

Bis(3,5-dibromophenyl)dimethylsilane: A useful synthon for organosilicon chemistry

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Abstract

The diarylsilyl compound, C₁₄H₁₂Br₄Si, was prepared from the reaction of 3,5-dibromophenyllithium with dimethyldichlorosilane, (CH₃)₂SiCl₂, at -78 °C, can be a good synthon for derivatization to produce efficient host materials for organic light emitting diodes (OLEDs). Crystal structure analysis shows a slight deviation from ideal tetrahedral symmetry around the Si atom, whose conformation is effective in ensuring the maximum separation of the two phenyl rings and the two methyl substituents. The directions of the two aromatic rings are almost perpendicular to each other. The molecule exists as a monomer in the solid state.

Keyword: organosilicon, organic light emitting diodes, crystal structure, diarylsilane, host material

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1. Introduction

Organic light emitting diodes (OLEDs) have become the next generation display means and their full-fledged applications to OLED-TV come into realization. To fabricate highly efficient OLED based display units, there still remains a big huddle to develop blue phosphorescence emitting layer materials and within this context development of the wide band-gap host is of uttermost urgency. In blue OLEDs, host materials with large triplet gap energy (>2.8 eV) is required by the following reasons. One is to avoid triplet excitons of the dopant from quenching by back energy

transfer from dopant to host, and the other is to confine the electro-generated triplet excitons in the dopant molecules. A variety of carbazole functional organic materials are known to meet such host material specifications and among them the most popular one is 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP). In order to facilitate effective charge balance and host/guest energy confinement as well as post film stability, much effort has been exerted in the derivatization at the CBP functional units. Historically CBPs proved to be highly efficient host materials for green or red phosphorescent electroluminescence. However, low glass transition temperature(62 °C)^[1] resulting in morphological instability^[2] and relatively low triplet state energy^[3] limit their utility for blue

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phosphorescence.

One way to overcome these shortcomings is to introduce the silicon atom either in the periphery or at the core of the organic functional groups. The silicon atom has been engaged in blue host materials due to their many advantages, such as conjugation blocking for a wide band gap and a tetrahedral geometry for morphology^[4-8]. In the previous study examining the efficacy of silicon atom incorporation, several phenylsilane-functionalized ultrahigh energy-gap hosts (UGHs) were prepared and used to fabricate deep-blue phosphorescent OLEDs^[4,5]. In the course of our ongoing research on silicon-based, phosphorescent OLED host materials, we synthesized bis(3,5-dibromophenyl) dialkylsilanes, (**3** and **4**), as a novel precursor for polyarylamino silanes and especially the tetrahedral silicon motif was introduced to construct a molecular architecture for the production of blue host materials.

2. Experimentals

2.1. General Considerations

All manipulations were performed under either a dry nitrogen atmosphere using either standard Schlenk techniques or inside a KK-011AS glove box. Tetrahydrofuran (THF) was purchased from Samchun Pure Chemical Company and dried over sodium/benzophenone before use. Glassware, syringes, magnetic stirring bars, and needles were dried overnight in a convection oven. 1,3,5-Tribromobenzene, *n*-butyllithium (*n*-BuLi) and dimethyldichlorosilane were purchased from Aldrich Chemicals. IR spectra were recorded on an Agilent Cary 600 Series FT-IR spectrometer using KBr disks. The ¹H and ¹³C NMR spectra were recorded on a Bruker 300 spectrometer

operating at 300.1 and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative to the internal residual CHCl₃ from the lock solvent (99.9% CDCl₃). Elemental analysis (Carlo Erba Instruments CHNS-O EA1108 analyzer) was performed by the Ochang branch of the Korean Basic Science Institute.

2.2. Synthesis of bis(3,5-dibromophenyl) dimethylsilane (**3**)

General Procedure. *n*-Butyllithium (2.5 M in hexane, 16.0 mL, 40 mmol) was added dropwise to a dry tetrahydrofuran solution (400 mL) containing 1,3,5-tribromobenzene (12.8 g, 40.0 mmol) under nitrogen atmosphere at -78 °C. The reaction solution was stirred for 2 h. Dichlorodimethylsilane (4.33 mL, 20 mmol) was then added dropwise to the solution. The solution was further stirred and gradually allowed to warm up to room temperature in 5 h, and then the reaction was quenched with water (300 mL). The mixture was extracted with diethyl ether (200 mL × 3). The product as a white solid was isolated by flash column chromatography using hexanes as eluent.

