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THE MOLECULAR STRUCTURE OF [DIMETHYL(PHENYL)SILYL]TRIS(TRIMETHYLSILYL)METHANE

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Summary

The structure of the crowded molecule $(Me_3Si)_3C(SiMe_2Ph)$ has been determined by single crystal X-ray diffraction. The steric strain manifests itself mainly in lengthening of the Me_3Si—C and Me_2PhSi—C bonds (average length 1.920(6) Å) and closing up of the C—Si—C angles within the Me_3Si and Me_2PhSi groups (average 105.2(10)°), with correspondingly large C(1)—Si—C angles (113.5(13)°; C(1) is the central carbon atom).

Introduction

Compounds of the type $(Me_3Si)_3CSiR_2X$ have been shown to have highly unusual properties arising from the serious steric crowding [1], and it seemed of interest to investigate the consequences of such crowding for the molecular structure of a representative compound of this type. The related compound $(Me_3Si)_3CH$ is known from electron diffraction studies to have an unusual structure, in which exceptionally large Me_3Si—C—$SiMe_3$ angles relieve the strain [2], but such angles enlargement is not possible in $(Me_3Si)_3CSiR_2X$. The most appropriatet etrasilylmethane derivative for comparison would be $(Me_3Si)_4C$, but its structure could not be determined by X-ray diffraction because only low angle data were obtained together with thermal diffuse scattering presumably arising from considerable rotational disorder of the nearly spherical molecules in the crystal. We therefore turned to the corresponding compound with one Me replaced by a phenyl group, i.e. $(Me_3Si)_3CSiMe_2Ph$, I.

Experimental

Preparation of $(Me_3Si)_3CSiMe_2Ph$

Tris(trimethylsilyl)methane (11.5 g, 0.050 mol) in THF (100 cm^3) was added to a solution of MeLi (0.06 mol) [prepared from MeCl and Li in ether

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(30 cm^3)] and the mixture was refluxed for 6 h. Subsequently, PhMe$_2$SiF [3] (7.71 g, 0.05 mol) was added dropwise during 30 min, and the mixture was refluxed for 42 h then cooled and added to an excess of ice-cold saturated aqueous NH$_4$Cl. The organic layer was separated and combined with ether washings of the aqueous phase, and the solution was dried (MgSO$_4$) then evaporated under reduced pressure to leave an oil. Ethanol (5 cm^3) was added to this oil and the mixture was kept overnight at —20°C. The white solid was filtered off and recrystallysed from EtOH to give (Me$_3$Si)$_3$CSiPhMe$_2$ (2.4 g, 13%), m.p. 186°C; ^{1}H NMR (CCl$_4$): δ 0.25 (s, 27 H, SiMe$_3$), 0.60 (s, 6 H, SiMe$_2$), 7.2—7.8 ppm (m, 5 H, aryl-H) (Found: C, 58.5; H, 10.4. Calcd. for C$_{18}$H$_{38}$Si$_4$: C, 58.9; H, 10.4%).

Crystal data. C$_{18}$H$_{28}$Si$_4$, M = 366.85, monoclinic, a = 15.744(2), b = 16.306(3), c = 8.979(4) Å, β = 92.52(2)°, U = 2302.9 Å^3, Z = 4, D_c = 1.06 g cm^3 $F(000)$ = 808. Mo-K_α radiation, λ = 0.71073 Å, μ = 2.5 cm^{-1}. Space group $P2_1/n$ from systematic absences of $0k0$ for k odd and $h0l$ for $h + l$ odd.

A needle crystal ca. 0.30 × 0.15 × 0.10 mm, obtained by recrystallisation from hexane, was used for data collection on an Enraf-Nonius CAD4 diffractometer. Data with $2 < \theta < 25$ were measured by a $\theta/2\theta$ scan using monochromated Mo-K$_\alpha$ radiation with a scan width of $\Delta\theta = (1.0 + 0.35 \tan\theta)^0$, The scan rate for each reflection was determined by a rapid pre-scan at 10^0 min^{-1} in θ, where reflections with $I/\sigma(I)$ less than 1 were coded as unobserved. The remainder were rescanned subject to a maximum $I/\sigma(I)$ of 50 or maximum recording time of 120 seconds. Three standard reflections monitored every 30 minutes showed no significant variation. After correction for Lorentz and polarisation effects

