

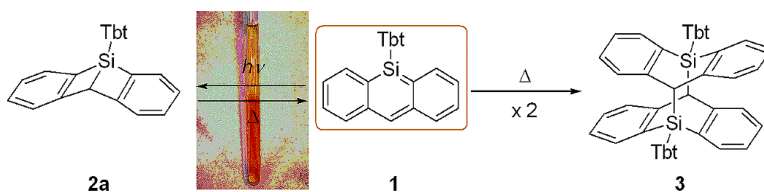
Communication

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Photochemical and Thermal Reactions of a Kinetically Stabilized 9-Silaanthracene: The First Spectroscopic Observation of a 9,10-Dewar-9-silaanthracene Isomer

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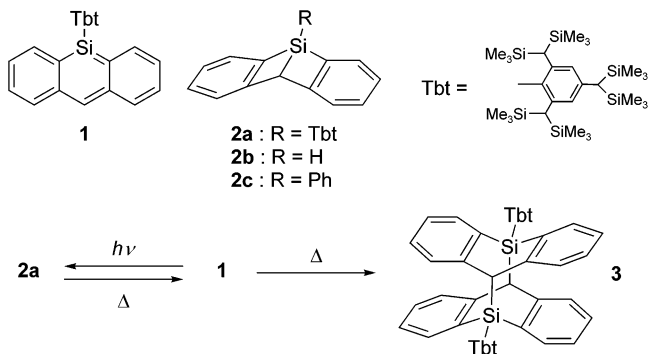
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Photochemical reactions of anthracenes are known to result in the formation of the dimers via [4 + 4] cycloaddition¹ or the corresponding 9,10-Dewar-anthracenes through valence isomerization,² depending on the substrates and/or reaction conditions. The anthracene dimers are known to revert to the monomers thermally, and this interconversion process has attracted much attention from the viewpoints of not only fundamental chemistry but also applications such as molecular switching. Most of 9,10-Dewar-anthracenes are thermally very unstable to regenerate the starting anthracenes in solution easily, and 9-*tert*-butyl-9,10-Dewar-anthracene is the only example structurally characterized so far.^{2d} On the other hand, much attention has been paid to the chemistry of silaaromatic compounds in recent decades, and several 9-silaanthracenes were prepared as transient species in low-temperature matrices.³ Although the photochemical conversion of 9-silaanthracenes into the corresponding Dewar isomers has also been examined, such a process was confirmed only by the disappearance of the original absorptions of 9-silaanthracene in the electronic spectra.^{3a} Since silaaromatic compounds are known to be thermally unstable and undergo ready dimerization and/or polymerization under ambient conditions,⁴ the details of photochemical behavior of 9-silaanthracenes have not been fully disclosed so far.

Meanwhile, we have already reported the syntheses of the first stable silabenzene and 2-silanaphthalene by taking advantage of kinetic stabilization utilizing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt).⁵ Quite recently, we further succeeded in the synthesis and isolation of Tbt-substituted 9-silaanthracene **1** as a stable crystalline compound and revealed its unique molecular structure and spectroscopic properties.⁶ As for the reactivity of these kinetically stabilized silaaromatic compounds, we have already described the similarities and differences in their addition reactions with methanol, benzophenone, mesitonitrile oxide, and 2,3-dimethylbuta-1,3-diene.^{5,6} Photochemically, however, we have only examined the irradiation of Tbt-substituted silabenzene with light of $\lambda = 290\text{--}350$ nm in benzene through Pyrex glass leading to the exclusive formation of the corresponding silabenzvalene isomer.^{5e} Since this result is in a sharp contrast to that of the photochemical conversion of the matrix-isolated silabenzene into the Dewar-type isomer postulated by Maier et al., it should be of great interest to investigate the photochemical reactions of stable 9-silaanthracene **1** for a part of systematic comparison. Here, we delineate the first spectroscopic observation of 9,10-Dewar-9-silaanthracene **2a** generated by the photochemical valence isomerization of **1** together with the kinetic study on the reverse tautomerization from **2a** to **1** and the formation of head-to-tail dimer **3** by thermolysis of **1** at high temperature.

When a degassed benzene-*d*₆ solution of **1** in a sealed Pyrex NMR tube was irradiated with light of $\lambda = 300\text{--}500$ nm through a UV cut filter at room temperature, the orange color of **1** disappeared and a new species, 9,10-Dewar-9-silaanthracene **2a**,

