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PERALKYLCYCLOTRISILANE: CRYSTAL AND MOLECULAR STRUCTURE OF $[(t\text{-}BuCH_2)_2Si]_3$ *

HAMAO WATANABE*, MOTOHIKO KATO, TADASHI OKAWA, YOICHIRO NAGAI*
Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

and MIDORI GOTO*
National Chemical Laboratory for Industry, Yatabecho, Tsukuba, Ibaraki 305 (Japan)

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Summary

The crystal and molecular structure of the first peralkylcyclotrisilane, $[(t\text{-}BuCH_2)_2Si]_3$, have been determined by X-ray diffraction. Crystal data: orthorhombic, space group *Pnna*, *a* 35.668(3), *b* 16.963(1), *c* 12.251(1) Å, d_{calcd} 0.9183 g cm^{-3} for $Z = 8$ and *V* 7392.8 Å^3. Final *R* factor, based on 851 reflections ($|F_0| > 3\sigma|(F_0)|$), 0.069. The Si–Si bond length in the Si_3 ring is the longest among those of various peralkylcyclopolysilanes, $[R^1R^2Si]_n$ (n = 3–6), and is comparable with that in the perarylcyclotrisilane $[2,6\text{-}Me_2C_6H_3)_2Si]_3$.

Introduction

Much attention is being paid to the preparation of small-ring peralkylcyclopolysilanes, because of their very unusual properties. Our recent communication described the first synthesis of a stable peralkylcyclotrisilane, hexaneopentylcyclotrisilane $[(t\text{-}BuCH_2)_2Si]_3$, which on photolysis gave the first peralkyldisilene, tetraneopentyldisilene $[(t\text{-}BuCH_2)_2Si{=}Si(CH_2\text{-}t\text{-}Bu)_2]$ [1]. That report closely followed that of the first successful synthesis, by Masamune and coworkers, of a perarylcyclotrisilane, hexakis(2,6-dimethylphenyl)cyclotrisilane, which similarly afforded the corresponding tetraaryldisilene, tetrakis(2,6-dimethylphenyl)disilene [2]. It seemed of interest to determine the structure of the title compound by X-ray analysis and to compare the crystallographic data with those of other related cyclopolysilanes as well as the hexaarylcyclotrisilane, since the latter compound has been found to have an extraordinarily long Si–Si bond length (average, 2.407 Å) in the Si_3 ring [2].

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* In honor of Professor Makoto Kumada for his many years of outstanding research and teaching in the field of organometallic chemistry.

Experimental

The $[(t\text{-}BuCH_2)_2Si]_3$ was prepared by the condensation of dineopentyldichlorosilane with lithium in tetrahydrofuran as previously described [1], and crystals suitable for X-ray analysis were obtained from an ethanol/pentane mixture. A single crystal with dimensions of $0.5 \times 0.1 \times 0.05$ mm^3 was used for the X-ray measurement. The crystal dimensions and diffraction intensities were measured on a Rigaku-Denki four-circle diffractometer (Model AFC-4) in the $2\theta/\omega$ scan mode, using Cu-K_α radiation with a graphite monochromator. Reflections with 2θ values up to 80° were collected and higher angle reflections were too weak to detect. A total of 851 reflections with $(|F_o| > 3\sigma|(F_o)|)$ were used for the analysis. No correction was made for absorption. The crystal data are summarized in Table 1.

Determination of the structure

The structure was solved by direct method with MULTAN 78 [3]. The number of 168 independent reflections with $|E| \geqq 1.2$ were used in the phase determining procedure. In the refinement and further calculations performed with UNICS III [4], anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic thermal factors were used for the hydrogen atoms of which the positions were determined from calculations. The final R-factor was 0.069. The final parameters are listed in Tables 2a and 2b.

Lists of anisotropic temperature factors and structure factors are available from the authors.

