Structure and Unusual Electronic Spectra of Decaisopropyl-7-oxabicyclo[2.2.1]heptasilane

Soichiro Kyushin, Haruaki Sakurai, Hiroyuki Yamaguchi, Midori Goto,† and Hideyuki Matsumoto*
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376
†*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305*

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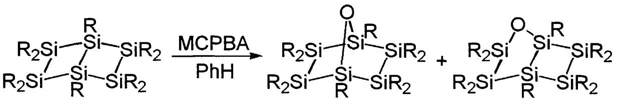
Decaisopropyl-7-oxabicyclo[2.2.1]heptasilane was synthesized by oxidation of decaisopropylbicyclo[2.2.0]hexasilane with *m*-chloroperbenzoic acid, and its structure was determined by X-ray crystallography. The compound shows unusual properties in the UV spectrum due to the interaction of the *n* orbital of the oxygen atom and the Si–Si σ bonds. The compound also shows far stronger fluorescence than the bicyclic ladder polysilane.

Since decaisopropylbicyclo[2.2.0]hexasilane was synthesized for the first time in 1987,[1] the structure, properties, and reactions of this bicyclic ladder polysilane have been studied by our group.[2] The unique properties of this compound arise from the highly strained polysilane skeleton. The introduction of a heteroatom such as oxygen to the ladder polysilane skeleton seems interesting because the heteroatom is expected to perturb the electronic properties of the Si–Si σ-conjugation system. We report herein the synthesis and structure of a novel 7-oxabicyclo[2.2.1]heptasilane system[3] and report its unusual electronic properties.

The oxidation of decaisopropylbicyclo[2.2.0]hexasilane (**1**) with a slightly deficient amount (0.7 equiv.) of *m*-chloroperbenzoic acid (MCPBA) gave decaisopropyl-7-oxabicyclo[2.2.1]heptasilane (**2**) in 32% yield and decaisopropyl-2-oxabicyclo[3.2.0]heptasilane (**3**) in 18% yield as monooxidation products.[4,5,6] The oxidation product which contains an oxygen atom in the terminal Si–Si rung was not formed under these conditions. The isomers **2** and **3** could be easily separated by recycle-type HPLC.



1 **2** (32%) **3** (18%)
R = *i*-Pr

The structure of **2** was confirmed by X-ray crystallography (Figure 1).[7,8] The oxygen atom connects two bridgehead silicon atoms with a Si–O bond length of 1.683(4) Å and a Si–O–Si bond angle of 120.2(4)°. The Si–O bond length is somewhat longer than those of other disiloxanes ($[(i\text{-Pr})_2\text{Si}]_4\text{O}$: 1.638 and 1.654 Å ,[9] $\text{Me}_3\text{SiOSiMe}_3$: 1.626(2) Å , [10] and $\text{Ph}_3\text{SiOSiPh}_3$: 1.616(1) Å[11]). The Si–O–Si bond angle is considerably smaller compared with other disiloxanes ($[(i\text{-Pr})_2\text{Si}]_4\text{O}$: 133.6°,[9] Me_3Si-OSiMe_3: 148.8(1)°,[10] and $\text{Ph}_3\text{SiOSiPh}_3$: 180°[11]). It is noted that the distance between two bridgehead silicon atoms (2.920 Å) is within the sum of the van der Waals radius[12] and the hard-sphere radius[13] of a silicon atom. The Si–Si bond lengths of **2** (average 2.402 Å) are almost the same as those of **1** (average 2.400 Å).[2a]

In the UV spectrum of **2**, new absorption bands appear at *ca.* 270–340 nm (Figure 2). The absorption maximum of the longest wavelength (313 nm) exists almost in the same position as that of **1** (310 nm), and the extinction coefficient (ε 5100) is fairly large. These results are quite remarkable in light of prior reports that insertion of an oxygen atom to catenated silicon atoms interrupts σ conjugation and results in the hypsochromic shift in the absorption spectrum.[14] On the other hand, the UV spectrum of **3** does not show such unique absorption and resembles that of **1**, especially in the region of 290–350 nm, indicating that the absorption spectra strongly depend on the position of the oxygen atom in the Si_6O framework. Therefore, the unique absorption bands of **2** seem to be due to the stereoelectronic effect of the oxygen atom at the 7-position.[15] In order to explain such an effect, we carried out the *ab initio* calculation (STO-3G) of the molecular orbitals of **2**.[16] As previously reported, the lobes of the HOMO of **1** are preferentially localized in the central Si–Si bond.[2c] In contrast, the lobes of the HOMO and the next HOMO of **2** are delocalized in both the lone pair of the oxygen atom and the pe-

