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A Refinement of the Crystal Structure of Tetraphenyl-Lead

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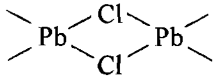
The crystal structure of the tetraphenyl-lead has been refined by X-ray analysis. Four parameters defining the position of one phenyl ring in the cell (molecular symmetry $\bar{4}$) have been systematically varied to the minimum value of the R factor. The Pb atom has tetrahedral valence angles and the plane of each phenyl ring is rotated by about 30° about the Pb–C bond, whose length is 2.19±0.03 Å. In this conformation each phenyl ring is perpendicular to the phenyl ring related to it by a diad axis, and makes an angle of about 60° to both the other two rings, thus being coplanar with the Pb–C bond of one of them. This molecular conformation is compared with that of tetraphenyl derivatives of C, Si, Ge and Sn.

Introduction

As a part of a program of research on organo-lead compounds, the crystal structure of diphenyllead-dichloride has been recently found[1,2] to consist of polymeric chains,  , in which the Pb–C distance appears to be rather short.[3,4]

Particularly noteworthy would therefore be the comparison with the covalent tetraphenyl derivative, on which a preliminary crystal structure analysis was previously carried out by other authors.[5,6]

More recently, the crystal structures of the tetraphenyl derivatives of Si, Ge, Sn and Pb have been also reported.[7-10] However, the analysis of the lead compound was based on packing considerations and on an assumed Pb–C bond length larger than 2.30 Å; the precise value, as well as the atomic coordinates, the structure factors and the R values, were not reported.

It seemed therefore worth-while to re-determine the crystal structure of tetraphenyl-lead, also for a reliable comparison of the Pb–C bond length in this compound and in the diphenyl derivative.

Experimental Section

Long transparent single crystals with square cross-section were obtained by slow evaporation of a tetraphenyl-lead solution in acetone at room temperature.

Cell parameters were accurately measured and the space group $P\bar{4}2_1c = D_{2d}^4$ confirmed by Weissenberg (CuKα radiation, Ni filter) and precession photographs (MoKα radiation, Zr filter, $\mu = 20°$); zero and upper layers including *hhl* reflections, were examined. Present results are compared in Table I with the values reported by previous authors; physical and crystallographic data are collected in Table II.

Table I. $Pb(C_6H_5)_4$ crystal data from present and previous works. Values in brackets have been calculated by using data reported by other authors.

a (Å)	*c* (Å)	V (Å^3)	d_{calc}	d_{obs}	Ref.
12.06	6.50	[941]	[1.810]	1.74	5
12.23	6.454	965	[1.773]	1.745	6
12.03	6.55	949	1.790	1.74	7-10
12.092	6.589	963	1.777	1.750	Present work

Table II. Physical and crystallographic data of $Pb(C_6H_5)_4$

M.W. = 515.61
M.P. = 227.7°C
Crystallographic system: Tetragonal
Space group $P\bar{4}2_1c = D_{2d}^4$
a = 12.092±0.003 Å
c = 6.589±0.002 Å
V = 963.4 Å^3
Z = 2; F(000) = 492
d_{obs} = 1.750 (by flotation)
d_{calc} = 1.777 g cm^{-3}
$\mu_{CuK\alpha}$ = 175 cm^{-1}; $\mu_{MoK\alpha}$ = 100 cm^{-1}

Seventy independent *hk0* reflections, out of 96 possible, and 38 *h0l* out of 59, were observed and integrated intensities obtained with a recording microdensitometer; correction for non linear behaviour of the X-ray films used (Ilford Industrial G),[11,12] and for usual Lorentz and polarization factors were applied.