Discussion

The molecular structure, with the numbering of the atoms, is shown in Fig. 1. In the unit cell, there are two kinds of crystallographically independent molecules, **A** and **B**, which are quite similar in conformation and have a two-fold axis of molecular symmetry. The cyclotrisilane ring in molecule A forms an isosceles triangle with Si(1A) at the apex and the two-fold axis passes through Si(1A) and the

TABLE 1

CRYSTAL DATA FOR $[(t\text{-}BuCH_2)_2Si]_3$

Molecular weight	511.119
Crystal system	Orthorhombic
Space group	*Pnna*
Cell constants	
a(Å)	35.646(3)
b(Å)	16.931(1)
c(Å)	12.251(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
Cell volume (Å^3)	7392.8(9)
Molecules/unit cell	8
d(calcd) (g cm^{-3})	0.9183

midpoint of the Si(2A)–Si(2′A) bond. In molecule **B**, these features of the Si_3 ring are identical to those of molecule **A**.

The bond lengths and angles are listed in Table 3a for molecules **A** and in Table 3b for molecule **B**. The unique Si–Si bond lengths of the two molecules are 2.367(8)–2.378(10) Å and the two equivalent bond lengths are 2.386(10)–2.414(10) Å. Thus, the difference between the two types of bonds is ca. 0.03 (average) Å. The Si–C bond lengths in the two molecules range from 1.89–1.94 Å. On the other hand, the bond angles in the cyclotrisilane rings are 59.0(0.3)–60.5(0.3)°. These bond lengths and bond angles are very close to those of hexakis(2,6-dimethylphenyl)cyclotrisilane prepared by Masamune et al. [2]. Table 4, in which the Si–Si bond lengths of other cyclopolysilane analogues [5–10] and related compounds

TABLE 2a

POSITIONAL PARAMETERS ($\times 10^4$) AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS IN $[(t\text{-}BuCH_2)_2Si]_3$

Atom	x	y	z	B_{eqv} (Å^2)
Molecule **A**				
Si(1A)	2500(0)	0(0)	6386(7)	3.3
Si(2A)	2306(2)	566(3)	4695(5)	3.5
C(1A)	2117(5)	−585(14)	7129(18)	4.9
C(2A)	1809(6)	−119(13)	7868(16)	5.4
C(3A)	2008(9)	331(18)	8786(24)	9.3
C(4A)	1551(8)	−737(21)	8313(32)	11.3
C(5A)	1592(9)	461(26)	7186(26)	12.3
C(6A)	2540(7)	1525(13)	4273(19)	5.5
C(7A)	2423(6)	2332(10)	4838(17)	5.3
C(8A)	2550(11)	2346(16)	6031(20)	9.9
C(9A)	1999(6)	2467(19)	4762(27)	8.1
C(10A)	2646(9)	2997(15)	4206(23)	8.3
C(11A)	1797(5)	412(17)	4329(16)	5.0
C(12A)	1689(6)	304(11)	3116(16)	4.4
C(13A)	1868(9)	−413(19)	2518(25)	9.3
C(14A)	1731(10)	1068(18)	2479(29)	10.8
C(15A)	1244(8)	179(23)	3084(33)	12.9
Molecule **B**				
Si(1B)	−403(0)	2500(0)	7500(0)	5.2
Si(2B)	188(2)	1890(4)	7978(5)	5.2
C(1B)	−675(6)	2937(14)	8689(18)	4.8
C(2B)	−914(6)	2463(15)	9508(19)	6.2
C(3B)	−1135(9)	3021(20)	10189(26)	11.1
C(4B)	−1198(11)	1973(23)	8849(30)	12.1
C(5B)	−676(10)	1935(29)	10120(35)	15.0
C(6B)	351(6)	971(13)	7182(18)	5.1
C(7B)	166(8)	129(14)	7388(27)	9.3
C(8B)	−235(9)	140(26)	7028(43)	15.0
C(9B)	199(12)	−98(23)	8591(33)	13.4
C(10B)	393(13)	−434(21)	6646(38)	14.2
C(11B)	306(6)	1962(19)	9491(20)	7.1
C(12B)	727(7)	2034(18)	9877(22)	8.2
C(13B)	948(12)	2587(36)	9283(47)	20.1
C(14B)	915(12)	1220(22)	9738(39)	14.0
C(15B)	728(11)	2167(30)	11079(34)	14.7

