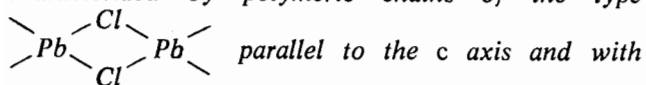


## Crystal Structure of Diphenyllead-Dichloride

M. Mammi, V. Buseti, and A. Del Pra

Received July 30, 1967

Diphenyllead-dichloride ( $C_6H_5)_2PbCl_2$ , crystallizes in the orthorhombic system, space group  $Pn\bar{m}=D_{2h}^{12}$ ,  $a = 17.965 \pm 0.005 \text{ \AA}$ ,  $b = 8.565 \pm 0.003 \text{ \AA}$ ,  $c = 4.005 \pm 0.003 \text{ \AA}$ ,  $Z = 2$ . The crystal structure, determined by two-dimensional X-ray analysis, is characterized by polymeric chains of the type



equivalent Pb-Cl bonds mutually perpendicular. The phenyl rings are normal to the chain axis, with the Pb-C bonds nearly perpendicular to the plane of the chain; the lead atoms are therefore octahedrally coordinated. The character of the Pb-Cl and Pb-C bond and the packing of the chains in the crystal are discussed.

### Introduction

Although many investigations have been reported in recent years on the chemistry of alkyl- and aryl-lead cations and their adducts with electron-pair donors,<sup>1-4</sup> very little is known on the structure of organo-lead compounds. It seemed therefore worth-while to carry out the X-ray crystal structure analysis of some of them, and the phenyllead-chlorides were preferred to the methyl and ethyl derivatives, owing to their relatively greater stability to light and radiations; moreover, it was expected that the larger contribution of the phenyl groups to the diffraction amplitudes and the known ring conformation would result in a more accurate determination of the light atom positions. Main interest was in fact in the type and symmetry of metal coordination and in the length and character of both metal-carbon and metal-chlorine bonds.

In this paper, the results obtained by X-ray analysis of diphenyllead-dichloride are reported.<sup>5</sup>

### Experimental Section

Crystallization from benzene solution, at room temperature, gave long transparent needles with rectangular cross-section. The crystals were examined in

(1) M. Dub, "Organo-metallic compounds", Vol. II, Springer-Verlag, Berlin (1961).

(2) N. A. Matwyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964) and references therein.

(3) K. Hills and M. C. Henry, *J. Organometal. Chem.*, **3**, 159 (1965).

(4) U. Croatto and R. Barbieri, *Ric. Sci.*, **35-11A**, 441 (1965) and references therein.

(5) A preliminary account of this work has been reported at the Sixth International Congress of I. U. Cr., Rome, September (1963).

Weissenberg and precession cameras, using  $CuK\alpha$  (Ni-filtered) and  $MoK\alpha$  (Zr-filtered) radiations respectively, with the oscillation axis parallel to the needle ( $c$ ) axis. Reflections occurred under the following conditions: ( $Ok$ ) only if  $k+l=2n$ , ( $hOl$ ) only if  $h+l=2n$ ; the diffraction symbol  $mmmPn\bar{m}$  corresponds to the orthorhombic space group  $D_{2h}^{12} = Pn\bar{m}$  (centro-symmetric) or  $C_{2v}^{10} = Pnn2$  (non-centro-symmetric); subsequent analysis showed the first to be the actual case. Physical and crystallographic data are collected in Table I.

