

# Synthesis and Electronic Properties of 9,10-Disilylanthracenes

Soichiro Kyushin,<sup>†</sup> Masanobu Ikarugi,<sup>†</sup> Midori Goto,<sup>‡</sup> Hiroshi Hiratsuka,<sup>†</sup> and Hideyuki Matsumoto<sup>\*,†</sup>

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan, and National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

Received October 2, 1995<sup>®</sup>

**Summary:** The sila-functional 9,10-disilylanthracenes  $An(SiR_2X)_2$  (**1**,  $R = i\text{-Pr}$ ,  $X = H$ ; **2**,  $R = i\text{-Pr}$ ,  $X = Cl$ ; **3**,  $R = Me$ ,  $X = H$ ) were synthesized, and the X-ray structure is reported for **1**. Compounds **1–3** as well as the related compound  $An(SiMe_3)_2$  exhibit intense fluorescence ( $\Phi_f > 0.9$ ) at room temperature.

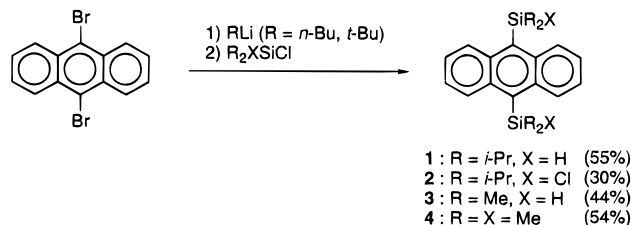
## Introduction

The electronic effect of silicon on benzene  $\pi$  systems has been the subject of considerable interest.<sup>1</sup> As part of our study on the perturbation of the  $\pi$  systems of aromatic compounds, we recently reported the syntheses of *cis*-dibenzo[*c,h*]-1,6-dialkyl-1,6-disilabicyclo[4.4.0]-deca-3,8-dienes<sup>2</sup> and dibenzo[*b,e*]-7,7,8,8-tetraalkyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes.<sup>3</sup> These compounds have some unique properties (e.g., formation of stable charge-transfer complexes with tetracyanoethylene) arising from strong  $\sigma$ - $\pi$  interaction.<sup>2,3</sup> We have now been interested in 9,10-disilylanthracene from the viewpoint of how silyl substituents at the 9- and 10-positions perturb the electronic properties of the anthracene  $\pi$  system. Prior to our work, several reports have appeared in the literature concerning 9,10-disilylanthracene.<sup>4–6</sup> However, much of the scientific interest in these reports has centered around the synthesis and structure of 9,10-bis(trimethylsilyl)anthracene (**4**)<sup>4</sup> except for one case. Thus, Shea and co-workers have reported the synthesis and the fluorescence spectrum of 9,10-bis(triethoxysilyl)anthracene.<sup>6</sup> However, in this example, the electronic absorption spectrum, the fluo-

rescence quantum yield, and the fluorescence lifetime of this particular compound were not given. In this work, sila-functional 9,10-disilylanthracenes  $An(SiR_2X)_2$  (**1**,  $R = i\text{-Pr}$ ,  $X = H$ ; **2**,  $R = i\text{-Pr}$ ,  $X = Cl$ ; **3**,  $R = Me$ ,  $X = H$ ) were synthesized. We present here the following new information: (1) the X-ray structure of **1**; (2) the unusual electronic absorption and emission spectra of **1–3** as well as a related compound **4**. A preliminary result of this work has been reported.<sup>7</sup>

## Results and Discussion

**Synthesis of  $An(SiR_2X)_2$ .** 9,10-Disilylanthracenes (**1–4**) were prepared by a modification of Raston's method.<sup>4e,6</sup> Thus, lithiation of 9,10-dibromoanthracene with butyllithium or *tert*-butyllithium followed by treatment with chlorosilanes gave 9,10-disilylanthracenes (**1–4**) in moderate yields.<sup>8</sup> By this method, 9,10-disilylanthracenes with bulky substituents such as **1** and **2** could be readily obtained.



