# First Preparation and Structural Determination of 1,1-Disubstituted Dibenzo[*bc,fg*][1,4]silathiapentalene Derivatives by X-ray Crystallographic Analysis and MO Calculations

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## ABSTRACT

*1,1-Dimethyldibenzo[bc,fg][1,4]silathiapentalene (1a) was prepared by treatment of 1,9-bis(methylsulfinyl)dibenzothiophene with EtMgBr or of dibenzothiophene with n-butyllithium, and then with dimethyl dichlorosilane. The structure of 4,4-dimethyldibenzo[bc,fg][1,4]silathiapentalene 1-oxide (2), obtained by oxidation of compound 1a with mCPBA, was determined by X-ray crystallographic analysis. The structure of compound 2 determined experimentally was compared to the structure obtained by semiempirical molecular orbital calculations (AM1). The MO calculations of compound 1a and its phenyl analog 1b were also performed by AM1 to evaluate their structures. © 1996 John Wiley & Sons, Inc.*

## INTRODUCTION

Thiophene and its related compounds have attracted much attention in the creation of new functional ma-

terials [1]. Recently, we reported the preparation of dibenzo[*bc,fg*][1,4]dithiapentalene and diselenapentalene as new thiophene and selenophene derivatives by photolysis and thermolysis of 1,9-bis(methylthio)dibenzothiophene and 1,9-bis(phenylseleno)dibenzoselenophene, respectively, and the determination of their structures by X-ray crystallographic analysis [2]. Furthermore, triphenyleno[4,5-*bcd*]thiophenes were obtained by photolysis of 1,9-bis(arylthio)dibenzothiophene with a high-pressure mercury lamp in benzene [3]. Also, dibenzodithiapentalene and triphenyleno[4,5-*bcd*]thiophene derivatives were revealed by cyclic voltammetry to have a similar behavior to polythiophenes on the electrode surface on measurement of their oxidation potentials.

In further extension of our work on the preparation of planar polyaromatic compounds bearing several heteroatoms, we attempted to prepare dibenzo[*bc,fg*][1]thiapentalene as an analogous planar molecule, but bearing only one sulfur atom, to dibenzo[*bc,fg*][1,4]dithiapentalene. Though the dibenzo[*bc,fg*][1]thiapentalene could not be obtained by photolytic and thermolytic procedures as described earlier, we have succeeded in the preparation of the monosilicon analogs, 1,1-disubstituted di-

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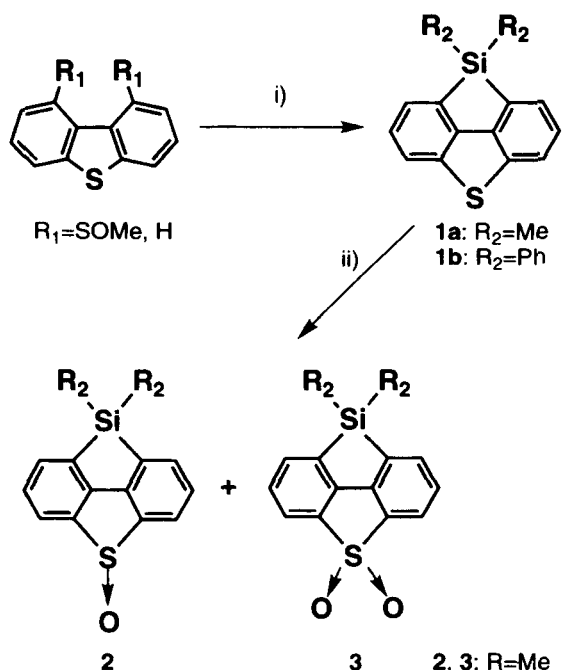
Scheme 1: i) R₁=SOMe, EtMgBr/Me₂SiCl₂/THF
(1a: R₂=Me, trace); R₁=H, n-BuLi/Me₂SiCl₂/heptane
(1a: R₂=Me, 7%); R₁=H, n-BuLi/Ph₂SiCl₂/heptane
(1b: R₂=Ph, 4%); ii) mCPBA/CH₂Cl₂ (2: R₂=Me, 66%;
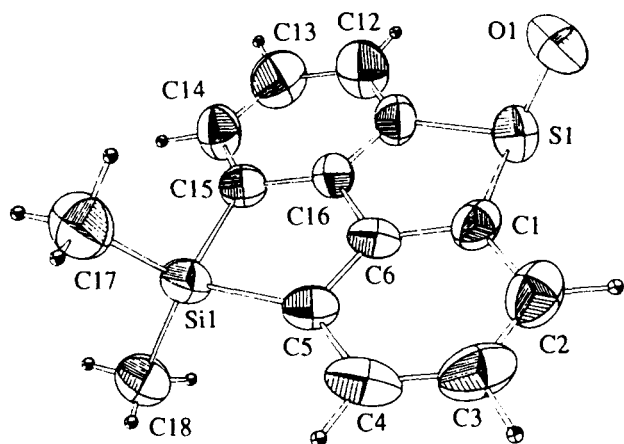3: R₂=Me, 4%).