Table I. Physical and crystallographic data for  $(C_6H_5)_2PbCl_2$

M.W. = 432.3
M.P. = $284 \div 286^\circ C$ (with decomposition)
Crystallographic system: orthorhombic
Space group $D_{2h}^{12} = Pn\bar{m}$
Unit cell parameters: $a = 17.965 \pm 0.005 \text{ \AA}$
$b = 8.565 \pm 0.003 \text{ \AA}$
$c = 4.005 \pm 0.003 \text{ \AA}$
$V = 616.3 \text{ \AA}^3$
$Z = 2$ ; $F(000) = 396$

$$d_{calc} = 2.33 \text{ g cm}^{-3}$$

$$d_{obs} = 2.28 \text{ g cm}^{-3} \text{ (by flotation)}$$

$$\mu_{CuK\alpha} = 311 \text{ cm}^{-1}; \mu_{MoK\alpha} = 161 \text{ cm}^{-1}$$

For the structure analysis, 153 independent  $hk0$  reflections, out of 202 possible, were observed on Weissenberg photographs (multiple film technique); all the 62  $hOl$  possible reflections were measured on precession photographs ( $\mu = 30^\circ$ ). Freshly prepared crystals were used to avoid the appearance of drawing out and compaction of spots, observed for the  $hk0$  reflections from aged crystals and presumably arising from slight chemical decomposition.

Integrated intensities were obtained with a recording microdensitometer. Non-linear behaviour of the X-ray films used (Ilford, Industrial G) was accounted for<sup>6,7</sup> and the usual Lorentz and polarization factors applied.

**Structure determination.** The space group symmetry requires the lead atoms to be packed in a body-centered lattice.

The (001) projection, which has  $pgg$  symmetry in both  $Pn\bar{m}$  and  $Pnn2$  space groups, was examined first; the corresponding Patterson map (Figure 1) clearly showed the Pb-Cl and the Pb-C vectors and the approximate  $x$  and  $y$  coordinates so obtained were

(6) M. Mammi, R. Bardi and S. Bezzi, *Acta Cryst.*, **16**, A149 (1963).

(7) H. Morimoto and R. Uyeda, *Acta Cryst.*, **16**, 1107 (1963).

refined by  $F_0$  and  $\Delta F$  syntheses. As a result, carbon atoms appeared to be localized in a regular hexagonal arrangement (see bond lengths and angles reported below in Table VI).

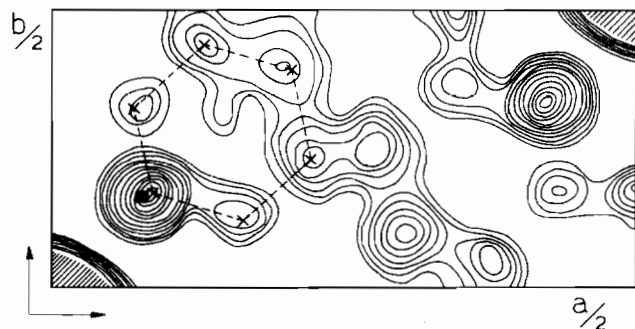


Figure 1. Patterson map, (001) projection. Contours are drawn at equal but arbitrary intervals, except for the origin peak, where the drawn contours are at quadruple intervals. Pb-Cl (■) and Pb-C (x) vectors, derived from final coordinates, are indicated.

Their position was however more precisely determined, first, by rotating the whole phenyl ring by a few degrees about the  $c$  axis, and secondly, by varying the phenyl-to-lead distance. A minimum R factor was observed at an angle  $\alpha$  of about  $42^\circ$  between the Pb- $C_1$  direction and the  $a$  axis, and at a Pb- $C_1$  distance of 2.12 Å, respectively.

The three-dimensional arrangement of atoms is controlled by diad axes parallel to  $c$ , which relate pairs of atoms in each molecule; therefore, they must have the same  $z$  coordinate, which must be zero or  $1/2$ , if the highest crystal symmetry Pnmm is obeyed, or any other value if the space group is Pnn2. For the Pb and Cl atoms, the two possible arrangements are shown in Figures 2a and 2b, respectively.