3: Yield: 6.8 g, 64%. M.p.: 65 °C. ¹H NMR (CDCl₃, ppm) δ 0.87 (s, 6H), 7.77 (s, 2H), 8.10 (s, 2H). ¹³C NMR (CDCl₃, ppm) δ 0.55 (Si-CH₃), 125.1 (C-Br), 136.1, 138.4 (C-H), 140.5 (C_{ipso}).

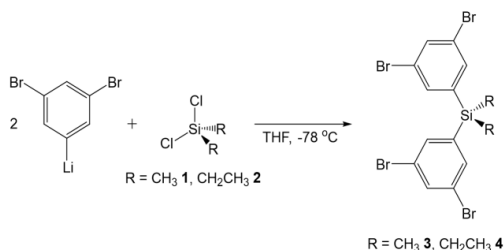
4: Yield: 7.9 g, 72%. M.p.: 61 °C. ¹H NMR (CDCl₃, ppm) δ 0.94 (q, 3JC-H = Hz, 6H), 1.51 (t, 3JC-H = Hz), 7.68 (s, 2H), 8.08 (s, 2H). ¹³C NMR (CDCl₃, ppm) δ 6.7 (Si-CH₂-CH₃), 12.5 (Si-CH₂CH₃), 125.2 (C-Br), 136.0, 138.3 (C-H), 140.3 (C_{ipso})

2.3. Crystal structure determination

Crystal of **1** was obtained from dichloromethane (CH_2Cl_2), sealed in glass capillaries under argon, and mounted on the diffractometer. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV \times 50 mA) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The *SMART* software package was used for data collection, and *SAINTE* was used for frame integration^[9]. Final cell constants were determined by a global refinement of *xyz* centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the *SHELXTL-PLUS* software package^[10].

3. Results and Discussion

The present structure determination of compound **3** was undertaken in order to understand the effects of 3,5-disubstituted phenyl groups on the geometry of the molecule, and to compare the results obtained with those of previously reported mono-substituted diphenylsilane derivatives.



Scheme 1. Synthesis of bis(3,5-dibromophenyl) dialkylsilanes (R = CH₃ **3**, CH₂CH₃ **4**).

Scheme 1 summarizes the synthesis of bis(3,5-dibromophenyl)dialkylsilanes. Treatment of 1,3,5-tribromobenzene with 1.2 equiv of *n*-BuLi in THF and then R₂SiCl₂ (R = CH₃ **1**, CH₂CH₃ **2**) afforded bis(3,5-dibromophenyl)dimethylsilane (**3**) and diethylsilane (**4**) in moderate yields (**3** 64%, **4** 72%). The new compound was characterized by ¹H and ¹³C NMR. Compounds **3** and **4** exhibit characteristic absorption bands in the infrared spectra at around 1520 ~ 1601 and 3010 cm⁻¹ reflecting the aromatic C=C and *sp*² C-H bond of the dibromophenyl groups. The ¹H NMR spectrum of **3** and **4** show resonances at around δ 0.87 ~ 1.51 due to the methyl and ethyl C-H protons and at around δ 7.68 ~ 8.10 due to the aromatic protons of the dibromophenyl moieties. The ¹³C NMR spectrum of **3** and **4** exhibit resonances at around δ 0.55 ~ 12.5 (Si-R), 125.1 ~ 125.2 (Br-C), 136.0 ~ 138.4 (aromatic C-H), and 140.3 ~ 140.5 (C_{ipso}) due to the dibromophenyl CH, respectively.

X-ray structural analysis of compound **3** was consistent with the structures proposed based on the NMR assignments. Selected crystallographic data and selected bond lengths and angles are summarized in Table 1 and 2, respectively. The ORTEP diagram in Figure 1 shows the molecular structure of **3** and confirms to be that of bis(3,5-dibromophenyl)dimethylsilane.

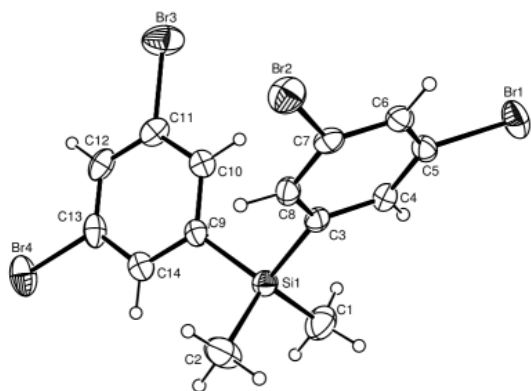


Figure 1. The structure of **3** showing 30% probability displacement ellipsoids and the atomic numbering scheme and H atoms are shown as small spheres of arbitrary radii.

