



# Fluorescence and phosphorescence of a series of silicon-containing six-membered-ring molecules



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## ARTICLE INFO

### Article history:

Received 13 July 2015

Received in revised form

28 December 2015

Accepted 31 December 2015

Available online 5 January 2016

### Keywords:

Silicon

Fluorescence

Phosphorescence

DFT

## ABSTRACT

Various silicon-containing six-membered-ring molecules were synthesized by Pd-catalyzed coupling reaction of 1,2-bis(dimethylsilyl)arenes with 1,2-diiodoarenes in moderate yields. Their optical properties were investigated via UV–vis absorption, fluorescence and phosphorescence spectroscopies, which indicated that the  $\sigma^*-\pi^*$  conjugated system expanded owing to the silicon atoms. Some of the compounds exhibited enhanced luminescence, larger Stokes shift, and phosphorescence in comparison with 9,9,10,10-tetramethyl-9,10-dihydroanthracene. Density functional theory (DFT) studies were also performed to investigate the photophysical properties of the compounds.

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## 1. Introduction

Much recent attention has focused on the unique properties of certain aromatic compounds bridged with hetero-atoms [1]. Red- or blue-shifts emerge in materials with  $\sigma-\pi$  conjugation, such as organosilicon compounds, as the energy gap between the HOMO and LUMO is tuned. Silicon-containing  $\sigma-\pi$  conjugated molecules are expected to be used in several kinds of materials such as fluorescent-emitting or electron-transporting devices [2]. Adding silicon directly to aromatic molecules induces hyperconjugation between the  $\sigma$  orbital of the silicon and the aromatic  $\pi$  orbital. UV–vis absorption and fluorescence spectra are red-shifted and the molecule's absorption coefficient and fluorescence intensity increase owing to the  $\sigma-\pi$  conjugation. These effects are evident in dibenzosilole, a five-membered ring molecule that contains silicon [3]. However, structurally similar silicon-containing molecules with six-membered-rings have been less well investigated due to limitations of their synthetic methodology [4]. During studies of the

reaction between hydrosilanes with aryl iodides, we have shown that this reaction provides a convenient route to various dibenzosiloles and dibenzogermoles [5]. In this work, we synthesized a series of 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracene, which are silicon-containing six-membered-ring compounds from their corresponding 1,2-bis(dimethylsilyl)arenes and 1,2-diiodoarenes, and investigated the fluorescence of the compounds at room temperature and their phosphorescence at 77 K.

## 2. Result and discussion

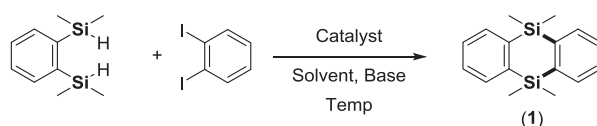
Initially, we screened the optimal conditions of coupling reaction between 1,2-bis(dimethylsilyl)benzene and 1,2-diiodobenzene as the model reaction, included the modification of solvents, bases, Pd catalysts, and temperature [6–8]. The reaction was monitored by GC, and the results were summarized in Table 1. We found that 1,2-diiodobenzene was completely converted at the end of the reaction and that Pd(P(*t*-Bu)<sub>2</sub>(4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>))<sub>2</sub> (catalyst) and *N,N*-diisopropylethylamine (base) in 1,2-dichloroethane or propionitrile (solvent) at rt (temperature) for 1 d were the best conditions after the careful optimization. Finally, the ratio of 1,2-bis(dimethylsilyl)benzene and 1,2-diiodobenzene was tested, and larger amount of 1,2-bis(dimethylsilyl)benzene could improve the yield of the

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**Table 1**  
Screening of optimal reaction conditions for 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracene (**1**).<sup>a</sup>



