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The Crystal and Molecular Structure of Octaphenylcyclotetrasilane, $C_{48}H_{40}Si_4$

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Octaphenylcyclotetrasilane, $C_{48}H_{40}Si_4$, crystallizes in the monoclinic space group $C2/c$ with four molecules in a unit cell of dimensions $a = 26{\cdot}799$, $b = 10{\cdot}201$, $c = 19{\cdot}084$ Å, $\beta = 128{\cdot}59°$. The structure was solved by direct methods and refined by an anisotropic least-squares procedure to a final $R = 0{\cdot}064$ for all 2474 independent reflections. The nucleus of the molecule is a quasi square-planar four-membered silicon ring. The Si–Si bond lengths are 2·370 and 2·381 Å and the Si–Si–Si bond angles are 89·7 and 89·6°. The Si–C bond lengths vary between 1·884 and 1·889 Å. The strained cyclotetrasilane ring is slightly folded across the diagonal. The molecule has a crystallographic twofold axis almost parallel to one of the Si–Si bonds.

Introduction

The first perphenylated cyclosilanes of the $(SiPh_2)_n$ type (n = 4, 5 and 6) were synthetized by Kipping & Sands (1921). The compound with n = 4 has the greatest reactivity and hence it was considered to be a biradical. The homocylic (cyclotetrasilane) ring structure was established by Gilman, Peterson, Jarvie & Winkler (1960).

The reactivity of cyclotetrasilanes is due to the strain in the four-membered ring; nevertheless these compounds are stabilized by large groups attached to the Si atoms. Octaphenylcyclotetrasilane (OPHCTSI) readily undergoes ring-opening, ring-fragmentation and ring-extension reactions; thus it serves as a starting material for the synthesis of five- and six-membered polysilanes, heteropolysilanes, halogenated silanes, *etc.* (Hengge, 1974). The title compound is of interest because the only cyclotetrasilane structure known hitherto is that of tetra-*tert*-butyltetramethylcyclotetrasilane, hereinafter TBMSI (Hurt, Calabrese & West, 1975) which possesses a non-planar four-membered ring with a mean Si–Si bond length of 2·377 Å.

Experimental

OPHCTSI was prepared from dichlorodiphenylsilane by the action of metallic lithium in tetrahydrofurane solution (Jarvie, Winkler, Peterson & Gilman, 1961; Hengge & Brichcy, 1966). After separation of the compounds $(SiPh_2)_n$ with $n > 4$, the crude material was recrystallized by cooling a hot toluene solution; opaque crystals of irregular shape were obtained. The crystal data are: $a = 26{\cdot}799\,(23)$, $b = 10{\cdot}201\,(7)$, $c = 19{\cdot}084\,(18)$ Å, $\beta = 128{\cdot}59\,(5)°$, $V = 4077{\cdot}9$ Å^3, $C_{48}H_{40}Si_4$, $M_r = 729{\cdot}19$; $D_x = 1{\cdot}187$, $D_m = 1{\cdot}175$ g cm^{-3}; μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = 1·77 cm^{-1}, space group $C2/c$, $Z = 4$. The intensities of 2474 independent reflections were collected on a Syntex $P2_1$ automatic four-circle diffractometer with monochromatic Mo $K\alpha$ radiation. Cell parameters and their e.s.d.'s were calculated from diffractometer data by a least-squares procedure. The space group was determined from the systematic absences and $N(Z)$ probability distributions. After data reduction the absolute scale and approximate temperature factor ($B = 1{\cdot}65$ Å^2) were obtained from a Wilson plot with all reflections. No absorption correction was made.

Determination of the structure

The phase problem was solved by direct methods with the 1976 version of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1976). For calculations of the normalized structure amplitudes the molecular scattering factor of the Si–Ph group was used instead of atomic scattering factors (Main, 1976). The K curve (Karle, Hauptman & Christ, 1958) was used for scaling

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structure factors to obtain E values, because both the Wilson plot and Debye curve were unsatisfactory. 350 reflections and 2800 sign relationships were used in the determination of signs. The E map calculated from the sign set with the highest combined figure of merit revealed the positions of all the non-hydrogen atoms. The atomic parameters of the non-hydrogen atoms were refined by anisotropic least-squares with the computer program *SHELX* 76 (Sheldrick, 1976). The H atoms were generated geometrically. The final R = 0·064 for all reflections. The final atomic coordinates are listed in Tables 1 and 2.* The atomic scattering factors were taken from Cromer & Mann (1968).

