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CYCLIC POLYSILANES

VIII*. THE CRYSTAL STRUCTURE OF 1,2,3,4-TETRA-tert-BUTYLTETRAMETHYLCYCLOTETRASILANE

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Summary

The crystal structure of $[Si(CH_3)(t\text{-}C_4H_9)]_4$ has been determined by single crystal X-ray diffraction. The crystals are tetragonal, $P4_2/n$; $a = b = 13.069(4)$, $c = 7.880(2)$ Å, $Z = 2$. The structure was determined using 745 independent data and refined with anisotropic least-squares to a final unweighted R-value of 3.5%. Each tetrameric molecule was found to be arranged about a $\bar{4}$ axis, with the independent crystallographic unit comprising one silicon atom, one methyl and one tert-butyl group. The four-membered ring of silicon atoms is nonplanar with an unusually large dihedral angle of 36.8°. The principal mean bond lengths are Si—Si 2.377(1), Si—C(methyl) 1.893(4), Si—C(tert-butyl) 1.918(3) Å, and the Si—Si—Si bond angle is 86.99°. The Si—Si bond length is somewhat longer than in other polysilanes.

Introduction

Although the chemistry of polysilanes has been extensively developed in recent years, few crystal structures have been determined and little is known about structural details for these molecules and how they compare to hydrocarbon analogs. Other than for disilanes, the only X-ray structure reported is that for dodecamethylcyclohexasilane, $(SiMe_2)_6$, by Carrell and Donohue [2]. Molecules of this substance have a structure entirely analogous to that of the chair form of cyclohexane, with tetrahedral bond angles at the silicon atoms.

In a recent communication [1] we reported the synthesis of 1,2,3,4-tetra-tert-butyltetramethylcyclotetrasilane, $[Si(CH_3)(t\text{-}C_4H_9)]_4$, in about 30% yield from the alkali metal condensation of $CH_3Si(t\text{-}C_4H_9)Cl_2$ in tetrahydrofuran. The product is air stable and rather unreactive, unlike the highly reactive permethyl

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[*] For part VII see ref. 1.

analog, $[(CH_3)_2Si]_4$. The crystalline product consists of an approximately 2/1 mixture of two isomers. The isomer formed in largest amount shows only singlets for the methyl and tert-butyl protons in the NMR spectrum, suggesting that it has a highly symmetrical structure. In this paper we report the structure of this isomer as determined by X-ray crystallography and a comparison of its molecular parameters with those of $(SiMe_2)_6$ and of carbocyclic four-membered rings.

Experimental

$[Si(CH_3)(t\text{-}C_4H_9)]_4$ was prepared by the condensation of tert-butylmethyldichlorosilane with sodium—potassium alloy in tetrahydrofuran as described earlier [1]. An irregularly shaped crystal of approximate dimensions 0.50 × 0.27 × 0.33 mm was cut from a large colorless block-like crystal grown by slow evaporation from diethyl ether. The crystal was mounted in the direction parallel to its longest axis and placed on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite monochromated Mo-K_α source. The preliminary Syntex routines [3] indicated a primitive tetragonal unit cell with dimensions $a = b = 13.069(4)$, $c = 7.880(2)$ Å; $V = 1345.8(6)$ Å^3. The $4/m$ (C_{4h}) Laue symmetry and associated lattice constants were verified by partial rotation projection photographs along each of the unit cell axes. The calculated density for $Z = 2$ of 0.987 g/cm^3 agrees within experimental error with the observed value of 0.992 g/cm^3 which was determined by flotation in a mixture of methyl formate and ethyl malonate.

Intensity data were collected in the usual $\theta - 2\theta$ variable scan speed mode (2-24°/min) for $3° < 2\theta < 50°$. Two standard peaks were monitored after every fifty reflections and indicated minimal intensity variations (±2%) over the entire data collection.