**Crystal Structure of **1**.** In Figure 1, the molecular structure of **1** determined by X-ray crystallography is shown. Crystallographic data and selected bond distances and angles are given in Tables 1 and 2. The molecule has a symmetry center, and the anthracene ring is planar. The bond distances of the anthracene ring of **1** are quite similar to those of anthracene,<sup>9</sup> while bond angles of the anthracene ring of **1** deviate to some extent from those of anthracene; the C(2)–C(1)–C(5) (117.8(3)°), C(3)–C(2)–C(5') (117.8(4)°), and C(6)–C(5)–C(2') (117.0(4)°) bond angles are relatively small, and the C(2)–C(3)–C(4) (122.4(4)°), C(1)–C(5)–C(2') (122.0(4)°), and C(5)–C(6)–C(7) (123.1(4)°) bond angles are relatively large. The silicon atoms and the hydrogen atoms bound to the silicon atoms exist in the anthracene plane. The Si–C(isopropyl) bonds are oriented out of

(7) Ikarugi, M.; Kyushin, S.; Matsumoto, H.; Goto, M. Presented at the 67th Annual Meeting of the Chemical Society of Japan, Tokyo, 1994; Abstracts I, p 352.

(8) It has been reported that addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) is essential to the synthesis of **3**.<sup>20</sup> However, we could obtain **1–4** with butyllithium in diethyl ether or *tert*-butyllithium in THF without using TMEDA.

(9) (a) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 470. (b) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547.

<sup>†</sup> Gunma University.

<sup>‡</sup> National Institute of Materials and Chemical Research.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1995.

(1) For reviews, see: (a) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. (b) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627. (c) Bock, H.; Solouki, B. *Chem. Rev.* **1995**, *95*, 1161.

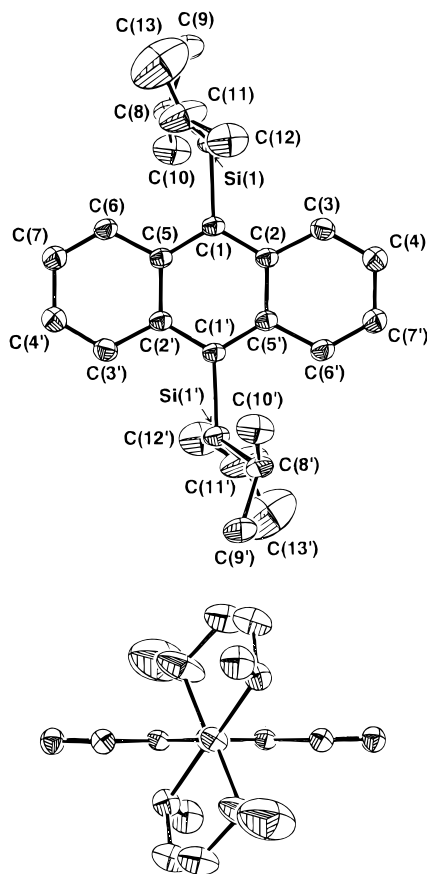
(2) (a) Kyushin, S.; Izumi, Y.; Tsunakawa, S.; Matsumoto, H. *Chem. Lett.* **1992**, 1393. (b) Kyushin, S.; Ikarugi, M.; Tsunakawa, S.; Izumi, Y.; Miyake, M.; Sato, M.; Matsumoto, H.; Goto, M. *J. Organomet. Chem.* **1994**, *473*, 19.

(3) (a) Matsumoto, H.; Arai, T.; Watanabe, H.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 724. (b) Kyushin, S.; Ikarugi, M.; Takatsuna, K.; Goto, M.; Matsumoto, H. *J. Organomet. Chem.*, in press.

(4) (a) Cho, H.; Harvey, R. G. *J. Org. Chem.* **1975**, *40*, 3097. (b) Roberts, R. M. G. *J. Organomet. Chem.* **1976**, *110*, 281. (c) Lehmkühl, H.; Mehler, K.; Benn, R.; Ruffińska, A.; Schroth, G.; Krüger, C. *Chem. Ber.* **1984**, *117*, 389. (d) Lehmkühl, H.; Shakoov, A.; Mehler, K.; Krüger, C.; Angermund, K.; Tsay, Y.-H. *Chem. Ber.* **1985**, *118*, 4239. (e) Alonso, T.; Harvey, S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* **1987**, *6*, 2110.