Scheme 1. Structures of **1–3** and Photochemical and Thermal Reactions of **1**



was formed exclusively (Scheme 1). Compound **2a** showed characteristic peaks at 4.43 ppm (singlet) in ¹H NMR and 48.60 ppm in ¹³C NMR. These peaks are most likely attributed to those of the methine hydrogen and carbon atoms at the 10-position of the Dewar isomer **2a**,⁷ respectively. They are considerably upfield-shifted compared with those of aromatic 9-silaanthracene **1** (7.72 and 116.13 ppm, respectively). In the ²⁹Si NMR measurement of **2a** using the INEPT technique, we observed a signal at 1.44 ppm assignable to that of the ring silicon atom. This assignment was reasonably supported by comparison of the experimentally observed chemical shift with those obtained for some model molecules, 9,10-Dewar-9-silaanthracene **2b** (−14.04 ppm) and 9,10-Dewar-9-phenyl-9-silaanthracene **2c** (3.55 ppm), by GIAO calculations.⁸ Furthermore, the monitoring of the photochemical conversion of **1** to **2a** in a degassed and sealed 3-methylpentane matrix at 77 K using UV/vis spectroscopy showed complete disappearance of the typical absorption bands of **1** at the range of 350 through 550 nm, indicating the formation of less conjugated system **2a** than **1**.

Although the spectroscopic studies strongly indicate the photochemical transformation of **1** to **2a**, the Dewar isomer **2a** prepared here could not be isolated as a stable compound due to its low thermal stability. **2a** was found to undergo gradual thermal tautomerization into **1** even at −80 °C in hexane. The conversion of **2a** to **1** in degassed hexane was monitored at six temperatures between −40 and 10 °C using UV/vis spectroscopy by observation of the increase of the absorption maximum for 9-silaanthracene **1** at 478 nm. As a result, this reaction was found to be a first-order reaction as well as thermal isomerization of 9,10-Dewar-anthracenes to anthracenes.⁹ The activation energy *E*_a and the preexponential factor deduced by the kinetic analysis were 4.34 kcal·mol^{−1} and 1.61, respectively. The activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were 3.83 kcal·mol^{−1} and −3.76 cal·mol^{−1}·K^{−1}, respectively. The half-life of **2a** in hexane at 10 °C was estimated to be about 5 min,¹⁰ the value of which is considerably shorter than that of the anthracene/9,10-Dewar-anthracene system, suggesting much less

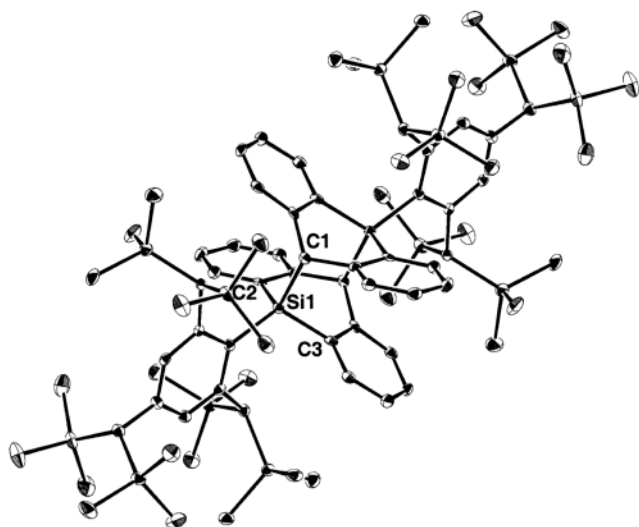


Figure 1. ORTEP drawing of 9-silaanthracene dimer **3**. Hydrogen atoms and a solvent molecule were omitted for clarity. Selected bond lengths (Å) Si1–C1 1.983(4), Si1–C2 1.874(4), Si1–C3 1.882(4).

stability of **2a** than 9,10-Dewar-anthracene. Moreover, it was found that the orange crystals of **1** in a degassed and sealed Pyrex glass tube changed into colorless crystals by irradiation with light of $\lambda = 300\text{--}500\text{ nm}$ through a UV cut filter. The ^1H NMR spectrum of the resulting crystals was identical to that of **2a** prepared in solution. Interestingly, **2a** underwent gradual tautomerization into **1** even in the solid state at room temperature in the dark, while the solid samples of 9,10-Dewar-anthracenes are reportedly stable at room temperature.

Next, we performed the pyrolysis of 9-silaanthracene **1** with the hope of obtaining the corresponding [4 + 4] dimer **3**, which is another possible candidate for the photochemical reaction product of **1** as can be seen in the cases of hydrocarbon analogues. When a benzene- d_6 solution of **1** was heated at $110\text{ }^\circ\text{C}$ in a sealed tube for 15 days, the orange color of **1** gradually diminished and the expected [4 + 4] dimer **3** was obtained in 42% yield as colorless crystals. Interestingly, the dimer **3** was formed more readily (58% yield) by thermolysis of **1** in the solid state at $180\text{ }^\circ\text{C}$ for 1 h (Scheme 1). These results indicate that **1** has high reactivity for cycloaddition at the 9- and 10-positions though it bears a bulky Tbt group on the central silicon atom. Dimer **3** is thermally very stable and no cycloreversion to monomer **1** was observed in the 1,2-dichlorobenzene- d_4 solution even at $200\text{ }^\circ\text{C}$ in a sealed tube. The ^1H and ^{13}C NMR data for dimer **3** were completely different from those of **2a**, and the ^{29}Si NMR signal of the central silicon atom of **3** was observed at -21.83 ppm . The head-to-tail type dimerization mode in the [4 + 4] dimer **3** was definitively determined by X-ray crystallographic analysis (Figure 1), which reveals that **3** has considerably elongated Si–C bonds [1.983(4) Å] probably due to the sterically congested 9-silaanthracene dimer structure.¹¹ The synthesis and characterization of **3** should be of great importance from the standpoints of not only the first example of a structurally characterized 9-silaanthracene dimer but also the requirement for the identification of 9,10-Dewar-9-silaanthracene **2a**.

