

Chapter 4

Photochemical Isomerization of 1,2,5-Trisilabicyclo[3.2.0]hepta-3,6-diene to 1,4,7-Trisilabicyclo[2.2.1]hepta-2,5-diene

Summary

Upon irradiation of a benzene- d_6 solution of 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diaryl-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene [**5a**: aryl = phenyl; **b**: aryl = 3,5-bis(trimethylsilyl)phenyl], 1,4,7,7-tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-di-aryl-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (**16a,b**) was formed *via* skeletal rearrangement.

Introduction

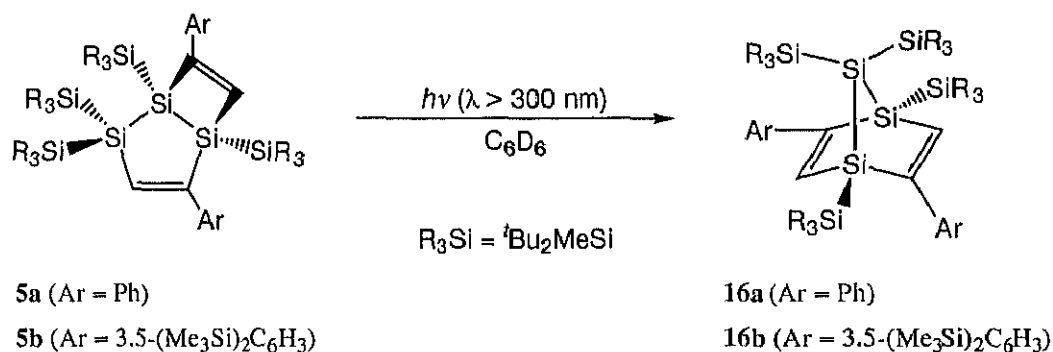
The photochemistry of organosilicon compounds is one of the most active areas for the creation of novel compounds and mechanistic studies.¹ As described in chapter 1, the author reported the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene (**3**) with phenylacetylene to give the unusual product of 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diaryl-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene (**5a**), which has disilacyclobutene and trisilacyclopentene rings fused in a bicyclic system. The reactivity of **5** promised to be quite interesting owing to its inherent ring strain and the presence of photosensitive Si-Si bonds. Thus, the author has examined the photochemical reaction of **5** and has found an entirely unexpected photochemical isomerization of **5** to the 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene derivatives **16a,b** containing several silicon atoms in the norbornadiene skeleton. This examples of 7-silabicyclo[2.2.1]hepta-2,5-diene derivatives with several silicon atoms in the skeleton are very rare, because of the synthetic difficulty associated with their preparation.² To best of my knowledge, the sole example of this type of structure is a dibenzo annulated derivative, which was reported by the reaction of the 9,10-disilaanthracene dianion with dichlorodimethylsilane.³

In this chapter, the isomerization of **5** to **16** and crystal structure of **16a** are described, along with a mechanistic discussion.

Result and Discussion

Synthesis and Structure of 1,4,7-Trisilanorbornadiene

Upon irradiation of a benzene- d_6 solution of **5a** in a sealed NMR tube with a high-pressure Hg lamp ($\lambda > 300$ nm), **5a** completely disappeared within one hour. After removal of the solvent, the reaction mixture was separated by HPLC equipped with a reversed phase column to afford 1,4,7,7-tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-diphenyl-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (**16a**) in 57% yield (Scheme 4-1). Compound **5b**⁴, which was prepared by the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene (**3**) with 3,5-bis-(trimethylsilyl)phenylacetylene, also isomerized to **16b** in 73% yield.



Scheme 4-1

The structure of **16a** was determined by mass spectrometry and by 1H , ^{13}C , and ^{29}Si NMR spectroscopy as well as X-ray crystallography. The NMR data on the structure of **16a** in benzene- d_6 indicate a highly symmetrical structure. For example, the 1H NMR spectrum showed only one set of peaks of olefinic protons at 8.03 ppm, as well as signals indicating the presence of two different tBu_2MeSi groups and one set of aromatic protons. The ^{29}Si NMR spectrum showed signals at -28.3, 15.2, 21.2, and 62.6 ppm. The high field signal ($\delta = -28.3$) can be assigned to the silicon atoms at the bridgehead position, and the low field signal ($\delta = 62.2$) is assigned to the silicon atom at the 7-position of the 1,4,7-trisilabicyclo-

[2.2.1]hepta-2,5-diene skeleton. Such a characteristic deshielding of the 7-silicon atom is typical for the 7-silabicyclo[2.2.1]hepta-2,5-diene system.⁵ The mass spectrum of **16a** showed a very weak parent ion at m/z 916, with fragmentation peaks at m/z 859 ($M^+ - ^t\text{Bu}$) and 759 ($M^+ - ^t\text{Bu}_2\text{MeSi}$). Fragmentations that are attributable to the expulsion of silylene [$(^t\text{Bu}_2\text{MeSi})_2\text{Si}:$] and formation of a 1,4-disilabenzene were not observed.