[11–14] are summarized, shows that the Si–Si bond lengths [2.391; 2.407 (average) Å] of the two cyclotrisilanes are the largest ever observed for an alkyl- or aryl-cyclopolysilane. It is noteworthy that in the peralkylcyclopolysilane series, the smaller the ring size the longer the Si–Si bond length (Fig. 2). The increase in the Si–Si bond length going from Si_6, Si_5, Si_4 to Si_3 is probably the result of increasing steric repulsions between the substituents on silicon and hence of ring strain. Further, for a particular ring size the Si–Si bond lengths depend primarily on the steric bulk of the substituents. Thus, as shown in Fig. 2, the Si–Si bond length of the cyclopentasilanes (Si_5) increases in the following order of substituents: H < Me < Ph.

TABLE 2b

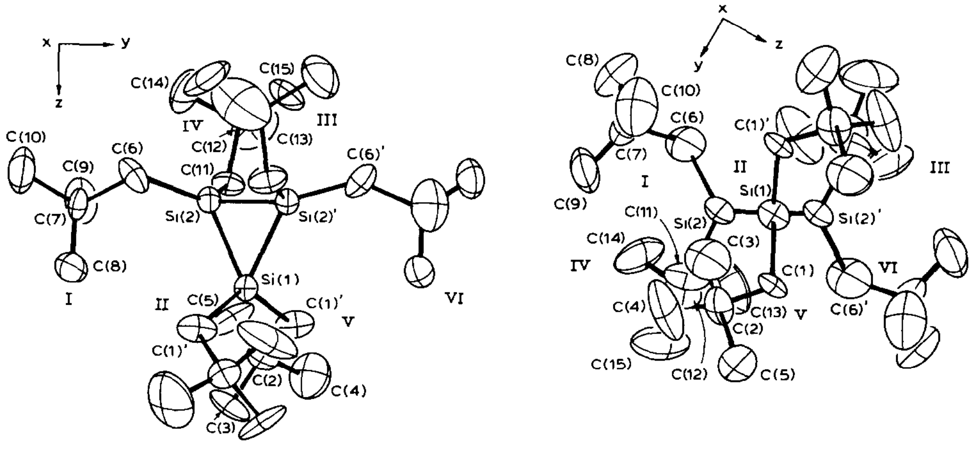
POSITIONAL PARAMETERS ($\times 10^3$) AND THERMAL PARAMETERS FOR HYDROGEN ATOMS IN $[(t\text{-}BuCH_2)_2Si]_3$

Atom [a]	*x*	*y*	*z*	*B* (Å)
Molecule **A**				
H(11)(C(1A))	224(5)	−98(13)	769(16)	10.2(4.4)
H(12)(C(1A))	190(5)	−83(11)	640(16)	8.5(4.2)
H(61)(C(6A))	245(9)	169(19)	332(28)	19.5(7.5)
H(62)(C(6A))	287(7)	146(13)	446(19)	12.1(5.2)
H(111)(C(11A))	158(8)	88(18)	465(24)	17.1(6.8)
H(112)(C(11A))	169(6)	−14(14)	475(19)	12.1(5.1)
H(31)(C(3A))	180(10)	63(23)	933(30)	23.2(9.5)
H(32)(C(3A))	216(10)	79(23)	844(30)	23.3(9.5)
H(33)(C(3A))	215(8)	−9(19)	933(23)	18.2(7.3)
H(41)(C(4A))	133(8)	−45(20)	883(26)	19.2(7.8)
H(42)(C(4A))	171(10)	−110(22)	880(31)	21.8(8.6)
H(43)(C(4A))	141(9)	−108(22)	769(32)	21.8(9.2)
H(51)(C(5A))	138(10)	78(23)	765(33)	22.7(9.5)
H(52)(C(5A))	144(11)	11(26)	653(33)	24.7(9.8)
H(53)(C(5A))	178(9)	82(20)	683(30)	20.7(8.7)
H(81)(C(8A))	246(8)	290(21)	643(25)	19.2(7.4)
H(82)(C(8A))	286(8)	226(20)	606(26)	19.5(8.0)
H(83)(C(8A))	238(9)	188(24)	654(28)	23.1(8.9)
H(91)(C(9A))	192(6)	307(18)	513(22)	14.4(5.8)
H(92)(C(9A))	184(8)	199(21)	528(26)	18.3(7.5)
H(93)(C(9A))	191(10)	253(23)	392(32)	22.1(8.5)
H(101)(C(10A))	257(10)	354(19)	454(27)	21.3(8.3)
H(102)(C(10A))	258(11)	300(24)	335(31)	23.4(9.2)
H(103)(C(10A))	296(11)	285(24)	432(32)	24.5(9.8)
H(131)(C(13A))	177(8)	−42(20)	160(26)	18.8(7.6)
H(132)(C(13A))	175(10)	−92(23)	310(30)	24.1(9.9)
H(133)(C(13A))	219(8)	−31(22)	244(26)	21.9(8.6)
H(141)(C(14A))	166(9)	96(18)	158(28)	18.9(7.6)
H(142)(C(14A))	202(9)	129(21)	250(31)	20.5(8.0)
H(143)(C(14A))	153(9)	153(21)	289(26)	19.4(7.6)
H(151)(C(15A))	113(9)	10(20)	217(27)	19.2(7.4)
H(152)(C(15A))	111(9)	69(20)	349(30)	19.6(7.8)
H(153)(C(15A))	119(9)	−38(23)	356(30)	20.8(8.5)
Molecule **B**				
H(11)(C(1B))	−89(5)	333(11)	830(14)	7.4(4.1)
H(12)(C(1B))	−47(6)	321(13)	922(18)	11.0(5.0)
H(61)(C(6B))	68(6)	88(11)	739(17)	9.9(4.4)
H(62)(C(6B))	28(5)	104(11)	623(17)	8.5(4.0)

