Preparation, Structure, and Properties of Tris(trimethylsilyl)silyl-substituted Anthracenes: Realization of Ideal Conformation for σ–π Conjugation Involving Eclipse of Si–Si σ-Bond with p-Orbital of Aromatic Ring

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Synthesis and X-ray diffraction analysis of 9- and 9,10-tris(trimethylsilyl)silyl (TTMSS)-substituted anthracenes were carried out to disclose that one of the Si–Si σ-bonds in the TTMSS-substituted anthracenes were perpendicular to the aromatic rings. The introduction of the TTMSS groups induced red shift of UV absorption and fluorescence emission maxima as compared with the parent and 9-pentamethyldisilanylated anthracenes. Theoretical calculation suggests LUMO levels of the TTMSS-substituted anthracenes are lowered by σ^*–π^* orbital interaction.

Introduction of a pentamethyldisilanyl group into arenes perturbs electronic structure of the parent π-conjugated systems via σ–π (σ^*–π^*) conjugation and hence leads to improvement of optical and/or electronic properties of the parent compounds.[1] To realize efficient σ–π conjugation, eclipse of a σ orbital of Si–Si bond and a p-orbital of an aromatic ring is essential (Figure 1, conformer A).[2] Therefore, use of tris(trimethylsilyl)-silyl (TTMSS) group as a source of a disilanyl group into an aromatic ring allows us to establish the eclipse alignment in any locally minimized conformer (Figure 1).[3,4] In addition, neither crystal structure, UV absorption, nor fluorescence of (bis)TTMSS-substituted arenes was reported.[5] We report here molecular structures disclosed by X-ray diffraction analysis, absorption and emission spectra, and theoretical study of TTMSS-substituted anthracenes **1** and **2**.[6]

Anthracenes **1** and **2** were prepared by lithium–bromine exchange of 9-bromo- and 9,10-dibromoanthracene with *t*-BuLi in THF followed by silylation with commercially available chlorotris(trimethylsilyl)silane in 75 and 29% yields, respectively.[7] The molecular structures of **1** and **2** disclosed by X-ray diffraction study are shown in Figure 2.[8,9] As expected, the Si(1)–Si(2) bond of **1** directs completely perpendicular to the anthracene plane, since **1** has a mirror plane which consists of Si(1),
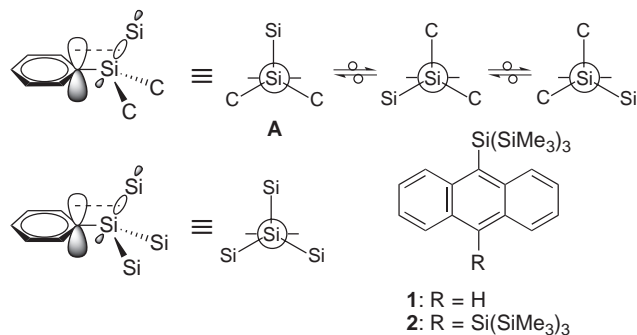

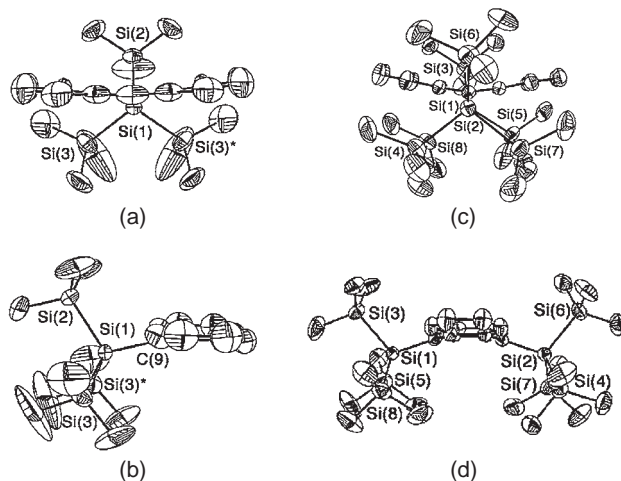**Figure 1.** Disilanyl and TTMSS group-substituted arenes.

Figure 2. ORTEP drawings of **1** and **2** (hydrogen atoms are not shown for clarity) (a) front view of **1**, (b) side view of **1**, (c) front view of **2**, (d) side view of **2**.