The molecular structure of **16a** has been confirmed by X-ray analysis of a single-crystal obtained by recrystallization from hexane–EtOH (Figure 4-1). The Si-Si bond lengths in the bicyclic skeleton are 2.4646(9) and 2.4811(8) Å, which are 5.6% longer than a normal Si-Si single bond (2.34 Å).

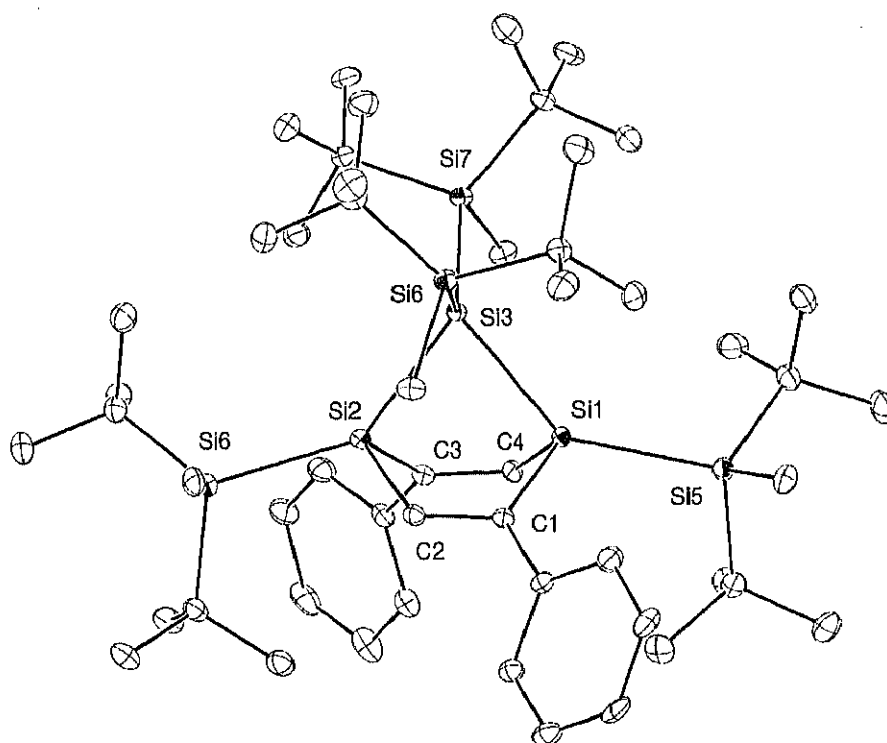
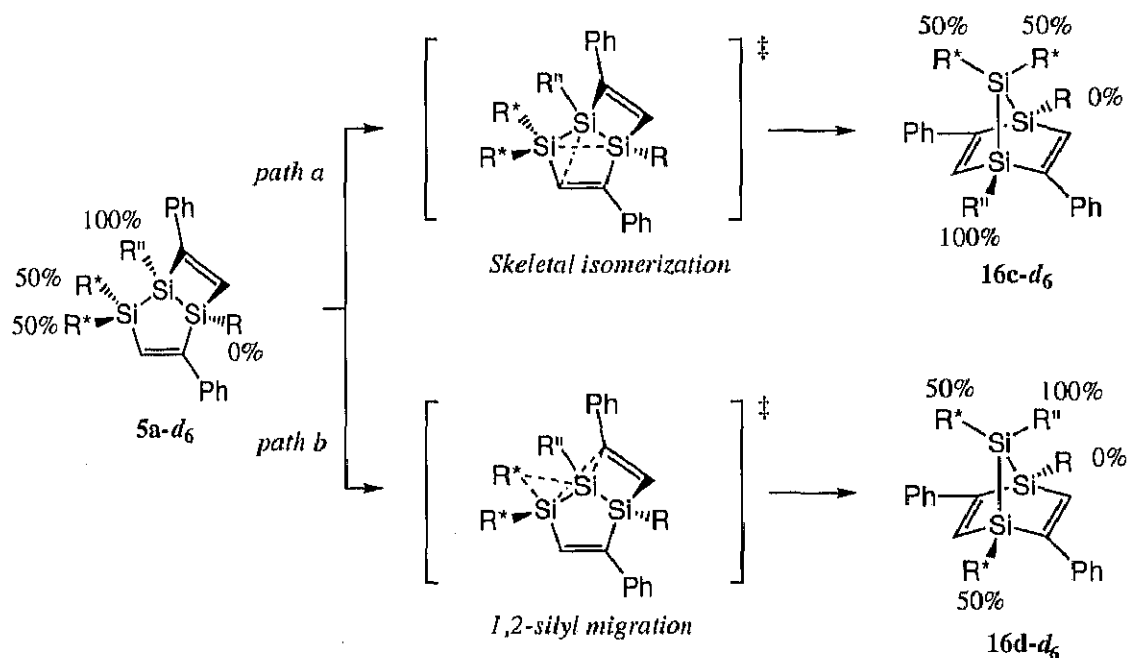


Figure 4-1. ORTEP drawing of 1,4,7-Trisilabicyclo[2.2.1]hepta-2,5-diene **16a**.

