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THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1,1,3,3,3-HEXAPHENYL-1,3-DISILAPROPANE

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Summary

Crystals of the title compound $H_2C(SiPh_3)_2$ are triclinic, space group $P\bar{1}$, with $a = 9.290(2)$, $b = 12.128(4)$, $c = 16.882(4)$ Å, $\alpha = 62.08(1)$, $\beta = 106.88(1)$, $\gamma = 117.28(2)°$ and $Z = 2$. The central skeletal angle SiCSi is 128.8(7)°. The structures of the molecules $H_2C(SiR_3)_2$ (R = H, CH_3, and Ph) are compared and discussed: a simple model for the skeletal geometry of species $H_2C(MR_3)_2$ is proposed, and tested against experimental data and theoretical calculations.

Introduction

The silicon μ-oxo compound $O(Ph_3Si)_2$ contains a linear SiOSi chain [1], whereas the μ-imino analogue $HN(Ph_3Si)_2$ contains a bent skeleton in which the angle SiNSi is 138.1° [2]: in each of these hexaphenyl species the skeletal bond angle is significantly larger than those in the analogous compound containing terminal methyl groups or hydrogens rather than phenyls, i.e. $X(SiMe_3)_2$ and $X(SiH_3)_2$ (X = O, NH) [3—5]. Here we report the crystal and molecular structure of a further member of the hexaphenyl series for $X = CH_2$, $H_2C(Ph_3Si)_2$: although the structure of the hexamethyl analogue appears to be unknown, the structure of $H_2C(SiH_3)_2$ has been determined by electron diffraction [6]. In $H_2C(SiH_3)_2$ the skeletal angle SiCSi is 114.4(2)°; in $H_2C(SiPh_3)_2$ we find this angle to be 128.8(7)°.

Experimental

A sample of $(Ph_3Si)_2CH_2$ was kindly provided by Professor A.G. Brook, University of Toronto. Crystals suitable for X-ray investigation were grown from light petroleum, b.p. 60—80°C.

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Data collection

Data were collected using a Stoe Stadi-2 two circle diffractometer with graphite-crystal monochromatised Mo-K_α radiation for a crystal of dimensions 0.2 × 0.3 × 0.3 mm mounted about c. The intensities of 2768 reflections in the hemisphere $\pm h$, $\pm k$, $+l$ with $4 \leqslant \theta \leqslant 30°$, $l = 0$—19 ($0 \leqslant \mu \leqslant 23.5730$) were measured using the ω—2θ scan mode. Standard reflections were measured every 50 reflections and showed only small random deviations from their mean values. Lorentz and polarisation correction were applied to the data, but no corrections for absorption were made.

Crystal data. 1,1,1,3,3,3-Hexaphenyl-1,3-disilapropane, $C_{37}H_{32}Si_2$, M_r =

TABLE 1

ATOM FRACTIONAL COORDINATES ($\times 10^4$) AND THE EQUIVALENT ISOTROPIC TEMPERATURE PARAMETERS (U_{iso}) [a] (/Å^2 × 10^{-3})

Atom	x	y	z	U_{iso}
Si(1)	1854(3)	6795(3)	7322(2)	42(2)
Si(2)	90(3)	3629(3)	7452(2)	39(2)
C(1)	1859(12)	5225(10)	7427(8)	51(7)
C(111)	2176(12)	8097(11)	6131(8)	42(7)
C(112)	1809(13)	9245(11)	5872(9)	56(8)
C(113)	2079(16)	10234(15)	5003(11)	64(9)
C(114)	2776(16)	10227(17)	4454(11)	67(10)
C(115)	3156(16)	9094(16)	4675(11)	75(11)
C(116)	2875(14)	8099(12)	5565(9)	54(8)
C(121)	3576(11)	7350(10)	8118(7)	39(6)
C(122)	3797(14)	6446(12)	9006(9)	60(8)
C(123)	5046(17)	6858(15)	9614(9)	62(10)
C(124)	6152(15)	8208(16)	9372(11)	69(10)
C(125)	5941(16)	9102(15)	8522(11)	72(10)
C(126)	4713(12)	8687(11)	7994(8)	50(7)
C(131)	−38(12)	6634(11)	7631(8)	43(7)
C(132)	−1460(12)	6515(11)	7011(9)	49(7)
C(133)	−2906(16)	6375(15)	7207(13)	68(10)
C(134)	−2916(18)	6328(16)	8004(14)	78(12)
C(135)	−1566(18)	6481(15)	8648(11)	77(11)
C(136)	−150(15)	6571(14)	8411(11)	60(9)
C(211)	−925(12)	2791(9)	8486(7)	28(6)
C(212)	−2168(14)	3044(13)	8554(9)	59(8)
C(213)	−2887(16)	2437(13)	9328(10)	65(9)
C(214)	−2379(20)	1494(16)	10092(11)	78(11)
C(215)	−1143(20)	1199(14)	10069(9)	69(10)
C(216)	−417(14)	1820(13)	9283(9)	58(8)
C(221)	−1438(11)	3932(11)	6457(7)	43(6)
C(222)	−1047(15)	5074(14)	5673(8)	66(9)
C(223)	−2171(21)	5274(16)	4921(10)	81(12)
C(224)	−3736(20)	4353(19)	4950(11)	79(13)
C(225)	−4227(16)	3221(16)	5771(13)	80(12)
C(226)	−3085(12)	3008(12)	6475(9)	49(7)
C(231)	903(11)	2476(10)	7467(6)	32(5)
C(232)	2544(13)	2657(12)	7735(9)	52(8)
C(233)	3124(15)	1769(15)	7745(10)	63(10)
C(234)	2120(18)	678(16)	7503(10)	76(11)
C(235)	480(18)	526(15)	7255(11)	78(11)
C(236)	−89(15)	1411(13)	7254(10)	59(10)

