# CRYSTAL STRUCTURE OF TETRAPHENYLSILANE, $C_{24}H_{20}Si$

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## Introduction

The X-ray crystal structure analyses of the tetraphenyl derivatives of the group of the IV/1 elements revealed the isomorphy of the compounds $(C_6H_5)_4C$, $(C_6H_5)_4Si$, $(C_6H_5)_4Ge$, $(C_6H_5)_4Sn$ and $(C_6H_5)_4Pb$. All these compounds crystallize in the same space group $P\bar{4}2_1c$ (No. 114). The unit cell dimensions are very similar with $Z = 2$ for all compounds.

The structures of tetraphenylmethane [1] and of tetraphenylstannane [2] had been determined so far. When our structure determination was under refinement, the structure of tetraphenylgermane [3] and somewhat later, the structure of tetraphenylsilane, was also published [4].

## Experimental

Crystals of tetraphenylsilane, m.p. 233—235° [5, 6] are colourless needles elongated along the $c$ axis. Unit, cell data were determined from precession photographs.

*Crystal data* — $M = 336.51$, $a = 11.466\ (7)$, $c = 7.083\ (2)$ Å, $U = 931.196$ Å$^3$, $F(000) = 356$, $D_m = 1.188$ g cm$^{-3}$ (by flotation), $D_X = 1.986$, $Z = 2$, $\mu(Cu-K_\alpha) = 10.9$ cm$^{-1}$. Systematic absences: hhl when l is odd, hh0 when h is odd, tetragonal space group $P\bar{4}2_1c$ (No. 114).

Data were collected on a Stoe two-circle diffractometer in the equiinclination arrangement for hk0 → hk6 layers by the $\omega$ scanning method using $CuK_{\bar{\alpha}}$ radiation, ($\lambda = 1.5418$ Å), scintillation counter with Ni filter and pulse-height discrimination. Reflections with $I \leq 1.5\ \sigma$ were taken as unobserved with an intensity of $I = \sigma/2$. After data reduction an absolute scale factor and an approximate overall temperature factor were determined by Wilson's method. No absorption correction was made.

*Structure analysis.* — The structure was assumed to be isomorphic to that of tetraphenylstannane. Thus, the silicon atom in the two-fold position (a)

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**Table 1**

Final fractional atomic co-ordinates with their e. s. d.'s in parentheses compared with those reported in [4] (given in the second lines) and the isotropic thermal parameters

| Atom | $x$ | $y$ | $z$ | B |
|---|---|---|---|---|
| Si | 0<br>0 | 0<br>0 | 0<br>0 | 2.2 |
| C (1) | 0.0166 (5)<br>0.0166 (6) | 0.1306 (6)<br>0.1309 (6) | 0.1546 (10)<br>0.1559 (11) | |
| C (2) | 0.0997 (7)<br>0.0989 (8) | 0.1337 (8)<br>0.1336 (8) | 0.2987 (12)<br>0.2988( 13) | |
| C (3) | 0.1157 (8)<br>0.1134 (8) | 0.2283 (9)<br>0.2286 (10) | 0.4161 (13)<br>0.4151 (13) | |
| C (4) | 0.0452 (8)<br>0.0455 (9) | 0.3257 (8)<br>0.3266 (8) | 0.3895 (13)<br>0.3893 (15) | |
| C (5) | −0.0382 (8)<br>−0.0391 (8) | 0.3286 (7)<br>0.3271 (7) | 0.2519 (14)<br>0.2535 (15) | |
| C (6) | −0.0539 (7)<br>−0.0544 (7) | 0.2301 (7)<br>0.2302 (6) | 0.1368 (14)<br>0.1389 (12) | |

Positions of the geometrically generated hydrogen atoms:

| | | | | |
|---|---|---|---|---|
| H (2) | 0.1519 | 0.0612 | 0.3195 | 2.1 |
| H (3) | 0.1774 | 0.2275 | 0.5195 | 2.3 |
| H (4) | 0.0569 | 0.3989 | 0.4762 | 3.3 |
| H (5) | −0.0915 | 0.3998 | 0.2385 | 2.4 |
| H (6) | −0.1196 | 0.2293 | 0.0376 | 1.9 |

**Table 2**

Anisotropic thermal parameters of non-hydrogen atoms in general positions with their e. s. d.'s in parentheses. The parameters are given in the form:

$$T = \exp\left[-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right]$$

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| C (1) | 39 (4) | 50 (4) | 150 (14) | − 9 (7) | 29 (14) | 23 (14) |
| C (2) | 62 (6) | 91 (7) | 160 (19) | 15 (12) | −16 (17) | 27 (18) |
| C (3) | 68 (6) | 109 (8) | 195 (20) | −50 (11) | −22 (19) | −25 (23) |
| C (4) | 105 (7) | 73 (6) | 160 (18) | −51 (12) | 21 (19) | −36 (19) |
| C (5) | 101 (8) | 57 (5) | 222 (20) | 8 (11) | 44 (22) | −8 (21) |
| C (6) | 66 (5) | 61 (6) | 231 (19) | 11 (10) | 18 (19) | 10 (20) |

