

Synthesis and Structures of New Silaanthracenophanes

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Received October 6, 2011, Accepted November 22, 2011

A new series of silaanthracenophanes **2-5** composed of 1,8-diethynylanthracene unit has been synthesized from silylation reactions of 1,8-di(lithioethynyl)anthracene with 1,3-dichloro-1,1,3,3-tetraalkyldisiloxanes and 1,2-dichlorotetramethyldisilane. The silaanthracenophane products **2-4** were characterized by spectroscopic methods and X-ray crystallographic analysis.

Key Words : Silaanthracenophanes, 1,8-Diethynylanthracene, Silylation, σ - π conjugations

Introduction

Many papers concerning the synthesis and their unique optical and electric properties of aromatic π -electron systems linked by an organosilicon unit $-(\text{SiR}_2)_n-$ have been reported.¹ The synthesis and properties of an alternating arrangement of a organosilicon unit and a π -electron system such as 9,10-diethynylanthrylene had been investigated.² From these reactions, the linear polymer composed of alternating 9,10-diethynylanthracene and organosilicon unit as a major product and the anthracenophanes as a minor product were afforded.^{2b} The optical properties of this alternating polymer containing 9,10-diethynylanthracenyl-ene and dialkyl- or diarylsilanyl-ene unit were affected through σ - π conjugation³ between diethynylanthracene and organosilicon unit in the backbone. Synthesis and structures of silacyclophanes with two disilanyl pillars and siloxane-bridge have been recently reported.⁴ However, the properties of silaanthracenophanes having 1,8-diethynylanthracene and organosilicon moieties have not been studied. If there are the substituents in 1- and 8-positions of anthracene (1,8-platinum-,⁵⁻⁷ 1,8-diethynyl-functionalized⁸ and 1,8-anthracene-based amine receptor⁹), these can be used as a optical sensor for metals and anions. It is of interest to us to examine synthesis and structure of new silaanthracenophanes having 1,8-diethynylanthracene and organosilicon moieties. In this paper, we report synthesis, optical properties and crystal structures of the silaanthracenophanes **2-5**.

Experimental Section

Materials. 1,8-Dichloroanthraquinone, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane, 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, 1,2-dichlorotetramethyldisilane, zinc, trimethylsilyl acetylene, ethylmagnesium bromide (2.0 M in THF) and *n*-BuLi (2.5 M in hexane) were obtained from Aldrich

Chemical Company and used without further purification. 1,8-Diethynylanthracene was prepared as reported in the literature.^{10,11} THF was distilled from sodium/benzophenone before use. All reactions were performed under a nitrogen atmosphere using standard techniques.

General Procedure. The progress of reaction was checked by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% methylphenylsilicone, 25 m) and thin layer chromatography. The final products were separated by a column chromatography using silica gel. All NMR spectra were recorded on a Bruker Avance 400 and a Varian 500 spectrometer. Chemical shifts were given as a δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as internal standard. Silicon chemical shifts are referenced to the signal of TMS. Mass spectra were measured on a Shimadzu QP5000 instrument. Elemental analysis were measured on FISOONS, EA1106 and melting points were measured with a Laboratory Devices-MEL-TEMP apparatus. UV-visible absorption spectra of the products in THF were measured on Jasco V-530 spectrophotometer and emission spectra were obtained by Jasco FP-6500 spectrofluorimeter.

X-ray Structure Determination. Data were collected on a STOE STADI4^{12a} four-circle diffractometer (**3** and **4**) and SMART CCD (**2**)^{12b} using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) by the 2θ - ω scans technique at 298(2) K (**3** and **4**) and ϕ - ω scans technique at 173(2) K (**2**). In each case, unit cell parameters were determined by a least-squares fit of 4237 (**2**), 22 (**3**) and 24 reflections (**4**) having 2θ values in the ranges of 2.37-27.21 (**2**), 19.0-21.0 (**3**) and 19.0-21.0 (**4**). A multi-scan absorption correction (SADABS)^{12c} for **2** and numerical absorption correction (X-SHAPE)^{12a} for **3** were made, and the transmission factors were 0.354/0.576 and 0.9810/0.9810 for **2** and **3**, respectively. Compound **4** was not applied. The structures were

solved by direct methods¹³ and refined on F^2 by full-matrix least-squares procedures.¹⁴ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model but were not refined. The data collection and structure solution parameters are given in Table 5, together with the standard discrepancy indices R and R_w .

