Benzo[1,2:4,5]bis(1,1,2,2-tetraisopropyldisilacyclobutene)

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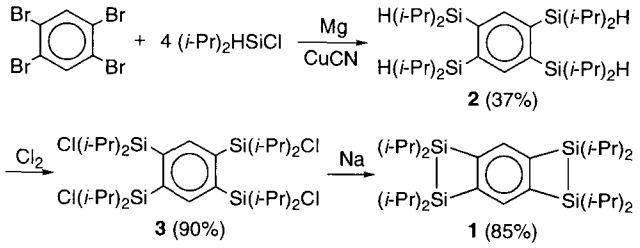
Benzo[1,2:4,5]bis(1,1,2,2-tetraisopropyldisilacyclobutene) (**1**) was synthesized. The X-ray crystal analysis shows that the benzene ring is deformed from the D_{6h} symmetry. Compound **1** shows an intense ^1L_b absorption band in the UV spectrum. In the emission spectrum, intense phosphorescence ($\Phi_p = 0.72$) was observed at 77 K.

Since the first benzodisilacyclobutene was synthesized in 1986,[1] the chemistry of this system has been studied extensively.[2–5] The benzodisilacyclobutene has a strained framework, and the Si–Si bond is easily cleaved by thermolysis,[1,2a] photolysis,[2b,c,3b] and by the action of a Lewis acid[1] and transition metal catalysts.[2d–j,3a,4,5] Recently, the structures of benzodisilacyclobutene and related benzene derivatives with fused disilacyclobutene rings have been calculated using 6-31G* methods.[6] However, no X-ray crystallographic data of the benzodisilacyclobutene derivatives have been reported so far, and the benzobis(disilacyclobutene)s have not yet been synthesized. Motivated by our recent study on organosilicon compounds containing aromatic rings,[7] we have attempted to construct benzene systems with fused disilacyclobutene rings. We report herein the synthesis, X-ray structure, and electronic properties of benzo[1,2:4,5]bis(1,1,2,2-tetraisopropyldisilacyclobutene) (**1**).

Compound **1** was synthesized by the following scheme. The reaction of 1,2,4,5-tetrabromobenzene with chlorodiisopropylsilane in the presence of magnesium and a catalytic amount of copper(I) cyanide gave **2**. Compound **2** was converted to **3** by chlorine. The intramolecular Si–Si bond formation of **3** was conducted with sodium to give **1** in high yield.[8] Compound **1** is stable in air in the crystalline form.[9,10]



The structure of **1** was determined by X-ray crystallography at −100 °C (Figure 1).[11] The benzo[1,2:4,5]bis(disilacyclobutene) skeleton has a planar structure; the benzene ring and four silicon atoms are located on a plane. The Si–Si bonds (2.350(1) Å) and Si–C bonds (1.900(3) and 1.885(3) Å) of the disilacyclobutene ring have normal bond lengths, but the annelated C–C bonds (1.417(4) Å) are significantly long compared with the other C–C bonds in the benzene ring (1.388(5) and 1.398(4) Å). The C–C–C bond angles in the benzene ring are nearly 120° (119.8(3)–120.3(3)°). The structural features of **1** are almost consistent with those of the calculated structure of unsubstituted benzo[1,2:4,5]bis(disilacyclobutene), in which the annelated C–C bonds are significantly longer than the other C–C bonds in the benzene rings.[6] The deformation of the benzene ring from the D_{6h} structure was also reported in the X-ray structure of benzo[1,2:4,5]dicyclobutene;[12] the C–C bond lengths in the benzene ring are almost the same (1.394 and 1.399 Å), but the C–C–C bond angles are deformed (112.1 and 124.0°).[12c] The difference in the deformation manner may be ascribed to the degree of strain by the four-membered rings.

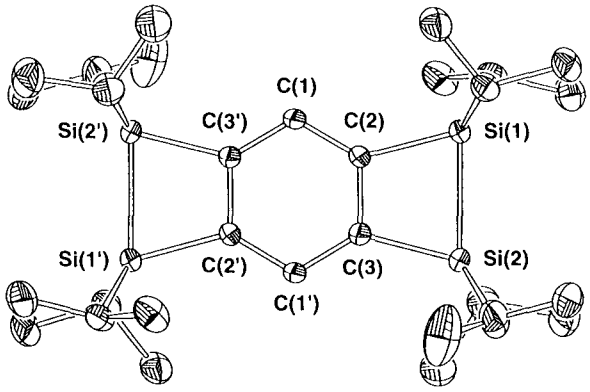


Figure 1. Molecular structure of **1** at −100 °C. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.350(1), Si(1)–C(2) 1.900(3), Si(2)–C(3) 1.885(3), C(1)–C(2) 1.388(5), C(1)–C(3') 1.398(4), C(2)–C(3) 1.417(4); Si(2)–Si(1)–C(2) 75.4(1), Si(1)–Si(2)–C(3) 76.0(1), C(2)–C(1)–C(3') 119.9(3), Si(1)–C(2)–C(1) 135.5(2), Si(1)–C(2)–C(3) 104.1(2), C(1)–C(2)–C(3) 120.3(3), Si(2)–C(3)–C(2) 104.3(2), Si(2)–C(3)–C(1') 135.9(3), C(2)–C(3)–C(1') 119.8(3).

