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THE MOLECULAR STRUCTURE OF TETRAKIS(DIPHENYLBROMOPLUMBYL)METHANE IN THE CRYSTAL

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SUMMARY

The crystal structure of tetrakis(diphenylbromoplumbyl)methane $(Ph_2BrPb)_4C$ has been determined by X-ray analysis. The crystals are monoclinic ($P2_1/n$) with $a=17.96$, $b=13.72$, $c=19.70$ Å and $\beta=91.92°$ ($Z=4$). The structure, solved by Patterson analysis and subsequent Fourier syntheses, was refined with 3591 independent three-dimensional diffractometer data to a final R value of 0.094. The central carbon atom is tetrahedrally surrounded by two types of lead atom, three being penta- and the fourth tetra-coordinated.

INTRODUCTION

The preceding paper[1] describes the syntheses of organolead compounds in which a carbon atom is thought to be surrounded by four lead atoms. On chemical and steric grounds such a configuration is very surprising, and definite confirmation of the proposed molecular structure was desirable. This paper reports the result of an X-ray investigation on one of these compounds, *viz.* $(Ph_2BrPb)_4C$.

EXPERIMENTAL

Petroleum ether (b.p. 40–60°) was added to a warm solution of tetrakis(diphenylbromoplumbyl)methane. After standing overnight block-shaped monoclinic crystals had settled. The unit-cell dimensions deduced from measurements [Cu–$K\alpha$ radiation, $\lambda(\alpha_1, \alpha_2)=1.5418$ Å] on a General Electric single crystal orienter were: $a=17.96$, $b=13.72$, $c=19.72$ Å and $\beta=91.92°$. From systematic absences the space group was uniquely determined as $P2_1/n$. With four molecules in the unit cell the calculated density was 2.43 $g \cdot cm^{-3}$.

The intensities were measured on an automatic Nonium three-circle diffractometer equipped with a monochromator, a scintillation counter, and a discriminator, using the ω-scan technique. The measurements were taken up to $\theta=26°$. For technical reasons the lower order reflections (up to $\theta=20°$) were determined with Cu–$K\alpha$ radiation. From $\theta=10°$ Mo–$K\alpha$ radiation was used. After the usual corrections for Lorentz and polarization factors and after isotropic absorption correction (dimen-

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES, THEIR STANDARD DEVIATIONS AND THERMAL PARAMETERS.

The β_{ij} coefficients are given by the expression for the temperature factor:

$$\sum_{i=1}^{3}\sum_{j=1}^{3} \exp(-h_i h_j \cdot \beta_{ij} \cdot 10^{-5})$$

Standard deviations positional parameters: $\sigma_{Pb}=0.002$ Å, $\sigma_{Br}=0.006$ Å, $\sigma_{C}=0.06$ Å.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
Pb(1)	0.1522	0.2476	0.4236	288	634	264	51	−13	−221
Pb(2)	0.2214	0.2574	0.6003	334	591	236	− 55	−34	− 78
Pb(3)	0.3452	0.3251	0.4578	331	514	231	−195	−20	−121
Pb(4)	0.2932	0.0713	0.4843	335	471	259	62	−10	−131
Br(5)	0.1969	0.4410	0.4167	335	547	286	− 42	38	−181
Br(6)	0.3472	0.2518	0.6697	410	959	366	−270	86	−288
Br(7)	0.4440	0.1836	0.5023	307	610	350	11	83	−260
Br(8)	0.1441	0.0273	0.4474	363	514	323	−172	18	−196

