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Synthesis and Structure of *all-trans*-1,2,3,4-Tetra-*tert*-butyl-1,2,3,4-tetrachlorocyclotetrasilane

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The synthesis of *all-trans*-[(*t*-Bu)ClSi]$_4$ (1) via chlorodephenylation of [(*t*-Bu)PhSi]$_4$ with HCl/AlCl$_3$ is described. Three isomers of [(*t*-Bu)PhSi]$_4$ (*cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2**) were separated, and each of them was subjected to chlorodephenylation. The X-ray structures are reported for *cis-cis-trans*-**2** and *cis-trans-cis*-**2**. Crystal data for *cis-cis-trans*-**2**: monoclinic, $P2_1/c$, a = 20.924(10) Å, b = 10.813(5) Å, c = 19.443(11) Å, β = 117.57(3)°, V = 3900(3) Å^3, Z = 4, R = 0.047, R_w = 0.047 for 2572 reflections. Crystal data for *cis-trans-cis*-**2**: monoclinic, $P2_1/n$, a = 15.407(4) Å, b = 23.798(6) Å, c = 10.852(2) Å, β = 94.93(2)°, V = 3964(2) Å^3, Z = 4, R = 0.043, R_w = 0.046 for 2905 reflections. The chlorodephenylation of *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2** gave **1** exclusively. The structure of **1** was established by X-ray crystallography. Crystal data for **1**: orthorhombic, $Pca2_1$, a = 14.848(2) Å, b = 13.719(1) Å, c = 13.074(4) Å, V = 2663(1) Å^3, Z = 4, R = 0.052, R_w = 0.077 for 1992 reflections. **1** has a folded structure, the dihedral angle being 26.6°, which accommodates the chlorine atoms in pseudoaxial positions and the *tert*-butyl groups in less hindered pseudoequatorial positions. The principal average bond distances are Si–Si 2.375 Å, Si–C 1.905 Å, and Si–Cl 2.086 Å. The Si–Cl bond distances are somewhat longer than usual.

Introduction

As part of an ongoing investigation of the chemistry of polycyclopolysilanes,[1] we have attempted to develop a convenient method for the synthesis of sila-functional cyclotetrasilanes of the type [R(Cl)Si]$_4$, which would serve as building blocks in the preparation of octasilacubanes and ladder polysilanes. Although a variety of alkyl- and aryl-substituted cyclotetrasilanes have been synthesized because of interest in their structures and properties,[2] the cyclotetrasilane [R(Cl)Si]$_4$ has not yet been reported except for one case. Thus, Masamune and co-workers reported that the reaction of 1,2-di-*tert*-butyl-1,1,2,2-tetrachlorodisilane with lithium naphthalenide had given *all-trans*-[(*t*-Bu)ClSi]$_4$ (**1**) in 8–20% yields as well as tricyclo[2.2.0.0^{2,5}]hexasilane and tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane.[3] However, even in this single example, the X-ray structure of **1** was not described.[4] In an attempt to prepare **1**, we studied the replacement of phenyl groups by chlorine atoms in the cyclotetrasilane [(*t*-Bu)PhSi]$_4$ (**2**). The earlier paper from our laboratory reported the synthesis of **2** by reductive coupling of (*t*-Bu)PhSiCl$_2$ with lithium.[5] However, compound **2** was identified as a mixture of the four possible isomers by spectroscopy, and the mixture was not separated into individual isomers by chromatography.[5] In this work, three isomers of **2**, *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2**, were separated and each of them was subjected to chlorodephenylation with HCl/AlCl$_3$.[6] We found that the chlorodephenylation proceeded smoothly to give **1** in high yield. In this paper, we present the following new information: (1) the X-ray structures of *cis-cis-trans*-**2** and *cis-trans-cis*-**2**; (2) stereochemistry of the chlorodephenylation of *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2**; (3) the X-ray structure of **1**.

Results and Discussion

Crystal Structures of *cis-cis-trans*-[(*t*-Bu)PhSi]$_4$ and *cis-trans-cis*-[(*t*-Bu)PhSi]$_4$. Cyclization of (*t*-Bu)PhSiCl$_2$ with an excess of lithium metal in tetrahydrofuran (THF) at −10 °C gave a 50% yield of [(*t*-Bu)PhSi]$_4$ (**2**). This represents a substantial improvement over the 32%

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1994.

[1] Nagai, Y.; Watanabe, H.; Matsumoto, H. Synthesis and Properties of Strained Cyclopolysilanes. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; Chapter 24 and references therein.

[2] (a) Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* 1975, *91,* 273. (b) Biernbaum, M.; West, R. *J. Organomet. Chem.* 1977, *131,* 179. (c) Biernbaum, M.; West, R. *J. Organomet. Chem.* 1977, *131,* 189. (d) Parkanyi, L.; Sasvari, K.; Barta, I. *Acta Crystallogr.* 1978, *B34,* 883. (e) Chen, Y.-S.; Gaspar, P. P. *Organometallics* 1982, *1,* 1410. (f) Helmer, B. J.; West, R. *Organometallics* 1982, *1,* 1458. (g) Matsumoto, H.; Minemura, M.; Takatsuna, K.; Nagai, Y.; Goto, M. *Chem. Lett.* 1985, 1005. (h) Matsumoto, H.; Takatsuna, K.; Minemura, M.; Nagai, Y.; Goto, M. *J. Chem. Soc., Chem. Commun.* 1985, 1366. (i) Watanabe, H.; Kato, M.; Okawa, T.; Kougo, Y.; Nagai, Y.; Goto, M. *Appl. Organomet. Chem.* 1987, *1,* 157. (j) Weidenbruch, M.; Thom, K.-L.; Pohl, S.; Saak, W. *J. Organomet. Chem.* 1987, *329,* 151. (k) Chrusciel, J.; Cypryk, M.; Fossum, E.; Matyjaszewski, K. *Organometallics* 1992, *11,* 3257.

[3] Kabe, Y.; Kuroda, M.; Honda, Y.; Yamashita, O.; Kawase, T.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* 1988, *27,* 1725.

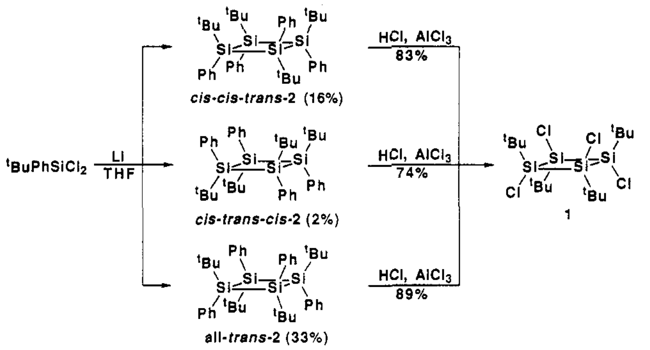
[4] Masamune *et al.* attempted X-ray structure determination for **1** and noted that, although strong diffractions of heavy atoms (Si, Cl) produced a satisfactory solution of the Si framework, severe disordering of *tert*-butyl groups had resulted in a moderate quality of the refinement (R value was not described).[3]

[5] Matsumoto, H.; Sakamoto, A.; Minemura, M.; Sugaya, K.; Nagai, Y. *Bull. Chem. Soc. Jpn.* 1986, *59,* 3314.

[6] Tamao, K.; Kumada, M. *J. Organomet. Chem.* 1971, *30,* 339.

0276-7333/94/2313-0795$04.50/0

Scheme 1



yield previously reported.[5] Three of the four possible isomers, *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2**, could easily be separated by reverse-phase recycle-type HPLC; yields of 16% (*cis-cis-trans*-**2**), 2% (*cis-trans-cis*-**2**), and 33% (*all-trans*-**2**) were obtained (Scheme 1).