**SCHEME 1**



**FIGURE 1**   ORTEP drawing of compound 2.

benzo[$bc,fg$][1,4]silathiapentalene derivatives (1), and we have verified their structures and oxidation potentials. This article reports the first preparations of 1,1-dimethyldibenzo[$bc,fg$][1,4]silathiapentalene (1a) and 1,1-diphenyldibenzo[$bc,fg$][1,4]silathiapentalene (1b), the structure determination of 1,1-dimethyldibenzo[$bc,fg$][1,4]silathiapentalene 4-oxide (2) by X-ray crystallographic analysis, and the

results of semiempirical molecular orbital calculations of compounds 1a, 1b, and 2 by AM1.

## RESULTS AND DISCUSSION

In order to prepare the dimethyl silathiapentalene (1a), 1,9-bis(methylsulfinyl)dibenzothiophene [4] was treated with EtMgBr and then dimethyl dichlorosilane in THF. Since only a trace amount of compound 1a could be obtained by this procedure, dibenzothiophene was treated with n-butyllithium in the presence of $N,N,N'N'$-tetramethylethylenediamine (TMEDA) in heptane and then with dimethyl dichlorosilane to give 1a as a colorless liquid in 7% yield (Scheme 1) [5]. Similarly, compound 1b was also obtained in 4% yield by the identical procedure using dibenzothiophene and diphenyl dichlorosilane. These silathiapentalene derivatives 1a and 1b are thermally very stable. To examine the reactivity of a typical silathiapentalene, compound 1a was oxidized with one equivalent of $m$-chloroperbenzoic acid ($m$CPBA) in $CH_2Cl_2$ at $-20°C$ to give compound 2 and 1,1-dimethyldibenzo[$bc,fg$][1,4]silathiapentalene 4,4-dioxide (3) in 66% and 4% yields, respectively, as colorless crystals (Scheme 1). The compounds 2 and 3 were stable in aprotic solvents, but they decomposed gradually in ethanol at room temperature to produce complex mixtures.

The structure of the monosulfoxide 2 was determined by X-ray crystallographic analysis, since compounds 1a and 1b did not give the desired crystalline forms suitable for X-ray analysis. The X-ray crystallographic analysis of compound 2 gave the following results. The orthorhombic cell parameters and calculated cell volume of compound 2 are $a = 12.149$ (1) Å, $b = 12.321$ (3) Å, $c = 17.312$ (1) Å, and $V = 2591.4$ Å³. The calculated density is 1.31 g/cm³ for $Z = 8$, and the formula weight = 256.40. The space group was determined to be Pbca from the systematic absences: $h, k, 0 : h = 2n; h, 0, l : l = 2n; 0, k, l : k = 2n$. The linear absorption coefficient is 3.1 cm⁻¹ for MoKα radiation. The structure was solved by the direct method. The 850 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 190 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.054$ and $R_w = 0.055$, respectively. As shown in Figure 1, the silathiapentalene 1-oxide (2) has a completely planar form similar to those of dibenzo-dithiapentalene derivatives [2]. In fact, the several torsional angles were found to be as follows: $Si_1-C_5-C_6-C_1$, 178.69 (0.68)°; $C_3-C_4-C_5-Si_1$, $-179.68$ (0.74)°; $Si_1-C_5-C_6-C_{16}$, $-1.05$ (0.82)°; $S_1-C_1-C_2-C_3$, $-178.06$ (0.69)°; $S_1-C_1-C_6-C_5$, 178.65 (0.65)°; $S_1-C_1-C_6-C_{16}$,

**TABLE 1** The Oxidation Potential (V) and UV Spectra

| | $Ep$ | $\lambda_{max}$ | | | |
|---|---|---|---|---|---|
| | $V$ | $nm$ $(\varepsilon)$ | | | |
| **1a** | 1.33 | 273 (8605) | 291 (2500) | 310 (3500) | 322 (3100) |
| **1b** | 1.42 | 274 (9800) | | 316 (4600) | 328 (4600) |
| DP | 1.16 | 270 (4300) | | | 329 (1900) |
| DT | 1.31 | | 285 (5000) | | 323 (1400) |

DP: dibenzodithiapentalene, DT: dibenzothiophene.