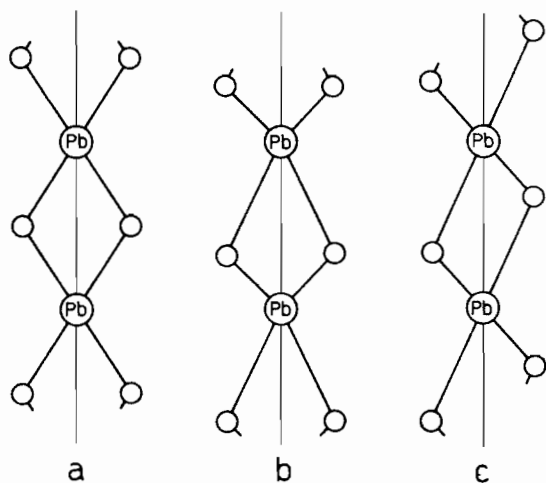


Figure 2. Possible arrangements of Pb and Cl atoms.

The Patterson projection along  $[010]$  (Figure 3) was consistent with the highest symmetry hypothesis a); the chlorine atoms of the molecule at the origin were

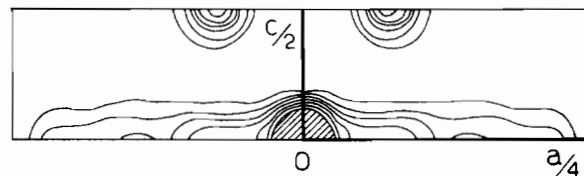


Figure 3. Patterson map, (010) projection. Contours are drawn at equal, but arbitrary intervals.

further confirmed to lie on the mirror plane at  $z = 1/2$  by  $h0l$  structure factor calculations and by difference Fourier maps, where no significant anisotropic electron density distribution was observed for the chlorine atoms.

However,  $h0l$  structure factors were also calculated for arrangement b), and the corresponding R values are plotted in Figure 4 vs. the Cl distance from the mirror plane at  $z = 1/2$  (white circles; upper scale); the R factor did not rise so sharply and suddenly as it could be expected, but this was not assumed as a supporting evidence for a shift of the chlorine atoms, that is, for the rather unreliable arrangement b), mainly because no definite minimum at a significant distance was observed.

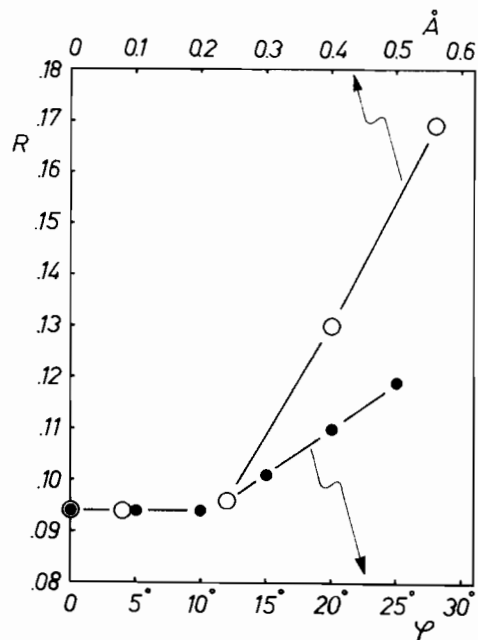


Figure 4. Variation of the R factor for  $h0l$  reflections by moving the Cl atom away from mirror plane (white circles, upper scale) and by rotating the phenyl ring about the Pb- $C_1$  bond (black circles, lower scale).

The arrangement shown in Figure 2c has been found in very similar structures, like dipyrindine-copper-dichloride<sup>8</sup> and dipyrindine-mercury-dichloride<sup>9</sup>; however, it would require a monoclinic symmetry, and was disregarded after both the hypotheses of a pseudo-

(8) J. D. Dunitz, *Acta Cryst.*, 10, 307 (1957).

(9) D. Grdenic and I. Krstanovic, *Archiv. Kem.*, 27, 143 (1955).