TABLE 2b (continued)

Atom [a]	*x*	*y*	*z*	*B* (Å)
H(111)(C(11B))	18(6)	149(15)	1000(21)	12.9(5.1)
H(112)(C(11B))	17(6)	245(14)	985(21)	13.0(5.0)
H(31)(C(3B))	-132(10)	272(25)	1077(32)	23.9(10.2)
H(32)(C(3B))	-135(11)	336(28)	968(38)	26.1(10.6)
H(33)(C(3B))	-93(11)	345(24)	1071(34)	25.3(10.8)
H(41)(C(4B))	-137(9)	165(22)	937(28)	19.5(8.3)
H(42)(C(4B))	-107(11)	154(22)	832(32)	22.8(9.5)
H(43)(C(4B))	-139(9)	242(26)	834(29)	23.4(9.7)
H(51)(C(5B))	-84(9)	163(21)	1076(29)	20.3(8.7)
H(52)(C(5B))	-45(10)	225(23)	1051(31)	23.6(9.7)
H(53)(C(5B))	-54(13)	151(27)	948(35)	26.2(10.6)
H(81)(C(8B))	-38(10)	-43(24)	719(32)	23.9(9.5)
H(82)(C(8B))	-26(10)	30(23)	625(30)	20.6(8.0)
H(83)(C(8B))	-41(10)	59(22)	757(29)	20.8(8.0)
H(91)(C(9B))	4(10)	-70(27)	868(34)	24.5(9.8)
H(92)(C(9B))	1(11)	38(28)	907(28)	24.7(10.4)
H(93)(C(9B))	52(12)	-12(27)	879(35)	27.7(11.3)
H(101)(C(10B))	29(10)	-102(23)	677(29)	22.3(9.0)
H(102)(C(10B))	70(10)	-42(23)	686(29)	22.6(9.1)
H(103)C(10B))	34(10)	-27(22)	580(25)	20.3(8.4)
H(131)(C(13B))	126(10)	267(21)	964(28)	21.4(8.6)
H(132)(C(13B))	84(10)	318(21)	943(32)	20.7(8.3)
H(133)(C(13B))	95(9)	245(24)	831(27)	20.8(8.7)
H(141)(C(14B))	123(11)	121(21)	1007(33)	23.7(10.2)
H(142)(C(14B))	92(9)	93(22)	880(35)	20.0(8.1)
H(143)(C(14B))	78(22)	76(22)	1032(34)	22.7(8.8)
H(151)(C(15B))	99(9)	221(21)	1147(27)	20.4(8.3)
H(152)(C(15B))	58(9)	163(20)	1155(25)	18.8(7.6)
H(153)(C(15B))	58(9)	279(21)	1132(27)	19.5(7.7)

[a] An example for notation, H(11)(C(1A)): Hydrogen(11) attached to Carbon(1) in molecule A.