Table 1. *Final fractional coordinates* ($\times 10^4$) *for the non-hydrogen atoms*

Estimated standard deviations are in parentheses.

	x	y	z
Si(1)	4870 (1)	2584 (1)	2992 (1)
Si(2)	4785 (1)	4911 (1)	2886 (1)
C(1)	4133 (2)	1592 (4)	2544 (3)
C(2)	3580 (2)	2104 (5)	2356 (3)
C(3)	3056 (2)	1299 (6)	2002 (4)
C(4)	3073 (3)	4 (6)	1829 (4)
C(5)	3610 (3)	−497 (6)	2010 (4)
C(6)	4133 (2)	284 (5)	2369 (4)
C(7)	5536 (2)	2002 (4)	4166 (3)
C(8)	5389 (2)	1647 (5)	4718 (3)
C(9)	5868 (3)	1282 (6)	5602 (4)
C(10)	6491 (3)	1261 (6)	5931 (4)
C(11)	6640 (3)	1604 (6)	5403 (4)
C(12)	6175 (2)	1980 (5)	4522 (3)
C(13)	3931 (2)	5495 (4)	2175 (3)
C(14)	3519 (2)	5384 (6)	1255 (4)
C(15)	2884 (3)	5765 (7)	761 (4)
C(16)	2664 (3)	6227 (7)	1183 (5)
C(17)	3051 (3)	6365 (6)	2084 (5)
C(18)	3683 (2)	5999 (5)	2575 (4)
C(19)	5280 (2)	5913 (4)	3947 (3)
C(20)	5347 (3)	7242 (5)	3866 (4)
C(21)	5724 (3)	8042 (5)	4596 (4)
C(22)	6048 (3)	7530 (6)	5433 (4)
C(23)	6002 (3)	6240 (6)	5542 (4)
C(24)	5615 (3)	5418 (5)	4804 (4)

Discussion

The numbering of the atoms is shown in Fig. 1 for the asymmetric part of the molecule, which is related to the remaining part by the crystallographic twofold axis to which the Si(1)–Si(2) bond is almost parallel. The symmetry-related atoms in the molecule are at x,y,z and $1-x$, y, $\frac{1}{2}-z$. The bond lengths and angles are given in Tables 3 and 4.

The nucleus of the molecule consists of four Si atoms forming a quasi-planar regular square with Si–Si–Si angles of 89·7 and 89·6°. The maximum deviation

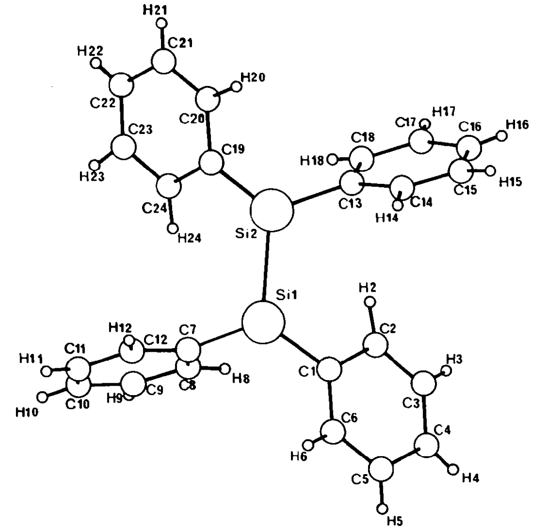

Fig. 1. Atomic numbering and identification of the atoms in the asymmetric part of the molecule projected down a direction parallel to a Si–Si bond.