1,8-Diethynylanthracene (1). Starting compounds, 1,8-dichloroanthracene and 1,8-bis(trimethylsilylethynyl)anthracene were prepared as described previously.^{10,11} Crude of 1,8-bis(trimethylsilylethynyl)anthracene above was treated with KOH/EtOH and then refluxed at 80 °C. The 1,8-diethynylanthracene (**1**) was identified by NMR spectroscopies. The spectral data of **1** are identical with the previously reported values.¹¹

Reactions of 1 with 1,3-Dichlorotetraalkyldisiloxanes. In a 50 mL two-necked round flask was charged with 1,8-diethynylanthracene (**1**, 0.50 g, 2.2 mmol) and THF (20 mL). To this was added 2.2 equiv of *n*-butyllithium solution (2.5 M solution in hexane) (1.9 mL, 4.8 mmol) at -78 °C. The resulting mixture was warmed to 0 °C. 1,3-Dichloro-1,1,3,3-tetra(*iso*-propyl)disiloxane (0.9 mL, 2.8 mmol) was added to the mixture and stirred for 2 h at 0 °C. The mixture was then hydrolyzed with water. The aqueous solution was extracted with methylene chloride and the organic layer was dried over CaCl₂. The solvent was evaporated by rotary evaporator. The resulting mixture was purified by column chromatography (silica gel, hexane:ethyl acetate = 8:1) and crystallized from the mixture of methylene chloride and ethanol to afford the siloxane-bridged¹⁵ silaanthracenophane **2** (0.36 g, 35% yield). Data for 3,3,5,5-tetra(*iso*-propyl)-4-oxa-3,5-disila[7](1,8)anthracenophane-1,6-diyne (**2**): pale yellow solids; mp 155-156 °C; MS m/z 468 (M^+); UV (λ_{max} , THF, $M^{-1}cm^{-1}$): 260 ($\epsilon = 98374$), 367 (68027), 387 (13578), 410 (13959); Emission (λ_{max} , THF): 412, 438, 467, 497; ¹H NMR (δ in CDCl₃): 1.14 (s, 28H), 7.42 (dd, 2H, $J = 6.9$ Hz, 8.7 Hz), 7.64 (d, 2H, $J = 6.9$ Hz), 7.99 (d, 2H, $J = 8.7$ Hz), 8.40 (s, 1H), 9.94 (s, 1H); ¹³C NMR (δ in CDCl₃): 14.06, 17.18, 99.57, 104.61, 121.59, 125.17, 126.19, 126.38, 127.50, 128.99, 131.31, 132.22; ²⁹Si NMR (δ in CDCl₃): -11.67; Anal. Calcd for C₃₀H₃₆OSi₂: C, 76.86; H, 7.74. Found: C, 76.78; H, 7.80.

The silylation reaction of **1** with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane under the same as above conditions afforded **3** (0.33 g, 42% yield). Data for 3,3,5,5-tetramethyl-4-oxa-3,5-disila[7](1,8)anthracenophane-1,6-diyne (**3**): pale yellow solids; mp 221-222 °C; MS m/z 356 (M^+); UV (λ_{max} , THF, $M^{-1}cm^{-1}$): 261 ($\epsilon = 99662$), 352 (3627), 368 (6040), 388 (10201), 408 (10470); Emission (λ_{max} , THF): 410, 437, 465, 497; ¹H NMR (δ in CDCl₃) δ 0.43 (s, 12H), 7.44 (dd, 2H, $J = 7.0$ Hz, 8.52), 7.64 (d, 2H, $J = 7.0$ Hz), 8.02 (d, 2H, $J = 8.52$ Hz), 8.42 (s, 1H), 9.93 (s, 1H); ¹³C NMR (δ in CDCl₃) δ 2.33, 101.88, 102.85, 121.19, 125.16, 125.90, 126.56, 127.76, 129.20, 131.26, 132.05; ²⁹Si NMR (δ in CDCl₃) δ -18.55; Anal. Calcd for C₂₂H₂₀OSi₂: C, 74.11; H, 5.65. Found: C, 74.14; H, 5.64.