Formation Mechanism of 1,4,7-Trisilabicyclo[2.2.1]hepta-2,5-diene

The formation of **16** is quite interesting which prompts to investigate the mechanism of isomerization. First, the photolysis of **5a** in the presence of MeOH, an effective trapping reagent for unsaturated silicon compounds; however, no MeOH trapped products were detected, indicating the absence of low-coordinated silicon compounds such as the trisilaheptatriene derivative with $>\text{Si}=\text{C}<$ bonds, which can be formed by the cleavage of the bridging Si-Si bond. It is likely that the reaction proceeds *via* concerted pathway a or pathway b (Scheme 4-2): a skeletal rearrangement with the breaking of two σ -bonds (Si-C and Si-Si) and formation of two new σ -bonds (Si-C and Si-Si) (path a); or an isomerization involving 1,2-silyl migration with cleavage of a Si-C bond in the four-membered ring (path b). The photochemically induced 1,2-silyl migration is already well established.⁶



Scheme 4-2

To differentiate between these possibilities, the photoreaction of the deuterium-labeled 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivative (**5a-d₆**), which was prepared by the reaction of deuterium-labeled cyclotrisilene with phenylacetylene, has been performed. If the isomerization occurs *via* path a, relative intensities of the two signals assigned to the methyl groups on silyl substituents at the 7- and 1,4-positions in the ¹H NMR spectrum should be the same. On the other hand, in the case of isomerization via 1,2-silyl migration, path b, the ratio of the intensities of the methyl groups on the 7-position to those on the 1,4-positions would be 3 : 1. In fact, the photoreaction of **5a-d₆** under the same conditions as shown in Scheme 4-1 produced **16c-d₆**, the ratio of two signals at 0.395 and 0.404 ppm assigned to methyl groups was 1 : 1, and these intensities were half the magnitude of those of **16a**. The result of deuterium-labeled experiment indicates that the isomerization of **5** to **16** occurs *via* a skeletal isomerization, rather than through a 1,2-silyl migration.

Conclusion

1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivatives (**5a,b**), which have disilacyclobutene and trisilacyclopentene rings fused in a bicyclic manner, were photochemically isomerized to 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene derivatives (**16a,b**). The NMR data and X-ray analysis on the structure of **16a** indicate a highly symmetrical structure. The isomerization of **5** to **16** occurs *via* a skeletal isomerization, rather than through a 1,2-silyl migration.

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^1H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan). trimethylsilylacetylene⁷ and 1-bromo-3,5-bis(trimethylsilyl)-benzene⁸ were prepared according to the literature procedure.

Preparation of [3,5-bis(trimethylsilyl)phenyl](trimethylsilyl)acetylene

(Ph_3P)₂PdCl₂ (0.32 g, 0.46 mmol) and CuI (80 mg, 0.42 mmol) were added to a Et₃N solution (40 mL) of 1-bromo-3,5-bis(trimethylsilyl)benzene (9.0g, 30 mmol) and trimethylsilylacetylene (4.2 g, 42 mmol). The reaction mixture was stirred at 60 °C for 2 h. After removal of the solvent in vacuo, the residue was extracted with Et₂O (50 mL x 3) and combined organic solutions were dried with sodium sulfate and concentrated on a rotary evaporator. The solid precipitate was recrystallized from EtOH to furnish colorless crystals of [3,5-bis(trimethylsilyl)phenyl](trimethylsilyl)acetylene (4.1 g, 43%). Colorless crystals; bp 140-150 °C / 3 mmHg; MS *m/z*(%) 318 (M^+ , 22), 303 (M^+ - Me, 100), 144 (19), 73 (46); ^1H NMR (CDCl_3 , δ) 0.25 (s, 9 H), 0.26 (s, 18 H), 7.56 (t, J = 1.2 Hz, 1 H), 7.59 (d, J = 1.2 Hz, 2 H); ^{13}C NMR (CDCl_3 , δ) -1.2, 0.1, 93.8, 105.9, 121.8, 137.2, 137.8, 139.4; ^{29}Si NMR (CDCl_3 , δ) -17.6, -3.3.