Atom	x	y	z	Atom	x	y	z
C(9)	0.2500	0.2281	0.4917	C(34)	0.3711	0.3271	0.3511
C(10)	0.1420	0.2257	0.3144	C(35)	0.3572	0.4126	0.3129
C(11)	0.0643	0.1991	0.2926	C(36)	0.3771	0.4073	0.2405
C(12)	0.0657	0.1870	0.2178	C(37)	0.4035	0.3299	0.2131
C(13)	0.1167	0.1969	0.1749	C(38)	0.4209	0.2401	0.2507
C(14)	0.1909	0.2211	0.1992	C(39)	0.4035	0.2357	0.3184
C(15)	0.1976	0.2340	0.2726	C(40)	0.3892	0.4490	0.5139
C(16)	0.0444	0.2711	0.4688	C(41)	0.3612	0.5435	0.4927
C(17)	− 0.0062	0.2073	0.4772	C(42)	0.3916	0.6198	0.5327
C(18)	− 0.0766	0.2210	0.4988	C(43)	0.4375	0.6108	0.5885
C(19)	− 0.0950	0.2983	0.5333	C(44)	0.4654	0.5225	0.6031
C(20)	− 0.0377	0.3718	0.5347	C(45)	0.4407	0.4344	0.5684
C(21)	0.0287	0.3590	0.5038	C(46)	0.3073	−0.0303	0.5745
C(22)	0.1598	0.1303	0.6490	C(47)	0.3770	−0.0469	0.5944
C(23)	0.1942	0.0979	0.7077	C(48)	0.3912	−0.1300	0.6408
C(24)	0.1478	0.0183	0.7478	C(49)	0.3306	−0.1759	0.6702
C(25)	0.0873	− 0.0154	0.7145	C(50)	0.2548	−0.1521	0.6475
C(26)	0.0560	0.0285	0.6586	C(51)	0.2445	−0.0802	0.5975
C(27)	0.0942	0.1098	0.6276	C(52)	0.3422	0.0168	0.3888
C(28)	0.1789	0.4014	0.6264	C(53)	0.3011	0.0295	0.3325
C(29)	0.1161	0.4053	0.6662	C(54)	0.3298	0.0012	0.2711
C(30)	0.0800	0.4994	0.6881	C(55)	0.4071	−0.0497	0.2665
C(31)	0.1202	0.5787	0.6672	C(56)	0.4341	−0.0483	0.3285
C(32)	0.1823	0.5826	0.6245	C(57)	0.4091	− 0.0248	0.3913
C(33)	0.2108	0.4968	0.6107				

sions of the crystal were: 0.2 × 0.2 × 0.4 mm) the data were scaled by means of reflections in common.

The lead atoms were located by means of Patterson analysis. After successive Fourier syntheses all the bromine and carbon atoms could be placed. Refinement by means of the least-squares technique (block-diagonal approximation), using scatte-

ring factors according to the analytical expression given by Moore[2], resulted in a final value of the conventional R index of 0.094. The variables were: (*i*) the scaling factor, (*ii*) all the positional parameters and (*iii*) the anisotropic temperature coefficients of the lead and bromine atoms; the isotropic temperature factors of the carbon atoms were kept fixed at 5 Å^2. Refinement was stopped after all parameter shifts became insignificant. The final parameters are given in Table 1. Observed and calculated structure factors are compared in Table 2.

DISCUSSION

The molecules of tetrakis(diphenylbromoplumbyl)methane are asymmetric and form a racemate in the crystal. The numbering of the atoms and of the phenyl groups is shown in Fig. 1. The central carbon atom is tetrahedrically surrounded by the lead atoms, the bond distances (Table 3) being quite well comparable to those found in tetramethyllead[3]. The distortion of the tetrahedral symmetry is mainly found in the enlargement of the edge Pb(2)–Pb(3). In this connection it should be noted that the bromine atoms bonded to these particular lead atoms are at a very short distance (3.89 Å) from each other.

Characteristic for the molecule is the inequivalency of the lead atoms. The configuration around Pb(2) is roughly tetrahedral; the ligands of the other lead atoms form an irregular trigonal bipyramid. The difference between these two types of lead