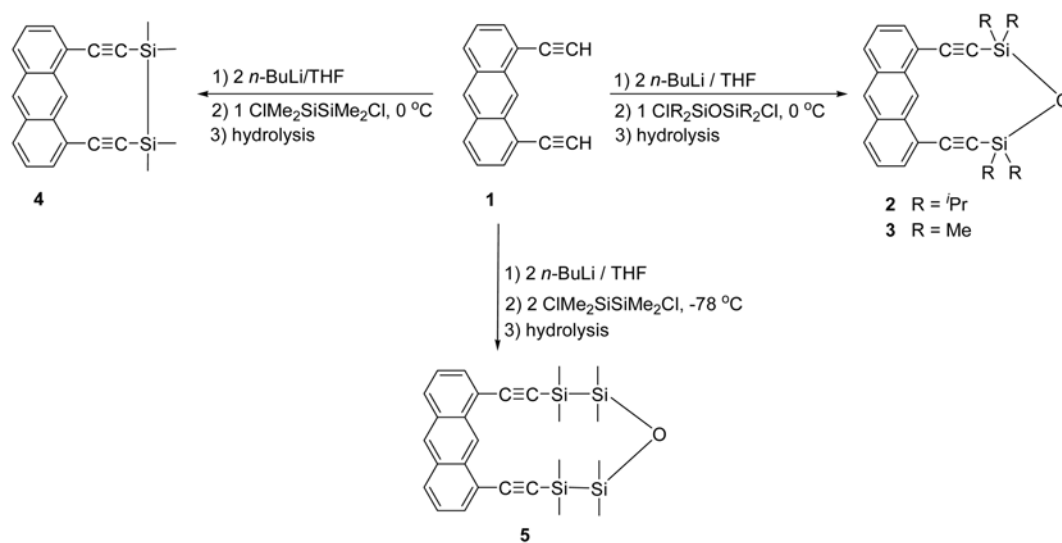
Reactions of 1 with 1,2-Dichlorotetramethyldisilane.

The silylation reaction of **1** with 1,2-dichlorotetramethyldisilane was carried out under the same as above conditions. The mixture was then hydrolyzed with water. The aqueous solution was extracted with methylene chloride and the organic layer was dried over CaCl₂. The solvent was evaporated by rotary evaporator. The resulting mixture was purified by column chromatography (silica gel, hexane:ethyl acetate = 8:1) and crystallized from the mixture of methylene chloride and ethanol to afford **4** (0.23 g, 31% yield) and a trace amount of **5**. The crystal **4** was included *n*-hexane during the purification process. Data for 3,3,4,4-tetramethyl-3,4-disila[6](1,8)anthracenophane-1,5-diyne (**4**): pale yellow solids; mp 197-199 °C; MS m/z 340 (M^+); UV (λ_{max} , THF, $M^{-1}cm^{-1}$): 264 ($\epsilon = 80103$), 354 (4375), 370 (6710), 390 (11148), 412 (11421); Emission (λ_{max} , THF): 414, 440, 469, 502; ¹H NMR (δ in CDCl₃) δ 0.46 (s, 12H), 7.44 (dd, 2H, $J = 7.0$ Hz, 8.56 Hz), 7.61 (d, 2H, $J = 7.0$ Hz), 8.01 (d, 2H, $J = 8.56$ Hz), 8.40 (s, 1H), 10.24 (s, 1H); ¹³C NMR (δ in CDCl₃) δ -1.96, 103.55, 107.00, 122.16, 125.39, 126.16, 126.61, 127.42, 129.01, 131.18, 131.72; ²⁹Si NMR (δ in CDCl₃) δ -34.75; Anal. Calcd for C_{23.50}H_{23.50}Si₂: C, 77.95; H, 6.54. Found: C, 77.86; H, 6.50.