Preparation of 3,5-Bis(trimethylsilyl)phenylacetylene

1 N NaOH aq. was added to a MeOH (20 mL) and Et₂O (20 mL) solution of [3,5-bis(trimethylsilyl)phenyl](trimethylsilyl)acetylene (2.5 g, 8.0 mmol). The course of the reaction is monitored by gas chromatography. Aqueous hydrochloric acid was slowly added to the reactants, and the aqueous phase was extracted with Et₂O (50 mL x 3) and combined organic solutions were dried with sodium sulfate and concentrated on a rotary evaporator. 3,5-Bis(trimethylsilyl)phenylacetylene was isolated by Kugelrohr distillation under reduced pressure as a colorless oil (1.5 g, 78%). A colorless oil; b.p. 100-120 °C / 3 mmHg; MS *m/z* (%) 246 (M⁺, 15), 235 (M⁺ - Me, 100), 108 (14), 73 (39); ¹H NMR (CDCl₃, δ) 0.26 (s, 18 H), 7.60 (t, *J* = 1.2 Hz, 1 H), 7.62 (d, *J* = 1.2 Hz, 2 H); ¹³C NMR (CDCl₃, δ) -1.3, 76.8, 84.3, 120.8, 137.2, 137.9, 139.0; ²⁹Si NMR (CDCl₃, δ) -3.5.

Preparation of 1,2,2,5-Tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-bis[3,5-bis(trimethylsilyl)phenyl]-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene (**5b**)

The red-orange crystals of **3** (50 mg, 0.070 mmol) were placed in a reaction vessel with a magnetic stirrer. Degassed 3,5-bis(trimethylsilyl)phenylacetylene (0.10 mL) and hexane (5.0 mL) were added, and the mixture was stirred for 15 h at room temperature. The solvent was removed in vacuo, the resulting residue being separated by a gel permeation chromatography to give **5b** (63 mg, 74%) as colorless crystals; mp 241 °C (dec); ¹H NMR (C₆D₆, δ) 0.10 (s, 3 H), 0.31 (s, 3 H), 0.38 (s, 18 H), 0.40 (s, 18 H), 0.50 (s, 3 H), 0.69 (s, 3 H), 0.92 (s, 9 H), 0.95 (s, 9 H), 0.97 (s, 9 H), 1.09 (s, 9 H), 1.28 (s, 9 H), 1.29 (s, 9 H), 1.34 (s, 9 H), 1.41 (s, 9 H), 7.34 (s, 1 H), 7.73 (s, 1 H), 7.79 (s, 2 H), 7.96 (s, 2 H), 8.03 (s, 1 H); ¹³C NMR (C₆D₆, δ) -3.4, -1.5, -1.3, -0.8, -0.4, -0.1, 21.7, 22.16, 22.22, 22.3, 22.4, 23.3, 23.6, 24.2, 30.2, 30.6, 31.1, 31.7, 31.8, 31.9, 32.1, 32.3,

127.9, 132.6, 135.2, 136.1, 138.0, 138.4, 143.0, 149.5, 155.2, 158.1, 164.0, 167.0; ^{29}Si NMR (C_6D_6 , δ) -54.8, -25.1, -20.3, -4.0, -3.7, 10.2, 17.9, 19.1, 19.5.

Synthesis of 1,4,7,7-Tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-diphenyl-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (16a)

A benzene- d_6 solution of **5a** (152 mg, 0.166 mmol) in a sealed NMR tube was irradiated with a high-pressure Hg lamp ($\lambda > 300$ nm) for 1 h. After removal of the solvent in vacuo, the reaction mixture was separated by HPLC equipped with a reversed phase ODS column (eluent: MeOH : $t\text{BuOMe} \approx 1 : 1$) to afford colorless crystals of **16a** (82 mg, 57%); mp 240 °C (dec.); MS (EI, 70 eV) m/z (%) 916 (M^+ , 10), 859 ($\text{M}^+ - \text{Me}$, 4.6), 759 ($\text{M}^+ - t\text{Bu}_2\text{MeSi}$, 32), 73 (100); ^1H NMR (C_6D_6 , δ) 0.395 (s, 6 H), 0.404 (s, 6 H), 0.80 (s, 18 H), 1.20 (s, 18 H), 1.26 (s, 18 H), 1.38 (s, 18 H), 7.05 (t, $J = 6.9$ Hz, 2 H), 7.22 (t, $J = 6.9$ Hz, 4 H), 7.53 (t, $J = 6.9$ Hz, 4 H), 8.03 (s, 2 H); ^{13}C NMR (C_6D_6 , δ) -2.9, 1.2, 22.3, 22.4, 22.5, 23.4, 30.6, 30.8, 31.9, 32.9, 126.8, 128.0, 128.4, 149.3, 165.5, 167.9; ^{29}Si NMR (C_6D_6 , δ) -28.3, 15.2, 21.2, 62.6; UV-Vis (hexane) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 264 (42700), 322 (6500); Anal. calc. for $\text{C}_{52}\text{H}_{96}\text{Si}_7$: C, 68.04; H, 10.54. Found: C, 68.05; H, 10.49%.

