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Synthesis and Structure of a Heavier Congener of Biphenyl: 1,1′-Disila-4,4′-biphenyl

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Summary: The 1,1′-disila-4,4′-biphenyl species **1**, *the first molecule bearing directly connected two silaaromatic rings, was synthesized and characterized by its spectroscopic and X-ray crystallographic data. The UV−vis spectrum of* **1** *showed not only a red shift but also a 6-fold increase in absorbance of the longest absorption maximum in comparison with those of Tbt-substituted silabenzene, indicating that the concept of conjugation through the single bond connecting two aromatic rings is applicable even in the silaaromatic systems.*

Biphenyl can be regarded as the simplest model compound for polyphenylenes, which have been widely used as attractive materials in many areas, and has been one of the most controversial molecules for a long time.[1] The important factor in the geometry of biphenyl is the torsion angle, which depends on the balance between π-electron conjugation and the steric repulsion of ortho hydrogen atoms. It is well-known that two phenyl rings of biphenyl in the crystalline state (at a temperature above 40 K) are coplanar dominantly due to crystal-packing forces[2] but are twisted across the central C−C bond in the vapor phase and in solution.[3] Detailed structural studies from such kinds of viewpoints are important to understand the conjugation effect for various types of aromatic compounds containing biphenyl skeletons.

As part of our ongoing research projects in the area of novel aromatic compounds, we have already succeeded in the incorporation of a silicon atom into various aromatic ring skeletons by the application of an efficient protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), to afford heavier analogues of benzene, naphthalene, anthracene, and phenanthrene.[4,5] Studies on their structural and spectroscopic properties together with theoretical calculations indicated that these silaaromatic compounds have much smaller energy gaps between their frontier orbitals than do those of the parent aromatic hydrocarbons, in addition to their high aromaticity. These results clearly show that silaaromatic frameworks are promising for the creation of novel π-conjugated systems containing heavier main-group elements.[6] That is, the connection or fusing of "ready-made" π-conjugated systems containing a heavier group 14 element(s) can be a new synthetic methodology to create novel extended π-conjugated systems. In order to understand the conjugation effect of a silaaromatic ring with the other π-unit, the biphenyl skeleton can be viewed as one of the simplest models. Herein, we wish to report the synthesis and structure of the 1,1′-disila-4,4′-biphenyl species **1**, the first compound bearing directly connected two silaaromatic rings.

As illustrated in Scheme 1, the bis(hydrosilane) **3**, bearing two SiC_5 rings, was obtained as a mixture of isomers by the coupling reaction of the corresponding silacyclohexadienide,[7] which was generated by the reaction of hydrosilane **2**[8] with *n*-BuLi.[9] Bis(chlorosilane) **5**, the potential precursor for the synthesis of disilabiphenyl, was prepared via bis(hydroxysilane) **4** according to the procedure for the synthesis of Tbt-substituted silabenzene.[8] The dehydrochlorination reaction of **5** with LDA afforded the title compound, the 1,1′-disila-4,4′-biphenyl species **1**, in 14% yield as colorless crystals. In the ^1H NMR spectrum of **1** in C_6D_6, signals assignable to the protons at the α- and β-positions of the silicon atoms (Si1) in the SiC_5 rings were observed at 7.12 and 8.22 ppm as doublet signals ($J = 12.8$ Hz), which were similar to those in the case of silabenzene. In the ^{29}Si NMR spectrum of **1**, the signal of Si1 was observed at 87.2 ppm, the value of which is shifted slightly upfield from that of silabenzene (93.6 ppm).[8] Due to its very low solubility, it was difficult to measure the ^{13}C NMR spectrum of **1** in C_6D_6, and hence, full characterization of **1** in solution was completed by using THF-d_8 as a solvent. In the ^{29}Si NMR spectrum in THF-d_8, a signal assignable to the Si1 atoms was observed at 91.0 ppm. It is known that the complexation of silenes (Si═C) with THF results in the remarkable upfield shift of ^{29}Si NMR

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(9) Experimental procedures and chemical data for the newly obtained compounds are given in the Supporting Information.

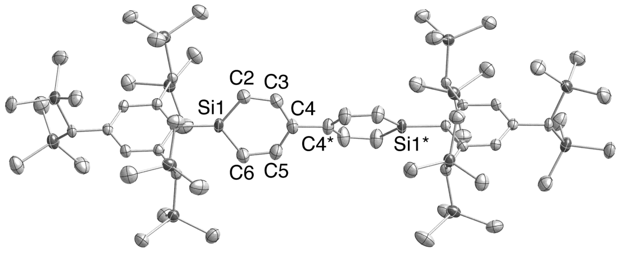
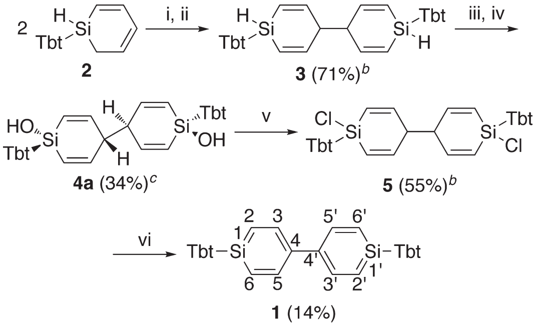