**Table VI.** Interatomic distances and angles, with standard deviations. Cl<sub>1</sub> and Cl<sub>2</sub> in the equivalent positions  $\bar{x}, \bar{y}, z$  and  $\bar{x}, \bar{y}, \bar{z}$ , respectively

Pb-Cl	2.795 ± 0.006 Å	Pb-Cl-Pb	91.5 ± 0.2°
Pb-Cl <sub>1</sub>	2.12 ± 0.02	Cl-Pb-Cl <sub>1</sub>	88.5 ± 0.2°
C <sub>1</sub> -C <sub>2</sub>	1.40 ± 0.03	C <sub>1</sub> -Pb-Cl	88.1 ± 0.5°
C <sub>2</sub> -C <sub>3</sub>	1.41 ± 0.03	C <sub>1</sub> -Pb-Cl <sub>2</sub>	91.9 ± 0.5°
C <sub>3</sub> -C <sub>4</sub>	1.41 ± 0.03	Pb-C <sub>1</sub> -C <sub>2</sub>	119.8 ± 1.2°
C <sub>4</sub> -C <sub>5</sub>	1.41 ± 0.03	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	119.8 ± 1.4°
C <sub>5</sub> -C <sub>6</sub>	1.41 ± 0.03	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	120.7 ± 1.4°
C <sub>6</sub> -C <sub>1</sub>	1.43 ± 0.03	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	120.2 ± 1.4°
Cl-Cl <sub>1</sub>	3.90 ± 0.01	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	119.2 ± 1.4°
		C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	120.5 ± 1.4°
		C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub>	119.8 ± 1.4°

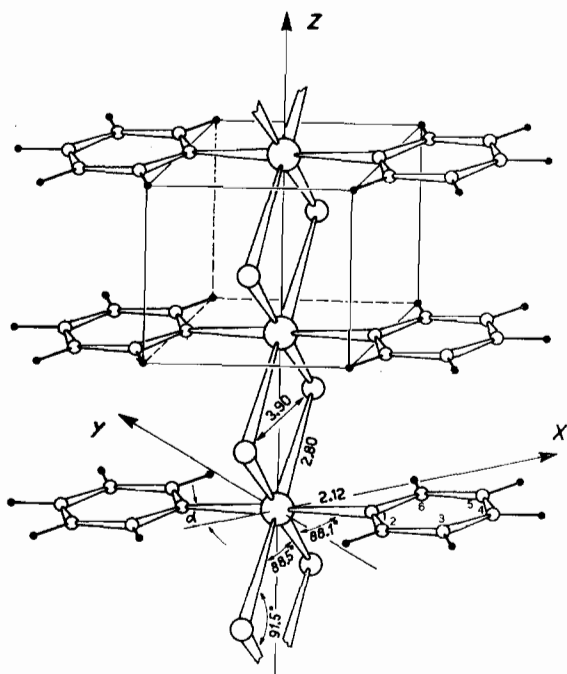


Figure 5. Perspective view of the (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PbCl<sub>2</sub> chain.

A perspective view of the crystal packing is shown in Figure 6: two polymeric chains cross the unit cell and are shifted by  $\frac{1}{2}c$  from each other; lead and chlorine atoms of the chain at the origin lie in a plane parallel to  $c$  and rotated by  $45.2^\circ$  counter-clockwise from the  $a$  axis direction, being therefore tilted by  $1.5^\circ$  only from the  $(\bar{2}10)$  crystallographic plane. The hydrogen atom positions were calculated assuming C-H, 1.08 Å; intermolecular distances are reported in Figure 7.

The strand structure is characterized by Pb-Cl bonds of 2.80 Å, which should be regarded as essentially ionic.

Distances of the same order have been reported for compounds of divalent lead with distorted coordination seven,<sup>15,16</sup> but no crystal structure of organo-lead compounds similar to the present one is reported in the literature.

As a matter of fact, the sum of covalent radii of Cl (0.99 Å) and Pb (tetrahedral, 1.46 Å; octahedral,

(15) M. Nardelli and G. Fava, *Acta Cryst.*, 12, 727 (1959).

(16) K. Sahl and J. Zemann, *Naturwiss.*, 48, 641 (1961).