Synthesis of 1,4,7,7-1,2,2,5-Tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-bis-[3,5-bis(trimethylsilyl)phenyl]-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (16b)

A benzene- d_6 solution of **5b** (63 mg, 0.052 mmol) in a sealed NMR tube was irradiated with a high-pressure Hg lamp ($\lambda > 300$ nm) for 1 h. After removal of the solvent in vacuo, the reaction mixture was separated by HPLC equipped with a reversed phase ODS

column (eluent: MeOH : ^tBuOMe = 1 : 1) to afford colorless crystals of **16b** (46 mg, 73%); mp >300 °C; ¹H NMR (C₆D₆, δ) 0.27 (s, 6 H), 0.40 (s, 36 H), 0.49 (s, 6 H), 0.79 (s, 18 H), 1.15 (s, 18 H), 1.28 (s, 18 H), 1.45 (s, 18 H), 7.62 (s, 4 H), 7.75 (s, 2 H), 7.97 (s, 2 H); ¹³C NMR (C₆D₆, δ) -3.4, -0.8, 1.8, 21.5, 22.1, 22.2, 23.4, 30.3, 30.8, 31.6, 32.7, 133.7, 136.0, 138.8, 149.0, 167.0, 169.2; ²⁹Si NMR (C₆D₆, δ) -29.8, -3.9, 17.1, 21.5, 56.0; UV-Vis (hexane) λ_{max}/nm (ε) 265 (42200), 320 (6800).

X-ray Crystal Structure Determination of **16a**•(hexane)

A single crystal of **16a**•(hexane) for X-ray diffraction was grown from a hexane-EtOH solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 4-1a. The final atomic parameters, the bond length, and the bond angles of **16a**•(hexane) are listed in Table 4-1b and Table 4-1c, respectively.

Table 4-1a. Crystal data and structure refinement for **16a•(hexane)**

| | | |
|--------------------------------------|---|---|
| Empirical formula | $\text{C}_{58}\text{H}_{110}\text{Si}_7$ | |
| Formula weight | 1004.09 | |
| Temperature | 120 K | |
| Wavelength | 0.71070 Å | |
| Crystal system, space group | Monoclinic, $P 2_1/c$ | |
| Unit cell dimensions | $a = 13.6260(3)$ Å $b = 35.7560(12)$ Å $c = 13.7020(5)$ Å | $\alpha = 90$ deg. $\beta = 110.604(2)$ deg. $\gamma = 90$ deg. |
| Volume | $6248.8(3)$ Å ³ | |
| Z, Calculated density | 4, 1.067 Mg/m ³ | |
| Absorption coefficient | 0.186 mm ⁻¹ | |
| F(000) | 2224 | |
| Crystal size | 0.30 x 0.25 x 0.20 mm | |
| Theta range for data collection | 2.14 to 27.92 deg. | |
| Limiting indices | $0 \leq h \leq 17$, $0 \leq k \leq 47$, $-18 \leq l \leq 16$ | |
| Reflections collected / unique | 14571 / 58842 [$R(\text{int}) = 0.0660$] | |
| Completeness to theta = 27.94 | 97.3 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 14571 / 0 / 587 | |
| Goodness-of-fit on F^2 | 1.033 | |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0562$, $wR_2 = 0.1430$ | |
| R indices (all data) | $R_1 = 0.0801$, $wR_2 = 0.1591$ | |
| Extinction coefficient | 0.0118(7) | |
| Largest diff. peak and hole | 0.611 and -0.467 e.Å ⁻³ | |