The structures of *cis-cis-trans*-**2** and *cis-trans-cis*-**2** were confirmed by X-ray crystallography.[7,8] In Figures 1 and 2, the structures of *cis-cis-trans*-**2** and *cis-trans-cis*-**2** are shown. Crystallographic data, positional parameters, and selected bond distances and angles are given in Tables 1–5. Both molecules adopt folded conformations, the dihedral angles being 27.7° in *cis-cis-trans*-**2** and 32.8° in *cis-trans-cis*-**2**. By comparison, the corresponding angles are 36.8° in *all-trans*-[(*t*-Bu)MeSi]$_4$[2a] and 12.8° in (Ph$_2$Si)$_4$.[2d] The Si–Si bond distances range from 2.419(2) to 2.432(2) Å in *cis-cis-trans*-**2** with an average of 2.423 Å, and in *cis-trans-cis*-**2** they range from 2.421(2) to 2.429(2) Å with an average of 2.424 Å. These values fall into the longer range of the reported values for cyclotetrasilanes, *e.g.*, 2.377 Å in *all-trans*-[(*t*-Bu)MeSi]$_4$[2a] and 2.445 Å in *cis-cis-trans*-[(*t*-Bu)(c-C$_6$H$_{11}$)Si]$_4$.[2j] In *cis-cis-trans*-**2**, the molecule exists in a relatively stable conformation, in which three *tert*-butyl groups occupy pseudoequatorial positions and one *tert*-butyl group occupies a pseudoaxial position, in order to minimize steric repulsion among the *tert*-butyl groups. In *cis-trans-cis*-**2**, two neighboring *tert*-butyl groups occupy pseudoequatorial positions and the remaining two *tert*-butyl groups occupy pseudoaxial positions.

In Figure 3, UV spectra of *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2** are shown. Although absorption spectra of the stereoisomers of **2** are rather different, absorption bands extend to the wavelength region of *ca.* 350 nm in every case. The lowest energy transitions occur at 318 nm (ϵ 500) in *cis-cis-trans*-**2**, 319 nm (ϵ 650) in *cis-trans-cis*-**2**, and 319 nm (ϵ 1500) in *all-trans*-**2**. The wavelength may be compared with that of *all-trans*-[(*t*-Bu)MeSi]$_4$ (λ_{max} 300 nm, ϵ 290).[2b] Probably, increasing strain in the silicon framework in [(*t*-Bu)PhSi]$_4$ or the interaction between the silicon–silicon σ bonds and the benzene rings is responsible for the shift of the absorption maxima to the longer wavelengths and the increase of the extinction coefficients.

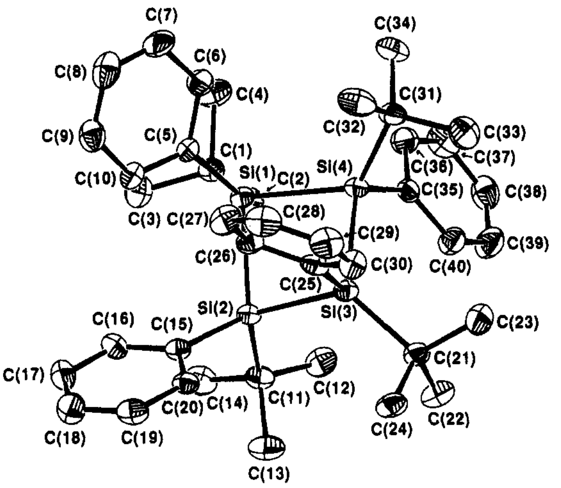


Figure 1. ORTEPII drawing of *cis-cis-trans*-**2** projected on the *ab* plane. Thermal ellipsoids are drawn at the 30% probability level.

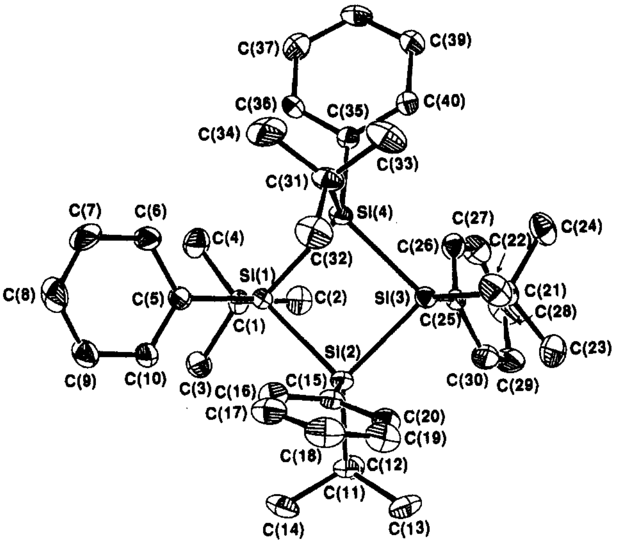


Figure 2. ORTEPII drawing of *cis-trans-cis*-**2** projected on the *ab* plane. Thermal ellipsoids are drawn at the 30% probability level.

Synthesis and Structure of 1. Chlorodephenylation of *cis-cis-trans*-**2**, *cis-trans-cis*-**2**, and *all-trans*-**2** could be effected by passing dry HCl at room temperature through its solution in benzene containing AlCl$_3$. It is noted that catalytic amounts of AlCl$_3$ were ineffective and that more than 0.5 equiv facilitated the chlorodephenylation. When *cis-cis-trans*-**2** was subjected to chlorodephenylation, the reaction reached completion in 2 h and *all-trans*-[(*t*-Bu)ClSi]$_4$ (**1**) was obtained in 83% yield as the sole product. Similarly, chlorodephenylation of *cis-trans-cis*-**2** and *all-trans*-**2** produced **1** in 74 and 89% yields, respectively. We found that the stereochemical course of the reaction was unaffected by reaction times. For example, when the reaction was quenched before complete consumption of the starting material, **1** was observed as the single stereoisomer. The result suggests that the inversion on the silicon atoms occurred rapidly to reach equilibrium during chlorodephenylation, in which the all-trans isomer

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(7) The structure of *all-trans*-**2** is assigned by NMR spectroscopy (Experimental Section). ^{1}H, ^{13}C, and ^{29}Si NMR indicate the presence of only one kind of *tert*-butyl group, one kind of phenyl group, and one kind of silicon atom, allowing the assignment to all-trans or all-cis structures. By considering the steric repulsion among *tert*-butyl groups, we assign the structure to all-trans. An X-ray structure determination is underway, and the preliminary results indicate the all-trans structure.

(8) A reviewer has commented that *cis-trans-cis*-**2** can be present in two different nonsuperimposable (diastereomeric) structures with equivalent energy because the flipping of the cyclotetrasilane ring should not occur in the solid state, and that reviewer has questioned why only one isomer appears to be present in crystalline *cis-trans-cis*-**2**. However, in actuality, we could not observe the formation of two kinds of crystals of *cis-trans-cis*-**2**, and only one kind of prism was obtained, the structure of which is discussed in the text.