The data were reduced as described previously [4] to yield 1284 independent reflections of which 745 were observed $(I > 2\sigma(I))$ and used throughout the structural analysis. Effects of crystal absorption were ignored since the variation in transmission coefficients for the block-like crystal ($\mu = 1.63$ cm^{-1}) was minimal. Systematic absences for $\{hk0\}$, $h + k = 2n + 1$ and $00l$, $l = 2n + 1$ unambiguously define the space group as $P4_2/n$ (C^4_{4h}, No. 86) [5]. The general equivalent positions were chosen in the standard orientation with the origin $\bar{1}$ at 1/4, 1/4, 1/4 from $\bar{4}$.

Structure solution and refinement

The structure was solved by the standard heavy-atom method. An electron density map* phased on the coordinates of the unique silicon atom revealed the entire structure. In accordance with $Z = 2$ and the eight-fold general equivalent positions, each tetrameric molecule was found to be arranged about a crystallographic $\bar{4}$ axis with the independent crystallographic unit comprising one silicon atom, one methyl and one tert-butyl group. Full matrix isotropic least-squares analysis of this model resulted in $R_1 = 11.8\%$ and $R_2 = 16.2\%$ where $R_1 =$

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* All crystallographic programs used in structural determination and least-squares refinement were written by the author (JCC). Plots were made using ORTEP (C.K. Johnson).

TABLE 1

ATOMIC PARAMETERS (× 10^4)[a]

Atom	x	y	z	β_{iso}
Si	1270.5 (5)	2265.4 (5)	2154.5 (10)	
C(1)	995 (3)	2206 (4)	−203 (5)	
C(2)	5 (2)	2024 (2)	3322 (4)	
C(3)	154 (4)	2075 (5)	5238 (6)	
C(4)	−775 (4)	2843 (6)	2828 (11)	
C(5)	−383 (5)	958 (5)	2867 (9)	
H(1A)	712 (28)	1596 (30)	−427 (44)	6.8 (10)
H(1B)	1629 (31)	2289 (28)	−829 (44)	7.2 (10)
H(1C)	541 (28)	2679 (28)	−503 (42)	6.4 (9)
H(3A)	−477 (35)	1970 (34)	5782 (49)	9.2 (11)
H(3B)	541 (36)	1450 (38)	5470 (55)	10.3 (15)
H(3C)	357 (38)	2786 (40)	5540 (57)	10.9 (16)
H(4A)	−1398 (43)	2767 (34)	3337 (61)	11.1 (14)
H(4B)	−480 (45)	3592 (47)	3141 (75)	4.6 (15)
H(4C)	−842 (32)	2627 (32)	1717 (57)	7.3 (14)
H(5A)	−973 (30)	868 (28)	3339 (47)	7.3 (10)
H(5B)	−431 (36)	886 (37)	1620 (65)	10.7 (15)
H(5C)	73 (50)	527 (51)	3282 (87)	15.6 (29)

ANISOTROPIC THERMAL PARAMETERS (× 10^4)[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	54.2 (5)	59.6 (5)	145.9 (13)	−2.0 (4)	−5.3 (7)	2.2 (7)
C(1)	93 (3)	91 (3)	163 (6)	−1 (3)	−36 (4)	3 (4)
C(2)	52 (2)	83 (2)	246 (7)	−5 (2)	5 (2)	24 (3)
C(3)	94 (3)	135 (5)	270 (9)	−17 (3)	67 (5)	7 (6)
C(4)	70 (3)	197 (7)	491 (20)	40 (4)	53 (7)	93 (10)
C(5)	108 (4)	151 (5)	381 (16)	−70 (4)	46 (7)	−12 (7)

[a] Numbers in parentheses are estimated standard deviation in the least significant digits in all Tables.