Table 4-1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **16a**•(hexane). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | $U(\text{eq})$ |
|-------|----------|---------|----------|----------------|
| Si(1) | 8666(1) | 1056(1) | 1883(1) | 16(1) |
| Si(2) | 10970(1) | 1035(1) | 3242(1) | 16(1) |
| Si(3) | 9507(1) | 1341(1) | 3616(1) | 16(1) |
| Si(4) | 7061(1) | 1119(1) | 372(1) | 20(1) |
| Si(5) | 12835(1) | 873(1) | 4069(1) | 19(1) |
| Si(6) | 9025(1) | 1025(1) | 4984(1) | 19(1) |
| Si(7) | 9628(1) | 2027(1) | 3449(1) | 19(1) |
| C(1) | 9245(2) | 563(1) | 2230(2) | 18(1) |
| C(2) | 10269(2) | 570(1) | 2849(2) | 18(1) |
| C(3) | 10669(2) | 1273(1) | 1902(2) | 18(1) |
| C(4) | 9631(2) | 1275(1) | 1342(2) | 19(1) |
| C(5) | 8731(2) | 205(1) | 1775(2) | 21(1) |
| C(6) | 7812(2) | 77(1) | 1902(2) | 27(1) |
| C(7) | 7343(2) | -256(1) | 1435(2) | 34(1) |
| C(8) | 7769(2) | -464(1) | 834(2) | 35(1) |
| C(9) | 8689(2) | -344(1) | 711(2) | 34(1) |
| C(10) | 9174(2) | -15(1) | 1189(2) | 26(1) |
| C(11) | 11411(2) | 1427(1) | 1424(2) | 19(1) |
| C(12) | 12240(2) | 1665(1) | 1961(2) | 26(1) |
| C(13) | 12932(2) | 1796(1) | 1486(2) | 32(1) |
| C(14) | 12806(2) | 1693(1) | 477(2) | 32(1) |
| C(15) | 11972(2) | 1465(1) | -76(2) | 30(1) |
| C(16) | 11285(2) | 1335(1) | 394(2) | 24(1) |
| C(17) | 7141(2) | 1628(1) | 2(2) | 27(1) |
| C(18) | 5717(2) | 1066(1) | 541(2) | 27(1) |
| C(19) | 5514(2) | 679(1) | 934(2) | 32(1) |
| C(20) | 5661(2) | 1361(1) | 1335(2) | 33(1) |
| C(21) | 4818(2) | 1144(1) | -498(2) | 35(1) |
| C(22) | 7166(2) | 823(1) | -778(2) | 26(1) |
| C(23) | 8313(2) | 769(1) | -708(2) | 31(1) |
| C(24) | 6672(2) | 432(1) | -833(2) | 32(1) |
| C(25) | 6601(2) | 1025(1) | -1821(2) | 36(1) |
| C(26) | 13760(2) | 1272(1) | 4119(2) | 27(1) |
| C(27) | 13184(2) | 717(1) | 5492(2) | 25(1) |
| C(28) | 13277(2) | 1068(1) | 6169(2) | 32(1) |
| C(29) | 12324(2) | 460(1) | 5604(2) | 34(1) |
| C(30) | 14248(2) | 512(1) | 5931(2) | 36(1) |
| C(31) | 13123(2) | 490(1) | 3203(2) | 23(1) |
| C(32) | 12837(2) | 91(1) | 3432(2) | 28(1) |
| C(33) | 14308(2) | 491(1) | 3376(2) | 32(1) |
| C(34) | 12544(2) | 572(1) | 2042(2) | 30(1) |
| C(35) | 9419(2) | 514(1) | 5005(2) | 27(1) |
| C(36) | 7518(2) | 1007(1) | 4620(2) | 23(1) |
| C(37) | 7102(2) | 739(1) | 3688(2) | 29(1) |
| C(38) | 7210(2) | 847(1) | 5519(2) | 31(1) |
| C(39) | 6966(2) | 1385(1) | 4310(2) | 31(1) |
| C(40) | 9746(2) | 1209(1) | 6383(2) | 24(1) |
| C(41) | 9287(2) | 1570(1) | 6639(2) | 36(1) |
| C(42) | 10896(2) | 1279(1) | 6517(2) | 33(1) |
| C(43) | 9742(2) | 911(1) | 7201(2) | 38(1) |
| C(44) | 9628(2) | 2118(1) | 2087(2) | 25(1) |
| C(45) | 8436(2) | 2312(1) | 3502(2) | 25(1) |
| C(46) | 8226(2) | 2270(1) | 4524(2) | 33(1) |
| C(47) | 7465(2) | 2180(1) | 2587(2) | 32(1) |
| C(48) | 8574(2) | 2733(1) | 3343(3) | 36(1) |
| C(49) | 10944(2) | 2229(1) | 4382(2) | 24(1) |
| C(50) | 11805(2) | 1934(1) | 4592(2) | 29(1) |
| C(51) | 11276(2) | 2564(1) | 3852(3) | 37(1) |
| C(52) | 10913(2) | 2363(1) | 5439(2) | 33(1) |
| C(53) | 4415(4) | 2425(2) | -797(5) | 92(2) |
| C(54) | 4481(5) | 2290(2) | -1764(5) | 108(2) |
| C(55) | 3549(5) | 2008(2) | -2341(5) | 116(2) |
| C(56) | 5895(4) | 1878(1) | -3640(4) | 80(1) |
| C(57) | 5136(3) | 2173(1) | -4204(4) | 74(1) |
| C(58) | 5224(3) | 2286(1) | -5228(4) | 73(1) |