(5) Although Suzuki and co-workers have quite recently reported that the copolymers of 9,10-bis(chloromethylpropylsilyl)anthracene and dichloromethylphenylsilane have strong emission properties, the structure and the emission properties of the monomer 9,10-bis(chloromethylpropylsilyl)anthracene itself have not been described. See: Suzuki, H.; Satoh, S.; Kimata, Y.; Kuriyama, A. *Chem. Lett.* **1995**, 451.

(6) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.



**Figure 1.** Top view (top) and side view (bottom) of the molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level.

the anthracene plane with the dihedral angles between the Si–C bond and the anthracene plane of  $56.2^\circ$  (Si(1)–C(8)) and  $70.1^\circ$  (Si(1)–C(11)). The planar structure of the anthracene ring of **1** is in contrast with the folded anthracene ring of **4** with the fold angle of  $14^\circ$ .<sup>4d</sup> The planar and folded structures do not seem to be determined by steric hindrance of silyl groups but by the symmetry of the silyl groups. In the case of **1**, the planar structure may be attributed to the diisopropylsilyl groups' almost symmetrical orientation on both sides of the anthracene plane, while the trimethylsilyl groups of **4** are not symmetrical on both sides of the anthracene plane.

**Electronic Absorption and Emission Spectra of 1–4.** In Figure 2, UV/vis spectra of **1–4** are shown together with that of anthracene. Intense absorption bands with a fine structure appear in the region of ca. 300–450 nm. The UV/vis absorption of **1–4** may arise from the transitions similar to that of anthracene ( $^1L_a \leftarrow ^1A$ ), but there are significant differences. The absorption maxima of the longest wavelength (**1**, 399 nm ( $\epsilon$  14 200); **2**, 413 nm ( $\epsilon$  11 200); **3**, 398 nm ( $\epsilon$  10 900); **4**, 401 nm ( $\epsilon$  9900)) show a bathochromic shift and increase of extinction coefficients compared with that of anthracene (374 nm ( $\epsilon$  8000)). The bathochromic shift observed is explained by the destabilization of the HOMO by silyl groups at the 9- and 10-positions.<sup>10</sup> Furthermore, the LUMO may be stabilized by the  $\sigma^*$ –

**Table 1.** Summary of Crystal Data, Data Collection, and Refinement for **1**

Crystal Data	
formula	C <sub>26</sub> H <sub>38</sub> Si <sub>2</sub>
<i>M<sub>r</sub></i>	406.76
cryst description	pale yellow plates
cryst size, mm	0.4 × 0.53 × 0.05
cryst system	monoclinic
space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> , Å	11.816(1)
<i>b</i> , Å	8.2382(3)
<i>c</i> , Å	12.801(2)
$\beta$ , deg	96.747(5)
<i>V</i> , Å <sup>3</sup>	1237.4(2)
<i>Z</i>	2
<i>D</i> <sub>measd</sub> , g cm <sup>-3</sup>	1.098
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.092
Data Collection	
diffractometer	Enraf-Nonius CAD-4
radiation ( $\lambda$ , Å)	Cu K $\alpha$ (1.5418)
$\mu$ , cm <sup>-1</sup>	14.33
abs corr	none
variation of stds	none
2 $\theta$ range, deg	6–130
range of <i>h</i>	0 to 13
range of <i>k</i>	0 to 9
range of <i>l</i>	–15 to 15
scan type	$\omega$ –2 $\theta$
scan width, deg	1.0 + 0.3 tan $\theta$
no. of reflcns measd	2186
no. of indepdt reflcns	1984
no. of obsd reflcns ( $ F_o  \geq 3\sigma(F_o)$ )	1369
Refinement	
<i>R</i>	0.060
<i>R<sub>w</sub></i>	0.061
weighting scheme	$w = 1/\sigma^2(F_o)$
<i>S</i>	0.971
( $\Delta/\sigma$ ) <sub>max</sub>	0.740
( $\Delta\rho$ ) <sub>max</sub> , e Å <sup>-3</sup>	0.3
( $\Delta\rho$ ) <sub>min</sub> , e Å <sup>-3</sup>	–0.31
no. of params	127