Table 2. *Final fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å^2) *of the hydrogen atoms*

Estimated standard deviations are in parentheses.

	x	y	z	B		x	y	z	B
H(2)	361 (2)	300 (5)	252 (3)	6·6	H(14)	366 (2)	503 (4)	93 (3)	4·3
H(3)	275 (2)	156 (5)	203 (3)	5·7	H(15)	266 (2)	574 (4)	15 (3)	8·5
H(4)	275 (2)	−50 (5)	170 (3)	6·9	H(16)	231 (2)	648 (4)	90 (3)	12·6
H(5)	361 (2)	−134 (5)	192 (3)	8·8	H(17)	290 (2)	671 (4)	243 (3)	5·0
H(6)	444 (2)	0 (5)	242 (3)	6·9	H(18)	392 (2)	598 (5)	314 (3)	4·7
H(8)	496 (2)	161 (5)	451 (3)	3·2	H(20)	512 (2)	751 (5)	329 (3)	5·5
H(9)	581 (2)	105 (5)	601 (3)	6·1	H(21)	576 (2)	884 (5)	449 (3)	5·5
H(10)	680 (2)	101 (5)	653 (3)	8·8	H(22)	625 (2)	801 (5)	591 (3)	4·0
H(11)	701 (2)	155 (5)	554 (3)	7·3	H(23)	622 (2)	586 (5)	611 (3)	7·7
H(12)	630 (2)	220 (5)	415 (3)	3·7	H(24)	556 (2)	453 (5)	482 (3)	5·2

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33109 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

from the best plane is 0·094 Å. The equations of the planes of the four-membered ring and the phenyl groups, referred to the crystal axes, with the deviations of atoms from the planes, are given in Table 5.

The phenyl rings attached in pairs to the Si atoms are positioned so that the planes of the two Si—C bonds at each Si are almost perpendicular to the plane of the Si_4 ring [87·3° at Si(1) and 92·3° at Si(2)] and they are parallel with the diagonal starting from the same Si atoms. The two Si—C bonds are inclined to plane *P*1 by angles of about 70 and 42° but in the opposite sense at Si(1) and Si(2) respectively (Fig. 2). In all cases the Si—C bonds are parallel to their phenyl rings (maximum deviation 5·5°). The dihedral angles of the phenyl-ring pairs are 95·9 and 101·8° at Si(1) and Si(2) respectively.

Table 3. *Bond lengths* (Å), *with their estimated standard deviations in parentheses*

Si(1)—Si(2)	2·381 (2)	C(8)—C(9)	1·390 (6)
Si(1)—Si(1)′	2·376 (1)	C(9)—C(10)	1·369 (6)
Si(2)—Si(2)′	2·370 (1)	C(10)—C(11)	1·341 (5)
Si(1)′—Si(2)′	2·381 (1)	C(11)—C(12)	1·383 (5)
Si(1)—C(1)	1·884 (5)	C(13)—C(14)	1·377 (5)
Si(1)—C(7)	1·889 (5)	C(13)—C(18)	1·386 (5)
Si(2)—C(13)	1·887 (5)	C(14)—C(15)	1·391 (6)
Si(2)—C(19)	1·885 (5)	C(15)—C(16)	1·346 (7)
C(1)—C(2)	1·391 (5)	C(16)—C(17)	1·352 (6)
C(1)—C(6)	1·375 (5)	C(17)—C(18)	1·381 (5)
C(2)—C(3)	1·385 (6)	C(19)—C(20)	1·389 (5)
C(3)—C(4)	1·369 (6)	C(19)—C(24)	1·380 (5)
C(4)—C(5)	1·353 (6)	C(20)—C(21)	1·368 (6)
C(5)—C(6)	1·368 (5)	C(21)—C(22)	1·359 (6)
C(7)—C(8)	1·383 (5)	C(22)—C(23)	1·350 (10)
C(7)—C(12)	1·394 (5)	C(23)—C(24)	1·393 (5)

Table 4. *Bond angles* (°), *with their estimated standard deviations in parentheses*