**TABLE 2** The Bond Distances (Å) and the Bond Angles (deg)

| | Distances (Å) | | | |
|---|---|---|---|---|
| Atoms | **2**[a] | **2**[b] | **1a**[b] | **1b**[b] |
| S1–O1 | 1.472(7) | 1.47 | | |
| S1–C1 | 1.810(8) | 1.76 | 1.72 | 1.72 |
| Si1–C5 | 1.922(8) | 1.88 | 1.88 | 1.89 |
| C1–C6 | 1.37(1) | 1.40 | 1.40 | 1.40 |
| C5–C6 | 1.37(1) | 1.39 | 1.40 | 1.40 |
| C6–C16 | 1.44(1) | 1.45 | 1.44 | 1.44 |
| | Angles (deg) | | | |
| C1–S1–C11 | 89.3(4) | 94.4 | 95.0 | 94.9 |
| C5–Si1–C15 | 91.8(3) | 94.5 | 97.0 | 96.5 |
| S1–C1–C6 | 110.8(6) | 108.7 | 109.3 | 109.4 |
| Si1–C5–C6 | 105.5(5) | 102.9 | 101.9 | 102.0 |
| C1–C6–C5 | 127.4(7) | 127.3 | 127.2 | 127.1 |
| C1–C6–C16 | 114.1(7) | 113.8 | 113.2 | 113.2 |
| C5–C6–C16 | 118.4(7) | 118.9 | 119.6 | 119.7 |

[a]The data are obtained by X-ray crystallographic analysis, and numbers in parentheses are estimated standard deviations in the least significant digits.
[b]The calculated distances and angles are for optimized structures (AM 1).

$-1.61$ (0.84)°; $C_5$–$C_6$–$C_{16}$–$C_{15}$, $-2.51$ (1.05)°; $C_1$–$C_6$–$C_{16}$–$C_{11}$, 179.68 (0.72)°. The bond lengths of the C–S and C–Si bonds of compound 2 are 1.810 (8) Å ($S_1$–$C_1$), 1.808 (8) Å ($S_1$–$C_{11}$), 1.922 (8) Å ($Si_1$–$C_5$), and 1.904 (8) Å ($Si_1$–$C_{15}$). The bond angles of the benzene ring of compound 2 are 127.4 (7)° ($C_1$–$C_6$–$C_5$), 117.8 (7)° ($C_2$–$C_1$–$C_6$), 117.3 (8)° ($C_1$–$C_2$–$C_3$), and 123.7 (8)° ($C_2$–$C_3$–$C_4$). Furthermore, the bond angles around the sulfur and silicon atoms are as follows: $O_1$–$S_1$–$C_1$: 110.5 (4)°, $O_1$–$S_1$–$C_{11}$: 111.2 (4)°, and $C_1$–$S_1$–$C_{11}$: 89.3 (4)°; $C_5$–$Si_1$–$C_{15}$: 91.8 (3)°, $C_5$–$Si_1$–$C_{17}$: 113.5 (4)°, $C_5$–$Si_1$–$C_{18}$: 114.2 (4)°, $C_{15}$–$Si_1$–$C_{17}$: 110.6 (4)°, $C_{15}$–$Si_1$–$C_{18}$: 114.8 (4)°, and $C_{17}$–$Si_1$–$C_{18}$: 110.0 (4)°. These values suggest that the configurations around the sulfur and silicon atoms are tetrahedral.

Meanwhile, the structure of compound 2 was found to be similar to those of dibenzothiophene and dibenzothiophene 4-oxide around the sulfur atom [6,7], and the two methyl protons of compound 2 were not coalesced at 150°C on measurement of the

$^1$H NMR spectrum, revealing that the sulfinyl oxygen of compound 2 does not undergo pyramidal inversion at this temperature. The central $C_6$–$C_{16}$ bond distance of compound 2 is 1.44 (1) Å, which is longer than that of dibenzodithiapentalene (1.386 Å) [2a,c], dibenzoselenathiapentalene (1.388 Å) [2b,c], and dibenzopentalene (1.392 Å) [8] and is shorter than that of biphenyl (1.507 Å) [9].