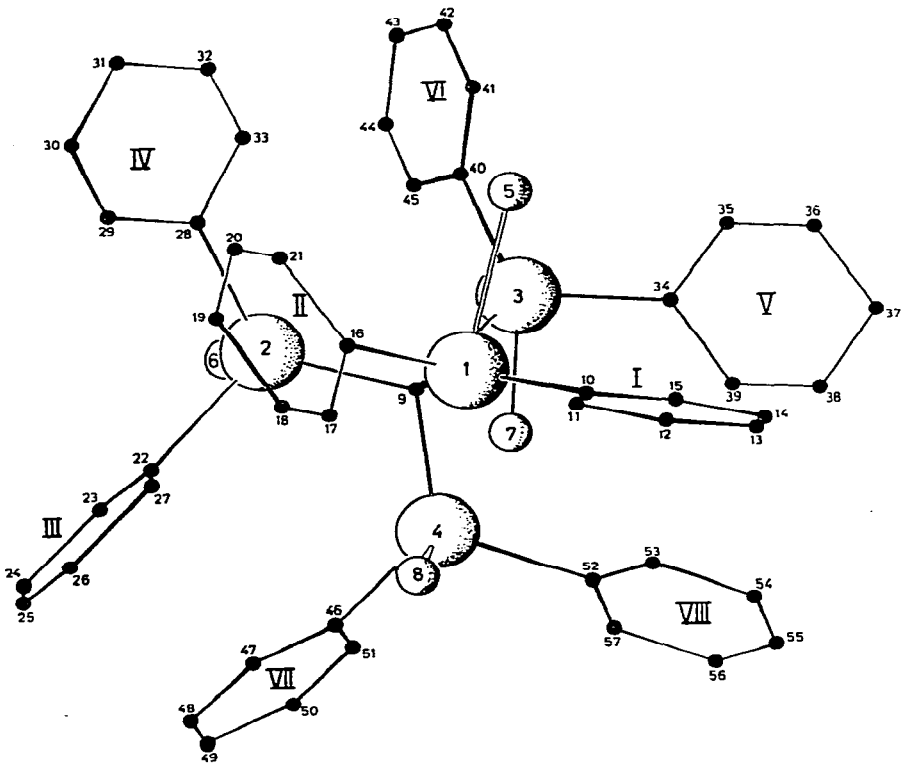

Fig. 1. Structure of the $(Ph_2BrPb)_4C$ molecule.

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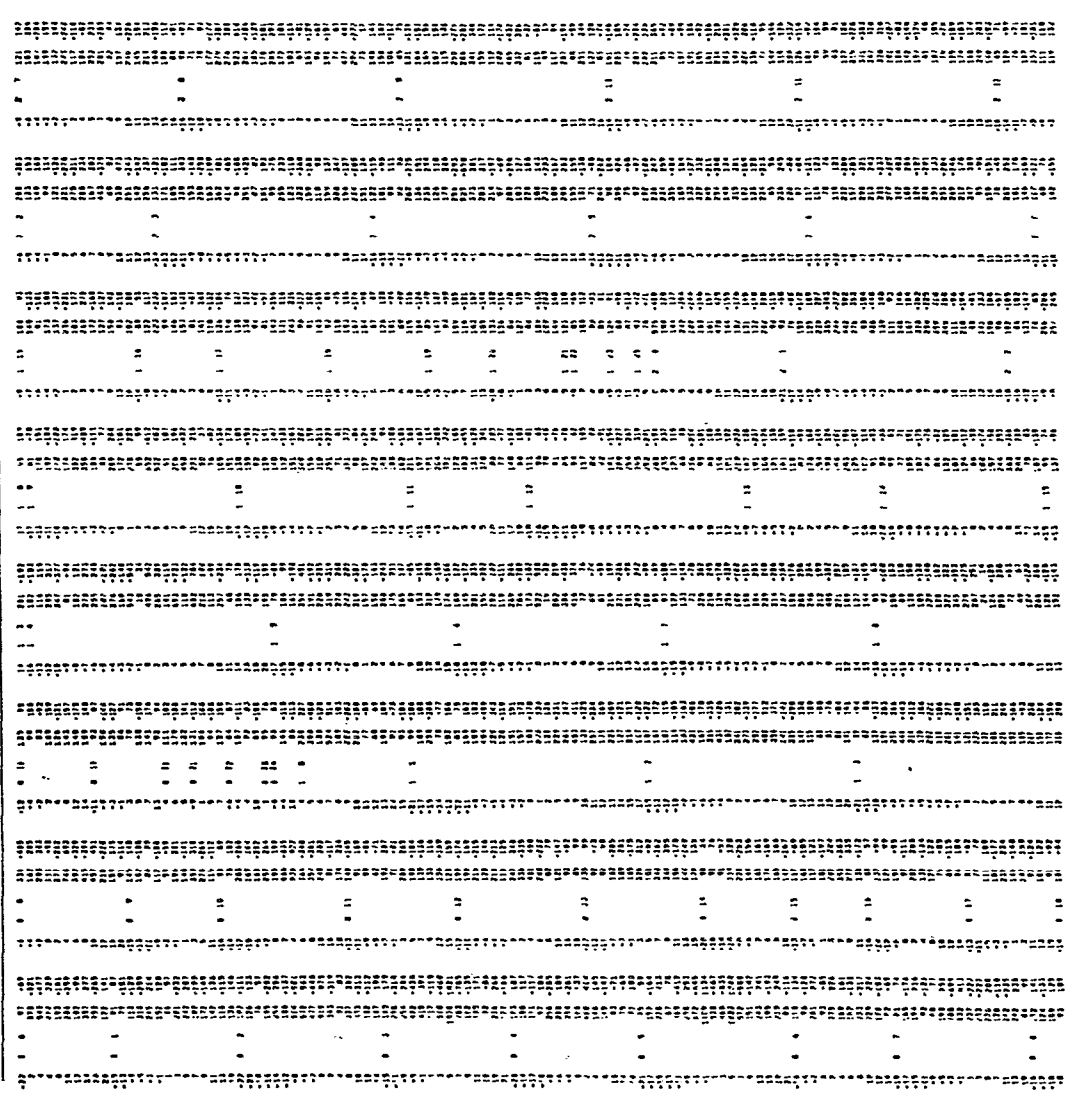
TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTORS