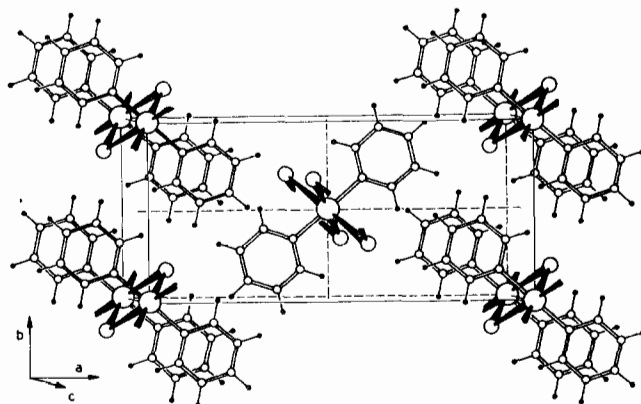


Figure 6. Packing of the polymeric chains in the unit cell.

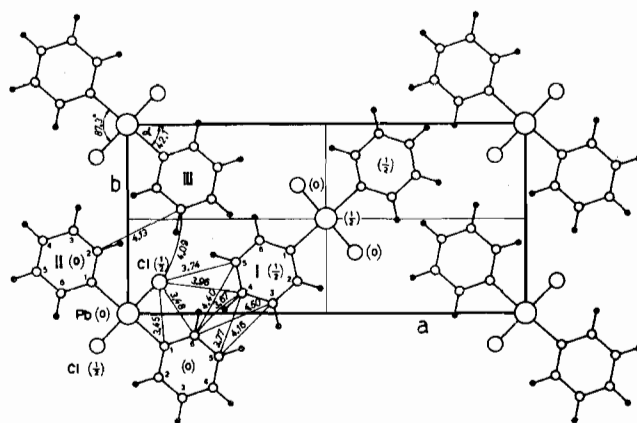


Figure 7. Crystal packing viewed along the  $c$  axis; interatomic contacts up to 4.50 Å are indicated.

1.50 Å)<sup>17</sup> would give a much shorter bond length, in agreement with the values found in covalently bonded compounds.<sup>18,19,20</sup> A square arrangement of four covalent Pb-Cl bonds of 2.50 Å would give normal approach between both chlorine and lead atoms, so allowing a stronger interaction (3.6 Å) between phenyl rings too. Loosening of the square arrangement of chlorine atoms and lengthening of Pb-Cl bonds to 2.80 Å is therefore not due to Pb-Pb nor to Cl-Cl interactions, for which much shorter contacts have been reported (Pb-Pb: 3.38 Å<sup>21</sup> and 3.50 Å<sup>22</sup>; Cl-Cl: 3.18 ÷ 3.40 Å in similar chain structures<sup>8,23,24</sup>).

A description of the diphenyllead-dichloride structure by ionic Pb-Cl bonds requires a Pb ionic radius of 0.99 Å (Cl, 1.81<sup>17</sup>). A similar value ( $R_2=0.95$  Å) is also obtained by the equation  $R_2=R_1 \cdot Z^{2/(n-1)}$ , using an "ionic univalent radii"  $R_1=1.08$  and a Bohr exponent  $n=12$ .<sup>17</sup>

(17) L. Pauling, "The Nature of the Chemical bond", Cornell University Press-Ithaca, New York (1960).

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

(19) M. Lister and L. E. Sutton, *Trans. Farad. Soc.*, 37, 406 (1941).

(20) G. Engel, *Z. Kristallogr.*, 90, 341 (1935).

(21) S. S. Tolkahev, *Sez. Fiz. Khim.*, N. 1, 152 (1958).

(22) H. P. Klug, *J. Am. Chem. Soc.*, 68, 1493 (1946).

(23) A. F. Wells, *Z. Kristallogr.*, 100, 189 (1938).

(24) A. F. Wells, *J. Chem. Soc.*, 1670 (1947).