The oxidation potentials of compounds 1a and 1b were determined by cyclic voltammetry using Ag/ 0.01 M AgNO$_3$ as a reference electrode in CH$_3$CN at 20°C (scan rate 200 mV/sec), and their cyclic voltammograms were found to be irreversible. Their peak potentials were 1.33 V (1a) and 1.42 V (1b), these values being higher than that of dibenzodithiapentalene (1.16 V) and similar to that of dibenzothiophene (1.31 V) (Table 1). The $\lambda_{max}$ and $\varepsilon$ values of the UV spectra of 1a and 1b were similar to those of dibenzodithiapentalene and dibenzothiophene (Table 1). On the other hand, it is reported that the electronic character of dibenzodithiapentalene is different from that of tetraphenylthieno[3,4-c]thiophene [2,10]. These spectroscopic results and the oxidation potentials of silathiapentalene derivatives (1a) and (1b) suggest that the sulfur and silicon atoms do not participate in $\pi$-electron delocalization similar to that observed for dibenzodithiapentalene and dibenzodiselenapentalene [2].

As a matter of theoretical interest, the experimentally determined structure of the silathiapentalene (2) was compared to the structure obtained by semiempirical molecular orbital calculations. The compound 2 calculated by the AM1 method indicates a planar form, and the bond length and bond angles are identical to those observed by X-ray crystallographic analysis (Table 2). Since the structures of compounds 1a and 1b could not be determined by X-ray crystallographic analysis, whereas the structure of compound 2 found by AM1 calculation is identical to the structure obtained by X-ray crystallographic analysis, MO calculations of compounds 1a and 1b were performed by AM1 to determine their structures and HOMO and LUMO levels. The structures of compounds 1a and 1b obtained by AM1 were similar to that of compound 2 with respect to the bond lengths and bond angles (Table 2), and, furthermore, these molecules, 1a and 1b, were calculated to have planar forms. The HOMO and LUMO of the silathiapentaleneoxide 2 were calculated with regard to the two structures, one determined by X-ray crystallographic analysis and not optimized by AM1, and the other, optimized by AM1, to be HOMO, $-9.333$ eV, and LUMO, $-0.541$ eV, for the nonoptimized structure, and HOMO, $-9.016$ eV, and LUMO, $-0.620$ eV, for the optimized structure.

On the other hand, the HOMO and LUMO levels of silathiapentalene derivatives **1a** and **1b** were calculated similarly by AM1 with respect to their optimized structures: **1a**: HOMO, $-8.171$ eV; LUMO, $-0.367$ eV; **1b**: HOMO, $-8.151$ eV; LUMO, $-0.351$ eV. Furthermore, the electron density of compound **1a** in the HOMO was found to be greater on the sulfur atom than on the carbon and silicon atoms.

## EXPERIMENTAL

### General

Infrared spectra were recorded on a JASCO FT/IR-5000 spectrometer. The NMR spectra were measured in $CDCl_3$ solution on a JEOL JNM-EX270 or a Bruker AM-500 spectrometer. Mass spectra were obtained with a JEOL JMX SX102 and a Shimadzu QP-2000 mass spectrometer. The X-ray data collection was performed on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer with MoK$\alpha$ radiation ($\lambda = 0.71073$ Å) at $23 \pm 1°C$, and all calculations for structure solution and refinement were carried out on a VAX computer using MolEN. MO calculations were carried out by use of a Fujitu S-Family 4/5 GX with MOPAC93 AM1 (J. J. P. Stewart and Fujitsu Limited, Tokyo, Japan). For measurement of oxidation potentials, a Hokuto Denko Co. Model HB-104 apparatus was used.