Compound **1** exhibits unique electronic properties. In Figure 2, the UV spectra of **1** and **2** are shown for comparison. The absorption maxima with the longest wavelength is 295 nm (ε 5600) in **1** and 290 nm (ε 1350) in **2**, and the intensity of **1** is larger than that of **2**. It is also noted that the intensity of **1** is greater than that of benzo[1,2:4,5]dicyclobutene (λ_{max} 286 nm (ε 3890)).[13] The molecular orbital calculation of **1** (PM3) shows that the π orbitals of benzene interact with eight Si–C(isopropyl) σ orbitals, and the energy levels of these σ–π orbitals are raised. The direction of the Si–C bonds in this interaction is inverse compared with that in the σ–π conjugation,[14] and this inverse σ–π conjugation is usually negligible in freely-rotating compounds such as trimethylphenylsilane. The rigid structure with nearly the parallel orientation of the Si–C σ bonds with π orbitals seems responsible for the appearance of this effect.[15]

In Figure 3, the emission spectra of **1** and **2** are shown. Both compounds show intense phosphorescence at *ca.* 370–550 nm, while the fluorescence of **1** was not detected, and weak fluorescence was observed at *ca.* 280–360 nm in the case of **2**. The phosphorescence quantum yields (Φ_p) of **1** and **2** are 0.72 and 0.97, respectively. Unfortunately, the emission spectra of benzo-

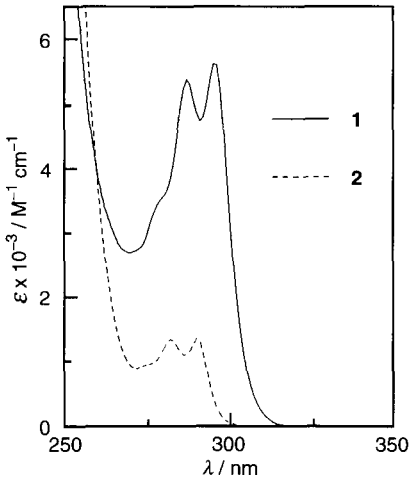


Figure 2. UV spectra of **1** and **2** in hexane at room temperature.

disilacyclobutenes have not been reported, and we cannot compare the quantum yields. However, these values are greater than those of benzene ($\Phi_p = 0.15$)[16] and other silyl-substituted benzenes.[17] These results indicate that intersystem crossing is far more rapid than fluorescence radiation in the excited singlet state, and the excited triplet state effectively emits phosphorescence.

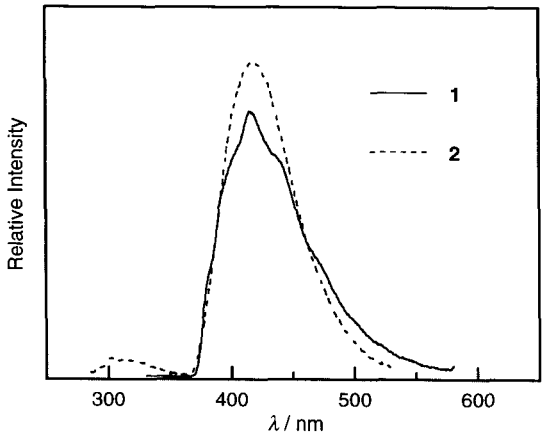


Figure 3. Emission spectra of **1** and **2** in 3-methylpentane at 77 K. The excitation wavelengths for **1** and **2** are 294 and 275 nm, respectively.

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8 A solution of **3** (0.910 g, 1.35 mmol) in toluene (5 ml) was added to a mixture of sodium (0.220 g, 9.57 mmol) and toluene (30 ml) under reflux. The reaction mixture was refluxed for 33 h. Insoluble materials were filtered off, and the solvent was removed under reduced pressure. The residue was recrystallized from hexane to give **1** (0.607 g, 85%) as colorless crystals.
9 **1**: mp 209–210 °C; ^{1}H NMR (C_6D_6) δ 1.18 (d, 24H, J = 7.4 Hz), 1.26 (d, 24H, J = 7.4 Hz), 1.40 (sept, 8H, J = 7.4 Hz), 7.90 (s, 2H); ^{13}C NMR (C_6D_6) δ 14.2, 20.18, 20.24, 136.9, 156.0; ^{29}Si NMR (C_6D_6) δ 16.0; IR (KBr, cm^{-1}) 2940, 2870, 1460, 1380, 1360, 1210, 1070, 1010, 870; MS m/z (%) 530 (M^+, 32), 487 (100), 445 (28), 403 (30), 73 (36), 58 (45); Anal. Found: C, 67.78; H, 11.16%. Calcd for $C_{30}H_{58}Si_4$: C, 67.84; H, 11.01%.
10 We also synthesized benzo[1,2:4,5]bis(1,1,2,2-tetramethyldisilacyclobutene). However, this compound is quite easily oxidized in air.
11 Crystal data for **1** at −100 °C: $C_{30}H_{58}Si_4$, F_w = 531.13, monoclinic, space group $C2/c$, a = 20.354(5), b = 12.54(2), c = 15.138(3) Å, β = 117.11(2)°, V = 3440(3) Å^3, Z = 4, D_c = 1.026 g cm^{-3}, R = 0.065, R_w = 0.089 ($w = 1/\sigma^2(F_o)$) for 2382 observed reflections.
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