As shown in Figure 1 and Table 1, the central Si1 atom has tetrahedral geometry, with the two phenyl and two methyl substituents. The average bond distance of Si-C_{ipso} 1.880(4) Å is very close to those found in bis(4-iodophenyl)dimethylsilane [1.882(4) and 1.878(4) Å]^[11] and bis(4-bromophenyl)dimethylsilane [1.873(3) and 1.877(3) Å]^[12], respectively, but longer than those of diphenylsilane-containing macrocycle compound [1.852(3) and 1.859(3) Å]^[13] and mono-substituted phenylsilane [1.859(5) Å]^[14]. The average Si-C_{methyl} distance [1.847(5) Å] is shorter than those of bis[4-(2-isopropyl-2*H*-tetrazol-5-yl)phenyl]dimethylsilane [1.853(4) Å]^[15] and bis(4-bromophenyl)dimethylsilane [1.852(4) and 1.858(4) Å]^[12], but longer than those of 9-(4-(trimethylsilyl)phenyl)-9*H*-carbazole [1.782(9), 1.795(10), and 1.798(7) Å]^[14]. The average bond distance of C_{phenyl}-Br of **3** is a 1.894(3) Å, which is shorter than those of bis(4-bromophenyl)dimethylsilane [1.899(3) and 1.903(4) Å]^[12]. The average C-C bond distance in the aromatic rings is 1.379(2) Å.

The range of angles around the Si1 atom

[107.9(2)-110.7(4)°] in **3** indicates a slightly distorted tetrahedral geometry. These values are similar to the range of 106.2(1) ~ 110.5(2)° [bis(4-bromophenyl)dimethylsilane]^[12] and 106.0(2) ~ 111.3(2)° [bis(4-iodophenyl)dimethylsilane]^[11] observed in the mono-substituted diphenylsilane derivatives. The angle 107.9(2)° (C3-Si1-C9) is larger than those of mono-substituted diphenylsilane derivatives [106.2(1)°^[11]; 105.63(19)°^[12]; 106.04(17)°]^[15], but smaller than that of 9-(4-(trimethylsilyl)phenyl)-9*H*-carbazole [108.90(7)°]^[14]. As a result, the angle between the two methyl units in **3** is expanded to 110.7(4)°.

The aryl ring Si1/C3/C4/C5/C6/C7/C8/Br1/Br2 in **3** is planar to within an r.m.s. deviation of 0.008 Å within the maximum deviation of 0.018(4) Å for C6 from the mean plane. Similarly, the aryl ring Si1/C9/C10/C11/C12/C13/C14/Br3/Br4 in **3** has an r.m.s. deviation of 0.011 Å and the maximum deviation of 0.021(4) Å for C12 with respect to its mean plane. The dihedral angle between these two planes is almost perpendicular to each other with 82.90(4)°, which is very large comparing with the dihedral angle 66.83(6)° between two aryl rings in the mono-substituted diphenylsilane derivative bis(4-(9*H*-carbazol-9-yl)phenyl)dimethylsilane^[14], but smaller than those of 88.86°^[11] and 84.03°^[12]. The latter two reference papers, however, do not provide detailed calculations of the dihedral angles. Therefore, we computed them using *SHELX97*^[10].

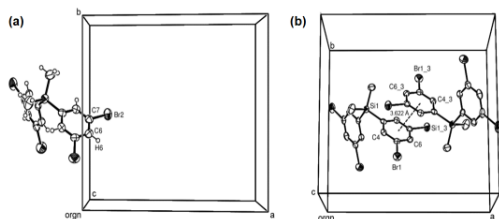


Figure 2. (a) An ORTEP diagram of **3** with the initial atomic coordinates given by *SHELX 97*^[10], where most of the atoms in the molecule are out of the unit cell. (b) A packing diagram drawn with the atomic coordinates displaced by $dx = 0.5$. The coordinate of the centroid C_{cent} of the phenyl ring C3/C4/C5/C6/C7/C8 is $x = 0.430183$, $y = 0.441083$, and $z = 0.354883$ [symmetry code: (i) $1-x, 1-y, 1-z$].