The silaanthracenophane **5** from the reaction of **1** with 1,2-dichlorotetramethyldisilane was prepared as follows. In a 50 mL two-necked round flask was charged with 1,8-diethynylanthracene (**1**, 0.50 g, 2.2 mmol) and THF (20 mL). To this was added 2.2 equiv of *n*-butyllithium solution (2.5 M solution in hexane) (1.9 mL, 4.8 mmol) at -78 °C. After the resulting mixture was stirred for 2 h at room temperature, 1,2-dichlorotetramethyldisilane (0.9 mL, 4.8 mmol) was added slowly to the mixture for 1 h by a syringe pump at -78 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 12 h. The mixture was then hydrolyzed with water. The aqueous solution was extracted with methylene chloride and the organic layer was dried over CaCl₂. The resulting mixture was purified by column chromatography (silica gel, petroleum ether:methylene chloride = 10:1) to afford **5** (0.42 g, 40% yield). Data for 3,3,4,4,6,6,7,7-octamethyl-5-oxa-3,4,6,7-tetrasila[9](1,8)anthracenophane-1,8-diyne (**5**): yellow solids; mp 143-144 °C. MS m/z 472 (M^+). UV (λ_{max} , THF, $M^{-1}cm^{-1}$): 266 ($\epsilon = 38505$), 354 (3500), 372 (7300), 392 (12800), 414 (12400). Emission (λ_{max} , THF): 420, 445, 474, 505; ¹H NMR (δ in CDCl₃) 0.36 (s, 12H), 0.39 (s, 12H), 7.40 (dd, 2H, $J = 7.0$, 8.54 Hz), 7.76 (d, 2H, $J = 7.0$ Hz), 7.96 (d, 2H, $J = 8.56$ Hz), 8.40 (s, 1H), 9.40 (s, 1H). ¹³C NMR (δ in CDCl₃) -2.69, 2.14, 98.67, 105.12, 121.65, 124.01, 124.95, 127.53, 128.99, 131.39, 131.43, 132.01. ²⁹Si NMR (δ in CDCl₃) -45.55, -45.07. Anal. Calcd for C₂₆H₃₂OSi₄: C, 66.04; H, 6.82. Found: C, 66.08; H, 6.90.

Results and Discussion

Synthesis and Characterization. For the synthesis of new type of silaanthracenophanes, the starting material of 1,8-diethynylanthracene (**1**) was prepared as described pre-



Scheme 1

viously.^{10,11} As shown in the synthetic routes of silaanthracenophanes (Scheme 1), all preparations of the products **2-5** were carried out under the similar reaction conditions. 1,8-Diethynylantracene (**1**) was readily lithiated by treating with *n*-BuLi in hexane producing 1,8-di(lithioethynyl)anthracene, which was then treated with 1,3-dichloro-1,1,3,3-tetraisopropylidisiloxane, 1,3-dichloro-1,1,3,3-tetramethylidisiloxane and 1,2-dichlorotetramethylsilane, respectively. It was observed that the reaction of 1,8-di(lithioethynyl)anthracene and 2.2 equivalents of 1,2-dichlorotetramethylsilane for 1 h by syringe pump at -78 °C afforded the siloxane-bridged product **5** through the hydrolysis of bis(chlorotetramethylsilyl) group of the intermediate. Unfortunately, several trials of crystallization of **5** were unsuccessful. The yields of silaanthracenophane products were moderate (Table 1). These products are highly soluble in common organic solvents (ether, toluene, THF, CHCl_3 etc.).

The structures of silaanthracenophanes **2-5** were identified through ^1H , ^{13}C and ^{29}Si NMR spectroscopy, mass spectra and elemental analysis. The ^1H NMR signals of the products appear in the normal range for alkyl protons of silyl groups

Table 1. Characterization and NMR data of silaanthracenophanes **2-5**

| Compound | Yield (%) ^a | mp (°C) | NMR (ppm) ^c | | |
|----------|------------------------|---------|------------------------|------------------|-----------------------------|
| | | | ^{29}Si | ^1H | |
| | | | | SiR ₂ | H ₉ ^d |
| 1 | 85 ^b | | - | - | 9.42 |
| 2 | 35 | 155-156 | -11.67 | 1.14 | 9.94 |
| 3 | 42 | 221-222 | -18.55 | 0.43 | 9.93 |
| 4 | 31 | 197-199 | -34.75 | 0.46 | 10.24 |
| 5 | 40 | 143-144 | -45.55, -45.07 | 0.36, 0.39 | 9.40 |

^aIsolated yields. ^boverall yield from 1,8-dichloroanthracene [Ref. (11)]. ^cTMS reference in CDCl_3 . ^dThe proton of 9-position of anthracenylene moiety.

and anthracenylene ring protons. Particularly, the proton of 9-position of anthracenylene moiety of a rigid silaanthracenophane **4** is shifted to more downfield at 10.24 ppm than that of flexible silaanthracenophanes **2** and **3** at 9.94 and 9.93 ppm, respectively in Table 1. This is because the H₉ of **4** is closer to the deshielding region of the triple bond as a π electron functional group.¹⁶ Distances between ethynyl group and H₉ atom of anthracenylene moiety of the crystal silaanthracenophanes **2-4** are given in Table 2.