[a] U_{iso} is defined as the geometric mean of the diagonal components of the diagonalised matrix of U_{ij}.

532.83. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2). $a = 9.290(2)$, $b = 12.128(4)$, $c = 16.882(4)$ Å, $\alpha = 62.08(1)$, $\beta = 106.88(1)$, $\gamma = 117.28(2)^\circ$; $U = 1486.75$ Å^3; $Z = 2$; $D_c = 1.190$ kg dm^{-3}; $F(000) = 564$. Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 0.106 mm^{-1}.

Structure solution and refinement

These were carried out using SHELX-76 [7]. The structure was solved using the general direct methods routine TANG: the best E-map gave the positions of all the non-H atoms. The structure was refined using 2134 reflections having $F_0 \geqslant 4\sigma(F_0)$ with the least-squares matrix blocked so in a given cycle the

TABLE 2

ANISOTROPIC TEMPERATURE PARAMETERS (/Å^2 × 10^{-3}) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	34(1)	37(2)	65(2)	−8(2)	2(1)	8(1)
Si(2)	31(1)	40(2)	50(2)	−7(1)	−2(1)	7(1)
C(1)	41(6)	55(7)	68(8)	−18(7)	8(6)	6(5)
C(111)	33(5)	50(7)	64(7)	−22(6)	10(5)	7(5)
C(112)	53(7)	47(7)	86(9)	−13(7)	−5(7)	17(6)
C(113)	56(8)	76(10)	77(10)	2(9)	2(7)	28(7)
C(114)	55(8)	79(12)	70(11)	8(10)	−3(7)	−1(8)
C(115)	61(9)	85(11)	89(12)	−19(10)	17(8)	−5(8)
C(116)	46(7)	57(8)	76(9)	−17(7)	19(6)	8(6)
C(121)	34(5)	45(6)	54(6)	−11(6)	14(5)	11(5)
C(122)	62(8)	57(8)	71(9)	2(7)	−3(7)	21(6)
C(123)	90(10)	94(11)	57(8)	−17(9)	−7(8)	63(9)
C(124)	59(8)	99(12)	92(11)	−49(10)	−14(8)	31(8)
C(125)	62(8)	73(10)	102(12)	−33(10)	−19(8)	5(7)
C(126)	37(6)	46(7)	76(8)	−9(7)	−6(6)	0(5)
C(131)	43(6)	41(6)	58(8)	−8(7)	13(6)	12(5)
C(132)	45(6)	55(7)	73(9)	−27(7)	0(6)	20(5)
C(133)	42(8)	78(10)	119(13)	−11(11)	−4(9)	23(7)
C(134)	52(9)	83(11)	133(16)	−14(13)	19(11)	17(8)
C(135)	79(10)	103(12)	96(11)	−35(10)	35(9)	22(9)
C(136)	51(7)	69(9)	92(11)	−15(9)	20(7)	26(7)
C(211)	43(6)	28(5)	56(7)	−31(5)	−7(5)	10(4)
C(212)	54(7)	66(8)	72(9)	14(8)	18(7)	19(6)
C(213)	87(9)	75(9)	80(10)	−31(9)	24(8)	31(8)
C(214)	102(12)	91(12)	71(10)	−22(10)	29(9)	22(10)
C(215)	115(13)	83(11)	46(8)	−3(8)	5(8)	48(10)
C(216)	55(7)	84(8)	60(8)	−8(8)	−9(6)	37(7)
C(221)	32(5)	62(7)	50(6)	−11(6)	0(5)	17(5)
C(222)	60(8)	90(10)	56(8)	0(8)	−1(6)	18(7)
C(223)	99(12)	129(14)	62(9)	19(10)	−5(9)	58(11)
C(224)	91(12)	157(16)	78(11)	−26(11)	−36(9)	79(12)
C(225)	48(8)	104(12)	147(17)	−44(13)	−36(9)	20(8)
C(226)	36(6)	62(8)	80(9)	−30(7)	−21(6)	13(5)
C(231)	32(5)	38(6)	39(6)	−1(5)	1(4)	19(4)
C(232)	39(6)	62(8)	92(10)	−24(8)	−7(6)	25(6)
C(233)	47(7)	89(10)	100(11)	−26(9)	5(7)	35(8)
C(234)	83(11)	90(11)	101(12)	−22(10)	−15(9)	54(9)
C(235)	90(11)	88(11)	116(13)	−61(10)	−31(10)	38(9)
C(236)	51(7)	71(9)	123(13)	−56(9)	−24(8)	32(7)