Table 1. Summary of Crystal Data, Data Collection, and Refinement

	cis-cis-trans-**2**	*cis-trans-cis*-**2**	**1**
Crystal Data			
formula	$C_{40}H_{56}Si_4$	$C_{40}H_{56}Si_4$	$C_{16}H_{36}Cl_4Si_4$
mol wt	649.23	649.23	482.62
cryst descr	colorless prisms	colorless prisms	colorless prisms
cryst size, mm	0.4 × 0.8 × 0.25	0.4 × 0.5 × 0.7	0.6 × 0.6 × 0.8
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$Pca2_1$
a, Å	20.924(10)	15.407(4)	14.848(2)
b, Å	10.813(5)	23.798(6)	13.719(1)
c, Å	19.443(11)	10.852(2)	13.074(4)
β, deg	117.57(3)	94.93(2)	
V, Å^3	3900(3)	3964(2)	2663(1)
Z	4	4	4
D_{measd}, mg m^{-3}	1.101	1.089	1.187
D_{calcd}, mg m^{-3}	1.106	1.088	1.204
Data Collection			
diffractometer	Rigaku AFC-6	Rigaku AFC-6	Enraf-Nonius CAD-4
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Cu Kα (1.5418)
μ, mm^{-1}	0.1724	0.1696	1.919
abs corr	none	none	empirical
variation of stds	<1%	<1%	3.9%
2θ range, deg	2–40	1–40	2–130
range of h	0–20	–14 to 14	0–15
range of k	0–10	0–22	0–16
range of l	–18 to 16	0–10	0–17
scan type	ω–2θ	ω–2θ	ω–2θ
scan width, deg	1.3 + 0.50 tan θ	1.3 + 0.50 tan θ	0.8 + 0.15 tan θ
no. of rflns measd	4053	4096	2393
no. of indep rflns	3914	3835	2393
no. of obsd rflns ($\lvert F_o\rvert \geq 3\sigma(F_o)$)	2572	2905	1992
Refinement			
R	0.047	0.043	0.052
R_w	0.047	0.046	0.077
weighting scheme	$w = 1/[\sigma^2(F_o) + 0.001117\lvert F_o\rvert^2]$	$w = 1/[\sigma^2(F_o) + 0.001387\lvert F_o\rvert^2]$	$w = 1/[0.00782\lvert F_o\rvert^2 - 0.20655\lvert F_o\rvert + 2.6109]$
S	0.2917	0.3697	2.4047
$(\Delta/\sigma)_{max}$	0.133	0.193	2.634
$(\Delta\rho)_{max}$, e Å^{-3}	0.085	0.120	0.263
$(\Delta\rho)_{min}$, e Å^{-3}	–0.102	–0.162	–0.480
no. of params	540	621	216

is the most thermodynamically favored over the other stereoisomers.[9] Similar inversion in chlorodephenylation of cyclotetragermane has been reported recently.[10]

A single-crystal X-ray determination confirmed the all-trans structure of **1**. Figure 4 shows two views of the molecular structure. Crystallographic data, positional parameters, and selected bond distances and angles are given in Tables 1, 6, and 7, respectively.[11] The cyclotetrasilane ring has a folded structure with a dihedral angle of 26.6°. The average distances of the Si–Si bonds (2.375 Å) and the Si–C(*tert*-butyl) bonds (1.905 Å) are normal compared with those in other cyclotetrasilanes reported so far.[2] The average distance of the Si–Cl bonds of **1** (2.086 Å) seems longer by 0.06 Å than those of typical Si–Cl bonds,[12] although no Si–Cl bond distances of chlorinated cyclotetrasilanes have been reported. The bulky *tert*-butyl groups are symmetrically arrayed in less hindered, equivalent pseudoequatorial positions; the chlorine atoms occupy the remaining pseudoaxial positions. Consistent with this structure, the ^{1}H NMR spectrum of **1** exhibits only one *tert*-butyl singlet at δ 1.29 ppm. Since the Si–Si–Cl bond angles (average 106.3°) are considerably smaller than the Si–Si–C(*tert*-butyl) bond angles (average 122.8°), two chlorine atoms on opposite silicon atoms of the Si_4 ring exist at close positions and two *tert*-butyl groups exist far from each other.

The packing diagram of **1** viewed along the c axis is shown in Figure 5. Four molecules of **1** are packed in the unit cell in the relatively rare space group, $Pca2_1$. Molecules of **1** lie perpendicular to one another inside a layer along the c axis. The arrangement of **1** is unique and interesting because most peralkylcyclotetrasilanes so far reported are packed parallel to one another.[2] Although the packing cannot be explained clearly at this moment, intermolecular repulsion between the chlorine atoms might play an important role, as well as stabilization by the most effective packing. The packing of **1** is also interesting from the viewpoint of isomorphism among organometals of group 14 elements. Recently, several examples have been reported, in which cyclic polysilanes and polyger-

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(9) The stereochemistry of the chlorodephenylation cannot be clearly explained at this moment. However, a concerted mechanism in which the chlorodephenylation proceeds in one step via the cyclic transition state consisting of Si–C(phenyl), hydrogen chloride, and aluminum chloride does not seem probable because the mechanism well demonstrates retention of configuration.[2c] We are examining the two possibilities that the chlorine atom attacks the trivalent silicon intermediate from the less crowded side and that the chlorinated cyclotetrasilane is converted to the thermodynamically favored all-trans isomer by the $AlCl_3$-catalyzed exchange of chlorine atoms.

(10) Sekiguchi, A.; Yatabe, T.; Naito, H.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1992**, 1697.

(11) The parameters of the unit cell of **1** are very close to those reported earlier (orthorhombic, $P2_12_12_1$, a = 13.057(2) Å, b = 14.854(2) Å, c = 13.698(2) Å, V = 2656 Å^3, Z = 4).[3] However, these values are not the same and the space group is apparently different. Probably, the crystals obtained in this work and the earlier work[3] have different modifications of the crystal structure of **1**.

(12) Sutton, L. E. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1965.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *cis-cis-trans*-2

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Si(1)	0.1856(1)	0.0377(1)	–0.0315(1)	0.0350(6)
Si(2)	0.2041(1)	–0.1819(1)	–0.0019(1)	0.0355(6)
Si(3)	0.3315(1)	–0.1389(1)	0.0747(1)	0.0380(7)
Si(4)	0.3126(1)	0.0539(1)	0.0047(1)	0.0372(7)
C(1)	0.1117(3)	0.0892(4)	–0.1322(3)	0.042(3)
C(2)	0.1191(4)	0.0302(6)	–0.1994(3)	0.056(3)
C(3)	0.0386(3)	0.0510(6)	–0.1369(4)	0.059(3)
C(4)	0.1110(5)	0.2316(6)	–0.1423(4)	0.065(4)
C(5)	0.1615(3)	0.1273(5)	0.0372(3)	0.036(2)
C(6)	0.1797(3)	0.2523(6)	0.0495(3)	0.051(3)
C(7)	0.1594(4)	0.3265(7)	0.0941(4)	0.069(4)
C(8)	0.1221(3)	0.2769(7)	0.1283(4)	0.073(4)
C(9)	0.1035(3)	0.1554(6)	0.1189(3)	0.062(3)
C(10)	0.1221(3)	0.0807(5)	0.0721(3)	0.046(3)
C(11)	0.1781(3)	–0.2994(5)	–0.0860(3)	0.048(3)
C(12)	0.2167(3)	–0.2716(5)	–0.1350(3)	0.060(3)
C(13)	0.1999(4)	–0.4294(5)	–0.0492(3)	0.068(4)
C(14)	0.0965(3)	–0.3036(6)	–0.1394(3)	0.063(3)
C(15)	0.1580(3)	–0.2449(4)	0.0547(3)	0.038(2)
C(16)	0.0832(3)	–0.2380(5)	0.0243(3)	0.047(3)
C(17)	0.0485(4)	–0.2910(6)	0.0619(4)	0.061(4)
C(18)	0.0859(4)	–0.3530(6)	0.1309(4)	0.063(3)
C(19)	0.1596(3)	–0.3600(5)	0.1618(3)	0.053(3)
C(20)	0.1955(3)	–0.3079(4)	0.1246(3)	0.043(3)
C(21)	0.4066(3)	–0.2593(5)	0.0908(3)	0.048(3)
C(22)	0.3965(3)	–0.3339(5)	0.0204(3)	0.066(3)
C(23)	0.4801(4)	–0.1954(7)	0.1208(5)	0.067(4)
C(24)	0.4083(3)	–0.3539(5)	0.1517(3)	0.058(3)
C(25)	0.3441(3)	–0.0906(4)	0.1749(3)	0.042(3)
C(26)	0.2852(3)	–0.0474(5)	0.1834(3)	0.046(3)
C(27)	0.2909(4)	–0.0052(6)	0.2525(4)	0.064(4)
C(28)	0.3567(4)	–0.0080(6)	0.3184(4)	0.067(4)
C(29)	0.4157(3)	–0.0495(5)	0.3134(3)	0.066(3)
C(30)	0.4104(3)	–0.0901(5)	0.2429(3)	0.053(3)
C(31)	0.3735(3)	0.1890(5)	0.0643(3)	0.051(3)
C(32)	0.3718(5)	0.2126(7)	0.1408(4)	0.073(4)
C(33)	0.4501(4)	0.1531(8)	0.0824(7)	0.092(5)
C(34)	0.3539(5)	0.3098(6)	0.0176(5)	0.067(4)
C(35)	0.3230(3)	0.0462(5)	–0.0870(3)	0.040(3)
C(36)	0.2958(3)	0.1392(6)	–0.1430(3)	0.055(3)
C(37)	0.3053(4)	0.1376(6)	–0.2085(3)	0.066(3)
C(38)	0.3383(3)	0.0413(6)	–0.2236(4)	0.065(3)
C(39)	0.3650(3)	–0.0525(6)	–0.1706(3)	0.069(3)
C(40)	0.3578(3)	–0.0488(5)	–0.1031(3)	0.055(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table 3. Bond Distances (Å) and Angles (deg) for *cis-cis-trans*-2