TABLE 1

FRACTIONAL ATOMIC COORDINATES (×10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
Si(1)	1352(2)	2869(2)	5172(3)
Si(2)	821(2)	2192(2)	1957(3)
Si(3)	1111(2)	4068(2)	2474(4)
Si(4)	2657(2)	2868(2)	2611(3)
C(1)	1486(6)	2987(6)	3062(10)
C(2)	2222(8)	3435(8)	6305(13)
C(3)	313(8)	3304(8)	5799(14)
C(4)	1386(7)	1781(7)	5937(11)
C(5)	2132(9)	1465(8)	6661(14)
C(6)	2122(10)	677(9)	7287(17)
C(7)	1407(10)	197(9)	7315(19)
C(8)	635(11)	528(8)	6661(17)
C(9)	615(9)	1310(8)	5951(14)
C(10)	1313(9)	1131(7)	2122(15)
C(11)	—294(6)	2059(8)	2578(13)
C(12)	680(7)	2439(8)	—101(12)
C(13)	—124(10)	4162(13)	2111(21)
C(14)	1402(9)	4902(8)	3883(16)
C(15)	1593(11)	4452(9)	676(15)
C(16)	3318(7)	3817(8)	3071(16)
C(17)	3192(7)	1997(8)	3645(15)
C(18)	2816(8)	2676(10)	602(15)

but not for absorption, equivalent data were averaged and 1650 reflections with $|F|^2 > \sigma(F^2)$ were used for the structure analysis. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.06I)^2]^{1/2}/Lp$.

The positions of the silicon and carbon atoms were found by routine heavy atom methods and refined by full matrix least squares with anisotropic temperature factors. A low angle difference map revealed the positions of most of the hydrogen atoms except those attached to atoms C(2) and C(6), and these were included in structure factor calculations with fixed positions and B(iso) values of 6.0. Further refinement converged at $R = 0.087$, $R' = 0.097$, with the weighting scheme $w = 1/\sigma^2(F)$, and all final shift to error ratios <0.01. A difference map was everywhere $<0.4\ e\ \text{Å}^{-3}$.

The structure solution and refinement was done on a PDP11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 4. Final atom coordinates are listed in Tables 1 and 2, and intramolecular distances and angles in Table 3, while the numbering

TABLE 2

HYDROGEN ATOM COORDINATES ($\times 10^3$)

	x	y	z
H(4)	82	219	196
H(5)	−43	188	389
H(6)	193	104	139
H(7)	14	209	−57
H(9)	143	490	387
H(10)	209	500	391
H(11)	−84	229	221
H(12)	32	330	580
H(13)	156	443	65
H(14)	375	188	332
H(15)	148	298	306
H(16)	139	178	593
H(17)	−11	417	218
H(18)	139	20	732
H(19)	333	382	306
H(20)	402	375	277
H(21)	64	54	667
H(22)	62	131	595
H(23)	125	395	0
H(24)	266	287	261
H(25)	211	67	728
H(26)	0	416	277
H(27)	282	265	59
H(28)	264	207	27
H(29)	152	270	0
H(30)	212	146	664
H(31)	132	112	206
H(32)	346	270	55
H(33)	111	407	247
H(34)	320	199	365
H(35)	96	82	139
H(36)	135	287	517
H(37)	222	344	632
H(38)	−11	417	218

TABLE 3

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a) Bonds			
Si(1)—C(1)	1.926(8)	Si(1)—C(2)	1.909(10)
Si(1)—C(3)	1.891(8)	Si(1)—C(4)	1.902(9)
Si(2)—C(1)	1.915(8)	Si(2)—C(10)	1.899(11)
Si(2)—C(11)	1.877(8)	Si(2)—C(12)	1.896(9)
Si(3)—C(1)	1.926(8)	Si(3)—C(13)	1.963(13)
Si(3)—C(14)	1.900(10)	Si(3)—C(15)	1.919(11)
Si(4)—C(1)	1.914(7)	Si(4)—C(16)	1.900(10)
Si(4)—C(17)	1.875(10)	Si(4)—C(18)	1.859(11)
C(4)—C(5)	1.415(12)	C(4)—C(9)	1.436(13)
C(5)—C(6)	1.403(14)	C(6)—C(7)	1.37(2)
C(7)—C(8)	1.43(2)	C(8)—C(9)	1.426(13)
b) Angles			
C(1)—Si(1)—C(2)	111.7(4)	C(1)—Si(1)—C(3)	112.9(4)
C(1)—Si(1)—C(4)	116.5(4)	C(2)—Si(1)—C(3)	105.7(5)
C(2)—Si(1)—C(4)	104.6(4)	C(3)—Si(1)—C(4)	104.6(4)
C(1)—Si(2)—C(10)	111.4(4)	C(1)—Si(2)—C(11)	114.9(4)
C(1)—Si(2)—C(12)	113.5(4)	C(10)—Si(2)—C(11)	104.8(4)
C(10)—Si(2)—C(12)	107.4(5)	C(11)—Si(2)—C(12)	104.0(4)
C(1)—Si(3)—C(13)	114.0(6)	C(1)—Si(3)—C(14)	114.2(4)
C(1)—Si(3)—C(15)	113.7(4)	C(13)—Si(3)—C(14)	105.3(6)
C(13)—Si(3)—C(15)	105.1(6)	C(14)—Si(3)—C(15)	103.5(5)
C(1)—Si(4)—C(16)	113.3(4)	C(1)—Si(4)—C(17)	112.8(4)
C(1)—Si(4)—C(18)	113.2(4)	C(16)—Si(4)—C(17)	106.2(5)
C(16)—Si(4)—C(18)	104.6(5)	C(17)—Si(4)—C(18)	106.0(5)
Si(1)—C(1)—Si(2)	111.2(4)	Si(1)—C(1)—Si(3)	108.4(4)
Si(1)—C(1)—Si(4)	110.2(4)	Si(2)—C(1)—Si(3)	108.9(4)
Si(2)—C(1)—Si(4)	109.4(4)	Si(3)—C(1)—Si(4)	108.8(4)
Si(1)—C(4)—C(5)	120.9(7)	Si(1)—C(4)—C(9)	119.4(7)
C(5)—C(4)—C(9)	119.1(9)	C(4)—C(5)—C(6)	120(1)
C(5)—C(6)—C(7)	124(1)	C(6)—C(7)—C(8)	117(1)
C(7)—C(8)—C(9)	121(1)	C(4)—C(9)—C(8)	119(1)