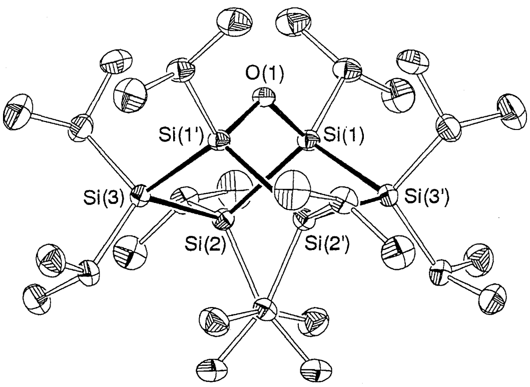


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.409(3), Si(1)–Si(3') 2.388(3), Si(1)–O(1) 1.683(4), Si(2)–Si(3) 2.408(3); Si(2)–Si(1)–Si(3') 111.8(1), Si(2)–Si(1)–O(1) 102.0(2), Si(3')–Si(1)–O(1) 97.3(1), Si(1)–Si(2)–Si(3) 95.2(1), Si(2)–Si(3)–Si(1') 95.2(1), Si(1)–O(1)–Si(1') 120.2(4).

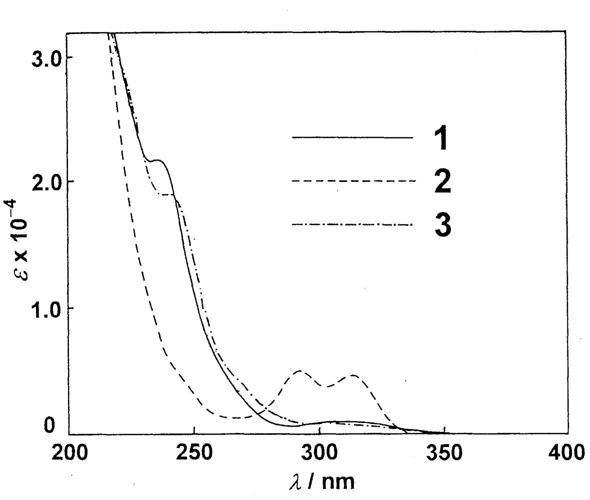


Figure 2. UV spectra of **1**–**3** in hexane at room temperature.

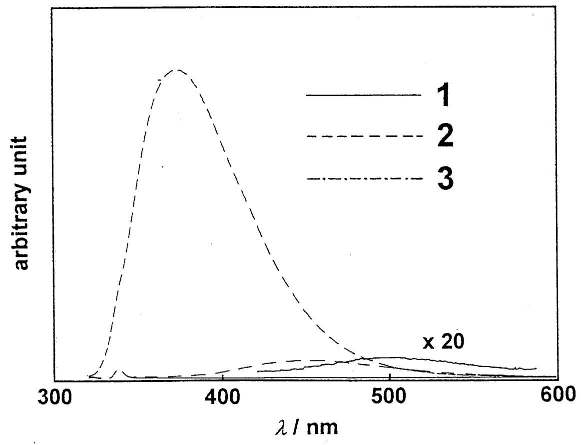


Figure 3. Fluorescence spectra of **1**–**3** in hexane at room temperature. The excitation wavelength is 310 nm.

ripheral Si–Si σ bonds. Especially in the HOMO, the n orbital of the oxygen atom is perpendicularly oriented to the Si(1)–O(1)–Si(1') plane. The result shows that the n orbital of the oxygen atom interacts with the Si–Si σ orbitals, and the novel σ–n conjugation may be the origin of the new absorption bands of **2**.

