A NEW EXAMPLE OF LINEAR DISILOXANE: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF BIS(2-SILOLYL)-TETRAMETHYLDISILOXANE^{*}

Shigehiro Yamaguchi, Ren-Zhi Jin, Motoo Shiro, and Kohei Tamao

Bis(2-silolyl)tetramethyldisiloxane has been obtained by an attempted Wurtz-type coupling of (2-silolyl)dimethylsilyl chloride using sodium metal, and its linear Si—O—Si geometry has been demonstrated by X-ray crystallography.

Organodisiloxanes having Si—O—Si linkage have long been investigated intensively because of their anomalous geometries at oxygen [1]. A striking feature is the rather flexible and wide Si—O—Si angles in disiloxanes, which vary in the range of 140-180°. Indeed, several examples of linear disiloxanes with a Si—O—Si angle of 180° have already been reported. In general, the Si—O—Si angle strongly depends on the substituents on silicon. Incorporation of electron-accepting groups, such as aryl groups, tends to widen the Si—O—Si angle [1-4]. Illustrative observations are the 180° Si—O—Si angle in Ph₃SiOSiPh₃ [5] versus 159° in Ph₃SiOSiPh₂Me [6].

We now present a new example of linear disiloxane, bis(2-silolyl)tetramethyldisiloxane I. In the course of our continuing research on the silole-containing new π -conjugated systems [7], we have fortuitously obtained the disiloxane I. X-ray crystal structural analysis has demonstrated its completely linear Si—O—Si linkage. Considering the substituents, two methyl groups and only one unsaturated C_{sp}2 group on each silicon atom, the occurrence of the linear geometry at oxygen seems to be unusual. Its synthesis and crystal structure are described herein.



*Dedicated to Professor E. Lukevics on the occasion of his 60th birthday.

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan. Rigaku Corporation, Akishima, Tokyo 196, Japan. Published in Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 180-185, February, 1997. Original article submitted November 21, 1996.

We attempted to prepare 1,2-bis(2-silolyl)disilane II by Wurtz-type coupling of chlorosilane III as a model compound for poly[(silole-2,5-diyl)disilanylene] IV. However, unexpectedly, disiloxane I was obtained as the major product, as shown in Scheme 1. The precursor III was prepared from readily available 2,5-dibromosilole V [8] as follows. Thus, as shown in Scheme 1, selective monolithiation of V using BuLi in ether formed 2-bromo-5-lithiosilole VI, which was subsequently treated with trimethylsilyl triflate to form 2-bromo-5-(trimethylsilyl) silole VII. After removal of the excess silyl triflate *in vacuo*, compound VII was further treated with BuLi in ether and then dimethylchlorosilane to afford unsymmetrically disilylated silole VIII. These procedures from V to VIII were carried out in one pot and the yield of VIII was 65% based on V. Palladium dichloride-catalyzed chlorination of VIII in refluxing CCl_4 [9] gave 2-(chlorosilyl)-5-(trimethylsilyl)silole III in 92% yield. Wurtz-type coupling of III using sodium in decane at 130°C for 15 h, followed by hydrolysis and recrystallization, afforded the disiloxane I in 55% yield. The mechanism of the formation of the Si-O-Si linkage is unclear at this stage.





The X-ray crystal structure of I is shown in Fig 1. The atomic coordinates, the B_{iso}/B_{eq} parameters, and the important bond lengths and angles are summarized in Tables 1 and 2, respectively. The structure has been crystallographically imposed on C_i symmetry with the center of symmetry at the O atom of the linear Si-O-Si skeleton having 180° angle. The Si-O bond length 1.5887(9) is rather short compared with those in the compounds Ph₃SiOSiPh₃ 1.616(1) [5] and Ph₃SiOSiPh₂Me 1.622(9) [6]. The two silole planes are arranged in parallel. The dihedral angle between the mean plane of silole and the mean plane consisting of O_1 -Si₁--C₃ is 91.6°. There is no significant abnormal features around the silicon atoms bonded to oxygen and in the silole part.

The short Si–O distance apparently implies the present linear Si–O–Si geometry is not ascribed to the steric congestion between the bulky silole moieties but to some electronic reasons. Several rationalizations for the wide Si–O–Si angle have been reported so far [10, 11]. According to the recent straightforward explanation by Schreiber and his coworkers [11], some $n-\pi^*$ mixing of the lone-pair orbitals on the oxygen with π^* group orbitals of silicon moieties crucially favors the wide Si–O–Si angle. In the present case, introduction of the highly electron-accepting silole ring [12, 13] into the silicon in disiloxane may cause a decrease in the level of the π^* group orbital of the silicon moiety to realize the efficient $n-\pi^*$ interaction, leading to the linear geometries at oxygen as well as the short Si–O distance.