Figure 2 gives two molecular diagrams of compound **3**. Figure 2(a) shows all atoms expect four atoms in a molecule are located out of the unit cell. The atomic coordinates of the molecule were obtained from *SHELX97*^[10]. Figure 2(b) shows two molecules related by an inversion center in a unit cell drawn with the atomic coordinates displaced by $dx = 0.5$. As shown in Figure 2(b), in the crystal packing structure of **3** the closest intermolecular $C_{cent} \dots C_{cent}^i$ distance [symmetry code: (i) $1-x, 1-y, 1-z$] of the phenyl ring C3/C4/C5/C6/C7/C8 is 3.622 \AA which is longer than that of the shortest intermolecular contact $Br4 \dots H2A^{ii}$ [3.273 \AA , symmetry code: (ii) $x, 1.5-y, -0.5+z$]. Therefore, there is no cofacial π - π stacking among phenyl rings. Examination of the structure with *PLATON* showed that there are no solvent accessible voids in compound **3** and no intra- and intermolecular hydrogen bonds exist.

4. Conclusions

In summary, we have discovered a good synthon for derivatization to produce efficient host materials, bis(4-dibromophenyl)dimethyl- and diethylsilane, for organic light emitting diodes. Compounds **3** and **4** were synthesized through a facile route, which is based on the design strategy of steric substitution on peripheral dibromophenyl moieties. As a result, we obtained highly efficient a good synthon for host materials for organic light emitting diodes.

Table 1. Crystal data and structure refinement for **3**.

| | |
|---|---|
| Identification code | K070509 |
| Empirical formula | $C_{14} H_{12} Br_4 Si$ |
| Formula weight | 527.97 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 \AA |
| Crystal system, space group | Monoclinic, $P 2_1/c$ |
| Unit cell dimensions | $a = 14.5324(12) \text{ \AA}$, $\alpha = 90.00^\circ$ $b = 13.2543(11) \text{ \AA}$, $\beta = 91.092(2)^\circ$ $c = 8.9589(7) \text{ \AA}$, $\gamma = 90.00^\circ$ |
| Volume | $1725.3(2) \text{ \AA}^3$ |
| Z, D_{calc} | 4, 2.033 g/cm^3 |
| m | 9.385 mm^{-1} |
| $F(000)$ | 1000 |
| Crystal size | $0.24 \times 0.21 \times 0.10 \text{ mm}$ |
| θ range for data collection | 1.40 to 28.34° |
| Limiting indices | $-19 \leq h \leq 19$, $-17 \leq k \leq 17$, $-11 \leq l \leq 11$ |
| Reflections collected / unique | 17625 / 4294 [R(int) = 0.0736] |
| Completeness to $\theta = 25.96$ | 99.8 % |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4294 / 0 / 175 |
| Goodness-of-fit on F^2 | 0.979 |
| Final R indices [$h2\sigma$ (h)] | $^a R_1 = 0.0397$, $^b wR_2 = 0.0798$ |
| R indices (all data) | $^a R_1 = 0.1144$, $^b wR_2 = 0.1052$ |
| Extinction coefficient | 0.0026(3) |
| Largest diff. peak and hole | 0.680 and $-0.659 \text{ e.\AA}^{-3}$ |

^a $R_1 = \sum \|F_o - |F_c|\| / \sum F_o$ (based on reflections with $F_o^2 > 2\sigma F^2$), ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ (also with $F_o^2 > 2\sigma F^2$)

Table 2. Selected bond lengths (Å), angles (°) and torsional angles (°) for **3**.

| | | | |
|--------------|-----------|----------------|-----------|
| Si1-C1 | 1.849(6) | Br1-C5 | 1.892(5) |
| Si1-C2 | 1.844(6) | Br2-C7 | 1.891(5) |
| Si1-C3 | 1.870(5) | Br3-C11 | 1.893(5) |
| Si1-C9 | 1.885(5) | Br4-C13 | 1.894(5) |
| C2-Si1-C1 | 110.6(3) | C1-Si1-C9 | 109.1(3) |
| C2-Si1-C3 | 109.4(3) | C3-Si1-C9 | 107.9(2) |
| C3-C4-C5-Br1 | -179.8(3) | C9-C10-C11-Br3 | 179.6(4) |
| Br2-C7-C8-C3 | 179.6(3) | Br4-C13-C11-C9 | -179.0(4) |

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- [16] References, should be collected at the end of your paper. Do not be in them on a new page unless this is absolutely necessary. They should be prepared according to a recognized style and your accumulated list should correspond to citations made in the text body. Above we have listed some references according to the numeric sequential system ^[1-4]. In this system references are numbered in the order in which they are cited in the text.