Bond Distances

Si(1)–Si(2)	2.432(2)	C(15)–C(16)	1.395(7)
Si(1)–Si(4)	2.421(2)	C(15)–C(20)	1.393(6)
Si(1)–C(1)	1.932(4)	C(16)–C(17)	1.371(12)
Si(1)–C(5)	1.897(6)	C(17)–C(18)	1.374(9)
Si(2)–Si(3)	2.421(2)	C(18)–C(19)	1.373(10)
Si(2)–C(11)	1.939(5)	C(19)–C(20)	1.383(10)
Si(2)–C(15)	1.894(6)	C(21)–C(22)	1.517(9)
Si(3)–Si(4)	2.419(2)	C(21)–C(23)	1.533(9)
Si(3)–C(21)	1.952(6)	C(21)–C(24)	1.552(9)
Si(3)–C(25)	1.913(6)	C(25)–C(26)	1.397(9)
Si(4)–C(31)	1.932(5)	C(25)–C(30)	1.407(6)
Si(4)–C(35)	1.897(6)	C(26)–C(27)	1.371(10)
C(1)–C(2)	1.524(10)	C(27)–C(28)	1.381(8)
C(1)–C(3)	1.544(9)	C(28)–C(29)	1.359(11)
C(1)–C(4)	1.552(8)	C(29)–C(30)	1.392(9)
C(5)–C(6)	1.394(8)	C(31)–C(32)	1.526(11)
C(5)–C(10)	1.382(9)	C(31)–C(33)	1.524(10)
C(6)–C(7)	1.384(11)	C(31)–C(34)	1.534(9)
C(7)–C(8)	1.348(12)	C(35)–C(36)	1.395(8)
C(8)–C(9)	1.358(10)	C(35)–C(40)	1.376(9)
C(9)–C(10)	1.402(10)	C(36)–C(37)	1.376(11)
C(11)–C(12)	1.537(11)	C(37)–C(38)	1.355(11)
C(11)–C(13)	1.547(7)	C(38)–C(39)	1.367(9)
C(11)–C(14)	1.536(7)	C(39)–C(40)	1.389(10)

Bond Angles

Si(2)–Si(1)–Si(4)	88.2(1)	Si(2)–C(11)–C(14)	112.3(4)
Si(2)–Si(1)–C(1)	119.1(2)	C(12)–C(11)–C(13)	109.7(5)
Si(2)–Si(1)–C(5)	113.4(2)	C(12)–C(11)–C(14)	109.0(4)
Si(4)–Si(1)–C(1)	122.0(2)	C(13)–C(11)–C(14)	106.4(5)
Si(4)–Si(1)–C(5)	111.8(2)	Si(2)–C(15)–C(16)	120.5(4)
C(1)–Si(1)–C(5)	102.6(2)	Si(2)–C(15)–C(20)	122.2(4)
Si(1)–Si(2)–Si(3)	88.1(1)	C(16)–C(15)–C(20)	117.1(6)
Si(1)–Si(2)–C(11)	119.2(2)	C(15)–C(16)–C(17)	121.2(5)
Si(1)–Si(2)–C(15)	114.9(2)	C(16)–C(17)–C(18)	121.5(7)
Si(3)–Si(2)–C(11)	116.3(2)	C(17)–C(18)–C(19)	118.1(8)
Si(3)–Si(2)–C(15)	115.1(1)	C(18)–C(19)–C(20)	121.4(5)
C(11)–Si(2)–C(15)	103.6(2)	C(15)–C(20)–C(19)	120.8(5)
Si(2)–Si(3)–Si(4)	88.5(1)	Si(3)–C(21)–C(22)	116.3(3)
Si(2)–Si(3)–C(21)	123.1(2)	Si(3)–C(21)–C(23)	110.6(4)
Si(2)–Si(3)–C(25)	105.8(2)	Si(3)–C(21)–C(24)	107.1(5)
Si(4)–Si(3)–C(21)	125.1(2)	C(22)–C(21)–C(23)	106.3(6)
Si(4)–Si(3)–C(25)	104.3(2)	C(22)–C(21)–C(24)	106.4(4)
C(21)–Si(3)–C(25)	107.3(2)	C(23)–C(21)–C(24)	110.0(5)
Si(1)–Si(4)–Si(3)	88.4(1)	Si(3)–C(25)–C(26)	119.9(3)
Si(1)–Si(4)–C(31)	124.0(2)	Si(3)–C(25)–C(30)	124.8(5)
Si(1)–Si(4)–C(35)	108.2(2)	C(26)–C(25)–C(30)	115.3(5)
Si(3)–Si(4)–C(31)	115.1(2)	C(25)–C(26)–C(27)	123.1(5)
Si(3)–Si(4)–C(35)	115.6(2)	C(26)–C(27)–C(28)	119.9(8)
C(31)–Si(4)–C(35)	105.4(3)	C(27)–C(28)–C(29)	119.3(7)
Si(1)–C(1)–C(2)	113.4(4)	C(28)–C(29)–C(30)	120.8(5)
Si(1)–C(1)–C(3)	106.8(4)	C(25)–C(30)–C(29)	121.5(6)
Si(1)–C(1)–C(4)	111.7(3)	Si(4)–C(31)–C(32)	113.9(5)
C(2)–C(1)–C(3)	109.1(5)	Si(4)–C(31)–C(33)	106.1(5)
C(2)–C(1)–C(4)	107.8(6)	Si(4)–C(31)–C(34)	111.6(3)
C(3)–C(1)–C(4)	107.9(6)	C(32)–C(31)–C(33)	108.3(6)
Si(1)–C(5)–C(6)	118.4(5)	C(32)–C(31)–C(34)	108.3(6)
Si(1)–C(5)–C(10)	124.8(4)	C(33)–C(31)–C(34)	108.6(7)
C(6)–C(5)–C(10)	116.5(6)	Si(4)–C(35)–C(36)	121.3(5)
C(5)–C(6)–C(7)	122.0(7)	Si(4)–C(35)–C(40)	123.3(4)
C(6)–C(7)–C(8)	119.6(7)	C(36)–C(35)–C(40)	115.4(6)
C(7)–C(8)–C(9)	120.9(8)	C(35)–C(36)–C(37)	122.1(6)
C(8)–C(9)–C(10)	119.7(7)	C(36)–C(37)–C(38)	121.1(6)
C(5)–C(10)–C(9)	121.1(5)	C(37)–C(38)–C(39)	118.6(7)
Si(2)–C(11)–C(12)	111.9(4)	C(38)–C(39)–C(40)	120.4(6)
Si(2)–C(11)–C(13)	107.3(4)	C(35)–C(40)–C(39)	122.4(5)

manes with the same substituents are isomorphous in the X-ray crystal structures.[13–16] However, molecules of the germanium analogue of 1 recently have been reported to be packed parallel to one another in the space group *Pbcm*.[10] Therefore, 1 and the germanium analogue provide an exception of isomorphism between cyclic polysilanes and polygermanes.