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(1) V. Busetti, M. Mammi and A. Del Pra, *Acta Cryst.*, *16*, A71 (1963).
(2) M. Mammi, V. Busetti, A. Del Pra and U. Croatto, *Inorg. Chim. Acta*, *1*, 419 (1967).
(3) H. A. Skinner and L. E. Sutton, *Trans. Farad. Soc.*, *36*, 1209 (1940).
(4) C. Wong and V. Schomaker, *J. Chem. Phys.*, *28*, 1007 (1958).
(5) W. H. George, *Proc. Roy. Soc.*, (London), *A 113*, 585 (1927).
(6) G. Giacomello, *Gazz. Chim. Ital.*, *68*, 422 (1938).
(7) G. S. Zhdanov and I. G. Ismailzade, *Dockl. Akad. Nauk. SSSR*, *68*, 95 (1949).
(8) G. S. Zhdanov and I. G. Ismailzade, *Zhur. Fiz. Khim.*, *24*, 1495 (1950).
(9) I. G. Ismailzade, *Zhur. Fiz. Khim.*, *26*, 1139 (1952).
(10) I. G. Ismailzade and G. S. Zhdanov, *Zhur. Fiz. Khim.*, *26*, 1619 (1952).
(11) M. Mammi, R. Bardi and S. Bezzi, *Acta Cryst.*, *16*, A149 (1963).
(12) H. Morimoto and R. Uyeda, *Acta Cryst.*, *16*, 1107 (1963).

Structure refinement. The two Pb atoms in the unit cell are arranged in a body-centered lattice at the special positions (0,0,0) and (½,½,½) and contribute to reflections with $h+k+l=2n$ only, while each phenyl ring occupies one of the eight general equivalent positions. Structure analysis required therefore determination of the coordinates of six carbon atoms.

The centrosymmetric *ab* projection was refined first; a Fourier synthesis calculated with the 54 reflections with $h+k=2n$, whose positive sign is required by the heavy atom contribution, showed the phenyl ring position roughly as reported by previous authors. These coordinates were used to allow for carbon atoms, and the residual R factor decreased from 0.11 (for reflections with $h+k=2n$ only) to 0.076, including all observed reflections; an overall isotropic temperature factor $B=2.50$ Å^2 was used. Refinement of x and y coordinates and temperature factors was then carried out by Fourier and ΔF syntheses.[13,14]

The overlapping of atoms on the non-centrosymmetric *ac* projection did not allow the z coordinate of each carbon atom to be refined independently with the usual techniques (see Figures 1 and 2).

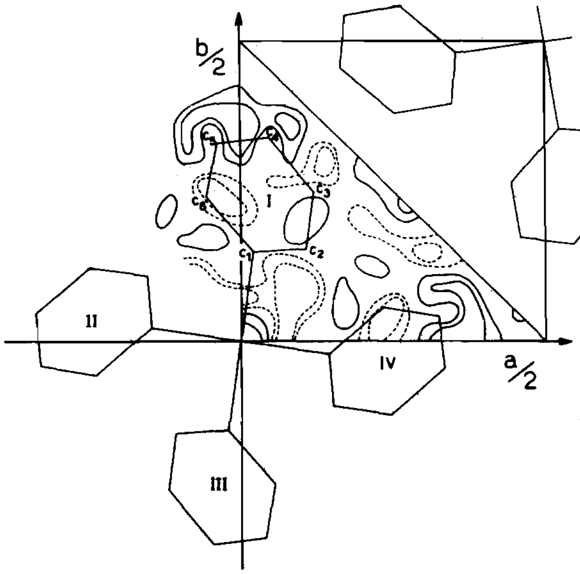

Figure 1. Tetraphenyl-lead: difference electron density projection on the *ab* plane. Countours are at intervals of 0.4 eÅ^{-2}; negative countours are broken and zero countour is omitted.