Molecule A

Molecule B

Fig. 1. Molecular structure of $[(t\text{-}BuCH_2)_2Si]_3$ (A and B). Atoms with prime mark: Symmetry operation code, $(\frac{1}{2}-x, \bar{y}, z)$ in A and $(x, \frac{1}{2}-y, \frac{1}{2}-z)$ in B.

Similarly, the Si–Si bond of $[Ph_2Si]_4 \approx [(t\text{-}BuMeSi]_4$ is longer than that of $[Me_2Si]_4$.

Interestingly, the lowest energy transitions in the electronic spectra for peralkylcyclopolysilanes, Si_6, Si_5, Si_4 and Si_3 occur at about 250–260, 260–280, 290–310

TABLE 3a

BOND DISTANCES AND ANGLES FOR $[(t\text{-}BuCH_2)_2Si]_3$ (MOLECULE A)[a]

Atoms	Distance (Å)	Atoms	Angle (°)
Si(1A)–Si(2A)	2.386(9)	Si(2A)–Si(1A)–Si(2′A)	59.5(0.3)
Si(2A)–Si(2′A)	2.367(8)	C(1A)–Si(1A)–C(1′A)	123.4(1.0)
Si(2A)–C(6A)	1.90(2)	C(1A)–Si(1A)–Si(12A)	114.5(0.7)
C(6A)–C(7A)	1.59(3)	C(1′A)–Si(1A)–Si(2A)	114.5(0.7)
C(7A)–C(8A)	1.53(3)		
C(7A)–C(9A)	1.53(3)	Si(1A)–Si(2A)–Si(2′A)	60.3(0.2)
C(7A)–C(10A)	1.58(2)	C(11A)–Si(2A)–C(6A)	118.4(1.1)
		C(11A)–Si(2A)–Si(2′A)	116.7(0.9)
Si(2A)–C(11A)	1.89(2)	C(11A)–Si(2A)–Si(1A)	115.4(0.7)
C(11A)–C(12A)	1.55(3)	C(6A)–Si(2A)–Si(2′A)	116.0(0.8)
C(12A)–C(13A)	1.56(4)	C(6A)–Si(2A)–Si(1A)	117.1(0.8)
C(12A)–C(14A)	1.52(4)		
C(12A)–C(15A)	1.60(4)	C(7A)–C(6A)–Si(2A)	120.3(1.6)
		C(2A)–C(1A)–Si(1A)	119.5(1.5)
Si(1A)–C(1A)	1.92(2)	C(12A)–C(11A)–Si(2A)	119.0(1.4)
C(1A)–C(2A)	1.62(3)		
C(2A)–C(1A)	1.50(4)		
C(2A)–C(3A)	1.53(4)		
C(2A)–C(5A)	1.51(4)		

[a] Atoms with prime mark: Symmetry operation code, $(\frac{1}{2}-x, \bar{y}, z)$.

TABLE 3b

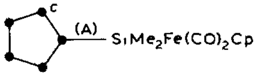
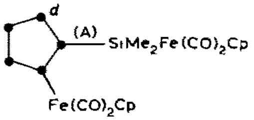
BOND DISTANCES AND ANGLES FOR $[(t\text{-}BuCH_2)_2Si]_3$ (MOLECULE B)[a]