It is interesting to compare the UV spectrum of 1 (Figure 3) with that of *all-trans*-[(*t*-Bu)MeSi]$_4$, since West and co-workers pointed out that substitution with chlorine in (Me$_2$Si)$_6$ (λ_{max} 253 nm, ϵ 1200) leads to a modest bathochromic shift of the lowest energy transition in ClMeSi(Me$_2$Si)$_5$ (λ_{max} 266 nm, ϵ 800) and that the major effect of chlorine in ClMeSi(Me$_2$Si)$_4$ (λ_{max} 284 nm, ϵ 80), compared with (Me$_2$Si)$_5$ (λ_{max} 272 nm, ϵ 970), is to decrease the extinction coefficient for the lowest energy absorption.[17] In 1 the lowest energy transition occurs at 284 nm with an extinction coefficient of 1000. The corresponding transition in *all-trans*-[(*t*-Bu)MeSi]$_4$ occurs at 300 nm with an extinction coefficient of 290.[2b] We feel that the hypochromic shift observed for 1 relative to *all-trans*-[(*t*-Bu)MeSi]$_4$ and the marked increase in intensity of the absorption band for 1 may be attributable to the strong

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Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *cis-trans-cis*-2

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Si(1)	0.1496(1)	–0.1186(1)	0.6482(1)	0.0325(5)
Si(2)	0.2528(1)	–0.1917(1)	0.7168(1)	0.0324(5)
Si(3)	0.3676(1)	–0.1241(1)	0.6926(1)	0.0324(5)
Si(4)	0.2611(1)	–0.0507(1)	0.7146(1)	0.0351(5)
C(1)	0.1077(3)	–0.1206(2)	0.4737(4)	0.037(2)
C(2)	0.1820(3)	–0.1214(2)	0.3889(5)	0.051(2)
C(3)	0.0486(3)	–0.1718(2)	0.4499(5)	0.051(2)
C(4)	0.0522(3)	–0.0687(2)	0.4395(5)	0.057(2)
C(5)	0.0445(3)	–0.1144(2)	0.7276(4)	0.039(2)
C(6)	0.0059(3)	–0.0628(2)	0.7473(5)	0.056(2)
C(7)	–0.0732(4)	–0.0593(3)	0.7979(6)	0.079(3)
C(8)	–0.1157(4)	–0.1069(3)	0.8300(6)	0.075(3)
C(9)	–0.0804(4)	–0.1581(2)	0.8098(5)	0.060(2)
C(10)	–0.0017(3)	–0.1617(2)	0.7590(5)	0.045(2)
C(11)	0.2487(3)	–0.2662(2)	0.6422(4)	0.038(2)
C(12)	0.2466(3)	–0.2656(2)	0.5022(5)	0.048(2)
C(13)	0.3283(4)	–0.3006(2)	0.6927(5)	0.061(2)
C(14)	0.1660(4)	–0.2957(2)	0.6790(5)	0.061(2)
C(15)	0.2486(3)	–0.2073(2)	0.8886(4)	0.038(2)
C(16)	0.1762(3)	–0.2018(2)	0.9535(5)	0.050(2)
C(17)	0.1774(4)	–0.2148(2)	1.0781(6)	0.066(3)
C(18)	0.2527(5)	–0.2352(3)	1.1392(5)	0.071(3)
C(19)	0.3253(4)	–0.2414(2)	1.0775(6)	0.066(3)
C(20)	0.3233(3)	0.2278(2)	0.9550(5)	0.050(2)
C(21)	0.4795(3)	–0.1233(2)	0.7904(4)	0.045(2)
C(22)	0.4737(4)	–0.1207(2)	0.9301(5)	0.067(2)
C(23)	0.5343(3)	–0.1749(2)	0.7595(6)	0.071(3)
C(24)	0.5280(3)	–0.0709(2)	0.7526(5)	0.062(2)
C(25)	0.3973(3)	–0.1273(2)	0.5268(4)	0.032(2)
C(26)	0.3917(3)	–0.0823(2)	0.4447(5)	0.043(2)
C(27)	0.4142(3)	–0.0861(2)	0.3252(5)	0.054(2)
C(28)	0.4449(5)	–0.1355(3)	0.2833(5)	0.066(3)
C(29)	0.4526(4)	–0.1812(2)	0.3595(6)	0.060(2)
C(30)	0.4287(3)	–0.1773(2)	0.4783(5)	0.048(2)
C(31)	0.2559(4)	–0.0201(2)	0.8794(5)	0.054(2)
C(32)	0.2409(4)	–0.0646(3)	0.9759(5)	0.075(3)
C(33)	0.3389(4)	0.0130(3)	0.9166(5)	0.082(3)
C(34)	0.1797(5)	0.0222(3)	0.8799(6)	0.088(3)
C(35)	0.2703(3)	0.0140(2)	0.6167(4)	0.038(2)
C(36)	0.1974(3)	0.0423(2)	0.5677(5)	0.049(2)
C(37)	0.2013(4)	0.0928(2)	0.5058(6)	0.064(2)
C(38)	0.2807(4)	0.1172(2)	0.4923(5)	0.061(2)
C(39)	0.3550(3)	0.0915(2)	0.5430(5)	0.053(2)
C(40)	0.3496(3)	0.0406(2)	0.6041(5)	0.043(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table 5. Bond Distances (Å) and Angles (deg) for *cis-trans-cis*-2

Bond Distances

Si(1)–Si(2)	2.429(2)	C(15)–C(16)	1.375(7)
Si(1)–Si(4)	2.422(2)	C(15)–C(20)	1.393(7)
Si(1)–C(1)	1.948(5)	C(16)–C(17)	1.386(8)
Si(1)–C(5)	1.901(5)	C(17)–C(18)	1.374(10)
Si(2)–Si(3)	2.421(2)	C(18)–C(19)	1.360(10)
Si(2)–C(11)	1.949(5)	C(19)–C(20)	1.366(8)
Si(2)–C(15)	1.908(5)	C(21)–C(22)	1.527(7)
Si(3)–Si(4)	2.422(2)	C(21)–C(23)	1.542(8)
Si(3)–C(21)	1.946(5)	C(21)–C(24)	1.528(7)
Si(3)–C(25)	1.896(5)	C(25)–C(26)	1.392(7)
Si(4)–C(31)	1.939(5)	C(25)–C(30)	1.403(7)
Si(4)–C(35)	1.883(5)	C(26)–C(27)	1.374(8)
C(1)–C(2)	1.530(7)	C(27)–C(28)	1.360(9)
C(1)–C(3)	1.531(7)	C(28)–C(29)	1.365(9)
C(1)–C(4)	1.529(7)	C(29)–C(30)	1.375(8)
C(5)–C(6)	1.390(7)	C(31)–C(32)	1.522(8)
C(5)–C(10)	1.390(7)	C(31)–C(33)	1.527(8)
C(6)–C(7)	1.382(9)	C(31)–C(34)	1.547(9)
C(7)–C(8)	1.369(9)	C(35)–C(36)	1.378(7)
C(8)–C(9)	1.360(9)	C(35)–C(40)	1.394(7)
C(9)–C(10)	1.376(8)	C(36)–C(37)	1.382(8)
C(11)–C(12)	1.516(7)	C(37)–C(38)	1.372(8)
C(11)–C(13)	1.535(7)	C(38)–C(39)	1.372(8)
C(11)–C(14)	1.538(7)	C(39)–C(40)	1.385(7)