A regular hexagonal arrangement of the phenyl ring was therefore assumed (C–C = 1.397 Å), and its position in the unit cell defined by the following parameters:

(1) α = angle between the PbC_1C_4 direction and the *c* axis ($2\alpha = C_1(I)PbC_1(III)$ = valence angle; see Figures 1 and 2);

(2) ω = angle between the ring plane and the $C_1(I)PbC_1(III)$ plane (this defines the rotation of the phenyl ring about the PbC_1C_4 direction);

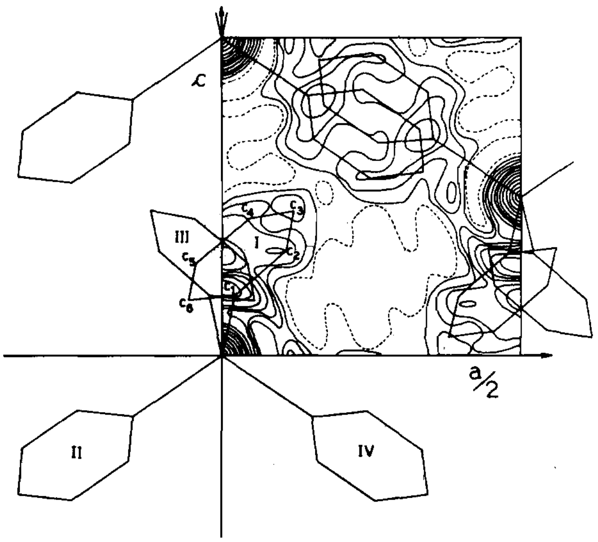

Figure 2. Tetraphenyl-lead: electron density projection on the *ac* plane. Countours are at intervals of 2 eÅ^{-2}, the zero line being omitted and the 2 eÅ^{-2} countour broken. For Pb atom, intervals are of 2 eÅ^{-2} up to 10, and then of 10 eÅ^{-2}.

(3) d = Pb–C bond length;

(4) φ = angle between the *b* axis and the projection of the PbC_1C_4 line on the *ab* plane (this defines the rotation of the whole molecule about the *c* axis).

The observed good agreement between the experimental x, y coordinates of carbon atoms and a regular ring projection on the *ab* plane, allowed preliminary values for the above four parameters to be calculated. Each of them was then varied systematically by steps in a short range and the corresponding R values calculated for *hk0* and *h0l* reflections. For instance, in Figure 3 the R value are plotted *vs.* d, keeping the other parameters fixed at their best (final) value.

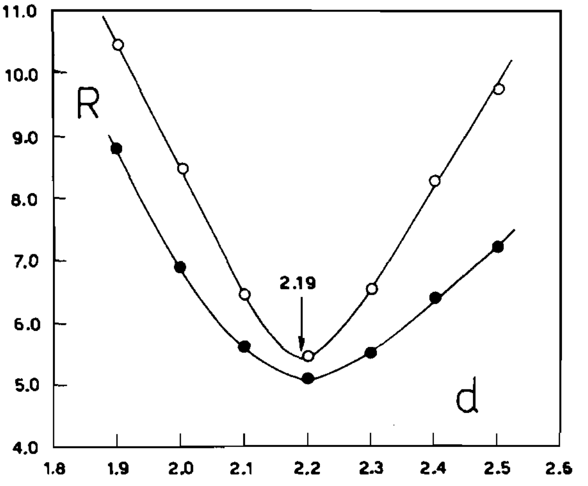

Figure 3. Residual R factor as a function of the Pb—C bond length, *d* (white circles: *hk0* reflections; black circles: *h0l* reflections).

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(13) W. Cochran, *Acta Cryst.*, *4*, 81 (1951).
(14) W. Cochran, *Acta Cryst.*, *4*, 408 (1951).

By interpolation, a minimum R value was found at $\alpha=55.8°$, $\omega=58.9°$, $d=2.19$ Å and $\varphi=7.5°$. The corresponding atomic coordinates are collected in Table III; final difference synthesis on *ab* projection is shown in Figure 1.

For the Pb atom, the isotropic temperature factor $B=2.50$ Å^2 was used for *hk0* reflections and $B=4.17$ Å^2 for *h0l* reflections; an overall value of 3.80 Å^2 was applied to carbon atoms.