was fixed to the origin at $\bar{4}$ and the carbon positional parameters of the tetraphenylstannane structure [2] were taken as the starting point for fullmatrix least-squares refinement, using the program written by ALBANO et al. [7] minimizing the function $\Phi = \Sigma_h w_h(F_{oh} - 1/G \mid F_{ch} \mid)^2$ where $G$ is the scaling factor. The weighting scheme suggested by CRUICKSHANK [8] $w_h = (a + bF + cF^2)^{-1}$ was used, with $a = 1.1$, $b = 1.0$ and $c = 0.013$.

The structure factor calculation with the tetraphenylstannane parameters resulted in a structure factor agreement of R = 0.316. After three cycles with isotropic and one cycle with anisotropic thermal parameters of the carbon atoms (R = 0.145), the positions of hydrogen atoms were geometrically generated. The isotropic thermal parameters of the hydrogen atoms were approximated by those of the corresponding carbon atoms after their isotropic refinement. Including these in the structure factor calculation, further three cycles of refinement in anisotropic mode for the parameters of the non-hydrogen atoms dropped R to the final value of 0.071 for observed, and 0.095 for all reflections. Throughout the calculations an isotropic thermal parameter was retained to the silicon atom. For structure factor calculations atomic scattering factors were taken from the International Tables for X-ray Crystallography [9].

Final atomic parameters with their estimated standard deviations are given in Tables 1 and 2. The positional parameters are compared with those given by GILDEWELL and SHELDRICK [4].

## Discussion

The molecule of tetraphenylsilane has a $\bar{4}$ symmetry. Least-squares plane of the phenyl group was calculated. The equation of the plane is $-0.6649x-0.3775y+0.6646z = 0.02407$, where x, y, and z are given in Å. The deviation of the phenyl group atoms from this plane are as follows:

| Atom | Distance, Å | Atom | Distance, Å |
|---|---|---|---|
| C (1) | −0.0109 | C (4) | −0.0036 |
| C (2) | 0.0009 | C (5) | −0.0067 |
| C (3) | 0.0063 | C (6) | 0.0140 |

The silicon atom is positional to this plane at a normal distance of −0.0241 Å.

The pairs of the four phenyl planes of the molecule, obeying the crystal symmetry, are inclined by two different angles. Noting the planes by the serial numbers of the symmetry positions (x,y,z; $\bar{x}$,$\bar{y}$,z; $\bar{y}$,x,$\bar{z}$; y,$\bar{x}$,$\bar{z}$), the inclination angles are

for (1—2) and (3—4): 99.6°
for (1—3), (2—3), (1—4), (1—3): 65.6°

The inclination of the phenyl planes to the 001 plane is ca. 50°.

The angle between the $a$ axis and the direction passing through the C (1) and C (4) atoms is ca. 8.4°, in agreement with the angle (8°) reported by ZHDANOV and ISMAILSADE [10] who obtained the structure on packing considerations.

The bond lengths and angles compare quite well with those given by GILDEWELL and SHELDRICK [4], as it is seen from Table 3. The phenyl ring is sligthly distorted in a similar way as reported in [4]. An unusual small C—C—C angle is found at the C (1) atom (Table 3). Some of the other angles show only slight differences. The Si—C bond length (1.863 (7) Å) is in agreement

**Table 3**

Bond lengths and angles with their e. s. d.'s in parentheses

| Present work | | Ref. [4] | Present work | | Ref. [4] |
|---|---|---|---|---|---|
| Si —C (1) | 1.863 (7) | 1.872 (7) | Si —C (1)—C (2) | 121.4 (5) | 121.1 (6) |
| C (1)—C (2) | 1.398 (11) | 1.386 (11) | Si —C (1)—C (6) | 122.9 (5) | 122.8 (5) |
| C (2)—C (3) | 1.377 (13) | 1.377 (13) | C (1)—C (2)—C (3) | 123.8 (7) | 122.6 (9) |
| C (3)—C (4) | 1.388 (13) | 1.379 (14) | C (2)—C (3)—3 (4) | 117.8 (9) | 119.7 (9) |
| C (4)—C (5) | 1.367 (13) | 1.367 (13) | C (3)—C (4)—C (5) | 122.0 (9) | 119.9 (8) |
| C (5)—C (6) | 1.402 (13) | 1.387 (12) | C (4)—C (5)—C (6) | 118.7 (8) | 119.9 (8) |
| C (6)—C (1) | 1.405 (11) | 1.402 (10) | C (5)—C (6)—C (1) | 122.0 (8) | 121.8 (8) |
| | | | C (6)—C (1)—C (2) | 115.7 (7) | 116.1 (7) |
| Mean C—C: | 1.389 Å | 1.388 Å | Mean C—C—C: | 120.6° | 120.4° |