The UV absorption and emission maxima of **2-5** are summarized in Table 3. The spectra of UV and emission of the products are quite similar, due to contain a same backbone of 1,8-diethynylantracene. UV absorption and emission maxima of **4** are slightly red-shifted than those of **2** and **3**. This is due to weak σ - π conjugation between the Si-Si σ -bond and the aromatic π -system of 1,8-diethynylantracenylene moiety in the silaanthracenophane **4**. The UV absorption maxima of **5** is slightly red-shifted than those of **2** and **3**. The increased σ conjugation length in silaanthraceno-

Table 2. Distances between ethynyl group and H₉ atom of anthracenylene moiety of **2-4**

| Compound | 2 | 3 | 4_A | 4_B |
|---------------------------|------------|------------|----------------------|----------------------|
| Distance (Å) ^a | 2.53, 2.54 | 2.56, 2.57 | 2.43, 2.43 | 2.44, 2.42 |

^aMeasurement from X-ray crystal analysis.

Table 3. Optical properties of the silaanthracenophanes **2-5**

| Compound | λ_{max} (nm) ^a | |
|----------|--|---------------------------------|
| | Absorption | Emission |
| | 2 | 260, 367, 387, 410 |
| 3 | 261, 352, 368, 388, 408 | 410, 437, 465, 497 |
| 4 | 264, 354(<i>sh</i>), 370, 390, 412 | 414, 440, 469, 502 |
| 5 | 266, 354, 372, 392, 414 | 420, 445, 474, 505(<i>sh</i>) |

^aMeasured in 10^{-5} M THF solution.