Figure 1. Thermal ellipsoid plot of [**1**·2toluene] drawn at the 50% probability level. Hydrogen atoms and toluene molecules are omitted for clarity. Selected bond lengths (Å): Si1−C2 = 1.737(4), C2−C3 = 1.395(5), C3−C4 = 1.393(6), C4−C5 = 1.396(5), C5−C6 = 1.401(5), C6−Si1 = 1.762(4), C4−C4* = 1.505(7).

Scheme 1. Synthesis of the 1,1′-Disila-4,4′-biphenyl Species 1[a]



[a] Conditions (i) *n*-BuLi (1 equiv), THF, −60 °C; (ii) $BrCF_2CF_2Br$ (1 equiv), THF, −60 °C then room temperature; (iii) NBS (2 equiv), CCl_4, 4 °C; (iv) $NaHCO_3$ (excess), THF/H_2O, 50 °C; (v) PCl_5 (excess) and NEt_3 (excess), Et_2O, reflux; (vi) LDA (1 equiv), hexane/THF, room temperature. [b] Mixture of isomers. [c] The isomer *syn*,*anti*-**4b** was obtained in 10% yield.

resonances (for example, from 144.2 to 52.4 ppm in the case of $Me_2Si{=}C(SiMe_3)\{SiMe(t\text{-}Bu)_2\}$).[10] Therefore, there is almost no interaction between the oxygen atom of THF and the ring silicon atoms of the disilabiphenyl unit because of the effective protection of the Tbt group around the sp^2 silicon atoms. ^{13}C NMR signals of the carbon atoms in the SiC_5 rings were observed at 144.2 (C3 and C5), 132.9 (C4), and 122.4 (C2 and C6) ppm, the values of which are quite similar to those of Tbt-substituted silabenzene (143.6 ppm for C3 and C5; 122.2 ppm for C2 and C6; 116.1 ppm for C4), except for C4.[8] The chemical shift of the signal for the C4 atom is shifted more downfield than that of Tbt-substituted silabenzene, as observed in the case of parent aromatic hydrocarbon systems: i.e., biphenyl and benzene.

Crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation from its toluene solution. Structural analysis has been completed satisfactorily on the basis of space group *C*2/*c*, and the two $TbtSiC_5H_4-$ moieties are crystallographically equivalent (Figure 1). The two SiC_5 rings are twisted with respect to each other with a dihedral angle of ca. 41°. The parent biphenyl has a coplanar structure due to packing forces in the crystalline state,[2] and its dihedral angles in solution or in the gas phase are ca. 45°.[3] On the other hand, it is known that bulky substituents at the 4- and 4′-positions in the parent biphenyl minimize the influence of crystal packing.[11] In the case of **1**, extremely bulky Tbt groups prevent intermolecular interactions between the disilabiphenyl units, resulting in the retention of a distorted structure even in the solid state. The length of the central C−C bond connecting the two SiC_5 rings is 1.505(7) Å, which is almost similar to that of the parent biphenyl.[2] The planar geometries of the two SiC_5 rings were clearly revealed, and the lengths of the two Si−C bonds and the four C−C bonds in the SiC_5 ring were found to be almost equal to each other, respectively, indicating the delocalization of π-electrons in each ring. These structural parameters, including the internal angles, are quite similar to those of Tbt-substituted silabenzene,[8] in spite of the connection of the two silaaromatic rings. These results suggested the absence of significant electronic correlations between the two silaaromatic rings in the crystalline state. In comparison with the parent biphenyl, the internal angle at the C3 position of **1** is larger by ca. 4°, owing to the introduction of a silicon atom, which has an atomic radius larger than that of a carbon atom.