[a] The isotropic temperature parameters refined to 0.06(2) for the methylene hydrogens and to 0.15(2), 0.12(2), 0.09(2), 0.10(2), 0.12(2) and 0.13(2) for the hydrogens in each of the phenyl rings.

TABLE 3

BOND DISTANCES (Å)

Si(1) · · Si(2)	3.336(5)	Si(1)—C(1)	1.830(15)	Si(2)—C(1)	1.870(10)
Si(1)—C(111)	1.889(11)	Si(1)—C(121)	1.852(11)	Si(1)—C(131)	1.877(15)
Si(2)—C(211)	1.839(12)	Si(2)—C(221)	1.867(10)	Si(2)—C(231)	1.858(15)

Within the phenyl rings C(*ijk*)—C(*ijl*)

k—*l*	*ij*					
	11	12	13	21	22	23
1—2	1.42(2)	1.41(2)	1.42(2)	1.37(2)	1.38(1)	1.40(2)
2—3	1.39(2)	1.38(2)	1.39(2)	1.36(2)	1.39(2)	1.40(3)
3—4	1.28(3)	1.41(2)	1.32(4)	1.40(2)	1.37(2)	1.39(3)
4—5	1.43(3)	1.36(2)	1.41(2)	1.37(3)	1.42(2)	1.41(2)
5—6	1.42(2)	1.39(2)	1.43(3)	1.38(2)	1.36(2)	1.40(3)
6—1	1.30(2)	1.41(1)	1.31(3)	1.44(2)	1.42(1)	1.34(2)

parameters for the atoms of one phenyl ring, the Si atom to which the phenyl ring was bonded and the central methylene group refined. With anisotropic temperature parameters for all non-hydrogen atoms and the hydrogen atoms in calculated positions (d(C—H) = 1.08 Å) with separate common isotropic temperature parameters for the methylene group and each phenyl ring, the refinement converged to give a conventional R index $[=\Sigma\Delta/\Sigma F_0, (\Delta = |F_0 - F_c|)]$ of 0.1098 and a generalised index $R_G[=(\Sigma\omega\Delta^2/\Sigma\omega F_0^2)^{1/2}]$ of 0.1150. In the final cycles of refinement 359 parameters were varied comprising 117 positional

TABLE 4

BOND ANGLES (°)

Si(1)—C(1)—Si(2)	128.8(7)		
C(1)—Si(1)—C(111)	110.2(7)	C(1)—Si(2)—C(211)	111.0(6)
C(1)—Si(1)—C(121)	104.8(6)	C(1)—Si(2)—C(221)	112.1(5)
C(1)—Si(1)—C(131)	115.3(5)	C(1)—Si(2)—C(231)	107.4(6)
C(111)—Si(1)—C(121)	110.7(4)	C(211)—Si(2)—C(221)	108.9(5)
C(111)—Si(1)—C(131)	107.9(6)	C(211)—Si(2)—C(231)	107.5(5)
C(121)—Si(1)—C(131)	107.9(7)	C(221)—Si(2)—C(231)	109.9(6)