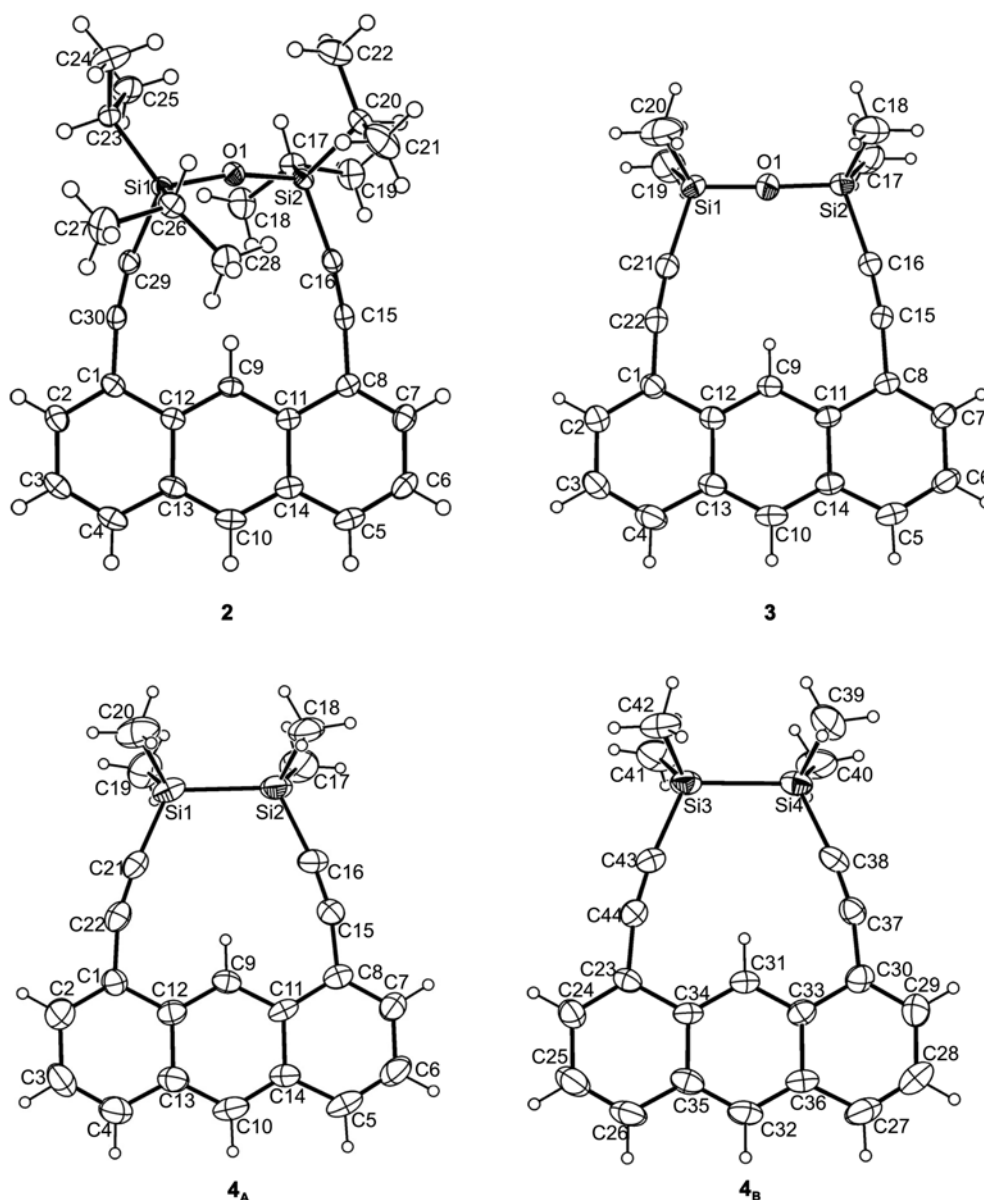


Figure 1. ORTEP diagrams for **2**, **3**, and **4** showing thermal ellipsoids at the 30% level.

phane **5** results in slight bathochromic shift in the UV spectrum of **5** when compared with those of **2** and **3**.^{2b,4a,15b,17}

The silylation reactions of 1,8-di(lithioethynyl)anthracene with dichlorodisiloxanes or dichlorodisilane allowed the connection of one 1,8-diethynylanthracene with one disiloxane or one disilane to afford siloxane-bridged anthracenophanes **2-3** or disilane-bridged anthracenophane **4**. The crystal structures of compound **2**, **3** and **4** were determined by X-ray single crystal diffraction studies. ORTEP diagrams for **2-4** are depicted in Figure 1. The crystal **4** were composed of a mixture of hexane which is from the purification by silica gel column chromatography (eluent: hexane/ethyl acetate). There are two symmetry independent molecules, **4_A** and **4_B** in the asymmetric unit.

Selected bond lengths and angles of the silanthracenophanes **2-4** are given in Table 4, and crystal data and struc-

ture refinement for **2-4** are given in Table 5, respectively.

Their structures of **4_A** and **4_B** are the same but have slightly different bond lengths and bond angles. In the compound with disilanyl group (**4**), the length of the Si-Si bond was 2.38 Å and was in the range of normal Si-Si bonds.¹⁸ The length of the C_{sp}-Si bonds of **2-4** were not affected by the presence of the disilanyl or disiloxane linkage and were in the range of 1.84-1.85 Å. In the compound with disiloxane linkage **2** and **3**, the length of the Si-O bonds were determined to be 1.63 and 1.61 Å and were in the range of normal Si-O bonds.¹⁹ The Si-O-Si bond angles of **2** and **3** were observed to be 166.57° and 177.0(3)° and were significant deviation from the normal Si-O-Si bond angles of hexamethyldisiloxane,¹⁹ six-membered cyclosiloxane²⁰ and siloxane-tethered cyclophane.^{15b} The Si-O-Si bond of **2** was more bent than that of **3**. In the case of tetramethyl-

Table 4. Selected bond lengths (Å) and angles (°) for **2-4**

| | 2 | 3 | 4_A | 4_B |
|---|------------------------|------------------------|----------------------|----------------------|
| <i>Bond lengths</i> | | | | |
| Si-Si | | | 2.378(5) | 2.380(4) |
| Si-O | 1.6268(14), 1.6260(14) | 1.606(3), 1.613(3) | | |
| C _{sp} -C _{sp} | 1.207(3), 1.209(3) | 1.204(6), 1.198(5) | 1.212(11), 1.198(11) | 1.187(11), 1.199(11) |
| Si-C _{sp} | 1.841(2), 1.844(2) | 1.839(5), 1.842(4) | 1.845(10), 1.848(9) | 1.851(10), 1.851(10) |
| <i>Bond angles</i> | | | | |
| Si-Si-C _{sp} | | | 114.8(3), 114.3(3) | 115.0(3), 114.1(3) |
| Si-O-Si | 166.56(9) | 177.0(3) | | |
| Si-C _{sp} -C _{sp} | 172.19(17), 161.76(17) | 172.4(4), 171.3(4) | 174.0(8), 173.0(9) | 173.3(9), 173.0(8) |
| O-Si-C _{sp} | 108.44(8), 109.62(8) | 107.42(19), 107.27(18) | | |
| C _{sp} -C _{sp} -C _{Ar} | 170.9(2), 169.1(2) | 171.1(5), 171.5(4) | 164.5(10), 167.1(10) | 166.5(10), 168.0(10) |