**Table 2.** Bond Distances (Å) and Angles (deg) for **1**<sup>a</sup>

Bond Distances			
Si(1)–C(1)	1.906(4)	C(4)–C(7)	1.412(6)
Si(1)–C(8)	1.880(5)	C(5)–C(6)	1.445(6)
Si(1)–C(11)	1.903(8)	C(6)–C(7)	1.355(7)
C(1)–C(2)	1.413(6)	C(8)–C(9)	1.545(7)
C(1)–C(5)	1.404(6)	C(8)–C(10)	1.532(8)
C(2)–C(3)	1.435(6)	C(11)–C(12)	1.582(9)
C(2)–C(5)	1.443(5)	C(11)–C(13)	1.318(12)
C(3)–C(4)	1.372(7)		
Bond Angles			
C(1)–Si(1)–C(8)	113.4(2)	C(1)–C(5)–C(6)	121.0(3)
C(1)–Si(1)–C(11)	108.5(2)	C(1)–C(5)–C(2)	122.0(4)
C(8)–Si(1)–C(11)	113.0(3)	C(6)–C(5)–C(2)	117.0(4)
Si(1)–C(1)–C(2)	122.6(3)	C(5)–C(6)–C(7)	123.1(4)
Si(1)–C(1)–C(5)	119.6(3)	C(6)–C(7)–C(4)	119.8(4)
C(2)–C(1)–C(5)	117.8(3)	Si(1)–C(8)–C(10)	111.0(4)
C(1)–C(2)–C(3)	122.0(3)	Si(1)–C(8)–C(10)	112.1(3)
C(1)–C(2)–C(5)	120.2(4)	C(9)–C(8)–C(10)	110.0(4)
C(3)–C(2)–C(5)	117.8(4)	Si(1)–C(11)–C(12)	107.2(5)
C(2)–C(3)–C(4)	122.4(4)	Si(1)–C(11)–C(13)	121.5(7)
C(3)–C(4)–C(7)	119.9(4)	C(12)–C(11)–C(13)	119.0(7)

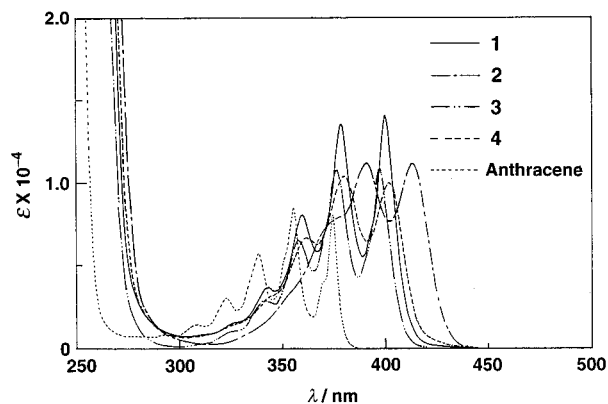
<sup>a</sup> Primed atoms are generated by the crystallographic symmetry operator  $-x, -y, -z$ .

$\pi^*$  interaction<sup>11</sup> between  $\sigma^*$  orbitals of Si–C(isopropyl) bonds and  $\pi^*$  orbitals of anthracene, which is effective in the coplanar structure of both orbitals (Figure 1). It is noted that the absorption bands of **2** shift significantly