The five columns contain the values of h, k, l, $|F_o|$ and F_c.



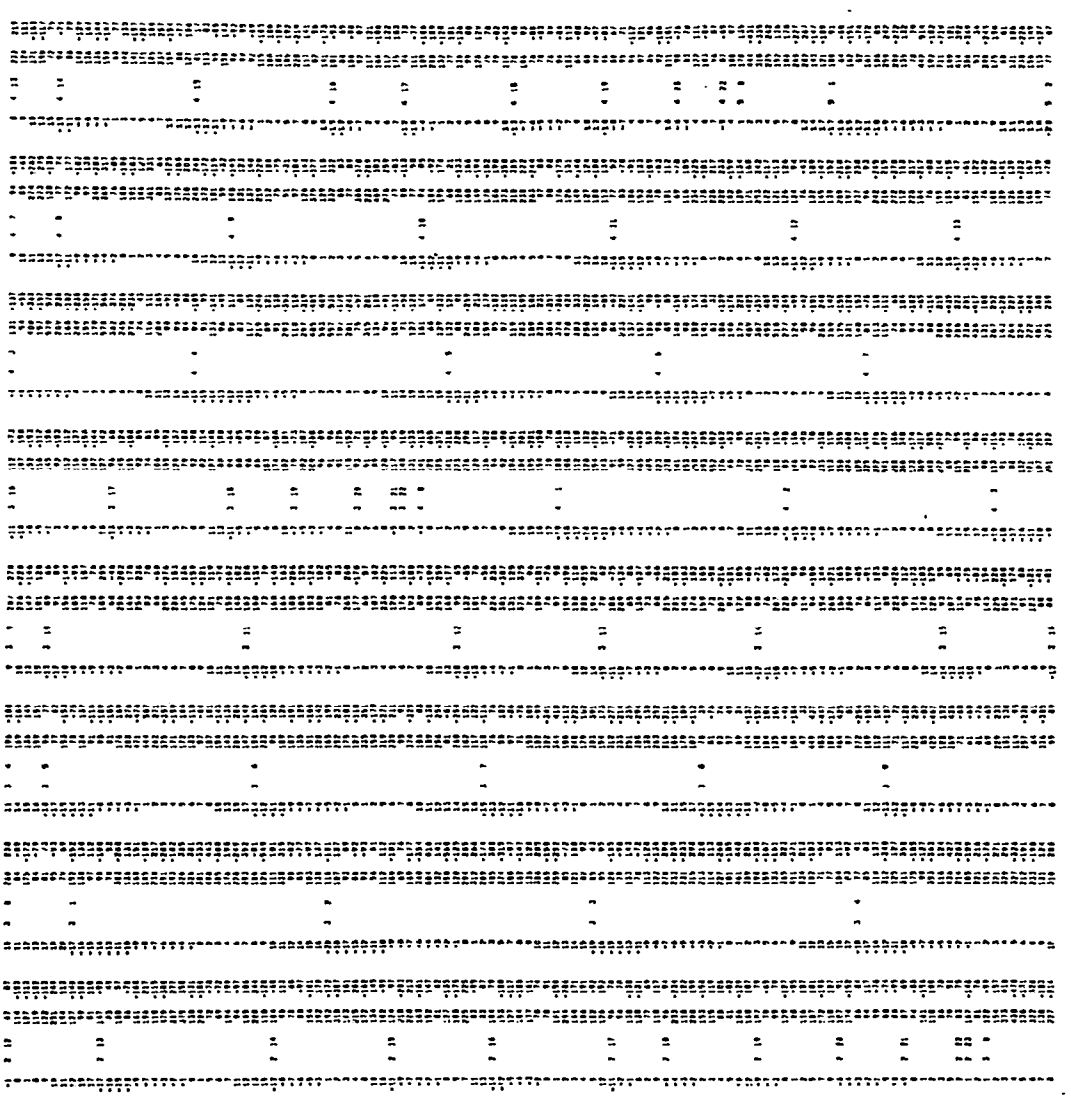