Within the phenyl rings C(*ijk*)—C(*ijl*)—C(*ijm*)/Si(*i*)

k—*l*—*m*/Si(*i*)	*ij*					
	11	12	13	21	22	23
1—2—3	118(2)	122(1)	122(2)	123(1)	122(1)	120(1)
2—3—4	124(2)	121(1)	117(1)	120(2)	120(1)	123(1)
3—4—5	120(1)	118(1)	125(1)	120(2)	119(1)	115(2)
4—5—6	115(2)	121(1)	114(2)	120(1)	119(1)	122(2)
5—6—1	125(2)	122(1)	124(1)	121(2)	122(1)	122(1)
6—1—2	117(1)	115(1)	117(1)	116(1)	117(1)	118(1)
2—1—Si(*i*)	117(1)	121(1)	119(1)	123(1)	122(1)	121(1)
6—1—Si(*i*)	125(1)	123(1)	124(1)	120(1)	121(1)	121(1)

TABLE 5

LEAST-SQUARES PLANES [a] THROUGH THE CARBON ATOMS C(*ijk*), k = 1—6 OF EACH PHENYL RING; DISTANCES OF ATOMS FROM THE PLANE AND DIHEDRAL ANGLES BETWEEN THE PLANES

	ij					
	11	12	13	21	22	23
A	—0.640(8)	0.890(4)	—0.104(4)	—0.246(1)	0.651(1)	0.218(4)
B	—0.675(3)	—0.351(1)	0.909(3)	—0.925(1)	—0.684(1)	0.215(3)
C	—0.366(4)	—0.292(1)	—0.403(3)	—0.289(3)	—0.329(1)	—0.952(2)
D	8.37(3)	12.33(1)	—7.12(2)	9.807(5)	13.24(3)	9.88(1)

Distances of atoms from the planes (Å X 10^{-2})

C(*ij*1)	2(3)	0(2)	1(3)	0(1)	2(3)	1(2)
C(*ij*2)	—2(3)	0(2)	0(3)	0(2)	—3(4)	—1(2)
C(*ij*3)	3(4)	1(2)	0(3)	0(2)	1(4)	0(2)
C(*ij*4)	—2(4)	1(2)	—2(3)	1(2)	4(4)	1(2)
C(*ij*5)	3(4)	—2(2)	3(3)	0(2)	—4(4)	0(2)
C(*ij*6)	—2(3)	1(2)	—2(3)	0(2)	0(3)	—1(2)
Si(*i*)	—9(3)	—7(1)	—2(2)	—3(1)	4(3)	0(1)

Dihedral angles between planes C(*ijk*) and C(*lmk*), k = 1—6 (°)

ij	*lm*		*ij*	*lm*		*ij*	*im*		*ij*	*lm*	
11	12	—77.0(5)	11	13	—66.4(3)	11	21	27.4(4)	11	22	80.5(3)
11	23	86.4(3)	12	13	—72.9(2)	12	21	79.0(1)	12	22	23.8(4)
12	23	66.6(3)	13	21	—45.7(2)	13	22	—56.2(2)	13	23	56.2(3)
21	22	55.4(1)	21	23	88.7(2)	22	23	72.0(2)			

[a] The planes are defined in orthogonal Ångstrom coordinates by the equation: $Ax + By + Cz + D = 0$

parameters, 234 anisotropic temperature components, 7 common isotropic temperature parameters and 1 overall scale factor. A final difference synthesis showed no significant residual features. The reductions in R_G at all stages of the refinement were significant at the 99.5% level [8]. Complex neutral-atom scattering factors [9] were employed for all atoms. The results of the final least-squares cycles are given in Tables 1 and 2. These, together with the covariance

TABLE 6

SELECTED TORSION ANGLES [a] (°)

C(111)—Si(1) · · Si(2)—C(211)	—152.6(6)	C(111)—Si(1) · · Si(2)—C(221)	—42.2(6)
C(111)—Si(1) · · Si(2)—C(231)	82.2(7)	C(121)—Si(1) · · Si(2)—C(211)	69.5(6)
C(121)—Si(1) · · Si(2)—C(221)	180.0(6)	C(121)—Si(1) · · Si(2)—C(231)	—55.7(7)
C(131)—Si(1) · · Si(2)—C(211)	—42.7(5)	C(131)—Si(1) · · Si(2)—C(221)	67.7(5)
C(131)—Si(1) · · Si(2)—C(231)	—167.9(7)	C(111)—Si(1) · · Si(2)—C(1)	88.7(10)
C(121)—Si(1) · · Si(2)—C(1)	—49.1(10)	C(131)—Si(1) · · Si(2)—C(1)	—161.4(10)
C(1)—Si(1) · · Si(2)—C(211)	118.6(10)	C(1)—Si(1) · · Si(2)—C(221)	—130.9(10)
C(1)—Si(1) · · Si(2)—C(231)	—6.6(10)		

[a] The torsion angle *i*—*j*—*k*—*l* is positive if, when viewed in the direction *j*—>*k*, the projection of *i*—*j* has to be rotated clockwise to coincide with the projection of *k*—*l*.