Atoms	Distance (Å)	Atoms	Angle (°)
Si(2B)–Si(1B)	2.414(10)	Si(2B)–Si(1B)–Si(2′B)	59.0(0.3)
Si(2B)–Si(2′B)	2.378(10)	C(1B)–Si(1B)–Si(2B)	115.4(0.7)
Si(2B)–C(11B)	1.91(3)	C(1B)–Si(1B)–Si(2′B)	117.7(0.7)
C(11B)–C(12B)	1.58(3)	C(1B)–Si(1B)–C(1′B)	118.3(1.0)
C(12B)–C(14B)	1.54(5)		
C(12B)–C(15B)	1.50(5)	Si(1B)–Si(2B)–Si(2′B)	60.5(0.3)
C(12B)–C(13B)	1.42(6)	C(11B)–Si(2B)–C(6B)	118.6(1.1)
		C(11B)–Si(2B)–Si(2′B)	115.0(1.0)
Si(2B)–C(6B)	1.93(2)	C(11B)–Si(2B)–Si(1B)	113.6(0.8)
C(6B)–C(7B)	1.59(3)	C(6B)–Si(2B)–Si(2′B)	117.0(0.7)
C(7B)–C(8B)	1.50(5)	C(6B)–Si(2B)–Si(1B)	119.1(0.9)
C(7B)–C(9B)	1.53(5)		
C(7B)–C(10B)	1.55(5)	C(12B)–C(11B)–Si(2B)	120.4(1.6)
		C(7B)–C(6B)–Si(2B)	121.3(1.7)
Si(1B)–C(1B)	1.91(2)	C(2B)–C(1B)–Si(1B)	125.3(1.7)
C(1B)–C(2B)	1.54(3)		
C(2B)–C(5B)	1.44(5)		
C(2B)–C(3B)	1.50(4)		
C(2B)–C(4B)	1.54(4)		

[a] Atoms with a prime mark: Symmetry operation code, $(x, \frac{1}{2}-y, \frac{1}{2}-z)$.

TABLE 4

COMPARISON OF Si–Si BOND LENGTHS IN CYCLOPOLYSILANES AND SOME RELATED COMPOUNDS

No.	Cyclopolysilane	Si–Si bond length	(Å) (average)	Ref.
1	$[Me_2Si]_6$	2.332–2.342	(2.338)	5
2	$[Ph_2Si]_5$	2.371–2.413	(2.396)	6
3	$[H_2Si]_5$	2.342 [a]		7
4	$[Ph_2Si]_4$	2.370–2.381	(2.377)	8
5	$[t\text{-}BuMeSi]_4$	2.377		9
6	$[Me_2Si]_4$	2.359–2.367	(2.363)	10
7	$[(2,6\text{-}Me_2C_6H_3)_2Si]_3$	2.375–2.425	(2.407)	2
8	$[(t\text{-}BuCH_2)_2Si]_3$	2.367–2.414	(2.391) [b]	this work
9		2.371(A) 2.343–2.360(ring)	 (2.353)	11
10		2.362(A) 2.355–2.376(ring)	(2.362)	11
11	$[Ph_2Si]_5O$	2.371–2.391	(2.382)	12
12	$Ph_3Si\text{-}SiMe_2Fe(CO)_2Cp$	2.373		13
13	$Mes_2SiH\text{-}SiHMes_2$ [e]	2.362		14

[a] By electron diffraction method (gas phase). [b] Average from both molecules A and B. [c] Nonamethylcyclopentasilyl group. [d] Octamethylcyclopentasilyl group. [e] Mes: mesityl group.

and 310–330 nm, respectively [15–17]. The bathochromic shift with decreasing ring size for the peralkylcyclopolysilanes parallels the trend in the Si–Si bond length in the peralkylcyclopolysilanes described here.

As a result of the molecular symmetry, the following pairs of neopentyl substituents are equivalent to each other: I and VI; II and V; III and IV (see Fig. 1).

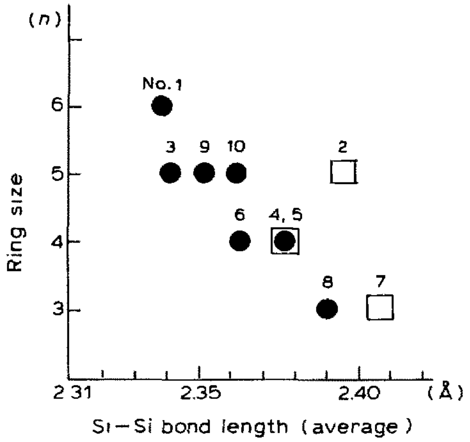


Fig. 2. Relationship between ring size (n) and Si–Si bond length in cyclopolysilanes, $[R^1R^2Si]_n$ (n = 3–6); ●: Peralkylcyclopolysilanes, □: Perarylcyclopolysilanes (see Table 4).