Si(1)—Si(2)—Si(2)′	89·7 (1)	C(6)—C(1)—C(2)	117·6 (5)
Si(2)—Si(2)′—Si(1)′	89·7 (1)	C(7)—C(8)—C(9)	120·6 (5)
Si(2)′—Si(1)′—Si(1)	89·6 (1)	C(8)—C(9)—C(10)	120·0 (6)
Si(1)′—Si(1)—Si(2)	89·6 (1)	C(9)—C(10)—C(11)	120·0 (6)
C(1)—Si(1)—Si(1)′	112·5 (2)	C(10)—C(11)—C(12)	121·4 (6)
C(1)—Si(1)—Si(2)	118·6 (2)	C(11)—C(12)—C(7)	119·9 (5)
C(1)—Si(1)—C(7)	108·5 (2)	C(12)—C(7)—C(8)	118·1 (5)
C(7)—Si(1)—Si(2)	112·6 (2)	C(13)—C(14)—C(15)	120·7 (6)
C(7)—Si(1)—Si(1)′	114·3 (2)	C(14)—C(15)—C(16)	120·0 (7)
C(13)—Si(2)—Si(1)	112·6 (2)	C(15)—C(16)—C(17)	121·5 (7)
C(13)—Si(2)—Si(2)′	113·3 (2)	C(16)—C(17)—C(18)	118·6 (7)
C(13)—Si(2)—C(19)	109·6 (2)	C(17)—C(18)—C(13)	122·2 (6)
C(19)—Si(2)—Si(2)′	112·2 (2)	C(18)—C(13)—C(14)	117·0 (5)
C(19)—Si(2)—Si(1)	118·9 (2)	C(19)—C(20)—C(21)	122·2 (6)
C(1)—C(2)—C(3)	119·7 (5)	C(20)—C(21)—C(22)	119·5 (6)
C(2)—C(3)—C(4)	120·9 (6)	C(21)—C(22)—C(23)	120·2 (6)
C(3)—C(4)—C(5)	119·5 (6)	C(22)—C(23)—C(24)	120·9 (6)
C(4)—C(5)—C(6)	120·1 (7)	C(23)—C(24)—C(19)	120·1 (6)
C(5)—C(6)—C(1)	122·1 (6)	C(24)—C(19)—C(20)	117·1 (5)

The four-membered ring is slightly folded about the diagonal of the square, the dihedral angle being 12·8°. This is much less than that of the cyclotetrasilane ring in TBMSI in which the corresponding angle is as large as 36·8°. It is noteworthy that no cyclobutane ring has been reported with a dihedral angle of less than 18° (Cotton & Frenz, 1974). The average Si—Si bond length of 2·377 Å is exactly the same as reported for TBMSI. The Si—Si non-bonding distances [3·351 Å (2×)] are longer by 0·08 Å than that in TBMSI, because of the smaller ring puckering. The greater regularity of the Si_4 square in OPHCTSI is also shown by the mean ring torsion angle of 9·0° (see Table 5) which is rather small compared with that of TBMSI (25·8°). The preferred conformation of the cyclotetrasilane ring seems to be puckered, similar to the four-membered C rings in substituted cyclobutanes (Cotton & Frenz, 1974). The differing degrees of puckering in OPHCTSI and TBMSI may be due to the different sizes of the substituents. Bulky phenyl groups sterically hinder the folding in OPHCTSI, probably causing a greater ring strain and an enhanced reactivity compared with TBMSI.

The Si—C distances (mean value 1·886 Å with maximum deviation of 0·003 Å) fall into the longer range of reported values (1·81–1·93 Å). Therefore any interaction between the π systems of the phenyl rings and Si atoms must be limited.

The phenyl groups are fairly planar, but the bond lengths and angles are somewhat distorted. The mean C—C bond length is 1·374 Å. Uncommonly short bond lengths are mainly at the peripheral part of the rings (1·346–1·369 Å) and are most probably due to the considerable thermal motion.