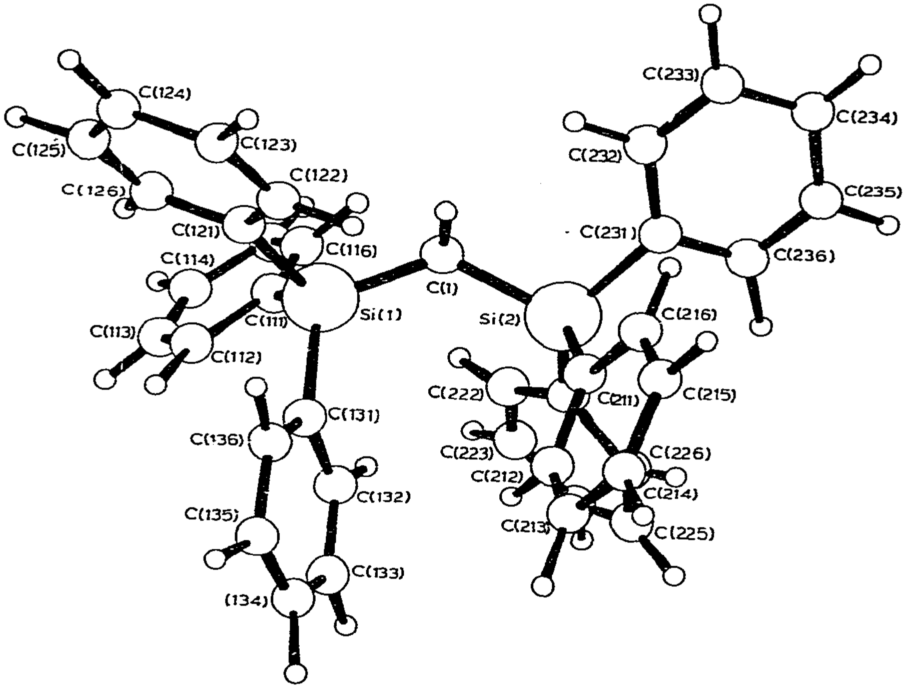

Fig. 1. A perspective view of the molecule showing the atom numbering scheme.

matrix were used to calculate the bond lengths and angles which are given with e.s.d.'s in Tables 3 and 4. Least-squares planes were calculated for each phenyl ring: these are given in Table 5. Table 6 gives selected torsion angles for the $C_3SiCSiC_3$ core of the molecule. Figure 1 is a perspective view of the molecule showing the atom numbering scheme. Figure 2 shows the unit cell. Tables of calculated and observed structure factors are available (from C.G.) on request.

Results and discussion

The structure consists of isolated molecules: the central SiC distances are similar to the value found in $H_2C(SiH_3)_2$: the terminal SiC distances are typical of those found in other aryl silicon compounds [1,2,10,11]. Similarly the central skeletal angle SiCSi, 128.8(7)° is significantly larger than that found in $H_2C(SiH_3)_2$ [6]: this again is typical of the μ-imino and μ-oxo series also, as is the observation of a longer Si · · · Si distance in the hexaphenyl compound than in the hexahydride or hexamethyl species. These relationships are summarised in Table 7.

No structure determination appears to have been undertaken for $H_2C(SiMe_3)_2$ itself although a number of metal complexes containing $[HC(SiMe_3)_2]^-$ as a ligand have been investigated [12—16]: in these the angles SiCSi fall within the range 112—118°. That one effect of complexation is to reduce the skeletal angle below the value in the free neutral molecule is suggested by the reduction in the angle SiCSi in the tris analogues from 117.2° in $HC(SiMe_3)_2$ [17] to

