	– 0.0021(Pb_1) – 0.0001(Pb_2)
(e) Other ions $(Pb_2Me_x)^+$								
$(Me_3PbPbMe_2)^+$ (4)	C_s	+ 880.3	2.197(x 3) 2.153(×2)	2.942	116.2(× 3) 104.2(× 1)	101.3(X 3) 127.9(x 2)		
$(Me_2PbPbMe)^+$ (7)	C_s	+ 778.4	2.152(x 2) 2.105(× 1)	2.911	102.0	129.q x 2) 94.3(x 1)	–	
$(Pb_2Me_2)^+$	C_2	*+827.5*	2.114	2.930	–	114.0	+ 0.0063	+ 0.0051
$(Pb_2Me)^+$ (8)	C_s	*+ 895.2*	2.127	2.857	–	102.7		–

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[a] Skeletal symmetry D_{2d} imposed: structure optimised with 38 independent geometric variables, (3N – 6) = 45.

alkyl derivatives of the heavier main-group elements, such as $SbMe_3$ [20] and $SeMe_2$ [21].

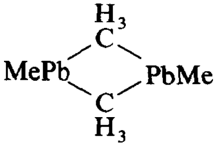
The HOMO of $PbMe_2$ is of a_1 symmetry, localised mainly on the lead atom, and can be described as a lone pair pointing along the two-fold rotation axis. The LUMO is an almost pure lead $6p$ orbital perpendicular to the skeletal plane. Single ionisation to provide $(PbMe_2)^+$ increases the calculated bond angle to 118.6 °, while double ionisation to $(PbMe_2)^{2+}$ gives a linear ion, isoelectronic and isostructural with $HgMe_2$ [22].

Isomeric forms of Pb_2Me_4 and of (Pb, Me,) $^+$

Although dimers of germylenes and stannylenes, Ge_2R_4 and Sn_2R_4, are well characterised structurally [23,24], very much less is known of the corresponding lead derivatives. Three constitutions for Pb_2Me_4 (l-3) were considered:

$Me_2Pb{=}PbMe_2$

(1)



(2)

$Me_3Pb{-}PbMe$

(3)

For both neutral and cationic species, the diplumbene **1** proved to have the lowest energies, and the cyclic system 2 to have the highest energies.

For 1 the neutral molecule was calculated to adopt the same C_{2h} conformation as found [23–25] for Ge_2R_4 and Sn_2R_4. The Pb-Pb bond, so far from being a double bond as suggested by representation **1**, is ca. *0.2* Å longer than that in ethane-like Pb_2Me_6, and has a bond order of only 0.168 (cf. 0.603 in Pb_2Me_6). Moreover the structure of each $PbMe_2$ fragment in neutral **1** is scarcely different (Table 1) from that of the isolated monomer $PbMe_2$. The weakness of the Pb-Pb bond in neutral **1** is partly due to the Pb-Pb antibonding character of the HOMO: ionisation to $[\mathbf{1}]^+$ thus causes a significant decrease in the Pb-Pb bond length.

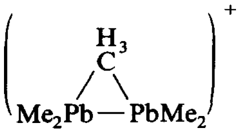
For the cyclic isomer 2, a C_{2v}(*syn*) conformation with both terminal methyl groups on the same side of the planar central Pb_2C_2 ring was found to be marginally more stable, by 6.0 kJ mol^{-1}, than the C_{2h}(*anti*) conformation having one terminal methyl group on either side of the ring. The behaviour of this dimer is thus very similar to that of Pb_2Cl_4 [9]. The two conformers, *syn* and *anti,* of $[\mathbf{2}]^+$ are of virtually identical energy.

Other ions (Pb, Me,) $^+$

Two isomeric forms of $(Pb_2Me_5)^+$ 4 and **5** were considered:

$(Me_3Pb{-}PbMe_2)^+$

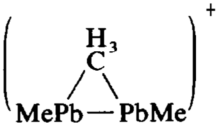
(4)



(5)

Optimisation of both led to a single minimum, in which the coordination of the three-coordinate Pb of 4 is accurately planar, while the Me_3Pb is nearly planar, perpendicular to the weak Pb-Pb bond (Table 1). This cation is best regarded as a donor-acceptor complex between $PbMe_2$ (acting as electron donor, with HOMO along the Pb-Pb bond) and $(PbMe_3)^+$ (acting as electron acceptor, with LUMO normal to its PbC_3 plane): the dinuclear cation is stabilised, by Pb-Pb bond formation, relative to its components by some 48 kJ mol^{-1}. No evidence was found for any minimum corresponding to 5.

On the other hand both cyclic and acyclic isomers 6 and 7 were found for $(Pb_2Me_3)^+$:



(6)

$(Me_2Pb—PbMe)^+$

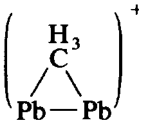
(7)

The cyclic isomer 6 has C_2 symmetry with one terminal methyl group on either side of the Pb_2C ring, while 7 of C_s symmetry, which is the more stable by some 40 kJ mol^{-1} is accurately planar at the three-coordinate lead atom. The unique angle C-Pb-Pb is only a little larger than 90°, and this ion is best thought as a donor-acceptor complex between neutral $PbMe_2$, acting as electron donor, and $(PbMe)^+$ acting as electron acceptor.