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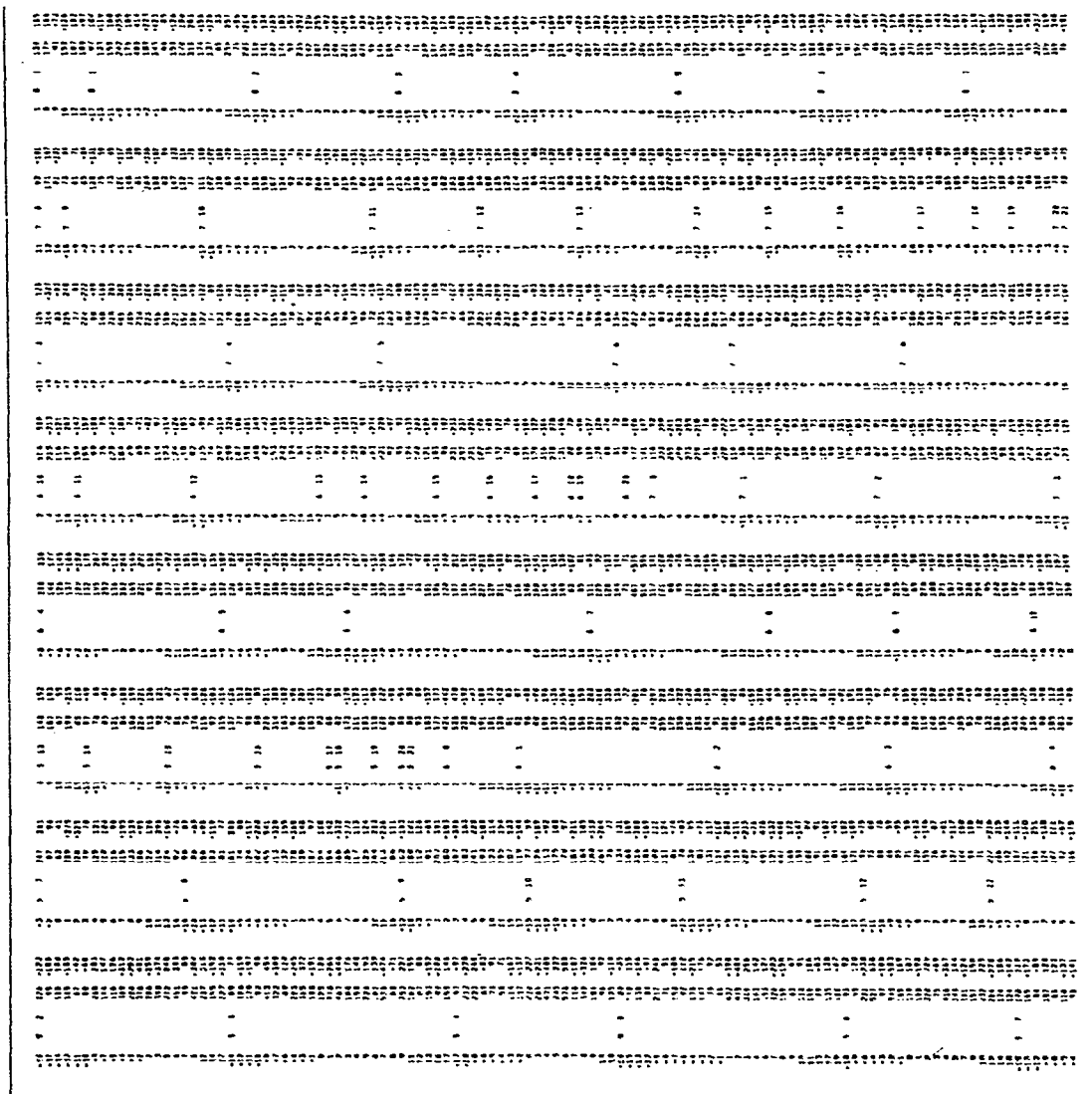
TABLE 2 (*continued*)