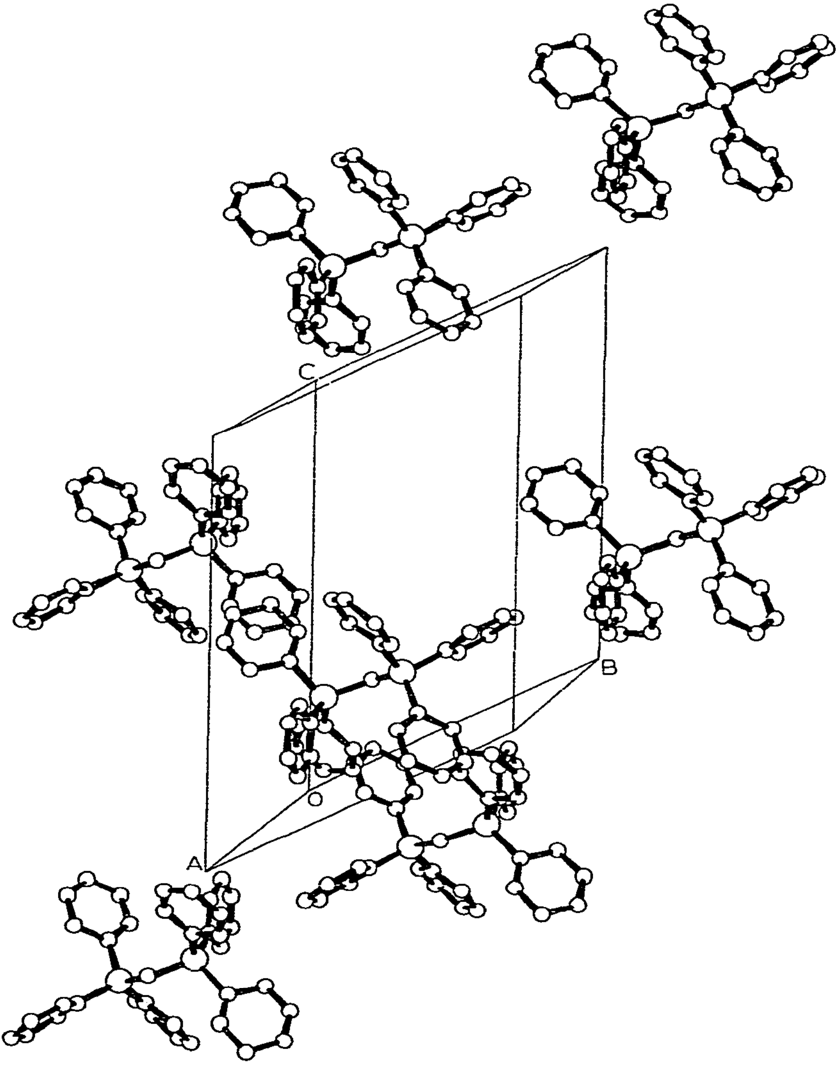

Fig. 2. A perspective view of the unit cell viewed perpendicular to the A face. All molecules whose centres lie in the range 0 to 1 in x and —0.5 to +1.5 in y and z are shown.

TABLE 7

GEOMETRY OF SOME $R_3SiXSiR_3$ ($X = CH_2$, NH, O) MOLECULES

	d(SiX) (Å)	d(Si ··· Si) (Å)	<(SiXSi) (°)	Reference
$H_2C(SiH_3)_2$	1.873(2)	3.149(3)	114.4(2)	6
$H_2C(SiMe_3)_2$	1.873 [a] 1.858 [b]	3.264 [a] 3.304 [b]	121.2 [a] 125.5 [b]	This work
$H_2C(SiPh_3)_2$	1.850(10)	3.336(5)	128.8(7)	This work
$HN(SiH_3)_2$	1.725(3)	3.097(6)	127.7(1)	5
$HN(SiMe_3)_2$	1.74(1)	3.08(5)	125(2)	3
$HN(SiPh_3)_2$	1.718(6)	3.209(5)	138.1(4)	2
$O(SiH_3)_2$	1.631(6)	3.086(2)	142.2(3)	4
$O(SiMe_3)_2$	1.626(5)	3.132(1)	148.8(2)	4
$O(SiPh_3)_2$	1.616(1)	3.232(1)	180.0(0)	1

[a] Calculated by molecular mechanics; see text. [b] Calculated by MNDO; see text.

only 112.6° in $Hg[C(SiMe_3)_2]_2$ [18]. On this basis the skeletal angle in $H_2C(SiMe_3)_2$ might be expected to lie somewhere in the range 117—123°. We have attempted to calculate the value of this angle both by semi-empirical SCF methods using the MNDO technique [19] and by molecular mechanics, using BIGSTRN-2 [20—23]: the values obtained are 125.5° using MNDO and 121.2° using molecular mechanics.