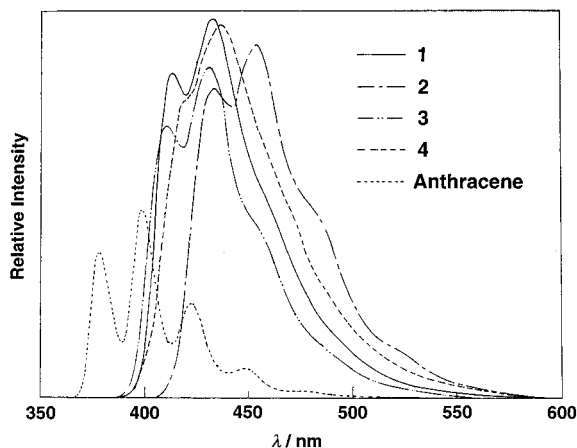
(10) The ionization potentials of 1,4-bis(trimethylsilyl)benzene (8.7 eV) and 1,4-bis(trimethylsilyl)naphthalene (7.85 eV) have been reported to be smaller than those of benzene (9.25 eV) and naphthalene (8.15 eV). See: Bock, H.; Solouki, B. Photoelectron Spectra of Silicon Compounds. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 9.

(11) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49.

(12) It has been reported that chlorine substitution on a silicon atom leads to a modest bathochromic shift in the UV spectrum of ClMeSi(Me<sub>2</sub>Si)<sub>2</sub>,<sup>21</sup> while in the case of *all-trans*-[(*t*-Bu)ClSi]<sub>4</sub>, a hypsochromic shift is observed.<sup>22</sup>



**Figure 2.** UV/vis spectra of **1–4** and anthracene in hexane at room temperature.



**Figure 3.** Fluorescence spectra of **1–4** and anthracene in cyclohexane at room temperature. The excitation wavelength is 355 nm.

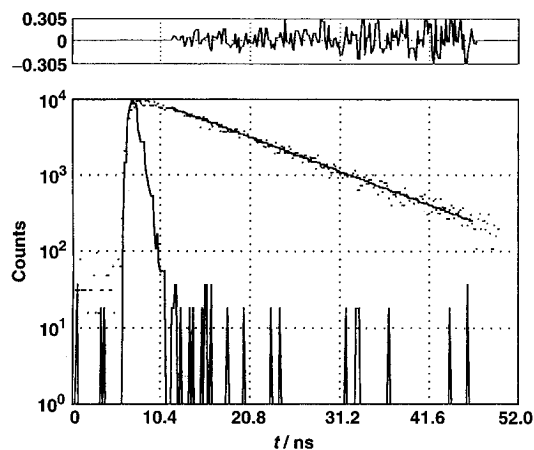
**Table 3. Photophysical Parameters of 1–4 and Anthracene in Cyclohexane at Room Temperature**

compd	$\lambda_{0-0}^a$ , nm	$\lambda_{0-0}^f$ , nm	$E_S$ , kJ mol <sup>-1</sup>	$\Phi_f$
<b>1</b>	400	416	299	0.90
<b>2</b>	416	433	288	0.92
<b>3</b>	398	411	301	0.97
<b>4</b>	402	420	298	0.95
anthracene	375	379	319	0.32

to a longer wavelength region than those of **1**, **3**, and **4**.<sup>12</sup> The bathochromic shift may be explained by the stabilization of the LUMO due to the electron-withdrawing chlorine atoms.

Compounds **1–4** show intense fluorescence as shown in Figure 3. The emission of the fluorescence occurs in the region of ca. 400–600 nm, and emission maxima of the shortest wavelength are 416 nm (**1**), 433 nm (**2**), 411 nm (**3**), and 420 nm (**4**). Since fluorescence of anthracene appears at ca. 370–500 nm with an emission maximum of the shortest wavelength at 379 nm, the fluorescence of 9,10-disilylanthracenes **1–4** shifts to a longer wavelength region than that of anthracene. In Table 3, several parameters of the fluorescence spectra are summarized. Fluorescence quantum yields of **1–4** are extremely high and nearly quantitative. The fluorescence quantum yields of **1–4** are far larger than that of anthracene ( $\Phi_f = 0.32$ ) and comparable to one of the strongest emitting species such as 9,10-diphenylanthracene ( $\Phi_f = 0.90$ ).<sup>13</sup> The intense fluorescence of **1–4** corresponds to the intense absorption in UV/vis spectra.

(13) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.