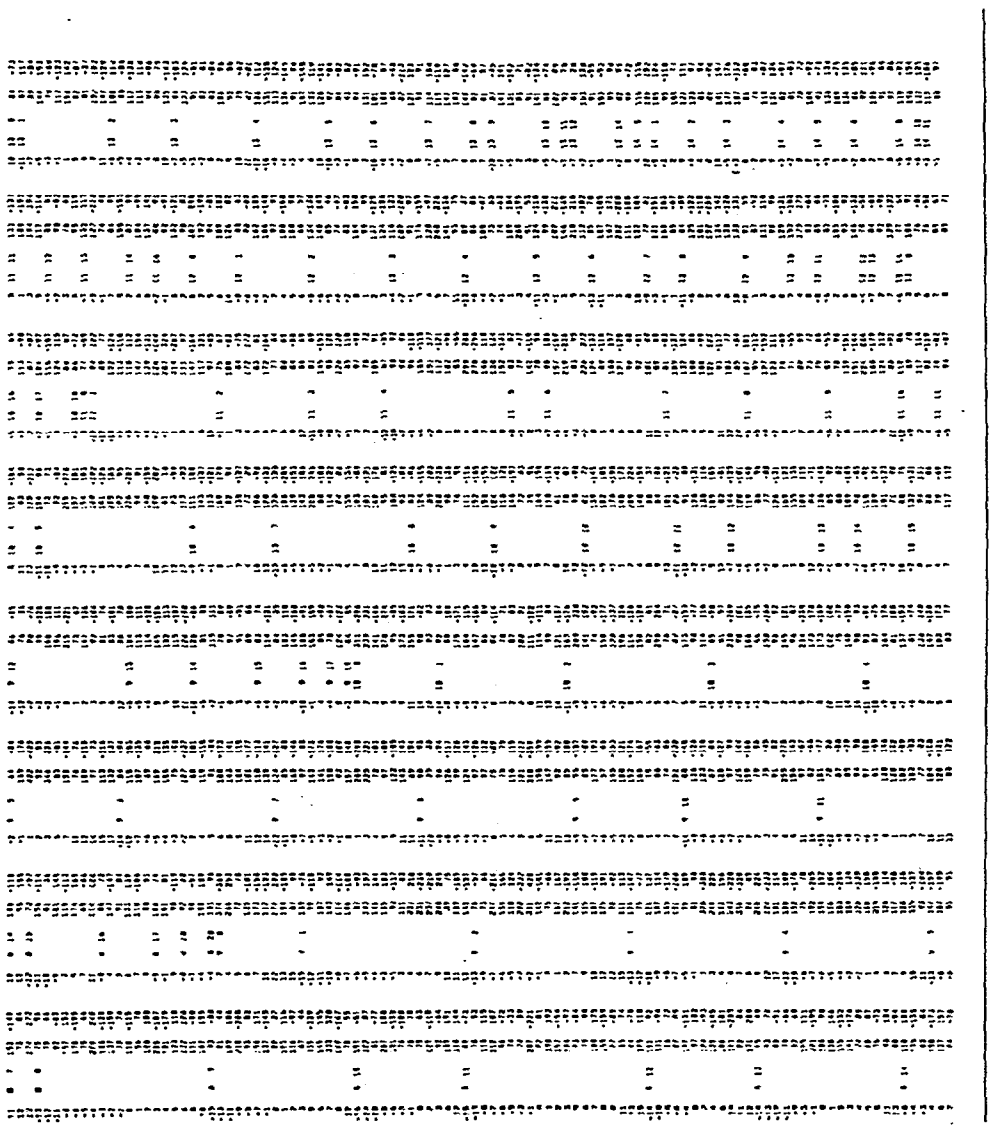


TABLE 3

INTERATOMIC DISTANCES AND BOND ANGLES IN TETRAKIS(DIPHENYLBROMOPLUMBYL)METHANE
The centres of the phenyl (Ph) groups are numbered with Roman figures.