On the other hand, by subtracting from the distances observed in the crystal structure of several Pb compounds<sup>16,20,21,25-37</sup> the known ionic radii of the bonded atoms, a mean value is obtained for the Pb ionic radius, which is 1.20 Å (corrected to 1.1 Å for the high radius ratio limit<sup>38</sup>) from the F, Cl and Br compounds of Pb<sup>2+</sup>, which have coordination number higher than 6,<sup>16,25-28</sup> while 1.05 Å is obtained from the less electronegative I, S, Se and Te derivatives<sup>29,33</sup> of Pb<sup>2+</sup>, and 0.76 Å from the Pb<sup>4+</sup> compounds.<sup>20,21,34-37</sup>

The empirical ionic radius of hexacoordinated lead is therefore expected to range approximately from 1.1 Å for Pb<sup>2+</sup> to 0.8 Å for Pb<sup>4+</sup>; the actual value will depend upon several factors besides the formal oxidation state, e.g., type and electronic distribution of surrounding atoms, radius ratio, crystal symmetry. The intermediate value of 0.99 Å seems therefore quite reasonable.

Finally, a fractional covalent bond number  $n=0.20$ , i.e., an 80% ionic character in the Pb-Cl bonds (leaving a formal charge of +1.6 on lead atoms) is obtained by the Pauling's equation,<sup>17</sup>  $D_n = D_1 - 0.60 \log n$ , using a covalent bond length,  $D_1$ , corrected from 2.49 to 2.39 Å for the difference in electronegativities.<sup>39</sup>

Therefore, we can conclude that Pb-Cl bonding in the present structure is essentially ionic in character.<sup>40</sup>

Two Pb-C bonds of 2.12 Å complete the Pb octahedral coordination. This length is slightly shorter than the few values reported in the literature:  $2.25 \pm 0.06$  Å in Pb<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>,<sup>41</sup>  $2.203 \pm 0.010$  Å in Pb(CH<sub>3</sub>)<sub>4</sub>,<sup>44</sup> and  $2.19 \pm 0.03$  Å in Pb(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>.<sup>45</sup> These values, which refer to molecules with tetrahedral coordination, agree with the sum of covalent radii, which give 2.23 Å, or 2.17 Å if allowance is made for difference in electronegativities.<sup>39</sup>

- (25) A. Bystrom, *Arkiv Kemi. Mineral. Geol.*, 24A, N. 33, 18 (1947).  
 (26) I. J. Yamzin, L. Z. Nozik and N. V. Belov, *Dokl. Akad. Nauk. SSSR*, 138, 110 (1961).  
 (27) W. Nieuwenkamp and J. M. Bijvoet, *Z. Kristallogr.*, 81, 469 (1932).  
 (28) W. Nieuwenkamp and J. M. Bijvoet, *Z. Kristallogr.*, 82, 157 (1932).  
 (29) R. S. Mitchell, *Z. Kristallogr.*, 111, 372 (1959).  
 (30) A. Ferrari, A. Braibanti, A. M. Lanfredi, *Acta Cryst.*, 14, 489 (1961).  
 (31) B. Wasserstein, *Am. Mineralogist.*, 36, 102 (1951).  
 (32) L. S. Ramsdell, *Am. Mineralogist.*, 10, 281 (1925).  
 (33) A. Nishiyama and T. Okada, *Mem. Fac. Sci. Kyushu Univ. Ser., B* 3, 3 (1960).  
 (34) R. Hoppe and W. Dähne, *Naturwiss.*, 49, 254 (1962).  
 (35) A. I. Zaslavskii, Y. D. Kandrashev and S. S. Tolkahev, *Dokl. Akad. Nauk. SSSR*, 75, 559 (1950).  
 (36) A. Bystrom and A. Westgren, *Arkiv. Kemi. Mineral. Geol.*, 16 B, N. 14, 7 (1943).  
 (37) S. T. Gross, *J. Am. Chem. Soc.*, 65, 1107 (1943).  
 (38) A. F. Wells, "Structural inorganic chemistry", Clarendon Press, Oxford (1962).  
 (39) V. Schomaker and P. D. Stevenson, *J. Am. Chem. Soc.*, 63, 37 (1941).  
 (40) A new set of empirical atomic radii has been recently proposed by Slater<sup>41,42</sup> as appropriate for atoms definitely forming bonds, either covalent or ionic; this set gives Pb-Cl=2.80 Å and Pb-C=2.50 Å with a tolerable accuracy extending to 0.3 Å for bonds involving Pb. The set is therefore very convenient, e.g., in preliminary approach to structures, rather than in detailed analyses within the range of bond variation.  
 (41) J. C. Slater, *J. Chem. Phys.*, 41, 3199 (1964).  
 (42) J. C. Slater, "Empirical atomic radii from crystal structures", Quarterly Progress Report No. 46, Solid-State and Molecular Theory Group, MIT, 6 (1962).  
 (43) H. A. Skinner and L. E. Sutton, *Trans. Farad. Soc.*, 36, 1209 (1940).  
 (44) C. Wong and V. Schomaker, *J. Chem. Phys.*, 28, 1007 (1958).  
 (45) V. Busetti, M. Mammi, A. Signor and A. Del Pra, *Inorg. Chim. Acta*, 1, 424 (1967).