The $(Pb_2Me)^+$ cation also has two isomeric forms, of which the acyclic isomer $(PbPbCH_3)^+$ (8) is more stable than the cyclic isomer 9 by ca. 11 kJ mol^{-1}.

$(Pb—PbMe)^+$

(8)



(9)

The paramagnetic cation $(Pb_2Me_2)^+$ has C_2 molecular symmetry (cf. H_2O_2) with a dihedral angle of 78.9 °.

Mass spectral fragmentation of $PbMe_4$ and Pb_2Me_6

In the mass spectrum of $PbMe_4$, the principal fragment ions, apart from the low abundance molecular ion $(PbMe_4)^+$ are $(PbMe_3)^+$, $(PbMe_2)^+$, and $(PbMe)^+$: the respective appearance potentials are 9.3, 10.1, 12.7 and 13.1 eV [26]. The calculated energies and symmetries of the valence shell orbitals for $PbMe_4$ are given in Table 2: the orbital order corresponds to that suggested in a photo-electron study [10], although there are serious discrepencies between the several reported values of the first ionisation energy of $PbMe_4$, with a range of reported values between 9.3 eV [26] and 8.0 eV [27]. The $\Delta H_f°$ data of Table 1, together with the calculated value of $\Delta H_f°$ for the methyl radical, + 103.0 kJ mol^{-1}, lead to calculated $\Delta H_f°$ values for the fragments: $(PbMe_3)^+ + CH_3^{\cdot}$, + 989.6 kJ mol^{-1}; $(PbMe_2)^+ + 2CH_3^{\cdot}$, + 1103.9 kJ mol^{-1}; $(PbMe)^+ + 3CH_3^{\cdot}$, + 1120.9 kJ mol^{-1}. All of the fragment ions could therefore be formed by ionisation of $PbMe_4$ from the t_1 level at − 13.85 eV: however there is some evidence [9] that the first ionisation energies for organolead compounds as calculated by MNDO are systematically high, although the effects on the higher ionisation energies have not been studied.

Table 2

Orbital symmetries and energies for $PbMe_4$ and Pb_2Me_6

Symmetry	Binding energy (eV)	Symmetry	Binding energy (eV)
(a) *PbMe₄*			
t_2	10.28	a_1	20.34
t_1	13.85	t_2	29.87
e	13.99	a_1	33.20
t_2	14.29		
(b) Pb₂Me₆			
a_{1g}	9.15	e_u	14.15
e_g	10.04	a_{1g}	14.43
e_u	10.51	a_{2u}	19.51
e_g	13.82	a_{1g}	22.31
e_g	13.89	e_g	29.65
e_u	13.90	e_u	29.89
e_g	14.09	a_{2u}	32.33
a_{2u}	14.14	a_{1g}	32.95

The mass spectrum of Pb_2Me_6 contains [28] all of the dinuclear ions $(Pb_2Me_x)^+$ ($0 \leqslant x \leqslant 6$) as well as the mononuclear ions $(PbMe_3)^+$, $(PbMe_2)^+$, and $(PbMe)^+$. The molecular ion $(Pb_2Me_6)^+$ is of low abundance, and the most prominent ions are the closed shell cations $(Pb_2Me_5)^+$, $(PbMe_3)^+$ and $(PbMe)^+$. The ΔH_f° data of Table 1 give calculated values for the fragments: $(Pb_2Me_5)^+ + CH_3^{\cdot}$, $+983.3$ kJ mol^{-1}; $(PbMe_3)^+ + PbMe_3$, $+ 1022.7$ kJ mol^{-1}; $(PbMe)^+ + PbMe_3 + 2CH_3^{\cdot}$, $+ 1154$ kJ mol^{-1}.

A noteworthy feature of each of these mass spectra [26,28] is the extreme weakness of the molecular ion peak: at 70 eV, the molecular ions $(PbMe_4)^+$ and (Pb_2Me_6) carry 0.3% and ca. 2% of the ion current respectively. These observations are readily understood in terms of the structures and energies calculated for the ions and described earlier: the C_{3v} isomer of $(PbMe_4)^+$ is well on the way to losing a methyl group, and is stabilised with respect to $(PbMe_3)^+$ and a free methyl radical by only 13.9 kJ mol^{-1}, so that if $(PbMe_4)^+$ is formed with no more than 0.15 eV of excess energy, dissociation to $(PbMe_3)^+$ will necessarily follow. Similarly $(Pb_2Me_6)^+$ is stabilised with respect to $(PbMe_3)^+$ and $PbMe_3$ by only 27.0 kJ mol^{-1}, so that formation of $(Pb_2Me_6)^+$ ions with an excess energy of only 0.3 eV can cause dissociation to give $(PbMe_3)^+$, easily the most abundant ion in the mass spectrum of Pb_2Me_6 [28]. In each case, the lowest-energy ionisation of the neutral parent molecule effectively directs the resulting molecular ion along a reaction channel towards the product ion $(PbMe_3)^+$.

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