Table III. Tetraphenyl-lead: atomic coordinates

	x/a	y/b	z/c
Pb	0.0000	0.0000	0.0000
C_1	0.0195	0.1483	0.1868
C_2	0.1068	0.1556	0.3247
C_3	0.1192	0.2503	0.4439
C_4	0.0444	0.3375	0.4251
C_5	−0.0428	0.3301	0.2871
C_6	−0.0553	0.2355	0.1679

Secondary extinction was found to affect the *hk0* intensity data by using the approximate relation proposed by Housty and Clastre;[15] the value $\alpha=-3.10^{-6}$ e^{-2} was found and applied, the twelve strongest reflections being thus appreciably corrected. No secondary extinction was observed to affect the *h0l* reflection intensities.

Observed and calculated structure factors of *hk0* and *h0l* reflections are listed in Tables IV and V, respectively; the residual factors are $R(hk0)=0.054$ and $R(h0l)=0.051$, including observed reflections only. Scattering factors by Forsyth and Wells[16] were used and allowance was made for anomalous scattering of lead atom.[17] Calculations were performed with the aid of an Olivetti Elea 6001 computer using the programs by the Centro di Strutturistica Chimica del C.N.R.[18]

Table IV. Tetraphenyl-lead: observed and calculated *hk0* structure factors (×10). Half the minimum observed intensity value was given to unobserved reflections, which are marked

H	K	$\|F_o\|$	F_c	H	K	$\|F_o\|$	F_c	H	K	$\|F_o\|$	F_c	H	K	$\|F_o\|$	F_c
0	2	1501	1483	2	5	109	107	4	4	727	779	6	9	30*	24
0	4	1175	1181	2	6	1394	1219	4	5	178	160	6	10	521	486
0	6	1215	1121	2	7	23*	-25	4	6	935	939	6	11	28*	-51
0	8	928	870	2	8	809	791	4	7	57	-27	6	12	359	336
0	10	437	377	2	9	28	-42	4	8	682	644	6	13	22*	25
0	12	488	477	2	10	525	532	4	9	29*	-39	6	14	232	253
1	1	1417	1564	2	11	129	125	4	10	569	543	7	7	732	735
1	2	145	154	2	12	556	574	4	11	30	-25	7	8	30*	7
1	3	1299	1295	2	13	26*	26	4	12	379	396	7	9	573	534
1	4	16*	43	2	14	339	351	4	13	24*	-15	7	10	29*	-15
1	5	1121	1046	2	15	16*	1	4	14	311	339	7	11	440	448
1	6	140	-142	3	3	1590	1449	5	5	735	825	7	12	23*	-27
1	7	956	950	3	4	209	209	5	6	100	-79	7	13	263	302
1	8	122	-95	3	5	1087	1046	5	7	795	725	8	8	622	571
1	9	807	834	3	6	260	230	5	8	105	-67	8	9	35	13
1	10	127	112	3	7	729	736	5	9	618	626	8	10	399	400
1	11	461	487	3	8	55	-43	5	10	30*	25	8	11	24*	19
1	12	77	79	3	9	605	606	5	11	445	459	8	12	298	306
1	13	410	435	3	10	30*	12	5	12	27*	-36	8	13	15*	30
1	14	23*	11	3	11	421	376	5	13	309	340	9	9	295	255
1	15	246	290	3	12	29*	-22	5	14	18*	4	9	10	25*	49
2	2	630	626	3	13	364	356	6	6	778	798	9	11	298	290
2	3	152	161	3	14	22*	4	6	7	28*	-65	10	10	302	327
2	4	1085	1124	3	15	249	280	6	8	606	586	10	11	18*	35

Table V. Tetraphenyl-lead: observed and calculated *h0l* structure factors (×10). Half the minimum observed intensity value was given to unobserved reflections, which are marked