In summary, it was experimentally demonstrated for the first time that 9-silaanthracene, as well as anthracene, can afford either the Dewar isomer or [4 + 4] dimer, depending on the reaction

conditions. Theoretical calculations on the molecular geometry and the relative energy of the real molecules **1**, **2a**, and **3** at the B3LYP/6-31G(d) level resulted in the conclusion that dimeric structure **3** was found to be more stable than the monomer **1** by $15.9\text{ kcal}\cdot\text{mol}^{-1}$ (per monomer unit) and Dewar isomer **2a** was less stable than 9-silaanthracene **1** by $13.4\text{ kcal}\cdot\text{mol}^{-1}$,⁸ which is consistent with the experimentally observed relative stability for **1**, **2a**, and **3**.

Further investigation on the reactivities of the Dewar isomer **2a** and the [4 + 4] dimer **3** is currently in progress.

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Supporting Information Available: Experimental details, X-ray structural report of **3**, spectroscopic data for **2a**, and kinetic analysis of **2a**. Crystallographic data for 9-silaanthracene dimer (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) NMR data of **2a**: ^1H NMR (300 MHz, rt , C_6D_6) δ 0.16 (br s, 54H), 1.51 (s, 1H), 2.58 (br s, 1H), 2.72 (br s, 1H), 4.43 (s, 1H), 6.63 (br s, 1H), 6.71 (br s, 1H), 6.99–7.09 (m, 4H), 7.20 (d, $J = 6.7\text{ Hz}$, 2H), 7.66 (d, $J = 7.8\text{ Hz}$, 2H). ^{13}C NMR (75 MHz, rt , C_6D_6) δ -0.71 (q), 0.90 (q), 1.01 (q), 29.75 (d), 30.01 (d), 31.33 (d), 48.60 (d), 118.52 (s), 122.48 (d), 125.52 (d), 126.27 (d), 128.29 (d), 130.77 (d), 132.44 (d), 142.21 (s), 146.67 (s), 147.09 (s), 157.02 (s \times 2); ^{29}Si NMR (60 MHz, rt , C_6D_6) δ 1.44, 2.17, 2.25.
- (8) The geometries of 9-silaanthracene derivatives and their isomers **1**, **2a**, **2b**, **2c**, and **3** were optimized using the Gaussian 98 program at the B3LYP/6-31G(d) level. GIAO-B3LYP calculations of **2b** and **2c** were carried out with 6-311G(3d) for Si and 6-311G(d) for C and H.
- (9) Kinetic analysis for the first-order reaction yielded the Arrhenius equation, $\ln k = 1.61 - (2.18 \times 10^3)/T$.
- (10) While the half-life of **2a** in hexane at $10\text{ }^\circ\text{C}$ is about 5 min, that in benzene- d_6 was estimated as about 16 min by monitoring the conversion of **2a** to **1** with ^1H NMR spectroscopy. We observed the ^{13}C and ^{29}Si NMR signals of **2a** by measuring the spectra just after the photoirradiation.
- (11) Dimer **3** has a poor solubility, and hence the full NMR data of **3** could not be attributed. Spectral data for **3**: white powder, mp $310\text{ }^\circ\text{C}$ (dec). ^{29}Si NMR (60 MHz, rt , CDCl_3) δ -21.83, 1.50, 1.57, 1.73, 1.80, 1.86, 1.94, 2.02, 2.08, 2.23, 2.27. Crystal data of **3**: $\text{C}_{36}\text{H}_{14}\text{Si}$; $\text{C}_{36}\text{H}_{14}\text{Si}$, MW = 1577.32, monoclinic, space group $P2_1/c$, $Z = 2$, $a = 12.155(6)$, $b = 22.181(11)$, $c = 18.561(10)$ Å, $\beta = 108.422(6)^\circ$, $V = 4748(4)$ Å³, D_{calc} = 1.103 g·cm⁻³, $\mu = 0.228\text{ mm}^{-1}$; R_1 ($I > 2\sigma(I)$) = 0.081, wR_2 (all data) = 0.171, GOF = 1.223 for 8321 reflections, 473 parameters, and 18 restraints.

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