Distances (Å)							Mean					
Pb(1)–C(9)	2.24	Pb(3)–C(9)	2.26	Pb(4)–C(9)	2.24		Pb–C (centr.)	2.25	Pb(2)–C(9)	2.28	Pb(1)–Pb(2)	3.659
Pb(1)–C(10)	2.17	Pb(3)–C(34)	2.17	Pb(4)–C(46)	2.27		Pb–C (phen.)	2.20	Pb(2)–C(22)	2.29	Pb(1)–Pb(3)	3.666
Pb(1)–C(16)	2.18	Pb(3)–C(40)	2.16	Pb(4)–C(52)	2.23				Pb(2)–C(28)	2.18	Pb(1)–Pb(4)	3.672
Pb(1)–Br(5)	2.78	Pb(3)–Br(7)	2.75	Pb(4)–Br(8)	2.82		Pb–Br	2.78	Pb(2)–Br(6)	2.60	Pb(2)–Pb(3)	3.755
Pb(1)–Br(8)	3.06	Pb(3)–Br(5)	3.18	Pb(4)–Br(7)	3.13		Pb–Br	3.12			Pb(2)–Pb(4)	3.688
											Pb(3)–Pb(4)	3.647
Bond angles (°)							Mean					
Br(5)–Pb(1)–C(9)	86	Br(7)–Pb(3)–C(9)	87	Br(8)–Pb(4)–C(9)	85		Br–Pb–C(centr.)	86	Br(6)–Pb(2)–C(9)	104	Pb(1)–C(9)–Pb(2)	108
Br(5)–Pb(1)–I	96	Br(7)–Pb(3)–V	99	Br(8)–Pb(4)–VII	98		Br–Pb–Ph	98	Br(6)–Pb(2)–III	99	Pb(1)–C(9)–Pb(3)	109
Br(5)–Pb(1)–II	98	Br(7)–Pb(3)–VI	101	Br(8)–Pb(4)–VIII	96				Br(6)–Pb(2)–IV	102	Pb(1)–C(9)–Pb(4)	110
											Pb(2)–C(9)–Pb(3)	112
I–Pb(1)–C(9)	129	V–Pb(3)–C(9)	118	VII–Pb(4)–C(9)	127		Ph–Pb–C(centr.)	123	III–Pb(2)–C(9)	115	Pb(2)–C(9)–Pb(4)	109
II–Pb(1)–C(9)	118	VI–Pb(3)–C(9)	125	VIII–Pb(4)–C(9)	119				IV–Pb(2)–C(9)	121	Pb(3)–C(9)–Pb(4)	108
I–Pb(1)–II	112	V–Pb(3)–VI	114	VII–Pb(4)–VIII	112		Ph–Pb–Ph	113	III–Pb(2)–IV	111		
Sum	359	Sum	357	Sum	358		Sum	347				

atoms manifests itself in the bond lengths and bond angles. This is revealed very clearly in the Pb–Br bonds. The pentagonally surrounded lead atoms and the bromine atoms bonded to them are approximately coplanar, the maximum distance to the least squares plane amounting to 0.08 Å. The bond C(9)–Pb(2) is perpendicular to it. It can be considered as a pseudo-trigonal axis if the bonds of Pb(2) and the orientations of the phenyl groups, which are presumably dictated by intermolecular forces are disregarded. The conformation about the bond C(9)–Pb(2) is staggered, while the conformations around the other lead atoms are characterized by the fact that the lead–phenyl bonds are nearly coplanar with C(9)–Pb(2).

The mean values of the C–C bond lengths and the C–C–C bond angles are 1.40 ± 0.01 Å and $120 \pm 1°$ respectively, in excellent agreement with theoretical values. No intermolecular contacts lower than 3.5 Å are present in this structure.

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