A shorter Pb-C value points out a partial  $\pi$  bonding between phenyl and lead, that is, resonance between the two aromatic rings "through" the metal atom. This is also supported by the coplanarity of the rings. Both phenyl groups lie, in fact, in the plane normal to the chain direction (Figure 5), thus differing from the very similar structures of Mn,<sup>46</sup> Co,<sup>8</sup> Cu<sup>8</sup> and Hg<sup>9</sup> dipyridine dichlorides, which show some tilt of the pyridine rings, besides asymmetric chlorine bridges. In these structures, which have shorter chain repeats (3.73, 3.66, 3.87 and 3.80 Å, respectively) a small tilt allows stronger interactions between the rings along the chain and better interchain approaches in the crystal packing. In diphenylead dichloride, a satisfactory approach of the aromatic rings along the chain, say 3.6 Å, would require a tilt of more than 25°, and though a small tilt (5-10°; see Figure 4) could be possible, no evidence was given by structure factor calculations and Fourier syntheses; moreover, the short distance observed between each chlorine and the carbon atoms in the *ortho*-position (3.48 Å) would be further reduced by tilting.

On the contrary, untilted phenyl groups give rise to the very symmetric arrangement shown in Figure 5, in which hydrogen atoms in the *ortho*-position lie at the corners of a rectangular prism, nearly a cube, with the Cl atoms about at the centres of two opposite faces.

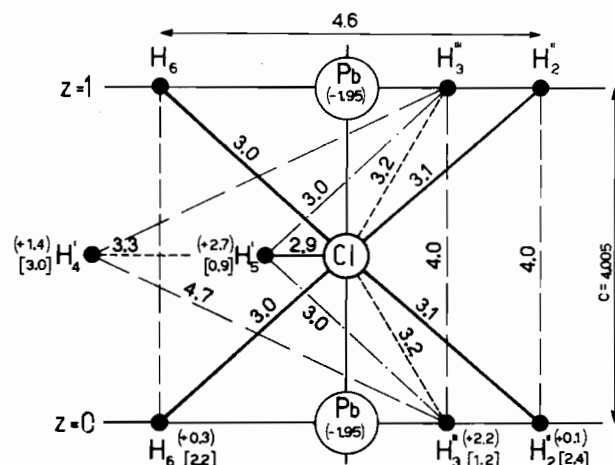


Figure 8. Outline of the Cl atom environment. The plane  $\pi$  of the paper, parallel to the  $c$  axis, is perpendicular to the Cl-Cl line and contains the Cl atom. H atoms are identified by the molecule numbering shown in Figure 7. ( ) distances from  $\pi$ ; [ ] distances from the Pb-Cl-Pb plane.

A more detailed outline of the Cl atom environment is reported in Figure 8: eight hydrogens surround each chlorine atom at about 3.1 Å, which is the normal Van der Waals distance, so that all the five hydrogen atoms of each phenyl group are involved in these contacts.

- (46) E. G. Cox, A. J. Shorter, W. Wardlaw and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).