**Figure 4.** Fluorescence decay of **1** in cyclohexane at room temperature.

The fluorescence lifetime of **1** was measured with a picosecond fluorescence lifetime measurement system (Figure 4). The fluorescence lifetime of **1** ( $\tau_S = 10.0 \pm 0.5$  ns) can be compared with that of anthracene ( $\tau_S = 5.25$  ns).<sup>14</sup> By using these parameters, several kinetic parameters in the excited state can be calculated according to the following relations, where  $k_f$ ,  $k_{ic}$ , and  $k_{ST}$  represent the rate constants for fluorescence radiation, internal conversion, and intersystem crossing processes, respectively, and the internal conversion rate constant is known to be negligible in aromatic hydrocarbons:<sup>15</sup>

$$\Phi_f = k_f / (k_f + k_{ic} + k_{ST}) \approx k_f / (k_f + k_{ST})$$

$$\Phi_f = k_f \tau_S$$

From these equations, it is obvious that the fluorescence radiative rate constant ( $k_f$ ) of **1** is larger than that of anthracene, and the intersystem crossing rate constant ( $k_{ST}$ ) of **1** is far smaller than that of anthracene. Therefore, the mechanism for the highly efficient fluorescence emission from 9,10-disilylanthracenes is similar to that of 9,10-diphenylanthracene, in which the high fluorescence quantum yield is attributed mainly to inhibition of intersystem crossing to the triplet state as well as the relatively rapid fluorescence radiation.<sup>14</sup>

In summary, silyl groups at the 9- and 10-positions of anthracene perturb the  $\pi$  system of anthracene considerably, which causes unusual electronic properties in UV/vis and fluorescence spectra. Moreover, 9,10-disilylanthracenes are found to be one of the most efficient light-emitting organosilicon materials.

## Experimental Section

All reactions were carried out under an argon atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. 9,10-Dibromoanthracene was prepared by a published procedure.<sup>16</sup> Butyllithium in hexane (Aldrich) and *tert*-butyllithium in pentane (Aldrich and Kanto) were purchased. Chlorodiisopropylsilane and Dichlorodiisopropylsilane were obtained from Petrarch Systems, Inc., and chlorotrimethylsilane and chlorodimethylsilane were obtained

(14) Hirayama, S.; Lampert, R. A.; Phillips, D. J. *Chem. Soc., Faraday Trans. 2* **1985**, *81*, 371.

(15) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(16) Heilbron, I. M.; Heaton, J. S. *Org. Synth., Coll. Vol. 1* **1941**, 207.

from Toshiba Silicone Co., Ltd. These chlorosilanes were distilled before use.

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were obtained with a JEOL JNM-A500 spectrometer. IR spectra were recorded on a JASCO A-102 spectrometer. UV/vis spectra were obtained with a JASCO Ubest-50 spectrophotometer. Fluorescence spectra were obtained with a Hitachi M-850 spectrofluorometer. Fluorescence quantum yields were measured in comparison with that of 9,10-diphenylanthracene ( $\Phi_f = 0.90$ ).<sup>13</sup> The fluorescence decay time was measured with a picosecond fluorescence lifetime measurement system (Hamamatsu Photonics C4780) by use of a nitrogen laser (Laser Photonics LN120C2, pulse width 300 ps). Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. Elemental analyses were performed by the Institute of Physical and Chemical Research.