Bond Angles

Si(2)–Si(1)–Si(4)	87.6(1)	Si(2)–C(11)–C(14)	107.7(3)
Si(2)–Si(1)–C(1)	115.7(1)	C(12)–C(11)–C(13)	108.1(4)
Si(2)–Si(1)–C(5)	117.4(2)	C(12)–C(11)–C(14)	108.6(4)
Si(4)–Si(1)–C(1)	118.2(1)	C(13)–C(11)–C(14)	108.5(4)
Si(4)–Si(1)–C(5)	116.1(2)	Si(2)–C(15)–C(16)	125.4(4)
C(1)–Si(1)–C(5)	102.6(2)	Si(2)–C(15)–C(20)	118.5(4)
Si(1)–Si(2)–Si(3)	87.5(1)	C(16)–C(15)–C(20)	116.0(5)
Si(1)–Si(2)–C(11)	121.9(1)	C(15)–C(16)–C(17)	122.4(5)
Si(1)–Si(2)–C(15)	111.3(2)	C(16)–C(17)–C(18)	119.2(6)
Si(3)–Si(2)–C(11)	123.8(2)	C(17)–C(18)–C(19)	119.8(6)
Si(3)–Si(2)–C(15)	108.8(2)	C(18)–C(19)–C(20)	120.1(6)
C(11)–Si(2)–C(15)	103.1(2)	C(15)–C(20)–C(19)	122.4(5)
Si(2)–Si(3)–Si(4)	87.8(1)	Si(3)–C(21)–C(22)	114.6(3)
Si(2)–Si(3)–C(21)	124.7(2)	Si(3)–C(21)–C(23)	110.5(3)
Si(2)–Si(3)–C(25)	108.3(1)	Si(3)–C(21)–C(24)	107.0(3)
Si(4)–Si(3)–C(21)	121.0(2)	C(22)–C(21)–C(23)	109.2(4)
Si(4)–Si(3)–C(25)	110.1(1)	C(22)–C(21)–C(24)	107.7(4)
C(21)–Si(3)–C(25)	104.1(2)	C(23)–C(21)–C(24)	107.5(4)
Si(1)–Si(4)–Si(3)	87.6(1)	Si(3)–C(25)–C(26)	124.8(4)
Si(1)–Si(4)–C(31)	116.1(2)	Si(3)–C(25)–C(30)	120.6(4)
Si(1)–Si(4)–C(35)	117.6(2)	C(26)–C(25)–C(30)	114.6(4)
Si(3)–Si(4)–C(31)	116.4(2)	C(25)–C(26)–C(27)	123.1(5)
Si(3)–Si(4)–C(35)	116.7(2)	C(26)–C(27)–C(28)	119.7(5)
C(31)–Si(4)–C(35)	102.9(2)	C(27)–C(28)–C(29)	120.1(5)
Si(1)–C(1)–C(2)	112.5(3)	C(28)–C(29)–C(30)	119.8(5)
Si(1)–C(1)–C(3)	109.0(3)	C(25)–C(30)–C(29)	122.6(5)
Si(1)–C(1)–C(4)	110.4(3)	Si(4)–C(31)–C(32)	113.2(4)
C(2)–C(1)–C(3)	110.7(4)	Si(4)–C(31)–C(33)	109.8(4)
C(2)–C(1)–C(4)	107.2(4)	Si(4)–C(31)–C(34)	109.9(4)
C(3)–C(1)–C(4)	106.9(4)	C(32)–C(31)–C(33)	110.5(4)
Si(1)–C(5)–C(6)	120.6(4)	C(32)–C(31)–C(34)	106.8(5)
Si(1)–C(5)–C(10)	122.9(4)	C(33)–C(31)–C(34)	106.4(5)
C(6)–C(5)–C(10)	116.3(4)	Si(4)–C(35)–C(36)	121.3(4)
C(5)–C(6)–C(7)	121.2(5)	Si(4)–C(35)–C(40)	122.5(3)
C(6)–C(7)–C(8)	120.6(6)	C(36)–C(35)–C(40)	115.6(4)
C(7)–C(8)–C(9)	119.6(6)	C(35)–C(36)–C(37)	123.0(5)
C(8)–C(9)–C(10)	119.9(5)	C(36)–C(37)–C(38)	119.8(5)
C(5)–C(10)–C(9)	122.4(5)	C(37)–C(38)–C(39)	119.3(5)
Si(2)–C(11)–C(12)	113.8(3)	C(38)–C(39)–C(40)	119.9(5)
Si(2)–C(11)–C(13)	109.9(3)	C(35)–C(40)–C(39)	122.3(4)

electronic perturbation of the Si_4 ring by polychloro substitution.

Experimental Section

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl. Benzene was distilled from lithium aluminum hydride. Hydrogen chloride was passed through sulfuric acid before use. *tert*-Butylphenyldichlorosilane, lithium wire, and ethyl acetate were used as received. Aluminum chloride (Wako Pure Chemical Industries, Ltd., extra pure grade) was sublimed before use. IR spectra were recorded on a JASCO A-102 spectrometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained with a JEOL JNM-A500 spectrometer. Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. UV spectra were obtained with a JASCO Ubest-50 spectrophotometer. Elemental analyses were performed by the Institute of Physical and Chemical Research.

Synthesis of [(*t*-Bu)PhSi]$_4$ (2). A solution of *tert*-butylphenyldichlorosilane (10.0 g, 42.9 mmol) in THF (35 mL) was added to a mixture of THF (50 mL) and finely cut lithium wire (0.83 g, 120 mmol) at −10 °C. The mixture was stirred for additional 3 h, and a large amount of hexane was added. After hydrolysis, the organic layer was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation. The residue was separated by silica gel chromatography (hexane elution) to give a mixture of 2. Each isomer of 2 was isolated by recycle-type HPLC (ODS, MeOH–THF (8:2) elution) and recrystallized from ethyl acetate. The yields of *cis-cis-trans*-2, *cis-trans-cis*-2, and *all-trans*-2 were 1.12 g (1.73 mmol, 16%), 0.102 g (0.157 mmol, 2%), and 2.26 g (3.48 mmol, 33%), respectively.

***cis-cis-trans*-2**: mp 272–276 °C. ^{1}H NMR (CD_2Cl_2): δ 0.78 (s, 9H), 1.00 (s, 9H), 1.45 (s, 18H), 6.81 (t, 4H, J = 7.7 Hz), 7.02 (t, 2H, J = 7.7 Hz), 7.33 (t, 2H, J = 7.3 Hz), 7.37–7.42 (m, 4H),

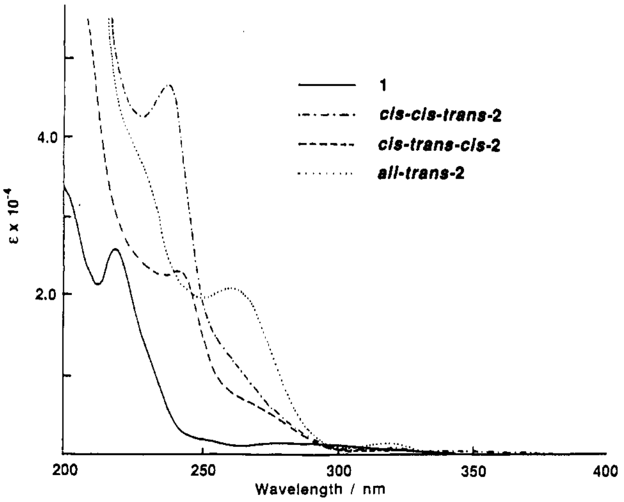

Figure 3. UV spectra of 1, *cis-cis-trans*-2, *cis-trans-cis*-2, and *all-trans*-2 in hexane.

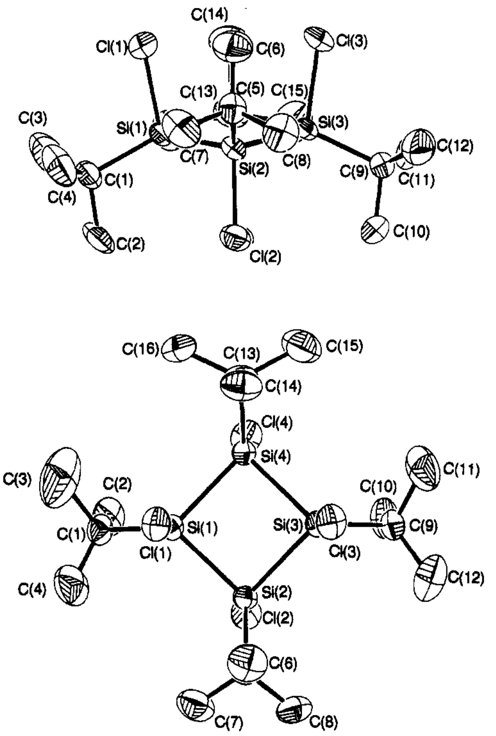

Figure 4. ORTEPII drawing of 1 viewed along the *c* axis (top) and in the direction perpendicular to the *c* axis (bottom). Thermal ellipsoids are drawn at the 30% probability level.