H	L	$\|F_o\|$	F_c	A_c	B_c	H	L	$\|F_o\|$	F_c	A_c	B_c	H	L	$\|F_o\|$	F_c	A_c	B_c
0	2	972	818	818	0	3	5	525	515	515	0	7	2	64*	14	0	-14
0	4	713	693	693	0	3	6	38*	64	0	64	7	3	577	569	569	0
0	6	436	441	441	0	4	0	1079	1124	1124	0	7	4	61*	41	0	-41
1	1	1264	1297	1297	0	4	1	204	195	0	195	7	5	271	339	339	0
1	2	208	233	0	-233	4	2	1008	1025	1025	0	8	0	768	738	738	0
1	3	880	841	841	0	4	3	171*	156	0	-156	8	1	65*	49	0	-49
1	4	175*	130	0	-130	4	4	604	622	622	0	8	2	627	627	627	0
1	5	596	577	577	0	4	5	61*	32	0	-32	8	3	64*	22	0	-22
1	6	51*	74	0	-74	5	1	1086	1222	1222	0	8	4	388	377	377	0
2	0	1538	1467	1467	0	5	2	58*	67	0	67	9	1	553	475	475	0
2	1	1067	1053	0	1053	5	3	594	622	622	0	9	2	64*	26	0	-26
2	2	969	1029	1029	0	5	4	65*	25	0	-25	9	3	421	416	416	0
2	3	58*	53	0	53	5	5	513	471	471	0	9	4	20*	49	0	49
2	4	687	711	711	0	6	0	1018	1021	1021	0	10	0	366	226	226	0
2	5	64	5	0	5	6	1	193	206	0	-206	10	1	62*	93	0	93
2	6	344	365	365	0	6	2	675	647	647	0	10	2	421	434	434	0
3	1	1163	1181	1181	0	6	3	64*	38	0	38	10	3	42*	18	0	18
3	2	284	302	0	302	6	4	471	532	532	0	11	1	389	386	386	0
3	3	762	838	838	0	6	5	52*	12	0	12	11	2	26*	34	0	34
3	4	176*	82	0	-82	7	1	777	766	766	0						

Results and Discussion

The phenyl ring lies on the plane $0.8126x+0.5793y-z=0$ which forms angles of 54.9°, 65.8° and 44.9° to the yz, xz and xy planes, respectively. Intermolecular distances shorter than 4.00 Å are observed only between atom C_4 and the atoms C_4 and C_5 at $(\frac{1}{2}-y;\ \frac{1}{2}-x;\ \frac{1}{2}+z)$ (3.76 and 3.86Å, respectively).

Standard deviation for the values of α (55.8°), ω (58.9°) and φ (7.5°), estimated on the basis of Cruickshank criteria[19,20] is about ± 1°; it means that observed differences of the Pb valence angles from the tetrahedral value ($C_1(I)PbC_1(III)=2\alpha=111.5°$; $C_1(I)PbC_1(II)=108.4°$) are not significant. Previously reported values of φ were 0° [6] and 5.5°.[10] The angle $\omega=58.9°$ corresponds to a rotation of the phenyl ring about the Pb–C bond by an angle $\psi=31.1°$, measured from the position in which the plane of the ring makes a minimum angle to the xy plane (*i.e.*, 35°16′ in the case of exactly tetrahedral bonds).

The molecular conformation may be described by the angles $\widehat{\pi_1\pi_3}=\widehat{\pi_2\pi_4}=89.9°$ and $\widehat{\pi_1\pi_2}=\widehat{\pi_2\pi_3}=\widehat{\pi_3\pi_4}=\widehat{\pi_4\pi_1}=59.9°$ between the planes of the rings, numbered as shown in Figure 1. This conformation, shown in Figures 4 and 5, is quite different

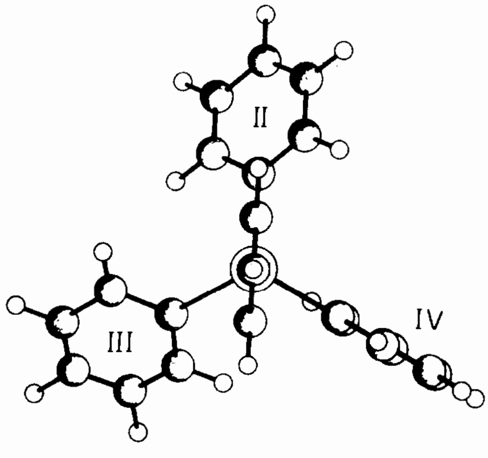

Figure 4. View of the tetraphenyl-lead molecule along the Pb–C_1 direction.