#### Synthesis of 9,10-Bis(diisopropylsilyl)anthracene (1).

A solution of butyllithium in hexane (1.6 M, 56 mL) was added dropwise to a suspension of 9,10-dibromoanthracene (10.0 g, 29.8 mmol) in diethyl ether (100 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm gradually to room temperature, and chlorodiisopropylsilane (15.2 g, 101 mmol) was added dropwise to the solution. The mixture was stirred at room temperature for 2 h and hydrolyzed with aqueous sodium hydrogen carbonate. The organic layer was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was passed through a short column of silica gel (hexane elution). Recrystallization of eluted materials from hexane gave 9,10-bis(diisopropylsilyl)anthracene (6.64 g, 55%) as pale yellow crystals. Mp: 221–226  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.86 (d, 12H,  $J = 7.6$  Hz), 1.30 (d, 12H,  $J = 7.2$  Hz), 1.64–1.73 (m, 4H), 4.87 (t, 2H,  $J = 4.9$  Hz), 7.48 (dd, 4H,  $J = 6.6$ , 3.1 Hz), 8.57 (dd, 4H,  $J = 6.6$ , 3.1 Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  14.2, 19.9, 20.6, 124.8, 130.2, 136.2, 137.4.  $^{29}\text{Si}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.8. IR (KBr): 3100, 2960, 2890, 2150, 1520, 1460, 1440, 1010, 880, 780, 750  $\text{cm}^{-1}$ . UV/vis ( $\lambda_{\text{max}}$  in hexane): 342 ( $\epsilon$  3500), 359 (8000), 378 (13 700), 399 nm (14 200). MS:  $m/z$  406 (85,  $\text{M}^+$ ), 363 (16), 321 (28), 249 (34), 247 (34), 55 (100). Anal. Calcd for  $\text{C}_{26}\text{H}_{38}\text{Si}_2$ : C, 76.77; H, 9.42. Found: C, 76.87; H, 9.49.

#### Synthesis of 9,10-Bis(chlorodiisopropylsilyl)anthracene (2).

A solution of *tert*-butyllithium in pentane (1.7 M, 26 mL) was added dropwise to a suspension of 9,10-dibromoanthracene (5.00 g, 14.9 mmol) in THF (50 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm gradually to  $-30^\circ\text{C}$ , and dichlorodiisopropylsilane (9.26 g, 50.0 mmol) was added dropwise to the solution. The mixture was stirred at room temperature for 12 h and poured into hexane (200 mL). After filtration, the solvent was evaporated. The residue was recrystallized from hexane to give 9,10-bis(chlorodiisopropylsilyl)anthracene (2.15 g, 30%) as yellow crystals. Mp: 143–147  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.91 (d, 12H,  $J = 7.3$  Hz), 1.33 (d, 12H,  $J = 7.3$  Hz), 1.98 (sep, 4H,  $J = 7.3$  Hz), 7.47 (dd, 4H,  $J = 6.7$ , 3.3 Hz), 8.50 (dd, 4H,  $J = 6.7$ , 3.3 Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  18.1, 18.3, 18.4, 124.7, 129.3, 134.9, 136.9.  $^{29}\text{Si}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  31.9. IR (KBr): 3080, 2940, 2860, 1520, 1460, 1440, 1007, 950, 880, 747, 680  $\text{cm}^{-1}$ . UV/vis ( $\lambda_{\text{max}}$  in hexane): 391 ( $\epsilon$  11 200), 413 nm (11 200). MS:  $m/z$  474 (100,  $\text{M}^+$ ), 247 (66), 93 (55). Anal. Calcd for  $\text{C}_{26}\text{H}_{36}\text{Cl}_2\text{Si}_2$ : C, 65.65; H, 7.63. Found: C, 65.87; H, 7.71.

(17) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; Univ. of York, England and Louvain, Belgium, 1978.

(18) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, 55, 69.

(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(20) Duerr, B. F.; Chung, Y.-S.; Czarnik, A. W. *J. Org. Chem.* **1988**, 53, 2120.

(21) Helmer, B. J.; West, R. *J. Organomet. Chem.* **1982**, 236, 21.

(22) Kyushin, S.; Kawabata, M.; Sakurai, H.; Matsumoto, H.; Miyake, M.; Sato, M.; Goto, M. *Organometallics* **1994**, 13, 795.