In order to clarify the properties of 1,1′-disila-4,4′-biphenyl in detail, theoretical calculations for several model compounds of **1** bearing a hydrogen atom or some substituted-phenyl groups instead of the Tbt group were carried out at the B3LYP level with 6-31G(d) basis sets (see the Supporting Information). In the optimized structures, the structural parameters of the disilabiphenyl units were almost similar regardless of the substituents, although the twist angles between the benzene ring of the substituents and the core silabenzene ring varied depending on the bulkiness of the substituents. The twist angles and the lengths of the central C−C bonds between the two silaaromatic rings were optimized to be 44.8−45.6° and 1.492−1.493 Å, respectively, both of which well reproduced those observed for **1** in the crystalline state. Understanding the rotational barrier of the parent 1,1′-disila-4,4′-biphenyl is a matter of vital importance to elucidate the π-conjugation effect in solution. The relative energy is the lowest when the twist angle is 45.5°. Meanwhile, a coplanar conformation is the most unstable geometry, and the difference between the energies of the most stable and unstable geometries is 5.4 kcal/mol. Although the rotational barrier of disilabiphenyl is estimated to be somewhat larger than that of the parent biphenyl (2.4 kcal/mol, calculated at the same level as that used for the aforementioned model compounds)[12] because of the inevitably greater steric repulsion between the hydrogen atoms on the β-carbons, the small energy barrier indicates that the two silaaromatic rings in the 1,1′-disila-4,4′-biphenyl skeleton can freely rotate around the central bond at room temperature.

In the UV−vis spectrum of **1** in hexane at room temperature, the longest absorption maximum was observed at 357 nm ($\varepsilon = 2.9 \times 10^4$) as a broad peak, as illustrated in Figure 2. On the other hand, Tbt-substituted silabenzene shows some vibrational fine structures and the longest absorption maximum at 331 nm ($\varepsilon = 5.0 \times 10^3$). It should be noted that the longest absorption maximum of 1,1′-disila-4,4′-biphenyl **1** is red-shifted 26 nm compared with that of the corresponding silabenzene, together with an increase in absorption intensity. These drastic differences may indicate that effective π-conjugation is achieved in solution between the two silaaromatic rings of **1** through the central C−C bond. The broadened absorption of **1** is most likely interpreted in terms

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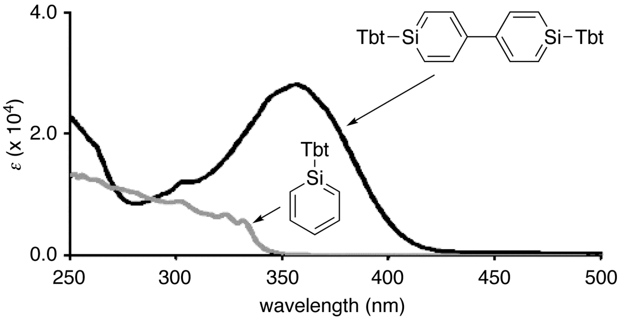

Figure 2. UV−vis spectra of the 1,1′-disila-4,4′-biphenyl species **1** and silabenzene.

of the free rotation between the two silaaromatic rings around the central C−C bond, as reported in the case of the parent biphenyl.[13] In order to assign the absorptions, TD-DFT calculations for the model compound bearing Dip (2,4,6-triisopropylphenyl) groups were performed with a conformation similar to that of the observed one, including the orientation of the aryl substituents (TD-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)). The calculated value of the longest absorption maximum was 373 nm ($f = 0.5535$), which is in good agreement with the observed one. Therefore, the absorption at 357 nm was found to be assignable to the electron transition from the π orbital (HOMO) of the disilabiphenyl unit to the π^* orbital (LUMO) of the disilabiphenyl unit together with the aryl substituents on the silicon atoms, as shown in Figure 3,[14] the results of which also support the existence of π-conjugation between two silaaromatic rings.

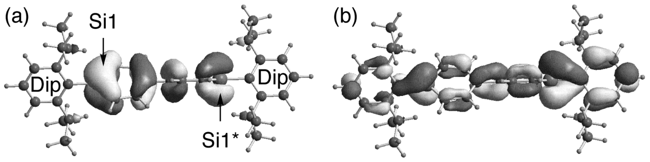

Figure 3. Frontier orbitals of a model compound bearing Dip groups: (a) HOMO; (b) LUMO.

In summary, we succeeded in the synthesis of the first compound bearing two silaaromatic rings in a molecule, i.e., the 1,1′-disila-4,4′-biphenyl species **1**. In the UV−vis spectrum of **1** in hexane, the longest absorption maximum is significantly red-shifted compared with that of Tbt-substituted silabenzene, indicating that silaaromatic rings can also conjugate with each other as well as the corresponding aromatic hydrocarbons. Construction of further extended π-conjugated systems containing more silaaromatic ring skeletons is ongoing.

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Supporting Information Available: Text, figures, and tables giving experimental procedures and spectral data for new compounds and a CIF file giving crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] The shape of the LUMO indicated that **1** would possess the character of a disilaquaterphenyl derivative in no small part. Actually, the longest absorption maximum calculated for the hydrogen-substituted disilabiphenyl was 343 nm ($f = 0.6066$), which was blue-shifted by 30 nm compared to that of the Dip-substituted one. This correlation resembles that between the longest absorption maxima of biphenyl (248 nm) and p-quaterphenyl (294 nm) in cyclohexane: Ozasa, S.; Hatada, N.; Fujioka, Y.; Ibuki, E. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2610.