Atom	x	у	2	Beq
Sim	0.87300(8)	0.04153(5)	0 57283(5)	4 37(2)
Sico	0.92135(7)	0,04133(3)	0,52205(5)	3,51(2)
Si(2)	0,92133(7)	0,11377(4)	0,71910(3)	3,31(2)
SI(3)	1,0000	0,11272(4)	0,92034(0)	5,65(2)
0(1) C(1)	0.7301/6)	0,000	0,5000	7,9(1)
C(1)	0,7391(3)	-0,0004(3)	0,4030(3)	8,8(1)
C(2)	0,8881(6)	0,1366(2)	0,4807(3)	9,5(1)
C ₍₃₎	0,8590(3)	0,0433(1)	0,6422(2)	3,66(6)
C(4)	0,7964(2)	-0,0053(1)	0,6906(2)	3,50(6)
C ₍₅₎	0,7919(2)	0,0109(1)	0,7863(2)	3,27(5)
C(6)	0,8521 (2)	0,0712(1)	0,8158(2)	3,44(6)
C(7)	1,0987(3)	0,1175(1)	0,7267(2)	4,01(6)
C(8)	1,1699(3)	0,1634(2)	0,6776(3)	6,7(1)
C(9)	1,3012(4)	0,1632(3)	0,6846(4)	8,6(1)
C(10)	1,3626(3)	0,1194(2)	0,7422(3)	7,4(1)
C(11)	1,2953(3)	0,0741 (3)	0,7915(3)	7,4(1)
C(12)	1,1651(3)	0,0728(2)	0,7836(2)	5,45(8)
C(13)	0,8491 (3)	0,2058(2)	0,7039(2)	4,13(6)
C(14)	0,7210(3)	0,2113(2)	0,6808(2)	5,61 (8)
C(15)	0,6584(4)	0,2767(3)	0,6831 (3)	7,6(1)
C(16)	0,7242(5)	0,3383(2)	0,7066(3)	7,6(1)
C(17)	0,8499(4)	0,3356(2)	0,7279(3)	6,5(1)
C(18)	0,9115(3)	0,2697(2)	0,7265(2)	5,28(8)
C(19)	0,7295(3)	-0,0717(2)	0,6587(2)	3,90(6)
C(20)	0,7946(3)	-0,1327(2)	0,6383(3)	6,27(9)
C ₍₂₁₎	0,7313(5)	-0,1950(2)	0,6125(4)	9,1(1)
C(22)	0,6035(5)	-0,1961(3)	0,6066(3)	8,9(1)
C(23)	0,5375(4)	-0,1375(3)	0,6267(3)	7,7(1)
C(24)	0,5994(3)	-0,0743(2)	0,6534(3)	5,98(9)
C(25)	0,7229(2)	-0,0405(1)	0,8417(2)	3,44(6)
C(26)	0,7766(3)	-0,1054(2)	0,8678(2)	4,29(7)
C(27)	0,7153(3)	-0,1515(2)	0,9220(2)	5,24(8)
C(28)	0,5984(3)	-0,1340(2)	0,9494(2)	5,69(8)
C(29)	0,5425(3)	-0,0707(2)	0,9241(2)	6,04(9)
C(30)	0,6047(3)	-0,0237(2)	0,8705(2)	4,77(7)
C(31)	0,8378(3)	0,0471 (2)	1,0154(2)	5,23(8)
C(32)	0,7051 (3)	0,1733(2)	0,9249(2)	5,55(8)
C(33)	0,9897(3)	0,1694(2)	0.9458(2)	5,46(8)

TABLE 1. Atomic Coordinates and Biso/Beg for I

EXPERIMENTAL

General. Melting point (mp) determinations were performed by using a Yanaco MP-S3 instrument and are uncorrected. ¹H, ¹³C, and ²⁹Si NMR spectra were measured with a JEOL EX-270 (270 MHz for ¹H, 67.8 MHz for ¹³C, and 53.5 MHz for ²⁹Si) spectrometer in CDCl₃. Chemical shifts are reported in δ ppm with reference relative to residual protio-solvent (i.e., CHCl₃) peak for ¹H, to CDCl₃ for ¹³C, and to TMS for ²⁹Si.

Materials. All the solvents were freshly distilled before use from the appropriate desiccants. 2,5-Dibromo-1,1,3,4-tetraphenylsilole V was prepared from bis(phenylethynyl)diphenylsilane according to the procedure described in [8].

All reactions were carried out under nitrogen unless otherwise stated.