#### Synthesis of 9,10-Bis(dimethylsilyl)anthracene (3).

A solution of *tert*-butyllithium in pentane (1.7 M, 26 mL) was added dropwise to a suspension of 9,10-dibromoanthracene (5.00 g, 14.9 mmol) in THF (50 mL) at  $-78^\circ\text{C}$ . Chlorodimethylsilane (4.6 g, 49 mmol) was added dropwise to the solution at  $-78^\circ\text{C}$ . The mixture was allowed to warm gradually to room temperature and hydrolyzed with aqueous sodium hydrogen carbonate. The organic layer was extracted with petroleum ether and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was passed through a short column of silica gel (hexane elution). Recrystallization of eluted materials from ethanol gave 9,10-bis(dimethylsilyl)anthracene (1.92 g, 44%) as pale yellow crystals. Mp: 98–100  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.72 (d, 12H,  $J = 4.2$  Hz), 5.47 (sep, 2H,  $J = 4.0$  Hz), 7.53 (dd, 4H,  $J = 6.7$ , 3.7 Hz), 8.60 (dd, 4H,  $J = 6.7$ , 3.7 Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -1.3, 125.0, 129.7, 136.6, 137.1.  $^{29}\text{Si}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -25.0. IR (KBr): 3080, 2950, 2900, 2150, 1515, 1440, 1245, 960, 890, 770, 735  $\text{cm}^{-1}$ . UV/vis ( $\lambda_{\text{max}}$  in hexane): 341 ( $\epsilon$  2900), 358 (6500), 377 (10 800), 398 nm (10 900). MS:  $m/z$  294 (42,  $\text{M}^+$ ), 235 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{Si}_2$ : C, 73.40; H, 7.53. Found: C, 73.52; H, 7.37.

#### Synthesis of 9,10-Bis(trimethylsilyl)anthracene (4).

A reaction analogous to that described for **3** but using *tert*-butyllithium in pentane (1.56 M, 40 mL), 9,10-dibromoanthracene (5.03 g, 15.0 mmol), and chlorotrimethylsilane (3.58 g, 33.0 mmol) gave 9,10-bis(trimethylsilyl)anthracene (2.60 g, 54%) as yellow crystals. Mp: 115–117  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.70 (s, 18H), 7.44 (dd, 4H,  $J = 6.9$ , 3.3 Hz), 8.40 (dd, 4H,  $J = 6.9$ , 3.3 Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  4.2, 124.1, 129.8, 136.9, 139.5.  $^{29}\text{Si}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -5.3. IR (KBr): 3070, 2950, 2890, 1510, 1435, 1405, 1250, 1160, 957, 835, 767, 680  $\text{cm}^{-1}$ . UV/vis ( $\lambda_{\text{max}}$  in hexane): 361 ( $\epsilon$  6400), 379 (10 300), 401 nm (9900). MS:  $m/z$  322 (83,  $\text{M}^+$ ), 307 (35), 249 (31), 219 (26), 73 (100).

#### X-ray Crystallographic Analysis of 9,10-Bis(diisopropylsilyl)anthracene (1).

Pale yellow crystals of 9,10-bis(diisopropylsilyl)anthracene were obtained from a hexane solution by slow evaporation. A crystal specimen was sealed in a glass capillary and used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu  $\text{K}\alpha$  radiation. Cell parameters were refined by the least-squares method using 25 reflections with  $17 < 2\theta < 53^\circ$ . Intensity data were collected in the range of  $6 < 2\theta < 130^\circ$  by the  $\omega$ - $2\theta$  scan technique at room temperature. Three standard reflections were measured after every 1 h, showing no decay. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN78.<sup>17</sup> Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using UNICSIII.<sup>18</sup> Thirteen hydrogen atoms were located by difference Fourier synthesis, and the remaining hydrogen atoms were located at calculated positions. All hydrogen atoms were not refined. Atomic scattering factors were taken from ref 19. All calculations were carried out on a FACOM M-380 computer. Details of crystal data, data collection, and refinement are listed in Table 1.

**Acknowledgment.** This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 05236206 and 06453034) from the Ministry of Education, Science, and Culture of Japan. We thank Shin-etsu Chemical Co., Ltd., Toshiba Silicone Co., Ltd., and Yuki Gosei Kogyo Co., Ltd., for financial support. We thank Mr. Y. Kawakami of Stanley Electric Co., Ltd., for measuring fluorescence lifetimes.

**Supporting Information Available:** Tables of complete atomic coordinates and thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** (4 pages). Ordering information is given on any current masthead page.

OM950776M