The mean endocyclic bond angle (α) of the phenyl groups (opposite to the Si atoms) is 117·4°, which fits ideally into the α-angle electronegativity correlation concept (Domenicano, Vaciago & Coulson, 1975). The electronegativity calculated from the above mean angle is exactly the value for Si (1·80) given by Pauling (1960). It is assumed therefore that the deviation of α from the ideal value (120°) is primarily caused by the

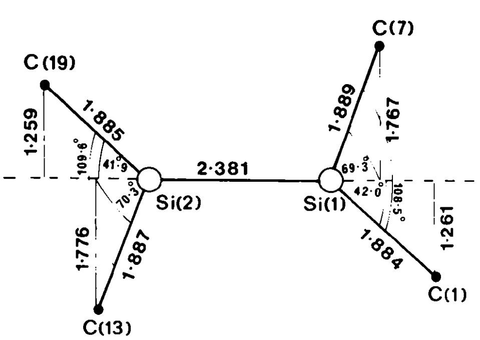

Fig. 2. The positions of the Si—C bonds relative to the plane of the Si_4 ring in the asymmetric part of the molecule. The Si_4 plane is at right-angles to the plane of the drawing.

electronegativity difference between C and Si and conjugative effects play a minor role.

An analysis of the arrangement of the H atoms in the molecule shows that there are a number of relatively short H···H intramolecular distances between the *ortho* H atoms (Table 6) which leave very little space for a reagent (*e.g.* metallic Li) to approach the cyclotetrasilane ring. The H(12), H(12)′ and H(14), H(14)′ atoms, related by the twofold axis (primed atoms are in positions $1-x$, y, $\frac{1}{2}-z$), are located almost exactly above and below the midpoints of the Si(1)–Si(1)′ and Si(2)–Si(2)′ bonds at distances of ±2·89 and ±2·90 Å, respectively, from plane *P*1, while the distances H(12)···H(14)′ and H(14)···H(12)′ (above and

Table 5. *Least-squares planes of the molecule with atomic deviations from the planes*

The plane constants ($AX + BY + CZ = D$) are referred to crystal axes and coordinates in Å.

Plane	*A*	*B*	*C*	*D*
*P*1	0·55375	0·0	0·30545	8·87732
*P*2	−0·27248	−0·21067	0·83805	0·69289
*P*3	−0·11114	1·08667	0·34465	3·34626
*P*4	0·27657	0·66289	−0·21128	5·72991
*P*5	1·35382	−0·25269	−0·80909	11·58825
*P*6	−1·76198	1·84095	1·89147	−7·34298
*P*7	0·42174	0·46093	−0·50898	4·91396
*P*8	0·46181	0·07510	0·36121	8·28760
*P*9	0·65926	−0·08411	0·24461	9·77903

Atomic deviations (Å)

*P*1	Si(1)	Si(2)	Si(1)′	Si(2)′	0·0939	−0·0941	−0·0939	0·0941
	C(1)	C(7)	C(13)	C(19)	−1·261	1·767	−1·776	1·259
*P*2	Si(1)	C(1)	C(2)	C(3)	−0·0192	0·0156	0·0087	−0·0018
	C(4)	C(5)	C(6)		−0·0126	−0·0076	0·0168	
*P*3	Si(1)	C(7)	C(8)	C(9)	0·0356	−0·0358	−0·0224	0·0117
	C(10)	C(11)	C(12)		0·0193	0·0079	−0·0163	
*P*4	Si(2)	C(13)	C(14)	C(15)	−0·0262	0·0224	0·0130	−0·0009
	C(16)	C(17)	C(18)		−0·0217	−0·0048	0·0182	
*P*5	Si(2)	C(19)	C(20)	C(21)	0·0502	−0·0505	−0·0249	0·0095
	C(22)	C(23)	C(24)		0·0246	0·0219	−0·0307	
*P*6	Si(1)	C(1)	C(7)		0·0	0·0	0·0	
*P*7	Si(2)	C(13)	C(19)		0·0	0·0	0·0	
*P*8	Si(1)	Si(2)	Si(2)′		0·0	0·0	0·0	
*P*9	Si(1)	Si(1)′	Si(2)′		0·0	0·0	0·0	

Dihedral angles in the molecule (°)

(*P*1,*P*2)	127·5	(*P*1,*P*6)	87·3	(*P*3,*P*4)	144·4
(*P*1,*P*3)	101·7	(*P*1,*P*7)	87·7	(*P*3,*P*5)	75·0
(*P*1,*P*4)	98·9	(*P*2,*P*3)	95·6	(*P*8,*P*9)	12·80
(*P*1,*P*5)	124·9	(*P*4,*P*5)	101·9		