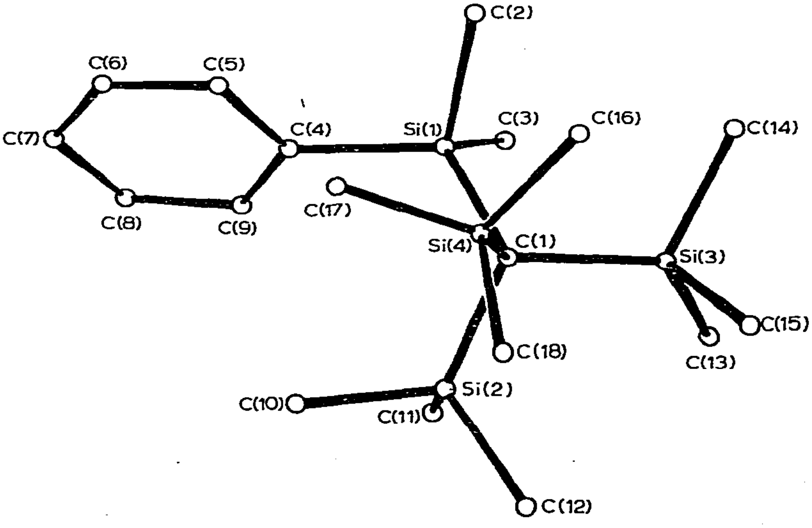

Fig. 1. Atom numbering scheme for $(Me_3Si)_3CSiMe_2Ph$.

scheme is shown in Fig. 1. Lists of temperature factors and final structure factors are available from the authors.

Discussion

The average dimensions in I, with r.m.s. deviations, are Si—C(1) 1.920(6) Å, other Si—C 1.899(26) Å, Si—C(1)—Si 109.5(10)°, C(1)—Si—C 113.5(13)°, and other C—Si—C 105.2(10)°. Thus the Si—C(1) bonds are consistently longer than normal (1.87 Å [5]), and the other Si—C bonds appear also to be slightly lengthened, although the difference is not statistically significant. The C(1)—Si—C and other C—Si—C angles are respectively larger and smaller than the tetrahedral value, and thus the steric strain mainly manifests itself in a closing up of the angles within the Me_3Si and Me_2PhSi groups and a lengthening of the Si—C(1) bonds. The closing of the angles within the Me_3Si and Me_2PhSi group results in Me—Me non-bonded contacts in the range 2.97—3.08 Å, while the shortest non-bonded contacts between Me groups attached to different silicon atoms are in the normal range of 3.4—3.6 Å.

For comparison, the average Si—C(1) bond length in $(Me_3Si)_3CH$ is 1.887 Å, and the Si—C—Si angles are 117.2° [2]. In $[(Me_3Si)_3C]_2Hg$, which is less crowded than I, there is again a marked closing up of the Me—Si—Me angles [106.0(11)°] and corresponding increase in the Me_3Si—C—$SiMe_3$ angles [112.6(2)°], but less lengthening of the Me_3Si—C bonds [1.887(4) Å] and normal Me—Si bonds [1.871(3) Å] [6].

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