5-Dimethylsilyl-2-trimethylsilyl-1,1,3,4-tetraphenylsilole (VIII). To a solution of 2,5-dibromosilole V (1.63 g, 3.00 mmol) was added a hexane solution of BuLi (1.63 M, 2.0 mL, 3.3 mmol) at -78°C. Stirring at the same temperature for 20

	T		·				
Bond length [A]							
S i1-O1	1,5887(9)	Si1-Ci	1,836(5)				
Si1-C2	1,851(4)	Si1-C3	1,870(3)				
Si2-C3	1,868(3)	Si2-C6	1,872(3)				
C3C4	1,361(4)	C4—C5	1,522(4)				
C5C6	1,354(4)	Si3—C6	1,871(3)				
Bond angle (*)							
Si1-O1-Si1	180,0	O_1 — Si_1 — C_1	108,9(2)				
01-Si1-C2	108,2(2)	O1-Si1-C3	109,63(9)				
Si2-C3-C4	105,8(2)	C3-Si2-C6	94,8(1)				
C4-C5-C6	117,4(2)	C3-C4-C5	116,5(2)				
Si2-C6-C5	105,4(2)	C7-Si2-Cl3	112,0(1)				

TABLE 2. Selected Bond Lengths and Angles for I

Fig. 1. ORTEP drawings of I, 30% thermal probability: a) a perspective view with atomlabeling scheme, and b) a side view, 3,4-phenyl rings on silole rings are omitted for clarity.

min followed by warming up to 0°C over 30 min afforded a light yellow suspension. Trimethylsilyl triflate (1.00 g, 4.50 mmol) was added to the mixture at -78°C. After stirring for 20 min at the same temperature, the mixture was stirred at 0°C for another 1 h. The excess silyl triflate and the solvents were removed *in vacuo*. The residue was dissolved in 40 mL of ether. A hexane solution of BuLi (1.63 M, 3.7 mL, 6.0 mmol) was added to the mixture at -78°C followed by stirring at 0°C for 20 min. Dimethylchlorosilane (0.85 g, 9.00 mmol) was added dropwise to the resulting red color solution at -78°C. The mixture was gradually warmed up to room temperature. After addition of water, the mixture was extracted with ether. The

combined extract was washed with brine, dried over anhydrous Na₂SO₄, and filtered. The filtrate was condensed under reduced pressure to afford a pale yellow solid. Recrystallization from hexane gave 1.01 g (1.95 mmol) of pure title compound in 65% yield as light yellow crystals: mp 152-154°C. ¹H NMR, δ : -0.36 (s, 9H), -0.35 (d, J = 3.8 Hz, 6H); 3.92 (sep, J = 3.8 Hz, 1H); 6.91-6.96 (m, 4H); 7.05-7.07 (m, 6H); 7.39-7.46 (m, 6H); 7.76-7.79 (m, 4H). ¹³C NMR, δ : -2.82, 0.83, 126.36, 127.08, 127.96, 128.52, 128.77, 129.83, 132.45, 135.72, 141.06, 141.98, 142.46, 143.97, 171.75, 172.34. ²⁹Si NMR, δ : -25.85, -8.84, 8.57.

Anal. Calcd. for C₃₃H₃₆Si₃: C 76.68; H 7.02. Found: C 76.82; H 7.12.

2-Chlorodimethylsilyl-5-trimethylsilyl-1,1,3,4-tetraphenylsilole (III). A mixture of VIII (0.80 g, 1.55 mmol) and PdCl₂ (30.2 mg, 0.17 mmol) in CCl₄ (15 mL) was refluxed for 2 h. To the resulting suspension was added a small amount of active carbon and the mixture was refluxed for an additional 10 min. After cooling to room temperature, the mixture was filtered. The filtrate was condensed under reduced pressure. The residue was washed with dry hexane (5 mL \times 3) to afford a spectroscopically pure title compound (0.79 g, 1.43 mmol) in 92% yield as a white powder: mp 200-202°C. ¹H NMR, δ : -0.39 (s, 9H); -0.12 (s, 6H); 6.92-16.97 (m, 4H); 7.06-7.09 (m, 6H); 7.42-7.48 (m, 6H); 7.82-7.85 (m, 4H). ¹³C NMR, δ : 0.67, 4.01, 126.47, 126.83, 127.13, 127.24, 127.98, 128.46, 128.77, 129.97, 291.73, 135.63, 135.72, 135.81, 140.05, 141.51, 141.96, 146.09, 170.92, 173.60. ²⁹Si NMR, δ : -8.49, 9.09, 17.11.