[b] The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

$[\Sigma||F_o|-|F_c||/\Sigma|F_o|] \times 100\%$ and $R_2 = [\Sigma w_i||F_o|-|F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100\%$. At this stage, refinement was continued allowing anisotropic thermal motion for the nonhydrogen atoms and including hydrogen atom coordinates in their idealized staggered positions as fixed atom contributors ($\beta_{iso} = 8.0$ Å^2). After several cycles, a difference electron density map revealed the actual hydrogen positions and these were allowed to vary isotropically in the last refinement series. The final data to parameter ratio was 7.3/1. At convergence, $R_1 = 3.5\%$, $R_2 = 4.4\%$ and the standard deviation of an observation at unit weight $[\Sigma w_i||F_o|-|F_c||^2/(m-n)]^{1/2}$ was 1.13.

All least-squares refinements were based on the minimization of $\Sigma w_i||F_o|-|F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from Hanson et al. [6] while those for the hydrogen atoms are from Stewart et al. [7]. Included in the least-squares was a correction for the anomalous dispersion of silicon [8].

The positional and thermal parameter output from the last least-squares cycle are presented in Table 1. Interatomic distances and angles with estimated

TABLE 2

INTERATOMIC DISTANCES (Å)[a]

Si—Si'	2.377 (1)	C(3)—H(3A)	0.940 (45)
Si—C(1)	1.893 (4)	C(3)—H(3B)	0.978 (47)
Si—C(2)	1.918 (3)	C(3)—H(3C)	0.995 (52)
C(2)—C(3)	1.524 (5)	C(4)—H(4A)	0.913 (54)
C(2)—C(4)	1.528 (6)	C(4)—H(4B)	1.080 (58)
C(2)—C(5)	1.526 (6)	C(4)—H(4C)	0.924 (41)
C(1)—H(1A)	0.897 (38)	C(5)—H(5A)	0.864 (39)
C(1)—H(1B)	0.970 (39)	C(5)—H(5B)	0.988 (49)
C(1)—H(1C)	0.889 (37)	C(5)—H(5C)	0.883 (65)

INTRAMOLECULAR ANGLES (°)[a]

Si'—Si—Si''	86.99 (2)	C(2)—C(4)—H(4A)	114.1 (31)
Si'—Si—C(1)	111.2 (2)	C(2)—C(4)—H(4B)	109.7 (32)
Si'—Si—C(2)	119.6 (1)	C(2)—C(4)—H(4C)	95.2 (28)
Si''—Si—C(1)	110.8 (2)	C(2)—C(5)—H(5A)	108.7 (26)
Si''—Si—C(2)	119.6 (1)	C(2)—C(5)—H(5B)	109.9 (29)
C(1)—Si—C(2)	107.4 (2)	C(2)—C(5)—H(5C)	105.7 (44)
Si—C(1)—H(1A)	108.0 (22)	H(1A)—C(1)—H(1B)	110.6 (33)
Si—C(1)—H(1B)	109.4 (21)	H(1A)—C(1)—H(1C)	106.8 (31)
Si—C(1)—H(1C)	111.1 (22)	H(1B)—C(1)—H(1C)	110.9 (32)
Si—C(2)—C(3)	111.0 (2)	H(3A)—C(3)—H(3B)	104.3 (38)
Si—C(2)—C(4)	109.8 (3)	H(3A)—C(3)—H(3C)	105.1 (39)
Si—C(2)—C(5)	108.9 (3)	H(3B)—C(3)—H(3C)	126.7 (42)
C(3)—C(2)—C(4)	107.9 (5)	H(4A)—C(4)—H(4B)	108.4 (45)
C(3)—C(2)—C(5)	108.4 (4)	H(4A)—C(4)—H(4C)	107.3 (42)
C(4)—C(2)—C(5)	111.0 (5)	H(4B)—C(4)—H(4C)	121.8 (46)
C(2)—C(3)—H(3A)	109.5 (24)	H(5A)—C(5)—H(5B)	111.1 (39)
C(2)—C(3)—H(3B)	102.4 (26)	H(5A)—C(5)—H(5C)	110.8 (52)
C(2)—C(3)—H(3C)	108.2 (27)	H(5B)—C(5)—H(5C)	110.5 (54)

