Crystal Chemistry of Tetraphenyl Derivatives of Group IVB Elements

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The crystal structures of the tetraphenyl derivatives of the Group IVB elements (MPh_4; M = C, Si, Ge, or Sn) are compared. All are tetragonal, $Z = 2$, space-group $P\bar{4}2_1c$, with $\bar{4}$ symmetry. Parameters obtained from a new determination of the crystal structure of $SiPh_4$ are in good agreement with those published earlier.

THE crystal structures of the tetraphenyl derivatives of the Group IVB elements were reported [1] in 1926, although no accurate bond lengths and angles were available; the isomorphism of this series of compounds was confirmed by the similarity of the *X*-ray diffraction patterns. Pascal [2] has shown that these substances form mixed crystals in any proportions and are strictly isomorphous. However, the Group IV elements heavier than carbon, especially silicon,[3] have empty *d* orbitals which can interact with filled lone-pair orbitals, of π-symmetry relative to the σ-bond, of the groups bound to them.[4] The difference in size of the central atoms in these series may also change the arrangement of the four phenyl groups. It was also noted [1] that the *c* axis decreases and *a* axis increases, *i.e.* c/a ratio decreases, as the central atomic size increases. There has been a great increase of interest in organometallic compounds of the Group IVB elements,[4] and the tetraphenyl derivatives are simple, basic compounds whose bond lengths could serve as standards for M–C(Ph) (M = Si, Ge, Sn, or Pb) bonds. The *X*-ray structure analyses of acetyl(triphenyl)-silane [5] and -germane [6] have revealed interesting differences between M–C(AcO) and M–C(Ph) (M = Si or Ge) bonds. The *X*-ray crystal structure analyses of tetraphenyl-germane [7] and -silane were undertaken in order to give reliable bond lengths and to study the isomorphism of this series of compounds. Recently a conformational analysis on this series of compounds was carried out,[8] and after the submission of previous versions of this paper, Glidewell and Sheldrick published the results of their studies on tetraphenylsilane.[9] Very good agreements were found between the two studies, even though different methods and radiations were used in collecting intensity data.* The cell constants in our study were obtained by least-squares methods based on diffractometer Cu-K_β 2θ values for 7 reflections and give $a = 11{\cdot}440(8)$, $c = 7{\cdot}060(4)$ Å, the corresponding values given in ref. 9 are 11·46(1) and 7·09(3). The Si–C(1) distances are 1·876(7) and 1·872(7).[9] The most important agreements of all are for the angles $C_{(xyz)}$–Si–$C_{(\bar{x}\bar{y}z)}$ 107·4(3) and 107·7(5),[9] and $C_{(xyz)}$–Si–$C_{(x\bar{y}\bar{z})}$, 110·5(3) and 110·3(3).[9]

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* Observed and calculated structure factors (for our determination) are listed in Supplementary Publication No. SUP 20,364 (2 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).

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DISCUSSION

The mean value of 1·874(7) Å found in tetraphenylsilane for Si–C is slightly greater (*ca.* 2σ) than the Si–C(Ph) bond, 1·864(8) Å, found in acetyltriphenylsilane[5] and this again is in accord with the previous explanation.[6]

Since the agreements in the two independent studies were good, the following conclusions were based on our results. The calculated potential energy as a function of θ' (Table 1) of each molecule,[8] showed a sharp minimum for tetraphenylmethane but the curves become flatter as the central atoms become larger, and therefore the possible ranges of rotation of the phenyl groups also increase. In Table 1, the values for θ' were calculated from the least-squares planes for the derivatives with the central atom Si, Ge, or Sn, but 55°[10] was a result from repeated trials by comparing the 'theoretical' Patterson projection with the Patterson projection calculated from observed intensities for tetraphenylmethane. The results calculated from ref. 8 are also included in Table 1 for comparison; good agreement was found in Ph_4Sn but not for Ph_4C and Ph_4Si.

The angle ψ (Table 1) decreases very slowly from Ph_4Si to Ph_4Sn which might be due to the fact that a increases while c decreases from tetraphenyl-methane to -stannane (Table 2) and hence releases the repulsion between the intermolecular hydrogens. The same trend was also found in the theoretical calculations.[8] The packing diagram of ref. 8 illustrates effectively that by having a small angle ψ, the H(4) atoms avoid pointing directly toward each other and therefore pack more efficiently than otherwise.