Torsion angles (°)

Si(1)–Si(2)–Si(2)′–Si(1)′	9·04	Si(2)′–Si(1)′–Si(1)–Si(2)	9·01
Si(2)–Si(2)′–Si(1)′–Si(1)	9·06	Si(1)′–Si(1)–Si(2)–Si(2)′	9·06

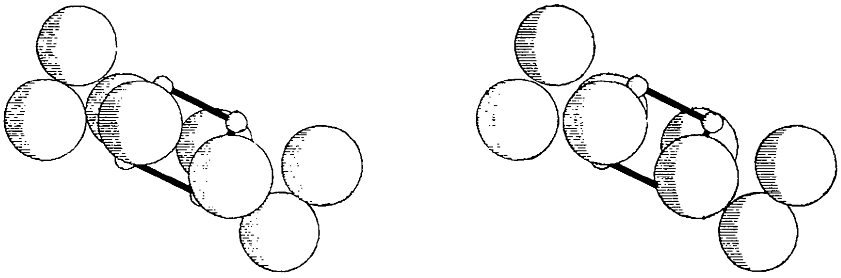

Fig. 3. Stereoscopic projection of the four-membered Si ring with the *ortho* H atoms (large circles correspond to the H van der Waals radius, 1·2 Å) maintaining short non-bonded intramolecular distances.

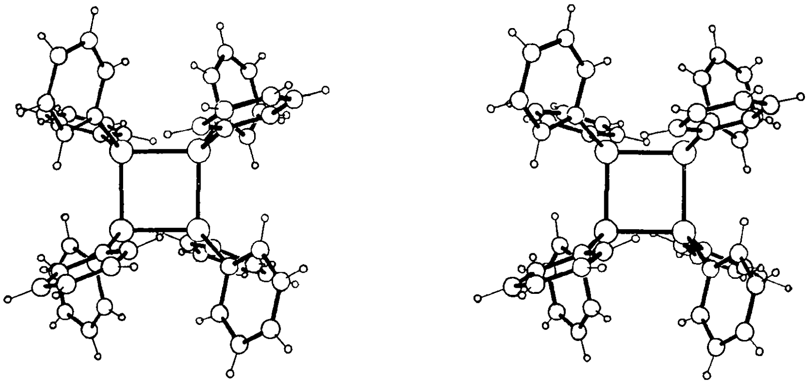

Fig. 4. Stereoscopic projection of the molecule down the normal to the Si_4 plane.

Table 6. *The shortest intra- and intermolecular* H–H *distances* (Å)

From atom at x,y,z	To atom	At position	Distance
(*a*) Intramolecular			
H(6)	H(6)′	$1-x, y, \frac{1}{2}-z$	2·821
H(12)	H(14)′	$1-x, y, \frac{1}{2}-z$	2·896
H(20)	H(20)′	$1-x, y, \frac{1}{2}-z$	2·662
(*b*) Intermolecular			
H(2)	H(23)	$1-x, 1-y, 1-z$	2·629
H(3)	H(17)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2·522
H(18)	H(23)	$1-x, 1-y, 1-z$	2·526

below the ring) are 2·90 Å. Even shorter distances are found between H(6) and H(6)′ (2·82 Å) and between H(20) and H(20)′ (2·66 Å) parallel to the Si(1)–Si(1)′ and Si(2)–Si(2)′ bonds respectively. Both H(6) and H(20) together with their symmetry-related pairs lie close to plane *P*1 (the deviations from the plane are ±0·88 and ±0·64 Å). When the van der Waals radius of H is considered, successful chemical attack at the cyclotetrasilane ring seems to be rather hindered from all directions other than perpendicular to the Si(1)–Si(2) [Si(1)′–Si(2)′] bonds in a plane close to that of the ring, as can be seen in Fig. 3. A stereoscopic projection of the whole molecule is given in Fig. 4.

The molecules in the spatial arrangement of the structure are held together by van der Waals forces. The shortest intermolecular H···H distances are also listed in Table 6.

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