[a] Equivalent related atoms are indicated by (′) for y, 1/2−x, 1/2−z, and by (″) for 1/2−y, x, 1/2−z.

standard deviations from the full variance-covariance matrix are listed in Table 2. A listing of the final values of the structure factor amplitudes is available.*

Discussion

The structure of $[Si(CH_3)(t\text{-}C_4H_9)]_4$ consists of a nonplanar four-membered ring of silicon atoms, with each silicon being four-coordinate and bonded to a methyl and tert-butyl group and to two other silicon atoms in the ring. The tert-butyl groups occupy alternate positions above and below the ring so as to make them all *trans* to each other (Fig. 1), as is required by the $\bar{4}$ symmetry of the molecule. All the hydrogen atoms are in staggered configurations.

Bond lengths and angles for the compound are given in Table 2. The Si—Si bond length of 2.377(1) Å is somewhat longer than usual; compare the Si—Si distances of 2.338(4) Å in dodecamethylcyclohexasilane [2] and 2.340(9) Å in

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* The table of structure factors has been deposited as NAPS Document No. 02552 with ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York 10016. A copy may be secured by citing the document and remitting \$1.50 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

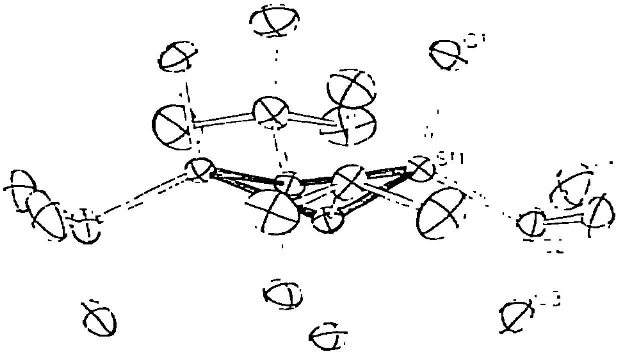

Fig. 1. A drawing of the $[Si(CH_3)(t\text{-}C_4H_9)]_4$ molecule. The 30% probability thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity.

hexamethyldisilane [9]. A similar, though smaller, trend of bond lengthening is observed in four-membered ring hydrocarbons. For example, the C—C bond length in cyclobutane of 1.548(3) Å [10] is slightly longer than that of 1.528(5) in cyclohexane [11].

A most interesting feature of the structure is the strongly folded configuration of the four-membered ring of silicon atoms. The dihedral angle between the two halves of the bent ring is 36.8°. This is considerably larger than the deviations from planarity observed in substituted cyclobutanes, where the dihedral angle is usually 26 ± 3° [12]. In $[Si(CH_3)(t\text{-}C_4H_9)]_4$, the large distortion probably takes place so as to allow the relatively large tert-butyl groups to become quasi-equatorial. In addition, the longer silicon—silicon distances allow greater ring folding without increased nonbonding repulsions. As expected from the puckering of the ring, the Si—Si—Si bond angle in the ring is significantly less than 90°, the actual angle being 86.99(2)°. The ring torsion angle is 25.8° and the silicon—silicon nonbonding distance across the ring is 3.272(1) Å.

The axial carbon atom is seen to bend away from the principal axis of the ring by 11.2°, minimizing the hydrogen nonbonding repulsions of the axial methyl with adjacent tert-butyl groups. The C(1)—Si—C(2) angle of 107.4(2)° is nearly tetrahedral. The axial C(1)—Si bond length is also observed to be larger than the equatorial C(2)—Si length by a distance of 0.025 Å. Similarly, Donohue and Carrell [2] found the axial bond lengths in dodecamethylcyclohexasilane to be 0.022 Å larger than the equatorial, and proposed that this difference was possibly significant. Our finding suggests that the difference is a real one, but we too offer no rationale for this phenomenon.

Acknowledgements

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