Table 6. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1

atom	x	y	z	B_{eq},[a] Å^2
Si(1)	0.3989(1)	0.1737(1)	0.2821(0)[b]	4.17(3)
Si(2)	0.4990(3)	0.2316(3)	0.4067(5)	4.1(1)
Si(3)	0.5670(1)	0.3324(1)	0.2800(5)	4.09(3)
Si(4)	0.5006(3)	0.2305(3)	0.1533(5)	3.97(9)
Cl(1)	0.2909(1)	0.2713(1)	0.2759(6)	6.68(5)
Cl(2)	0.5889(3)	0.1169(3)	0.4342(5)	6.3(1)
Cl(3)	0.4947(1)	0.4625(1)	0.2771(7)	6.73(5)
Cl(4)	0.5918(3)	0.1193(3)	0.1255(5)	6.6(1)
C(1)	0.3521(4)	0.0454(4)	0.2843(17)	5.9(2)
C(2)	0.4258(7)	–0.0267(4)	0.2620(15)	8.4(4)
C(3)	0.3072(16)	0.0263(15)	0.3806(17)	11.2(6)
C(4)	0.2855(20)	0.0294(17)	0.1921(26)	18.0(11)
C(5)	0.4587(11)	0.2822(13)	0.5352(11)	5.8(4)
C(6)	0.3993(16)	0.3630(18)	0.5203(18)	9.8(7)
C(7)	0.4178(14)	0.2032(15)	0.5927(13)	9.6(6)
C(8)	0.5401(15)	0.3006(14)	0.6030(13)	8.5(4)
C(9)	0.6930(4)	0.3645(4)	0.2843(16)	5.3(2)
C(10)	0.7475(5)	0.2734(5)	0.2721(24)	7.8(4)
C(11)	0.7126(13)	0.4181(20)	0.1858(20)	12.0(9)
C(12)	0.7184(12)	0.4258(15)	0.3775(19)	11.0(7)
C(13)	0.4614(13)	0.2745(12)	0.0238(11)	6.5(4)
C(14)	0.3921(16)	0.3649(18)	0.0371(15)	9.3(7)
C(15)	0.5444(18)	0.3260(15)	–0.0305(15)	11.2(6)
C(16)	0.4049(15)	0.1879(16)	–0.0303(12)	9.0(5)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{eq} = (4/3)\sum_i\sum_j B_{ij}\mathbf{a}_i\mathbf{a}_j$. [b] The z coordinate of Si(1) was fixed to define the origin.

Table 7. Bond Distances (Å) and Angles (deg) for 1

Bond Distances			
Si(1)–Si(2)	2.344(9)	C(1)–C(2)	1.503(12)
Si(1)–Si(4)	2.393(10)	C(1)–C(3)	1.448(30)
Si(1)–Cl(1)	2.091(2)	C(1)–C(4)	1.574(36)
Si(1)–C(1)	1.893(5)	C(5)–C(6)	1.431(29)
Si(2)–Si(3)	2.382(7)	C(5)–C(7)	1.452(26)
Si(2)–Cl(2)	2.095(6)	C(5)–C(8)	1.519(26)
Si(2)–C(5)	1.913(16)	C(9)–C(10)	1.498(10)
Si(3)–Si(4)	2.381(7)	C(9)–C(11)	1.511(32)
Si(3)–Cl(3)	2.084(2)	C(9)–C(12)	1.528(29)
Si(3)–C(9)	1.923(6)	C(13)–C(14)	1.621(30)
Si(4)–Cl(4)	2.072(6)	C(13)–C(15)	1.589(30)
Si(4)–C(13)	1.889(17)	C(13)–C(16)	1.617(27)
Bond Angles			
Si(2)–Si(1)–Si(4)	88.8(2)	Si(1)–C(1)–C(2)	110.0(5)
Si(2)–Si(1)–Cl(1)	107.3(3)	Si(1)–C(1)–C(3)	110.5(13)
Si(2)–Si(1)–C(1)	122.5(7)	Si(1)–C(1)–C(4)	110.4(12)
Si(4)–Si(1)–Cl(1)	104.4(3)	C(2)–C(1)–C(3)	112.7(14)
Si(4)–Si(1)–C(1)	123.0(7)	C(2)–C(1)–C(4)	102.5(15)
Cl(1)–Si(1)–C(1)	108.3(2)	C(3)–C(1)–C(4)	110.6(15)
Si(1)–Si(2)–Si(3)	88.9(3)	Si(2)–C(5)–C(6)	110.7(13)
Si(1)–Si(2)–Cl(2)	105.6(2)	Si(2)–C(5)–C(7)	108.3(12)
Si(1)–Si(2)–C(5)	122.3(5)	Si(2)–C(5)–C(8)	108.9(11)
Si(3)–Si(2)–Cl(2)	106.6(2)	C(6)–C(5)–C(7)	113.0(16)
Si(3)–Si(2)–C(5)	122.2(6)	C(6)–C(5)–C(8)	116.2(16)
Cl(2)–Si(2)–C(5)	108.8(6)	C(7)–C(5)–C(8)	98.9(14)
Si(2)–Si(3)–Si(4)	88.2(2)	Si(3)–C(9)–C(10)	109.3(4)
Si(2)–Si(3)–Cl(3)	106.9(3)	Si(3)–C(9)–C(11)	105.9(11)
Si(2)–Si(3)–C(9)	121.6(6)	Si(3)–C(9)–C(12)	113.0(11)
Si(4)–Si(3)–Cl(3)	106.1(3)	C(10)–C(9)–C(11)	102.2(17)
Si(4)–Si(3)–C(9)	123.9(6)	C(10)–C(9)–C(12)	114.3(15)
Cl(3)–Si(3)–C(9)	107.8(2)	C(11)–C(9)–C(12)	111.3(13)
Si(1)–Si(4)–Si(3)	87.9(3)	Si(4)–C(13)–C(14)	110.1(11)
Si(1)–Si(4)–Cl(4)	107.2(2)	Si(4)–C(13)–C(15)	107.6(13)
Si(1)–Si(4)–C(13)	122.7(6)	Si(4)–C(13)–C(16)	108.5(11)
Si(3)–Si(4)–Cl(4)	106.5(2)	C(14)–C(13)–C(15)	101.5(15)
Si(3)–Si(4)–C(13)	124.3(6)	C(14)–C(13)–C(16)	106.3(16)
Cl(4)–Si(4)–C(13)	106.2(6)	C(15)–C(13)–C(16)	122.3(14)

7.64 (d, 4H, J = 7.7 Hz), 7.77 (d, 2H, J = 7.3 Hz), 8.06–8.08 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 21.4, 23.5, 23.9, 30.4, 30.8, 32.3, 126.5, 127.0, 127.3, 128.1, 128.7, 129.0, 136.3, 136.4, 137.4, 139.0, 139.5, 139.8. ^{29}Si NMR (CD_2Cl_2): δ −8.8, 0.7, 8.5. IR (KBr): 1430, 1395, 1370, 1190, 1095, 1005, 810, 735, 705 cm^{-1}. Mass spectrum m/z: 648 (M$^+$, 11), 591 (26), 513 (34), 197 (65), 135 (100). UV (λ_{max} in hexane): 237 (ε 47 000), 319 nm (650). Anal. Calcd for $C_{40}H_{56}Si_4$: C, 74.00; H, 8.69. Found: C, 73.21; H, 8.67.