Table 4-1c. Bond lengths [Å] and angles [deg] for **16a•(hexane)**

| | | | | | |
|--------------------|------------|-------------------|------------|-------------------|------------|
| Si(1)-C(4) | 1.892(2) | Si(1)-C(1) | 1.920(2) | Si(1)-Si(4) | 2.4360(8) |
| Si(1)-Si(3) | 2.4646(8) | Si(2)-C(2) | 1.898(2) | Si(2)-C(3) | 1.933(2) |
| Si(2)-Si(5) | 2.4591(8) | Si(2)-Si(3) | 2.4811(8) | Si(3)-Si(6) | 2.4686(8) |
| Si(3)-Si(7) | 2.4741(8) | Si(4)-C(17) | 1.903(3) | Si(4)-C(18) | 1.934(2) |
| Si(4)-C(22) | 1.945(3) | Si(5)-C(26) | 1.890(2) | Si(5)-C(27) | 1.920(3) |
| Si(5)-C(31) | 1.938(2) | Si(6)-C(35) | 1.899(2) | Si(6)-C(40) | 1.936(3) |
| Si(6)-C(36) | 1.937(2) | Si(7)-C(44) | 1.894(3) | Si(7)-C(49) | 1.938(2) |
| Si(7)-C(45) | 1.938(2) | C(1)-C(2) | 1.355(3) | C(1)-C(5) | 1.487(3) |
| C(3)-C(4) | 1.351(3) | C(3)-C(11) | 1.491(3) | C(5)-C(10) | 1.403(3) |
| C(5)-C(6) | 1.400(3) | C(6)-C(7) | 1.396(3) | C(7)-C(8) | 1.381(4) |
| C(8)-C(9) | 1.389(4) | C(9)-C(10) | 1.394(3) | C(11)-C(16) | 1.401(3) |
| C(11)-C(12) | 1.399(3) | C(12)-C(13) | 1.401(3) | C(13)-C(14) | 1.382(4) |
| C(14)-C(15) | 1.388(4) | C(15)-C(16) | 1.390(3) | C(18)-C(20) | 1.538(4) |
| C(18)-C(21) | 1.542(3) | C(18)-C(19) | 1.545(4) | C(22)-C(25) | 1.543(4) |
| C(22)-C(24) | 1.542(3) | C(22)-C(23) | 1.544(3) | C(27)-C(28) | 1.540(4) |
| C(27)-C(29) | 1.539(3) | C(27)-C(30) | 1.544(3) | C(31)-C(34) | 1.535(3) |
| C(31)-C(32) | 1.542(3) | C(31)-C(33) | 1.547(3) | C(36)-C(39) | 1.532(3) |
| C(36)-C(37) | 1.537(3) | C(36)-C(38) | 1.544(3) | C(40)-C(41) | 1.529(4) |
| C(40)-C(42) | 1.532(3) | C(40)-C(43) | 1.548(3) | C(45)-C(46) | 1.532(4) |
| C(45)-C(47) | 1.542(4) | C(45)-C(48) | 1.545(3) | C(49)-C(50) | 1.529(3) |
| C(49)-C(52) | 1.540(3) | C(49)-C(51) | 1.547(3) | C(53)-C(54) | 1.442(8) |
| C(53)-C(58') | 1.512(7) | C(54)-C(55) | 1.594(8) | C(56)-C(57) | 1.488(6) |
| C(57)-C(58) | 1.504(7) | C(58)-C(53') | 1.512(7) | | |
| C(4)-Si(1)-C(1) | 101.33(9) | C(4)-Si(1)-Si(4) | 99.67(7) | C(1)-Si(1)-Si(4) | 117.57(7) |
| C(4)-Si(1)-Si(3) | 93.10(7) | C(1)-Si(1)-Si(3) | 97.49(7) | Si(4)-Si(1)-Si(3) | 138.97(3) |
| C(2)-Si(2)-C(3) | 101.49(10) | C(2)-Si(2)-Si(5) | 105.04(7) | C(3)-Si(2)-Si(5) | 112.41(7) |
| C(2)-Si(2)-Si(3) | 94.87(7) | C(3)-Si(2)-Si(3) | 94.77(7) | Si(5)-Si(2)-Si(3) | 141.62(3) |
| Si(1)-Si(3)-Si(6) | 112.56(3) | Si(1)-Si(3)-Si(7) | 110.19(3) | Si(6)-Si(3)-Si(7) | 124.67(3) |
| Si(1)-Si(3)-Si(2) | 75.73(3) | Si(6)-Si(3)-Si(2) | 113.67(3) | Si(7)-Si(3)-Si(2) | 109.56(3) |
| C(17)-Si(4)-C(18) | 105.75(11) | C(17)-Si(4)-C(22) | 106.05(12) | C(18)-Si(4)-C(22) | 112.69(11) |
| C(17)-Si(4)-Si(1) | 101.36(8) | C(18)-Si(4)-Si(1) | 119.60(9) | C(22)-Si(4)-Si(1) | 109.79(8) |
| C(26)-Si(5)-C(27) | 104.97(12) | C(26)-Si(5)-C(31) | 106.16(11) | C(27)-Si(5)-C(31) | 112.68(11) |
| C(26)-Si(5)-Si(2) | 114.01(8) | C(27)-Si(5)-Si(2) | 112.52(7) | C(31)-Si(5)-Si(2) | 106.45(7) |
| C(35)-Si(6)-C(40) | 105.67(11) | C(35)-Si(6)-C(36) | 103.94(10) | C(40)-Si(6)-C(36) | 112.86(10) |