Anal. Calcd. for C₃₃H₃₅ClSi₃: C 71.89; H 6.40. Found: C 72.09; H 6.47.

1,3-Bis(5-trimethylsilyl-1,1,3,4-tetraphenyl-2-silolyl)-1,1,3,3-tetramethyldisiloxane (I). A mixture of III (0.44 g, 0.80 mmol) and sodium (36 mg, 1.56 mmol) in 6 mL of decane was stirred at 130°C for 15 h. The mixture was poured into methanol to afford a light yellow precipitate, which was dissolved in CH_2Cl_2 . The solution was washed with water and dried over anhydrous Na₂SO₄. After filtration and evaporation, the mixture was recrystallized from hexane and chloroform to give the title compound (0.23 g, 0.22 mmol) in 55% yield as colorless crystals: mp 229-231°C. ¹H NMR, δ : -0.71 (s, 12H); -0.43 (s, 18H); 6.67-7.06 (m, 20H); 7.32-7.41 (m, 12H); 7.74-7.71 (m, 8H). ¹³C NMR, δ : 0.79, 2.43, 126.04, 126.16, 126.81, 126.92, 127.91, 128.80, 128.90, 129.63, 132.60, 135.78, 142.10, 142.60, 142.75, 144.29, 171.46, 172.33. ²⁹Si NMR, δ : -8.94, -6.29, 8.87.

Anal. Calcd. for C₆₆H₇₀OSi₆: C 75.66; H 6.73. Found: C 75.47; H 6.77.

X-ray Crystal Structure Analysis of I. A single crystal of I suitable for X-ray structural determination was obtained by recrystallization from THF. Crystal data are as follows: $C_{66}H_{70}OSi_6$, FW = 1047.79, crystal size $0.40 \times 0.20 \times 0.15$ mm, monoclinic, space group P2₁/c (No. 14), a = 10.560(4) Å, b = 18.474(4) Å, c = 15.555(3) Å, $\beta = 92.34(2)^\circ$, V = 3032(1)Å³, Z = 2, $D_c = 1.148$ g cm⁻³, μ (Cu K α) = 15.90 cm⁻¹. Intensity data were measured at 23°C on a Rigaku AFC7R diffractometer with graphite monochromated Cu K α radiation ($\lambda = 1.54178$ Å) using the ω -28 scan technique to $2\theta_{max} = 110.2^\circ$, and 4151 unique reflections were collected. The structure was solved by the direct method (SIR92) and refined anisotropically by full-matrix least squares to R = 0.040, $R_W = 0.065$, and S = 1.40. Hydrogen atoms were included but not refined.

ACKNOWLEDGMENT

This work was supported by Grants-in-Aid (No. 07555280) from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

- W. S. Sheldrick, in: The Chemistry of Organic Silicon Compounds, S. Patai and Z. Rappoport (eds.), Wiley, New York (1989), Vol. 1, Chapter 3.
- 2. E. Lukevics, O. Pudova, and R. Sturkovich, Molecular Structure of Organosilicon Compounds, Ellis Horwood, Chichester (1989), p. 175.
- 3. W. Wojnowski, B. Becker, K. Peters, E. M. Peters, and H. G. Schnering, Z. Anorg. Allg. Chem., 563 (1988).
- 4. E. Lukevics, S. Belyakov, L. Ignatovich, and N. Shilina, Bull. Soc. Chim. Fr., 132, 545 (1995).
- 5. C. Glidewell and D. C. Liles, Acta Crystallogr., B34, 124 (1978).

- 6. M. G. Voronkov, D. Yu. Nesterov, A. I. Gusev, N. V. Alexeev, and M. B. Lotarev, Dokl. Akad. Nauk SSSR, 257, 1377 (1981).
- 7. K. Tamao and S. Yamaguchi, Pure Appl. Chem., 68, 139 (1996).
- 8. K. Tamao, S. Yamaguchi, and M. Shiro, J. Am. Chem. Soc., 116, 11715 (1994).
- 9. Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori, and M. Hayashi, J. Organomet. Chem., 9, 21 (1967).
- 10. W. Ries, T. Albright, J. Silvestre, I. Bernal, W. Malisch, and C. Burschka, Inorg. Chim. Acta, 111, 119 (1986).
- 11. S. Shambayati, J. F. Blake, S. G. Wierschke, W. L. Jorgensen, and S. L. Schreiber, J. Am. Chem. Soc., 112, 697 (1992), and references cited therein.
- 12. S. Yamaguchi and K. Tamao, Bull. Chem. Soc. Jpn., 69, 2327 (1996).
- 13. K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, and S. Yamaguchi, J. Am. Chem. Soc., in press.