Si(2), and C(9) (Figures 2a and 2b). Similarly, both Si(1)–Si(3) and Si(2)–Si(6) bonds of **2** are oriented in the same direction with almost perpendicular alignments to the anthracene plane. Due to steric repulsion between anthracene skeleton and the trimethylsilyl groups, all silicon–silicon bond lengths ranging from 2.3523(10) to 2.3950(10) Å in **1** and **2** were longer than the normal value of Si–Si bond (2.34 Å), and the TTMSS groups are slightly deviated from the planes consisting of anthracene frameworks of **1** and **2**. In addition, the anthracene moiety in **2** is fairly bent because of the steric repulsion against trimethylsilyl groups (Figures 2c and 2d).

UV and fluorescence spectra of **1**, **2**, 9-(pentamethyldisilanyl)anthracene (**3**), and anthracene measured in cyclohexane at room temperature are shown in Figures 3 and 4, and the data are summarized in Table 1. Anthracenes **1** and **2** exhibited a bathochromic shift of λ_{max} compared with anthracene and **3** (Figure 3). In addition, molar extinction coefficients of **1** and **2** are larger than those of anthracene and **3**. Vibrational structure of absorption spectra of **2** was very broadened: although the reason is not clear at present, the broadening may be ascribed to the bent framework of **2**. Emission maxima upon irradiation by a UV light ($\lambda = 355$ nm) red-shifted in the order of anthracene, **3**, **1**, and **2** (Figure 4).[10]

Theoretical calculation of 9- and 9,10-$(H_3Si)_3$Si-substituted anthracenes (**1′** and **2′**) were carried out by DFT method at HF/6-31G*//B3LYP/6-31G* level (Table 2). The optimized structure was the same as those determined by X-ray. Introduction of TTMSS groups into anthracene induced considerable lower-

Table 1. Photophysical characteristics of **1**, **2**, **3**, and anthracene[a]

	$\lambda_{\max}$ /nm	$\lambda_{\rm em}$ /nm	ε /M^{-1} cm^{-1}	$\Phi_{\rm f}$
1	400	452	10,760	0.52
2	433	483	12,870	0.51
3	393	432	8700	0.60
anthracene	376	378	7700	0.32

[a]Irradiation was effected with an UV light ($\lambda = 355$ nm).
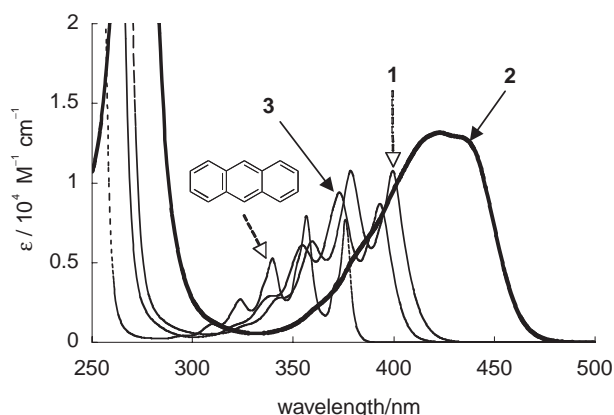
Figure 3. UV spectra of **1**, **2**, **3**, and anthracene.
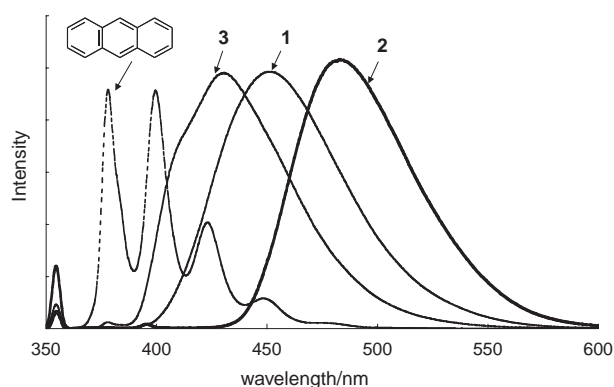
Figure 4. Fluorescence spectra of **1**, **2**, **3**, and anthracene.

ing LUMO levels, resulting in decrease of HOMO–LUMO gap which was consistent with red shift of absorption maxima. As shown in Figure 5, such lowering of LUMOs probably results from σ^*–π^* conjugation between σ^* orbital of Si–Si bond and π^* orbital of anthracene.

In summary, use of a TTMSS group as a σ-conjugation module is demonstrated to be a versatile way for attaining ideal conformation for efficient σ–π (σ^*–π^*) conjugation system with anthracene as a model of π-framework. Further studies on preparation of TTMSS-substituted π-conjugated molecules and their application to functional organic materials are in progress in our laboratory.