TABLE 5

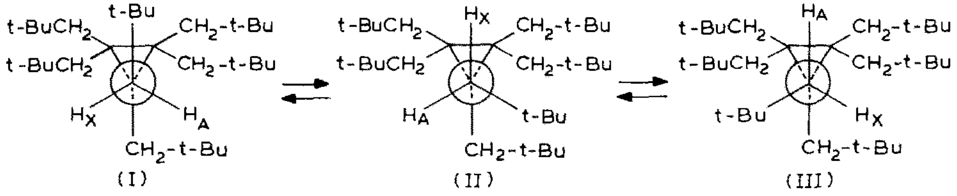
INTRAMOLECULAR H–H DISTANCES BETWEEN VICINAL METHYLENE GROUPS OF NEOPENTYL SUBSTITUENTS IN $[(t\text{-}BuCH_2)_2Si]_3$

Atoms [a]	Distance (Å)
Molecule **A**	
H(12)–H(112)	2.5
H(112)–H(6′2)	2.7
H(6′2)–H(12)	2.8
Molecule **B**	
H(6′2)–H(12)	3.0
H(12)–H(112)	2.7
H(112)–H(6′2)	2.9

[a] Atoms with a prime: Symmetry operation code, $(\frac{1}{2} - x, \bar{y}, z)$ in molecule **A**; $(x, \frac{1}{2} - y, \frac{1}{2} - z)$ in molecule **B**.

The planes of the Si–C bond pairs at each Si atom are nearly perpendicular to the plane of the Si_3 ring. As can be seen from Table 2, large temperature factors were observed for the terminal groups (methyls in neopentyl substituents), indicating a wide-range thermal motion of the groups at the temperature measured (r.t.), whereas the methylene groups attached to the ring silicons appear to be fairly rigid. The methylene groups show rather close near intramolecular atomic approaches between the hydrogens of vicinal methylenes from the two sets of the substituents, I/II/III and IV/V/VI. Thus, for example, the H–H distances observed between H(112)–H(6′2) (molecule **A**) and between H(12)–H(112) (molecule **B**) are about 2.7 Å (Table 5). Since the Van der Waals radius of H is 1.2 Å, the two sets of the "H · H · H ring" consisting of the methylene hydrogens are of similar size to that of the Si_3 ring which was sandwiched between the former two "rings". Therefore, chemical attack at the Si_3 ring from the two directions perpendicular to the plane of the Si_3 ring might be rather hindered, but attack from the three directions parallel to the plane of the Si_3 ring is not.

As shown in the previous paper [1], the title compound shows ^1H NMR ($CDCl_3$, TMS) signals (two singlets at room temperature) for methylene hydrogens at δ 0.93 ppm and for methyl hydrogens at δ 1.07 ppm, respectively, and the former signal is temperature dependent. Below −20°C, the methylene hydrogens are magnetically non-equivalent and two pairs of AX-type signals were observed at δ 0.44 ppm for H_A and at δ 1.44 ppm for H_X (J_{AX} 15.2 Hz) [18], respectively *. The non-equiva-



SCHEME 1.

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* With increasing temperature from ca. −40°C, the AX quartet decreased in intensity until no signal was observable at −20°C, and then a weak singlet, which appeared at δ 0.93 ppm at −15°C, became as intense as the normal signal at room temperature.

lence of the methylene hydrogens can be explained in terms of the hindered rotation around the Si–C bond(s) by the bulky neopentyl groups (Scheme 1). In fact, it is likely that H_X and H_A in conformations II and III, respectively, are not equivalent to the other four hydrogens (H_X and H_A in I, H_A in II and H_X in III), and the two sets of hydrogens are equivalent in each set. This non-equivalence between the two types of the hydrogens can also apply to all the other methylene hydrogens. Accordingly, in respect of the conformation of the methylene hydrogens, the NMR spectral behavior below −20°C is in harmony with the result of the crystallographic analysis described above.

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