| C(35)-Si(6)-Si(3) | 107.64(8) | C(40)-Si(6)-Si(3) | 114.70(8) | C(36)-Si(6)-Si(3) | 111.15(8) |
| C(44)-Si(7)-C(49) | 105.39(11) | C(44)-Si(7)-C(45) | 103.74(11) | C(49)-Si(7)-C(45) | 111.87(10) |
| C(44)-Si(7)-Si(3) | 106.48(8) | C(49)-Si(7)-Si(3) | 112.63(8) | C(45)-Si(7)-Si(3) | 115.62(8) |
| C(2)-C(1)-C(5) | 120.45(19) | C(2)-C(1)-Si(1) | 112.43(15) | C(5)-C(1)-Si(1) | 126.49(16) |
| C(1)-C(2)-Si(2) | 119.86(16) | C(4)-C(3)-C(11) | 119.0(2) | C(4)-C(3)-Si(2) | 111.86(16) |
| C(11)-C(3)-Si(2) | 129.05(16) | C(3)-C(4)-Si(1) | 120.49(17) | C(10)-C(5)-C(6) | 118.1(2) |
| C(10)-C(5)-C(1) | 119.3(2) | C(6)-C(5)-C(1) | 122.5(2) | C(7)-C(6)-C(5) | 120.4(2) |
| C(8)-C(7)-C(6) | 120.8(2) | C(7)-C(8)-C(9) | 119.6(2) | C(8)-C(9)-C(10) | 120.1(3) |
| C(9)-C(10)-C(5) | 120.9(2) | C(16)-C(11)-C(12) | 117.7(2) | C(16)-C(11)-C(3) | 119.6(2) |
| C(12)-C(11)-C(3) | 122.7(2) | C(11)-C(12)-C(13) | 120.6(2) | C(14)-C(13)-C(12) | 120.7(2) |
| C(13)-C(14)-C(15) | 119.5(2) | C(16)-C(15)-C(14) | 120.0(3) | C(15)-C(16)-C(11) | 121.6(2) |
| C(20)-C(18)-C(21) | 107.9(2) | C(20)-C(18)-C(19) | 108.0(2) | C(21)-C(18)-C(19) | 107.7(2) |
| C(20)-C(18)-Si(4) | 107.54(16) | C(21)-C(18)-Si(4) | 110.46(18) | C(19)-C(18)-Si(4) | 115.04(17) |
| C(25)-C(22)-C(24) | 108.1(2) | C(25)-C(22)-C(23) | 106.2(2) | C(24)-C(22)-C(23) | 107.8(2) |
| C(25)-C(22)-Si(4) | 110.02(18) | C(24)-C(22)-Si(4) | 112.16(17) | C(23)-C(22)-Si(4) | 112.28(17) |
| C(28)-C(27)-C(29) | 109.3(2) | C(28)-C(27)-C(30) | 106.5(2) | C(29)-C(27)-C(30) | 108.8(2) |
| C(28)-C(27)-Si(5) | 108.30(18) | C(29)-C(27)-Si(5) | 110.43(17) | C(30)-C(27)-Si(5) | 113.39(18) |
| C(34)-C(31)-C(32) | 108.3(2) | C(34)-C(31)-C(33) | 106.6(2) | C(32)-C(31)-C(33) | 107.20(19) |
| C(34)-C(31)-Si(5) | 111.04(15) | C(32)-C(31)-Si(5) | 114.12(17) | C(33)-C(31)-Si(5) | 109.26(17) |
| C(39)-C(36)-C(37) | 108.6(2) | C(39)-C(36)-C(38) | 107.6(2) | C(37)-C(36)-C(38) | 107.9(2) |
| C(39)-C(36)-Si(6) | 114.57(16) | C(37)-C(36)-Si(6) | 106.37(15) | C(38)-C(36)-Si(6) | 111.59(17) |
| C(41)-C(40)-C(42) | 108.6(2) | C(41)-C(40)-C(43) | 108.0(2) | C(42)-C(40)-C(43) | 106.8(2) |
| C(41)-C(40)-Si(6) | 114.17(17) | C(42)-C(40)-Si(6) | 108.39(17) | C(43)-C(40)-Si(6) | 110.67(18) |
| C(46)-C(45)-C(47) | 109.3(2) | C(46)-C(45)-C(48) | 107.1(2) | C(47)-C(45)-C(48) | 107.2(2) |
| C(46)-C(45)-Si(7) | 114.30(18) | C(47)-C(45)-Si(7) | 107.49(17) | C(48)-C(45)-Si(7) | 111.25(17) |
| C(50)-C(49)-C(52) | 108.1(2) | C(50)-C(49)-C(51) | 106.9(2) | C(52)-C(49)-C(51) | 108.1(2) |
| C(50)-C(49)-Si(7) | 109.69(15) | C(52)-C(49)-Si(7) | 114.26(16) | C(51)-C(49)-Si(7) | 109.51(19) |
| C(54)-C(53)-C(58') | 115.7(5) | C(53)-C(54)-C(55) | 111.8(6) | C(56)-C(57)-C(58) | 113.9(4) |
| C(57)-C(58)-C(53') | 112.5(4) | | | | |

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z+1/2 #2 x,-y+1/2,z-1/2

Reference and Notes

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