***cis-trans-cis*-2**: mp 270–271 °C. ^{1}H NMR (CD_2Cl_2): δ 1.01 (s, 36H), 7.24 (t, 8H, J = 7.3 Hz), 7.32 (t, 4H, J = 7.3 Hz), 7.88 (d, 8H, J = 7.3 Hz). ^{13}C NMR (CD_2Cl_2): δ 22.9, 31.3, 127.0, 128.6, 136.5, 139.7. ^{29}Si NMR (CD_2Cl_2): δ −0.8. IR (KBr): 1430, 1395, 1370, 1190, 1095, 1005, 810, 735, 705 cm^{-1}. Mass spectrum m/z: 648 (M$^+$, 12), 591 (35), 513 (53), 197 (68), 135 (100). UV (λ_{max} in hexane): 243 (ε 23 000), 318 nm (500). Anal. Calcd for $C_{40}H_{56}Si_4$: C, 74.00; H, 8.69. Found: C, 72.61; H, 8.66.

***all-trans*-2**: mp 270–273 °C. ^{1}H NMR (CD_2Cl_2): δ 1.08 (s, 36H), 7.10 (t, 8H, J = 7.3 Hz), 7.25 (t, 4H, J = 7.3 Hz), 7.91 (d, 8H, J = 7.3 Hz). ^{13}C NMR (CD_2Cl_2): δ 24.8, 31.5, 127.3, 128.5, 136.8, 139.2. ^{29}Si NMR (CD_2Cl_2): δ −2.4. IR (KBr): 1430, 1395, 1370, 1190, 1095, 1005, 810, 735, 705 cm^{-1}. Mass spectrum m/z: 648 (M$^+$, 19), 591 (42), 513 (82), 197 (76), 135 (100). UV (λ_{max} in hexane): 261 (ε 21 000), 319 nm (1500). Anal. Calcd for $C_{40}H_{56}Si_4$: C, 74.00; H, 8.69. Found: C, 72.60; H, 8.63.

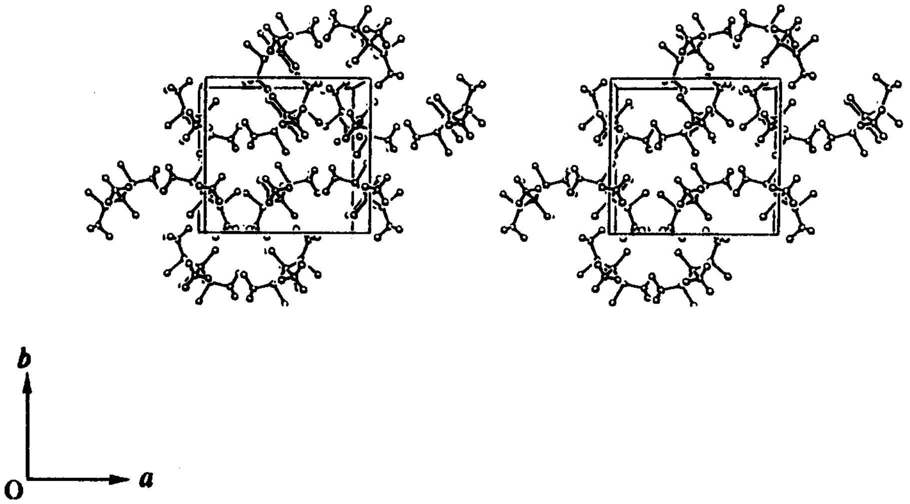

Figure 5. Stereoview of the molecular packing of 1 projected along the *c* axis.

Synthesis of *all-trans*-[(*t*-Bu)ClSi]$_4$ (1). Typical procedures are described for the case of *cis-cis-trans*-[(*t*-Bu)PhSi]$_4$ as a starting material. To a solution of *cis-cis-trans*-[(*t*-Bu)PhSi]$_4$ (0.420 g, 0.647 mmol) and aluminum chloride (0.041 g, 0.31 mmol) in benzene (5 mL) was passed hydrogen chloride for 2 h at room temperature. A small amount of acetone was added to the reaction mixture in order to deactivate aluminum chloride. After filtration of the mixture, the solvent was removed by evaporation. The residue was recrystallized from 1,2-dimethoxyethane to give *all-trans*-[(*t*-Bu)ClSi]$_4$ (0.259 g, 0.537 mmol) as colorless crystals. The yield was 83%: mp 216–217 °C. ^{1}H NMR (C_6D_6): δ 1.29 (s, 36H). ^{13}C NMR (C_6D_6): δ 26.6, 28.4. ^{29}Si NMR (C_6D_6): δ 18.8. IR (KBr): 1460, 1395, 1365, 1190, 810 cm^{-1}. Mass spectrum *m/z*: 482 (M$^+$, 61), 426 (16), 369 (20), 85 (77), 73 (100). UV (λ_{max} in hexane): 219 (ϵ 26 000), 284 nm (1000). Anal. Calcd for $C_{16}H_{36}Cl_4Si_4$: C, 39.82; H, 7.52. Found: C, 39.90; H, 7.58.

More conveniently, a stereoisomeric mixture of 2 obtained by silica gel chromatography (*vide supra*) was used as a starting material for the preparation of *all-trans*-[(*t*-Bu)ClSi]$_4$. To a solution of a mixture of 2 (2.00 g, 3.08 mmol) and aluminum chloride (0.205 g, 1.54 mmol) in benzene (20 mL) was passed hydrogen chloride for 30 min at room temperature. By a procedure similar to that above, *all-trans*-[(*t*-Bu)ClSi]$_4$ (1.097 g, 2.27 mmol) was obtained in 74% yield.

X-ray Crystallographic Analysis of *cis-cis-trans*- and *cis-trans-cis*-[(*t*-Bu)PhSi]$_4$ (2). Colorless crystals of *cis-cis-trans*- and *cis-trans-cis*-[(*t*-Bu)PhSi]$_4$ were obtained from an acetone solution by slow evaporation. A crystal specimen was sealed in a glass capillary and used for data collection on a Rigaku AFC-6 diffractometer using graphite-monochromated Mo Kα radiation. Cell parameters were refined by the least-squares method using 20 reflections with 8° < 2θ < 17° (*cis-cis-trans*-2) and 11° < 2θ < 20° (*cis-trans-cis*-2). Intensity data were collected in the range 2° < 2θ < 40° (*cis-cis-trans*-2) and 1° < 2θ < 40° (*cis-trans-cis*-2) by the ω–2θ scan technique at room temperature. Three standard reflections were measured after every 100 reflections, showing no decay. The structure was solved by direct methods using SHELXS86.[18] Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using SHELX76.[19] In the case of *cis-cis-trans*-2, 29 hydrogen atoms were located from difference Fourier and refined isotropically. The remaining hydrogen atoms were located at calculated positions and constrained to ride on the atoms to which they are bonded during refinement. In the case of *cis-trans-cis*-2, all hydrogen atoms were located from difference Fourier and refined isotropically. Atomic scattering factors were taken from ref 20. All calculations were carried out on a HITAC M-682H computer. Details of crystal data, data collection, and refinement are listed in Table 1.

X-ray Crystallographic Analysis of *all-trans*-[(*t*-Bu)ClSi]$_4$ (1). Colorless crystals of *all-trans*-[(*t*-Bu)ClSi]$_4$ were obtained by recrystallization from 1,2-dimethoxyethane. A crystal specimen was sealed in a glass capillary and used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu Kα radiation. Cell parameters were refined by the least-squares method using 25 reflections with 20° < 2θ < 30°. Intensity data were collected in the range 2° < 2θ < 130° by the ω–2θ scan technique at room temperature. Three standard reflections were measured after every 1 h, and they varied less than 3.9%. The structure was solved by direct methods using MULTAN78.[21] Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using UNICSIII.[22] Nine hydrogen atoms were located from difference Fourier, and the remaining hydrogen atoms were located at calculated positions. All hydrogen atoms were not refined. Atomic scattering factors were taken from ref 20. All calculations were carried out on a FACOM M-380 computer. Details of crystal data, data collection, and refinement are listed in Table 1.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles for 1, *cis-cis-trans*-2, and *cis-trans-cis*-2 (22 pages). Ordering information is given on any current masthead page.

OM930636H

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