Tetrahedral angles:

| | Present work: | Ref. [4]: | |
|---|---|---|---|
| C (1)—Si—C (1') | 108.2 (3) | 107.7 (5) | (2X) |
| C (1)—Si—C (1'') | 110.1 (5) | 110.3 (3) | (4X) |
| Mean: | 109.5° | 109.4° | |

**Table 4**

The shortest intermolecular atomic distances

| From atom in $x, y, z$ | To atom | In position | Distance, Å |
|---|---|---|---|
| H (3) | H (6) | $1/2+x, 1/2-y, 1/2-z$ | 2.414 |
| H (4) | C (5) | $1/2-y, 1/2-x, 1/2+z$ | 2.842 |
| H (4) | H (5) | $-1/2+y, 1/2+x, 1/2+z$ | 2.590 |
| H (4) | H (5) | $1/2-y, 1/2-x, 1/2+z$ | 2.928 |
| H (5) | H (6) | $-1/2+y, 1/2+x, 1/2+z$ | 2.960 |

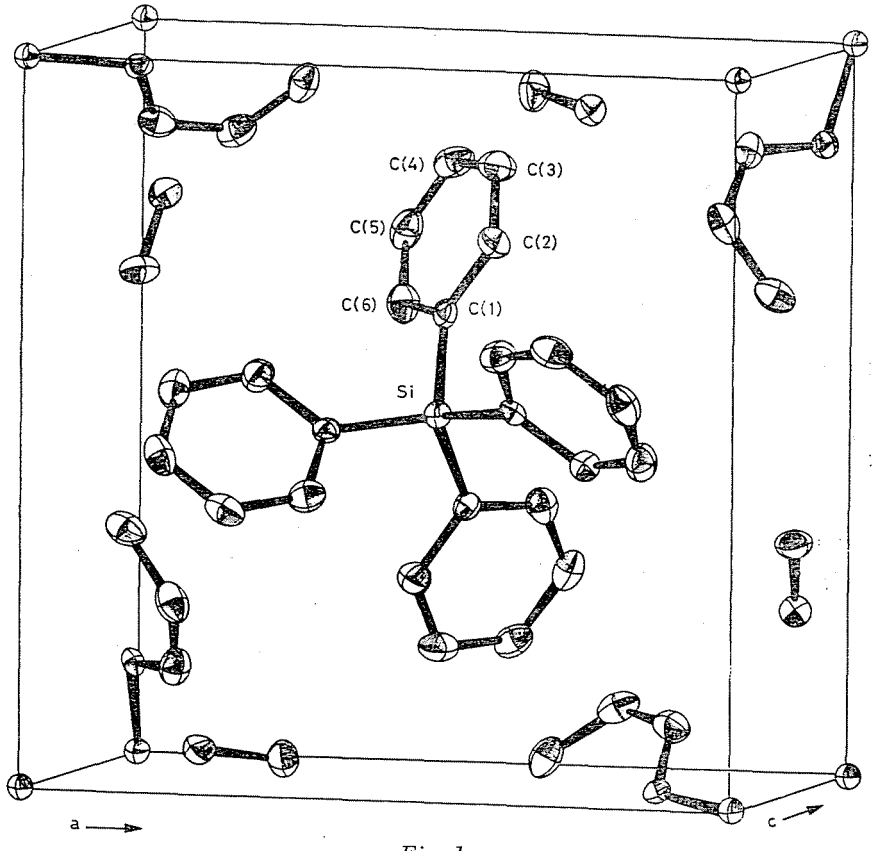


*Fig. 1*

with bond lengths found in mono-methyl silanes (1.867 Å) [11], in (+)-phenyltriphenyl-sylil-carbinol (1.86 (1) Å) [12], and bond length determined in tetraphenylsilane by electron diffraction (1.87 (3) Å) [13]. The average C—C bond length (1.389 Å) compares to the value of 1.394 (5) Å [14] accepted in the literature.

The spatial packing of the molecules is conform to the molecular close packing, with the shortest intermolecular atomic distances given in Table 4.

The unit-cell with two molecules is shown in Fig. 1.

## Summary

Tetraphenylsilane, $C_{24}H_{20}Si$, crystallizes in the tetragonal space group $P\bar{4}2_1c$, a = = 11.466, c = 7.083 Å, with two molecules in the unit-cell. The structure was determined on the basis of isomorphy of the tetraphenyl derivatives of the group IV/1 elements, starting from the atomic co-ordinates of tetraphenylstannane. Intensity data were collected on a Stoe two-circle diffractometer and calculations led to the final R = 0.071 for 408 observed, and R = 0.095 for all (511) reflections. The molecular symmetry is $\bar{4}$ with Si—C bond length 1.863 (7) and mean C—C bond length 1.389 Å. The mean C—Si—C angle is 109.5°. Results are compared with the work of *C. Gildewell* and *G. M. Sheldrick*.

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