## PREPARATION

### 1,1-Dimethylbenzo[bc,fg] [1,4]silathiapentalene (1a)

To a heptane (150 mL) solution of dibenzothiophene (460 mg, 2.5 mmol), $N,N,N',N'$-tetramethylethylenediamine (TMEDA, 0.75 mL, 0.5 mmol) and 1.61 M $n$-BuLi (3.1 mL, 5 mmol) were added dropwise under an $N_2$ atmosphere. The solution was stirred for 1 hour at reflux temperature and then dichlorodimethylsilane (0.75 M in heptane, 10 mL, 7.5 mmol) was added slowly at room temperature. The solution was stirred for 15 hours and was treated with $H_2O$ (5 mL). After the usual workup, the solution was extracted with $CH_2Cl_2$ (3 × 150 mL), and the extracts were dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography (silica gel, $n$-hexane) and preparative HPLC to give **1a** (43 mg, 7%); **1a**: colorless liquid; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.62 (s, 6H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.78 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ $-2.1$, 123.4, 127.6, 128.0, 134.7, 135.0, 148.9; UV ($CH_2Cl_2$) $\lambda_{max}$ nm ($\varepsilon$) 273 (8605), 291 (2500), 310 (3500), 322 (3100); HRMS ($m/z$); calcd for $C_{14}H_{12}SSi$ 240.0429. Found: 240.0470 (M$^+$).

### 1,1-Diphenylbenzo[bc,fg][1,4]silathiapentalene (1b)

To a heptane (250 mL) solution of dibenzothiophene (1.84 g, 10 mmol), TMEDA (0.75 mL, 0.5 mmol) and 1.61 M $n$-BuLi (12.5 mL, 20 mmol) were added dropwise under an $N_2$ atmosphere. The solution was stirred for 1 hour at reflux temperature, and then dichlorodiphenylsilane (1.0 M in heptane, 50 mL, 50 mmol) was added slowly at room temperature. The solution was stirred for 15 hours and was treated with $H_2O$ (5 mL). After the usual workup, the solution was extracted with $CH_2Cl_2$ (3 × 600 mL), and the extracts were dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography (silica gel, $n$-hexane, and $n$-hexane:$CH_2Cl_2$ = 1:1) and preparative HPLC to give **1b** (135 mg, 4%); **1b**: 151–152°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.36 (t, $J = 7.2$ Hz, 4H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.71 (d, 4H, $J = 7.2$ Hz), 7.76 (d, $J = 7.4$ Hz, 2H), 7.82 (d, $J = 7.4$ Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 124.0, 128.2, 128.3, 129.1, 130.3, 131.9, 132.6, 135.2, 135.4, 149.7; UV ($CH_2Cl_2$) $\lambda_{max}$ nm ($\varepsilon$) 274 (9800), 316 (4600), 328 (4600); MS ($m/z$) 364 (M$^+$); anal. calcd for $C_{24}H_{16}SSi$: C, 79.08; H, 4.42. Found: C, 78.86; H, 4.31.

### 1,1-Dimethyl Benzo[bc,fg][1,4]silathiapentalene 4-oxide (2) and 1,1-Dimethylbenzo[bc,fg] [1,4]silathiapentalene4,4-dioxide (3)

To a $CH_2Cl_2$ (20 mL) solution of **1a** (24 mg, 0.1 mmol), $m$CPBA (17 mg, 0.1 mmol, in 10 mL $CH_2Cl_2$) was added slowly at $-20°C$. The solution was stirred for 18 hours at $-20°C$ and then was treated with $NH_3$ gas until a white precipitate was produced. The white precipitate was filtered off, and the solvent was evaporated. Then the residue was purified by column chromatography (silica gel, $CH_2Cl_2$ and $CH_2Cl_2$:methanol = 1:1) to give **2** (17 mg, 66%) and **3** (1 mg, 4%), respectively; **2**: mp 189–191°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.560 (s, 3H), 0.564 (s, 3H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.69 (d, $J = 7.4$ Hz, 2H), 7.83 (d, $J = 7.4$ Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ $-2.8$, $-2.4$, 127.4, 130.0, 135.5, 136.3, 141.5, 149.5; IR (KBr) 1038 cm$^{-1}$ (SO); MS ($m/z$) 256 (M$^+$); anal. calcd for $C_{14}H_{12}OSSi$: C, 65.58; H, 4.72. Found: C, 65.30; H, 4.54; **3**: mp 188–190°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.57 (s, 6H), 7.43 (t, $J = 7.1$ Hz, 2H), 7.66 (d, $J = 7.1$ Hz, 2H), 7.74 (d, $J = 7.1$ Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ $-3.0$, 122.8, 130.8, 135.4, 135.7, 137.7, 142.9; IR (KBr) 1307, 1158 cm$^{-1}$ (SO$_2$); MS ($m/z$) 272 (M$^+$); anal. calcd for $C_{14}H_{12}O_2SSi$: C, 61.73; H, 4.44. Found: C, 61.39; H, 4.30.

## ACKNOWLEDGMENTS

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