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(15) J. Housty and J. Clastre, *Acta Cryst.*, *10*, 695 (1957).
(16) J. B. Forsyth and M. Wells, *Acta Cryst.*, *12*, 412 (1959).
(17) "International Tables for X-Ray Crystallography", Vol. III, 215, Kynoch Press Birmingham, England (1962).
(18) C. Panattoni and E. Frasson, *Ric. Sci.*, *32*, II-A, 376 (1962).
(19) D. W. J. Cruickshank, *Acta Cryst.*, *2*, 65 (1949).
(20) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, *6*, 698 (1953).

from that described by Zhdanov and Ismailzade, who reported values of 50.5°[7,9] and 50°±3°[10] for the angle ψ, obtained on the basis of geometrical calculation of the "best" intermolecular distances between hydrogen atoms.

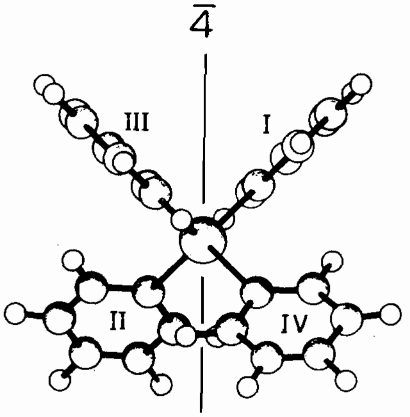

Figure 5. View of the tetraphenyl-lead molecule along the intersection of the planes of two perpendicular rings.

The tetraphenyl derivatives of C,[21] Si,[9,10] Ge,[9] Sn[9,10] and Pb, crystallize in the same space group, their *a* and *c* parameters vary rather regularly with the covalent radius of the central atom M, and their orientation in the unit cell (φ angle) is nearly the same, as shown in Table VI; however, the reported ψ angles for Si, Ge, and Sn fluctuate irregularly in between the two extreme values of 55° and 31.1° observed for the C and Pb compounds.

Comparison is made more evident in Figure 6, where the phenyl rings, projected onto the *ab* plane of their unit cells, are shifted in such a way that all the C_1 atoms and all the C_1-to-M lines are made coincident. For Si, Ge and Sn, the phenyl rings were drawn using the reported x and y coordinates calculated by geometrical analysis[9,10] and assuming regular hegaxonal rings.[22] For Si and Sn compounds, the carbon atom positions localized on the Fourier maps[10] are shown by white and black circles, respectively.

Table VI. Comparison of molecular and crystallographic parameters of tetraphenyl compounds with different central atoms

Central atom	C	Si	Ge	Sn	Pb	Pb
ψ°	55	37	52.5	42	50	31.1
φ°	7.5	8	7	7	5.5	7.5
a (Å)	10.87	11.30	11.60	11.85	12.03	12.09
c (Å)	7.23	7.05	6.85	6.65	6.55	6.59
Tetrahedral covalent radii (Å)	0.77	1.17	1.22	1.40	1.46	1.46
References	21	10	9	10	10	Present work

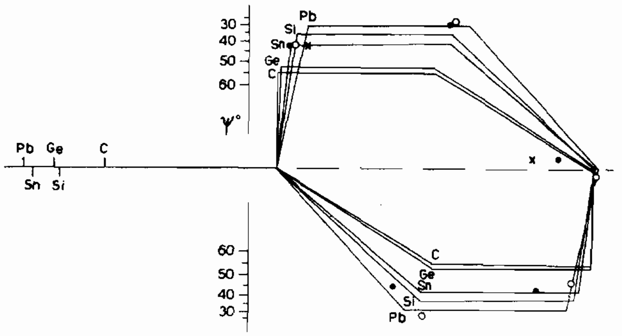

Figure 6. Tetraphenyl derivatives: projections of the phenyl rings on to the *ab* plane. The position of all the C_1 atoms and all the C_1 to central atom lines have been made coincident. Distances between horizontal bonds of the rings are the cosψ projection of the phenyl ring width, as shown by the angular scale on the left.