Entry	Catalyst	Temp (°C)	Solvent	Base	1,2-bis(dimethylsilyl)benzene/1,2-diiodobenzene	Yield (%) <sup>b</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	rt	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	0
2	Pd(P( <i>t</i> -Bu) <sub>3</sub> ) <sub>2</sub>	rt	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	6
3	Pd(P( <i>t</i> -Bu) <sub>2</sub> Ph) <sub>2</sub>	rt	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	22
4	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	27
5	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	50	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	22
6	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	0	THF	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	6
7	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CN	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	33
8	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	42
9	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	toluene	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	19
10	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>2</sub> Cl <sub>2</sub>	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	36
11	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CHCl <sub>3</sub>	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	15
12	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	ClCH <sub>2</sub> CH <sub>2</sub> Cl	( <i>i</i> -Pr) <sub>2</sub> EtN	1.2	38
13	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	Et <sub>3</sub> N	1.2	40
14	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	DABCO	1.2	4
15	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	<i>c</i> -C <sub>6</sub> H <sub>11</sub> MeN	1.2	31
16	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN		1.2	34
17	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN		1.2	0
18	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	DBU	1.2	0
19	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	K <sub>3</sub> PO <sub>4</sub>	1.2	21
20	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	Cs <sub>2</sub> CO <sub>3</sub>	1.2	16
21	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	KOAc	1.2	10
22	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	KO( <i>t</i> -Bu)	1.2	0
23 <sup>c</sup>	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	CH <sub>3</sub> CH <sub>2</sub> CN	( <i>i</i> -Pr) <sub>2</sub> EtN	1.5	42
24 <sup>c</sup>	Pd(P( <i>t</i> -Bu) <sub>2</sub> (4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> )	rt	ClCH <sub>2</sub> CH <sub>2</sub> Cl	( <i>i</i> -Pr) <sub>2</sub> EtN	1.5	43

<sup>a</sup> Reaction conditions: Pd catalyst (0.025 mmol), 1,2-bis(dimethylsilyl)benzene (0.60 mmol), 1,2-diiodobenzene (0.50 mmol), base (3.0 mmol), solvent (1.0 mL), rt, 1 d.

<sup>b</sup> GC yield with dodecane as an internal standard.

<sup>c</sup> The amount of 1,2-bis(dimethylsilyl)benzene was 0.75 mmol.

product (**1**) in up to 43%. In the improved synthetic protocol, silicon-containing six-membered-ring molecules **1–8** shown in Table 2 were synthesized by coupling 1,2-bis(dimethylsilyl)arenes and 1,2-diiodoarenes under the optimized conditions. Compound **9**, the carbon analog of **1**, was commercially available and used for comparison. Although all the compounds were obtained here in moderate yields in one-step reaction, it was difficult to prepare unsymmetrical 9,10-dihydro-9,10-disilaanthracenes **2–7**, including double cyclized product **8**, using previous methods. Importantly, delicate functional groups toward organometallic reagents such as the ester substituent of **6** were compatible with the reaction. The main byproducts were reduced arene compounds and non-cyclized products. Analytically pure compounds **1–8** were isolated by purification with a GPC column (eluent: CHCl<sub>3</sub>) or by recrystallization of the crude product because the separation of cyclized and non-cyclized products was difficult with SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> column. These pure compounds were stable under air in the solid state and could be stored without special precautions.

The optical properties of compounds **1–9** were investigated by UV–vis absorption, fluorescence, and phosphorescence spectroscopies. The UV–vis and fluorescence spectral data are listed in Table 3. Compound **1**, the simplest 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracene congener, exhibited UV absorption at 266 nm, 271 nm (shoulder peak). The carbon analog, 9,9,10,10-tetramethyl-9,10-dihydroanthracene (**9**), exhibited absorption at similar wavelengths (256 nm, 263 nm, and 271 nm). The

absorption maxima of **2** and **3**, which contained methyl groups on the aromatic ring, were slightly different from that of **1**. However, the extended  $\pi$ -conjugation of **4** caused its absorption maximum to shift to a longer wavelength (286 nm) with stronger molecular absorption coefficient relative to that of **1**. Similar to **4**, the absorption maxima of **5**, **6**, **7**, and **8** were also shifted to longer wavelengths, 277 nm, 292 nm, 297 nm, and 289 nm, respectively. This indicates that conjugated systems were expanded by the introduction of functional group through 1,2-bis(dimethylsilyl)benzene moiety.

Next, the luminescence of these compounds in hexane solution has been investigated. Compound **1** exhibited very weak fluorescence when excited at 266 nm ( $\Phi_F$ : < 0.01), while **9** (its carbon analog) exhibited fluorescence at 286 nm ( $\Phi_F$ : 0.08). Compound **1** in hexane showed a lower fluorescence quantum yield than did its carbon analog. Similar to the UV absorption behavior, the fluorescence wavelength of **2** was close to that of **3**, whereas the fluorescence maximum of **4** was shifted to a longer wave-length and higher quantum yield ( $\Phi_F$ : 0.13). Electron-withdrawing groups on the aromatic ring dramatically reduced the fluorescence quantum yield (**5** and **6**,  $\Phi_F$ :  $\leq$  0.01). Compound **7** showed red-shifted fluorescence in high quantum yield due to its expanded  $\pi$ -conjugation ( $\lambda_{em}$ : 344 nm,  $\Phi_F$ : 0.09). The 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracenes showed larger Stokes shifts than did 9,9,10,10-tetramethyl-9,10-dihydroanthracene (**9**), indicating that their conformational changes from the ground state to the

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