Table 2. HOMO and LUMO energies of **1′**, **2′**, and anthracene[a]

	Anthracene	**1′**	**2′**
LUMO/eV	1.71	1.20	0.73
HOMO/eV	−6.86	−7.06	−7.16
LUMO–HOMO/eV	8.57	8.26	7.89

[a]Calculated at HF/6-31G*//B3LYP/6-31G* level.
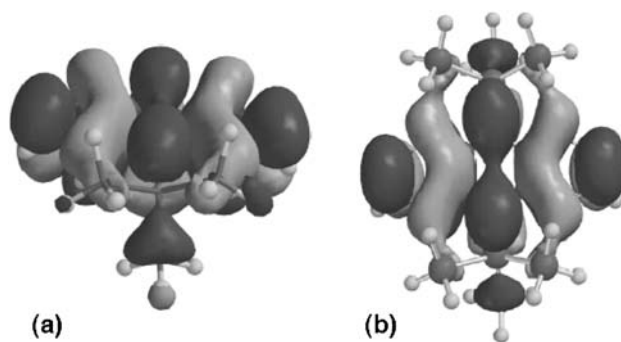
Figure 5. LUMOs of **1′** (a) and **2′** (b).

References and Notes
1   H. Sakurai, *J. Organomet. Chem.* **1980**, *200*, 261.
2   H. Sakurai, S. Tasaka, M. Kira, *J. Am. Chem. Soc.* **1972**, *94*, 9285.
3   Examples of TTMSS-substituted aromatics: a) M. J. Sanganee, P. G. Steel, D. K. Whelligan, *J. Org. Chem.* **2003**, *68*, 3337. b) L. F. Brough, R. West, *J. Organomet. Chem.* **1982**, *229*, 113. c) H. J. Sipe, Jr., R. West, *J. Organomet. Chem.* **1974**, *70*, 353. d) M. A. Cook, C. Eaborn, D. R. M. Walton, *J. Organomet. Chem.* **1970**, *23*, 85.
4   Preparation and such properties as photoelectron spectra, first ionization energy, and ESR/ENDOR spectra of 1,4-bis(TTMSS)benzene were reported without any crystal structures: a) H. Bock, J. Meuret, K. Ruppert, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 414. b) H. Bock, J. Meuret, R. Baur, K. Ruppert, *J. Organomet. Chem.* **1993**, *446*, 113; See also, H. Bock, B. Solouki, *Chem. Rev.* **1995**, *95*, 1161.
5   In Refs. 4a and 4b, a single crystal structure of 1,4-bis[(trimethylsilyl)*methyl*]benzene is reported. One benzylic carbon–silicon bond is shown to be aligned with the plane of the benzene ring.
6   Examples of 9- and 9,10-silylated anthracenes: a) S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka, H. Matsumoto, *Organometallics* **1996**, *15*, 1067. b) T. Karatsu, T. Shibata, A. Nishigaki, K. Fukui, A. Kitamura, *Chem. Lett.* **2001**, 994, and references cited therein.
7   See Supporting Information.
8   Crystal data of **1**: C$_{23}$H$_{34}$Si$_4$, fw 422.86, orthorhombic, space group *Cmc*2$_1$, $a = 17.5529(13)$, $b = 8.9994(7)$, $c = 16.7129(12)$ Å, $V = 2640.1(3)$ Å^3, $T = 298$ K, $Z = 4$, $D_{\rm calcd} = 1.064$ Mg/m^3, $R_1 = 0.0495$ ($I > 2\sigma(I)$), $wR_2 = 0.143$ (all data). CCDC-613895.
9   Crystal data of **2**: C$_{32}$H$_{62}$Si$_8$, fw 671.52, monoclinic, space group $P2_1/c$, $a = 15.2329(10)$, $b = 14.9587(10)$, $c = 19.5634(13)$ Å, $\beta = 103.5120(10)°$, $V = 4334.4(5)$ Å^3, $T = 298$ K, $Z = 4$, $D_{\rm calcd} = 1.029$ Mg/m^3, $R_1 = 0.0509$ ($I > 2\sigma(I)$), $wR_2 = 0.137$ (all data). CCDC-613896.
10 For fluorescence of aryldisilanes, see: H. Sakurai, H. Sugiyama, M. Kira, *J. Phys. Chem.* **1990**, *94*, 1837, and references cited therein.