As a final note, **2** shows relatively strong fluorescence in the region of 330–550 nm (λ_{max} = 373 nm) as shown in Figure 3. The fluorescence quantum yield of **2** (Φ_f = 0.014) is far larger than that of **1**,[2b] while **3** shows relatively weak fluorescence (Φ_f = 1.0×10^{-3}). The strong fluorescence of **2** corresponds to the relatively large extinction coefficient in the UV spectrum. It is also noted that the Stokes shift in the fluorescence of **2** (5100 cm^{-1}) is not as large as that of **1** (12400 cm^{-1}). The difference in the Stokes shifts is explained by the following consideration. The norbornane skeleton of **2** seems rigid, and the structural change by excitation may be relatively small. In the case of **1**, the central Si–Si bond is considerably weakened by the one-electron excitation because the lobes of the HOMO of **1** are localized in the central Si–Si bond as already mentioned. Since the central Si–Si bond is the most strained bond in **1**, the excited singlet state of **1** is postulated to be significantly changed.

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4 A benzene solution (15 ml) of **1** (200 mg, 0.33 mmol) and MCPBA (60 mg, assay 70%) was stirred for 6 h at room temperature. The reaction mixture was passed through a short column of silica gel and the solvent was removed by evaporation. Separation of the residue by the recycle-type HPLC (ODS, MeOH/THF = 7/3) gave recovered **1** (77 mg), **2** (40 mg, 32%), **3** (23 mg, 18%), and a dioxidation product of which structure has not been determined (50 mg, 39%). The yields are based on consumed **1**.

5 **2**: Mp 260–265 °C; ^{1}HNMR (C_6D_6) δ 1.352 (d, 24H, J = 7.3 Hz), 1.355 (d, 12H, J = 7.3 Hz), 1.37 (d, 12H, J = 7.6 Hz), 1.38 (d, 12H, J = 7.4 Hz), 1.50 (sep, 4H, J = 7.4 Hz), 1.66 (sep, 4H, J = 7.4 Hz), 1.88 (sep, 2H, J = 7.5 Hz); ^{13}CNMR (C_6D_6) δ 15.0, 15.1, 17.4, 18.9, 22.1, 23.3, 23.5, 24.4; ^{29}SiNMR (C_6D_6) δ −15.2, 23.8; IR (KBr, cm^{-1}) 2880, 1460, 1380, 1360, 1220, 1070, 1020, 1000, 990, 870, 690; UV (λ_{max} in hexane) 245 nm (sh, ε 4800), 292 nm (ε 5500), 313 nm (ε 5100); MS m/z (%) 614 (M^+, 100), 571 (86), 529 (45); HRMS. Found: 614.4053. Calcd for $C_{30}H_{70}OSi_6$: 614.4043.

6 **3**: Mp 198 °C; ^{1}HNMR (C_6D_6) δ 1.17–1.48 (m, 60H), 1.58 (sep, 2H, J = 7.5 Hz), 1.65 (sep, 2H, J = 7.3 Hz), 1.71 (sep, 4H, J = 7.6 Hz), 1.77 (sep, 2H, J = 7.4 Hz); ^{13}CNMR (C_6D_6) δ 13.4, 13.6, 14.2, 14.3, 14.8, 16.8, 17.1, 18.1, 18.2, 18.36, 18.43, 18.7, 18.9, 19.1, 20.4, 20.6, 21.0, 21.8, 22.6, 22.77, 22.84, 22.9, 23.02, 23.03, 23.2, 23.3, 24.1, 24.9, 25.1; ^{29}SiNMR (C_6D_6) δ −40.8, −13.1, 0.9, 9.7, 17.9, 31.2; IR (KBr, cm^{-1}) 2850, 1450, 1380, 1360, 1220, 1060, 990, 940, 870; UV (λ_{max} in hexane) 240 nm (ε 19000), 270 nm (sh, ε 3800), 310 nm (sh, ε 800); MS m/z (%) 614 (M^+, 97), 571 (100), 529 (54); HRMS. Found: 614.4030. Calcd for $C_{30}H_{70}OSi_6$: 614.4043.

7 Crystal data for **2**: $C_{30}H_{70}OSi_6$, F_w = 615.40, monoclinic, space group $C2/c$, a = 13.280(1), b = 16.075(1), c = 18.331(1) Å, β = 94.517(2)°, V = 3901.1(3) Å^3, Z = 4, D_o = 1.040, D_c = 1.048 g cm^{-3}, R = 0.051, R_w = 0.058 (w = $1/\sigma^2(F_o)$) for 2569 observed reflections.

8 The preliminary X-ray analysis of **3** indicates the structure of decaisopropyl-2-oxabicyclo[3.2.0]heptasilane.

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