Indeed, the molecular conformation of the Pb compound ($\psi \simeq 30°$) would still be possible for all the other derivatives, except for tetraphenylmethane, and it has been already proposed by Yokoi for tetraphenylsilane.[23] By shortening the M–C_1 bond length *d*, the intramolecular distances are shortened too; the most significant of them, collected in Table VII for the structures with the two extreme ψ values (Pb and C), are observed between hydrogen atoms. By decreasing *d* in the Pb conformation ($\psi = 31.1°$), the Van der Waals contact of 2.4 Å[24] would be reached first by the $H_2(I)–H_6(IV)$ distance, at a *d* values of about 1.8 Å, so that the same conformation is allowed for the Sn, Ge and even for the Si compound ($d = 1.87$ Å). On the contrary, for $d = 1.47$ Å (tetraphenylmethane), the $H_2(I)–H_6(IV)$ distance would be 2.17 Å and the molecule changes its conformation increasing the ψ angle to 55° (observed distance, 2.37 Å).

The result which we were mainly concerned with, is the Pb–C bond length, $d = 2.19$ Å ($\sigma = \pm 0.03$ Å). The Pb covalent tetrahedral radii is 1.44÷1.46 Å,[24,25]

Table VII. Intramolecular shortest contacts, calculated assuming C–H=1.10 Å. (For molecule numbering, see Figures 1 and 2)

	Pb	C
$H_2(I)–H_2(III)$	4.56 Å	2.55 Å
$H_2(I)–H_6(III)$	4.28	3.91
$H_2(I)–H_6(IV)$	2.76	2.37
	Present work	Ref. 22

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(21) H. T. Sumsion and D. McLachlan Jr., *Acta Cryst.*, 3, 217 (1950).

(22) The z coordinates for the Si and Sn compounds are not reported, while for Ge they are wrongly coupled, atoms C_2 through C_6 being given the z cordinates of atoms C_6 through C_2. We also note that the two carbon atom positions marked by an X in Figure 6, reported for the Sn compound,[10] are clearly inconsistent with any regular hexagon and have been corrected in the drawing to the best agreement with the other ring-positions.

(23) M. Yokoi, *J. Chem. Soc. Japan*, 73, 822 (1952).

(24) L. Pauling, "The nature of the chemical bond", Cornell University Press-Ithaca, New York (1959).

(25) M. Lister and L. E. Sutton, *Trans. Farad. Soc.*, 37, 393 (1941).

and that of the carbon atom may be assumed 0.76÷0.77 Å, even in a bond from an aromatic ring.[26-28] Calculated Pb–C distance is therefore 2.23 Å, that should be reduced to 2.17 Å by applying the correction for difference in electronegativities.[29]

The same result (2.16 Å) is obtained by increasing the C–C_{ring} value of 1.47 Å found in tetraphenylmethane,[21] by 0.69 Å, correspondent to the difference between covalent tetrahedral radii of Pb and C.[24] By the same way, the Si–C_{ring} value of 1.87 Å found in tetraphenylsilane[23] should be increased by 0.29 Å, giving Pb–C=2.16 Å. The shorter Pb–C bond length determined in the crystal structure of diphenyllead dichloride (2.12 Å)[1,2] seems therefore due to resonance of the coplanar phenyl rings.

Finally we note that the rather surprising difference in the distances to central atom, between $C(CH_3)_4$ (1.54 Å)[27] and $C(C_6H_5)_4$ (1.47 Å),[21] is not observed between $Pb(CH_3)_4$ (2.203 Å)[4] and $Pb(C_6H_5)_4$ (2.19 Å).

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(26) F. A. Keidel and S. H. Bauer, *Ann. Rev. Phys. Chem.*, *4*, 236 (1953).

(27) L. Pauling and L. O. Brockway, *Am. Chem. Soc.*, *59*, 1223 (1937).

(28) A. Hargreaves and S. Hasan Rizvi, *Acta Cryst.*, *15*, 365 (1962).

(29) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, *63*, 37 (1941).