The comparisons of parameters for the tetraphenyl derivatives of Group IVB elements are summarized in Table 2. The ratio c/a decreases from C to Pb. The relation between the ratios and the distances M–C is a smooth curve, however it is more complicated than linear. The angle C_{xyz}–M–$C_{\bar{x}\bar{y}z}$ (two-fold) increases while the angle C_{xyz}–M–$C_{x\bar{y}\bar{z}}$ (four-fold) decreases from Si to Sn. These results suggest that the molecule becomes flatter as the central atom becomes larger. This kind of distortion might lower the interaction energy. For the reflection 021 the central atom has no contribution to the calculated structure factor and yet variations among the derivatives are small (Table 1).

The compound $Ph_3Ge(COPh)$ was found to have the same type of structure as the tetraphenyl derivatives; however, the differences are not yet known.

TABLE 1

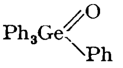
Comparison of the mean planes of the phenyl ring in the tetraphenyl derivatives of the Group IVB elements

M	C	Si	Ge	Sn
l [a]		0·6486	0·6385	0·5810
m		0·3927	0·3932	0·4150
n		−0·6520	−0·6616	−0·7002
ψ [b]	7° 30′	7° 41′	7° 35′	7° 8′
θ' [c]	55° [44°] [d]	44° 3′ [51°] [d]	43° 13′	58° 40′ [59°] [d]
Max. displacement from mean plane/Å [e]		0·03	0·008	0·02
Reflections 021				
F_o	(Not included)	102·3	105·5	100·7
F_c		102·7	104·2	100·3

[a] Equations of mean planes in the form $lX + mY + nZ = 0$ where X, Y, Z are co-ordinates in Å to a, b, and c. [b] The angle ψ of rotation of the entire molecule about the z axis measured horizontally from the xz plane for M = C and from the yz plane for M = Si, Ge, and Sn owing to different choices of co-ordinates. [c] The angle θ' of rotation of the phenyl groups about the tetragonal bonds of the central atom measured from a vertical plane through z. [d] Results from ref. 8. [e] Not including H.

TABLE 2

Comparison of data for the tetraphenyl derivatives of Group IVB elements [a] with estimated standard deviations in parentheses

M	C	Si	Ge	Sn	Pb	Disorder [b] 
a	10·87	11·440(8)	11·613(4)	12·058(1)	12·06	11·358(7)
c	7·23	7·060(4)	6·904(2)	6·568(1)	6·50	17·816(3)
c/a	0·665	0·617	0·595	0·545	0·54	0·688
M–C	1·50	1·876(5) [1·872] [d]	1·954(1)	2·144(14)		
C_{xyz}–M–$C_{\bar{x}\bar{y}z}$: 2-fold	109·5 [c]	107·4(3) [107·7] [d]	108·8(2)	110·8(9)		
C_{xyz}–M–$C_{x\bar{y}\bar{z}}$ 4-fold	109·5 [c]	110·5(3) [110·3] [d]	109·8(2)	108·8(9)		
Mean C–C(Ph)	1·39 [c]	1·378(1)	1·380(1)	1·41(1)		
Mean C–C–C(Ph)	120° [c]	120·0(1)	120·0(1)	120(1)		
D_c	1·266	1·208	1·357	1·485		1·346
D_m	1·173	1·179	1·36	1·49	1·74	1·341
R		0·068	0·045 [e] 0·050	0·076		
No. of obs. reflections.	34 [f]	294	437 [e]	366		

[a] All have $Z = 2$, space-group $P\bar{4}2_1c$, and $\bar{4}$ symmetry. [b] In preparation. [c] Assumed values in ref. 10. [d] Ref. 9. [e] Stationary-crystal–stationary-counter data were given here. [f] Systematic absent and nonequivalent reflections have been omitted for this number.

I thank Drs. W. B. Pearson and D. M. Adams for valuable discussions, and the National Research Council of Canada and the University of Waterloo for financial support and computer facilities.

[1/2151 *Received*, 15*th November*, 1971]

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