Table 5. Crystal data and structure refinement for **2-4**

| | 2 | 3 | 4 |
|--|--|--|--|
| Empirical formula | C ₃₀ H ₃₆ OSi ₂ | C ₂₂ H ₂₀ OSi ₂ | C ₂₂ H ₂₀ Si ₂ , 0.5(C ₆ H ₁₄) |
| Formula weight | 468.77 | 356.56 | 362.10 |
| Temperature (K) | 298(2) | 298(2) | 298(2) |
| Wavelength (Å) | 0.71069 | 0.71069 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 1 | <i>P</i> 1 |
| Unit cell dimensions | a = 18.5143(7) Å b = 8.8846(3) Å c = 17.4837(7) Å α = 90.00° β = 112.558(1)° γ = 90.00° | a = 8.663(1) Å b = 9.385(2) Å c = 12.649(2) Å α = 76.59(2)° β = 81.24(2)° γ = 84.77(2)° | a = 11.469(2) Å b = 14.384(3) Å c = 14.784(3) Å α = 98.12(3)° β = 108.65(3)° γ = 106.82(3)° |
| Volume (Å ³) | 2655.90(17) | 987.0(3) | 2137.2(11) |
| Z | 4 | 2 | 4 |
| Density (Mg/m ³ , calcd) | 1.172 | 1.200 | 1.125 |
| Absorption coefficient (mm ⁻¹) | 0.154 | 0.186 | 0.169 |
| Reflections collected/unique | 15848 / 5795 [R(int) = 0.0587] | 4519 / 2371 | 7475 / 2886 |
| Goodness-of-fit on F ² | 1.044 | 1.122 | 1.198 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0435, wR ₂ = 0.1167 | R ₁ = 0.0830, wR ₂ = 0.1665 | R ₁ = 0.1231, wR ₂ = 0.2332 |

disiloxane-bridged anthracenophane **3**, the bond angles of Si-C_{sp}-C_{sp} (Si-C≡C bond) are 171.3(4) and 172.4(4), respectively. On the other hand, the bond angles of Si-C_{sp}-C_{sp} of tetra(*iso*-propyl)disiloxane-bridged **2** are 161.8 (2) and 172.2 (2), respectively. One of Si-C_{sp}-C_{sp} bonds of **2** was more bent than those of **3**. The torsion angle of C_{sp}-Si-Si-C_{sp} of **4_A** was observed to be 1.2(5)°. The geometry of the C_{sp}-Si₁ and C_{sp}-Si₂ bonds of **4_A** can be in almost syn periplanar geometry.

Conclusion

The silylations of 1,8-di(lithioethynyl)anthracene with 1,3-dichloro-1,1,3,3,-tetra(*iso*-propyl)disiloxane, 1,3-dichloro-1,1,3,3,-tetramethyldisiloxane and 1,2-dichlorotetra-methyldisilane allowed the connection of one diethynyl-anthracene ring with one disiloxane or one disilane to afford siloxane-bridged **2-3** or disilane-bridged silanthraceno-

phane **4**. The siloxane-bridged **5** in the ratio of one diethynylanthracenylene moiety to two of disilanylene moiety was also afforded at -78 °C. The UV absorption maxima of **5** is slightly red-shifted when compared with those of **2-4**. The increased conjugation length in anthracenophane skeleton **5** containing two disilanylene moieties results in bathochromic shift in the UV spectrum of **5**. The crystal structures of compound **2-4** were determined by X-ray single crystal diffraction studies. The torsion angle of C_{sp}-Si-Si-C_{sp} of **4_A** was observed to be 1.2(5)°. The geometry of the C_{sp}-Si₁ and C_{sp}-Si₂ bonds of **4_A** was found to be in almost syn periplanar geometry.

Supplementary Material. Crystallographic data have been registered at the Cambridge Crystallographic Data Center (CCDC), CCDC Nos. 841922 (**2**), 841923 (**3**) and 841924 (**4**). Copies of these informations may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-003; E-

mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments. This research was supported by Kyungpook National University Research Fund, 2008.

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