Since in the $HN(SiR_3)_2$ and $O(SiR_3)_2$ series the skeletal angle SiXSi for both the R = Me compounds is closer to that for R = H than for R = Ph, whereas this is not so for the calculated angle in $H_2C(SiR_3)_2$, we have sought to assess the reliability of our calculated values by comparison of the experimental values in the related compounds $H_2C(CMe_3)_2$ and $HC(SiMe_3)_3$ with those we calculated by MNDO and by molecular mechanics. The calculated value of the central angle CCC in $H_2C(CMe_3)_2$ is 127.0° by both MNDO and molecular mechanics using the same force field as for $H_2C(SiMe_3)_2$: the experimental value found from electron diffraction [24] is 125° if the central and terminal CC distances are assumed to differ by 0.02 Å and 128° if they are assumed to be equal, neatly spanning our two calculated values. In $HC(SiMe_3)_3$ the value found for the angle SiCSi by electron diffraction [17] is 117.2°, while the values calculated by MNDO and molecular mechanics are respectively 116.0 and 115.3°. Because of the good overall agreement between on the one hand values calculated by two entirely independent techniques, and on the other the experimental values for $H_2C(CMe_3)_2$ and $HC(SiMe_3)_3$, we can have confidence in our calculated values for $H_2C(SiMe_3)_2$, and conclude that the angle SiCSi in this latter molecule lies somewhere in the range 121—125°. This angle is much bigger than that found in $H_2C(SiH_3)_2$, and is in fact much closer to the value of 128.8° found here for the hexaphenyl derivative than might have been expected from the analogous μ-imino and μ-oxo series.

In $H_2C(SiPh_3)_2$ there are no unusually short distances either between a silicon atom and the phenyl groups in the other half of the molecule, or between phenyl groups attached to different silicon atoms. Consistent with this are the very small calculated strain energies, 1.35 kJ mol^{-1} and 0.008 kJ mol^{-1} respectively, associated with the angles SiCSi in $H_2C(SiMe_3)_2$ and $HC(SiMe_3)_3$: in both these molecules the only significant strain energies arise from the gearing of the methyl groups. In each of the molecules $H_2C(SiR_3)_2$ (R = H, CH_3, Ph) the central skeletal angle SiCSi is significantly larger than the approximately tetrahedral angle predicted by the VSEPR model: similarly the non-bonded distances Si · · · Si are all larger, very much so for R = CH_3 or Ph, than the 3.10 Å characteristic of the limiting distance between two non-bonded silicon atoms [25]: in the absence of either lone pair effects [26] or serious steric (non-bonded) interactions between the two SiR_3 groups when R = CH_3 or Ph, the occurrence of such large angles at 4-coordinate carbon is unexpected (but see below).

The molecular conformation of $H_2C(SiPh_3)_2$ (Fig. 1 and Table 6) has the central $C_3Si \cdots SiC_3$ fragment in an essentially staggered arrangement, perturbed somewhat by the bridging CH_2 group. In general, staggered or near-staggered conformations are characteristic of species X_3MYMX_3 having large central angles MYM [27,28], while eclipsed or near-eclipsed conformations are usually found in species having small central angles. While it is tempting to associate the conformation in $H_2C(SiPh_3)_2$ with the unusual magnitude of the angle SiCSi, we note that a very similar conformation occurs in $S[Ge(CH_2Ph)_3]_2$ where the central angle GeSGe is only 106.6° [29].

A bonding model for $H_2C(MR_3)_2$

Although the hydrogen atoms of the central CH_2 group were not explicitly located in the experimental studies of $H_2C(SiH_3)_2$ and $H_2C(SiPh_3)_2$, the calculated structure for $H_2C(SiMe_3)_2$ whether by MNDO or by molecular mechanics indicates no abnormal structural feature in the CH_2 group: the calculated values for the distance d(CH) and the angle HCH are 1.105 Å and 107.7° by MNDO, and 1.093 Å and 110.8° by molecular mechanics. We must therefore look to the SiCSi fragment only for any rationalisation of the geometries.

One approach is to regard each molecule $H_2C(SiR_3)_2$ as resulting from the interaction of a singlet carbene H_2C with two SiR_3 fragments. Using our usual simple approximation of a single σ orbital on each of the SiR_3 groups lying along the 3-fold axes of these groups, the following orbitals are relevant to the bonding in the SiCSi fragment: in phase and out of phase combinations of the two σ orbitals from silicon, of symmetry classes a_1 and b_2 respectively (the H_2CSi_2 fragment has local C_{2v} symmetry); a carbon orbital of a_1 symmetry, parallel to the local C_2 axis and composed of both C(2*s*) and C(2*p*); and a carbon 2*p* orbital of b_2 symmetry. Of the two carbon orbitals, that of a_1 symmetry is the tighter bound, because of its 2*s* component: (in the isolated carbene this orbital is occupied, while the pure 2*p* orbital is not).

As the silicon orbitals become more tightly bound with change in substituent R, the a_1 interaction becomes more important, while as these orbitals become less tightly bound, as with a group SiR_3 of low electronegativity, the b_2 interaction becomes the more important. Because of the spacial properties of the two carbon orbitals, the magnitude of the a_1 interaction is essentially independent of the angle SiCSi, but the b_2 interaction is maximised when this angle approaches 180°. Hence SiR_3 substituents of low electronegativity cause the b_2 bonding interaction to assume greater importance than the a_1, which in turn requires a larger angle SiCSi. A similar argument may be applied to molecules $HN(SiR_3)_2$ by simply replacing the singlet carbene H_2C with the singlet nitrene HN; the magnitude of the angle SiXSi in each series increases as R varies $H < CH_3 < Ph$. This is precisely the order deduced [30] from the properties of oxo compounds $O(MR_3)_2$ for the force constants for the skeletal bending vibration δ(MOM), and mirrors the order of decreasing electronegativity $SiH_3 > SiMe_3 > SiPh_3$. The key to this model is the breaking of the T_d symmetry at carbon and its lowering to effective C_{2v} symmetry: if the symmetry-breaking by the substituents in a generalised species $H_2C(MR_3)_2$ is insufficient and the carbon then behaves as in effective T_d symmetry, this model will be inapplicable.

Some computational support for this model can be obtained from MNDO calculations on the series $H_2C(MH_3)_2^{n+}$ for M = Be^{2-}, B^-, C, N^+; Al^-, Si, P^+. For the first row M, the calculated values of the skeletal angle MCM are as follows: Be, 143.8°; B, 124.7°; C, 116.8°; N, 114.3°; and for second row M the values are: Al, 125.7°; Si, 116.4°; P, 117.8°: (when M = O or S, the molecules $H_2C(MH_3)_2^{4+}$ dissociate to 2 MH_3^+ and CH_2^{2+}). For first row M there is, as expected, a steady decrease in the skeletal angle as M becomes more electronegative, and its bonding orbitals more tightly bound: for second row M, the calculated angle in the aluminium derivative is larger than for silicon and phosphorus, as anticipated, but the latter two values are rather similar. Overall however the variation of the calculated values is in satisfactory agreement with the simple model.

Experimental structures for molecules or ions of type $H_2C(MR_3)_2$ are rather few in number, and when the species are anionic the structure is rather sensitive to the nature of the cation; thus for the anion $H_2C(SO_3)_2^{2-}$ the skeletal angle SCS is 119.7° in the potassium salt [31], 117.7° in the silver salt [32], and 113.4° in the calcium salt [33]. However we note the following pairs, which may be relevant to this discussion: in the phosphine oxide $H_2C[P(O)Ph_2]_2$, when chelated to sodium ions, the value of the angle PCP is 112° in the bromide [34] and 114.1° in the iodide [35], while in the analogous uncomplexed selenide $H_2C[P(Se)Ph_2]_2$ this angle is 128.2° [36]: similarly oxidation of $H_2C(SC_6H_4Br)_2$, in which the angle SCS is 114.9° [37] to $H_2C(SO_2C_6H_4Br)_2$ causes a decrease in the skeletal angle to 111.5° [38].

Apart from these species, the oxo compounds $O(MPh_3)_2$ and $O[M(CH_2Ph)_3]_2$ (M = C, Si, Ge, Sn), and the cation $[N(PPh_3)_2]^+$, which we have discussed elsewhere [27], the closest isoelectronic analogues of the present molecule are species $C(PR_3)_2$; $C(PPh_3)_2$ has a very flexible central angle PCP whose value varies between 130.1 and 143.8° in different molecular forms in the solid state [39,40], while in $C(PPh_2Me)_2$ the angle observed is only 121.8° [41]. On the other hand $C(PMe_3)_2$ has a very flexible skeleton as determined by gas phase electron diffraction [42]; the averaged value of the angle PCP is 147.6°, but the skeleton may be linear at equilibrium, or this may be an example of a quasilinear molecule.

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