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Modification of the electronic structure of silole by the substituents on the ring silicon

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Abstract

A series of 3,4-dimethyl-2,5-bis(trimethylsilyl)siloles having various substituents on the ring silicon atom have been prepared and their UV absorption spectra have been determined. Their absorption maxima steadily shifted to longer wavelengths as the 1,1-substituents on the ring silicon atom become more electronegative. Ab initio calculations at the HF/6-31G(d) level of theory showed that the nature of the 1,1-substituents strongly affects the HOMO and LUMO energy levels of the silole ring mainly due to inductive effects. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silole; Substituent effect; $\sigma^*-\pi^*$ Conjugation; UV absorption spectra; Ab initio calculation

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1. Introduction

Silole (silacyclopentadiene) has now received much attention as a new building unit of π-conjugated compounds due to its unique electronic structure [1–5]. The most characteristic feature is its high electron affinity, that is, the low lying LUMO level, which is realized by $\sigma^*-\pi^*$ conjugation between the σ^* orbital of two-exocyclic σ-bonds on the ring silicon and the π^* orbital of the butadiene moiety, as shown in Fig. 1 [2]. Indeed, based on this electronic structure, silole-based π-conjugated compounds have potential applicabilities as electron-transporting materials in organic electroluminescent (EL) devices [1]e.

To design new silole-based π-electronic systems, it is essential to elucidate the electronic structure of the silole ring in detail. We are now interested in substituent effects on the electronic structure of the silole ring by the groups on the ring silicon atom, namely the 1,1-substituents. It is anticipated that the 1,1-substituents would strongly perturb only the LUMO level through the $\sigma^*-\pi^*$ conjugation, because the σ orbital of the two exocyclic σ-bonds on the ring silicon cannot participate in the HOMO of the silole ring due to orbital symmetry (Fig. 1).

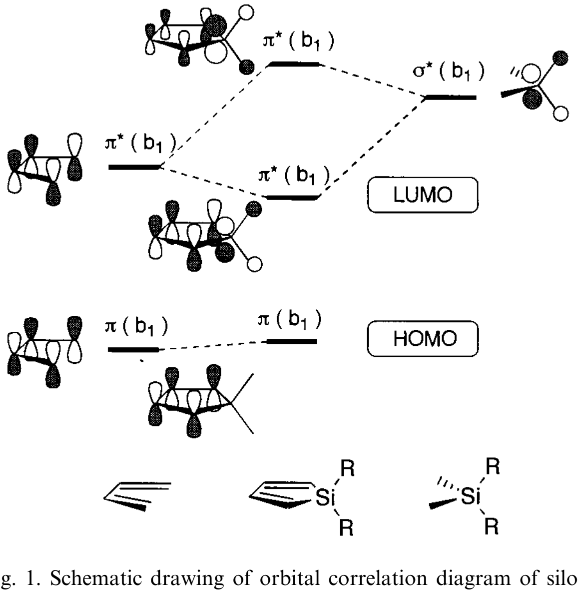

Fig. 1. Schematic drawing of orbital correlation diagram of silole.

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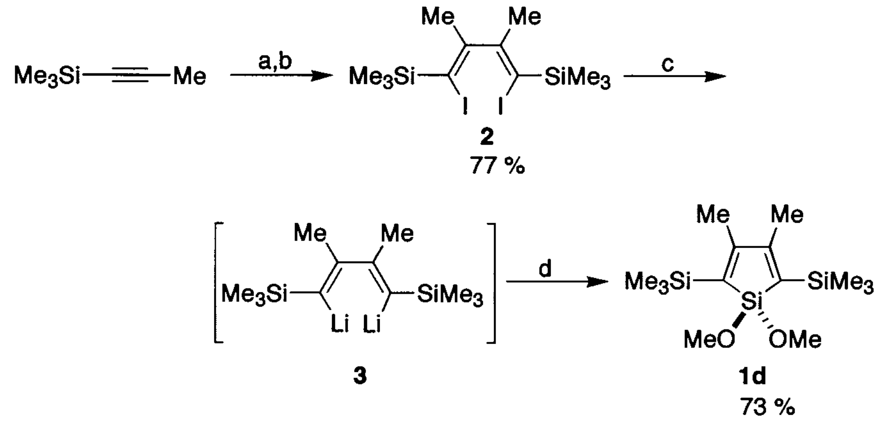
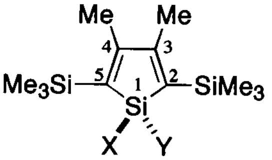


Scheme 1. Reagents and conditions: (a) Cp_2ZrCl_2 (10.5 mol. amt.), *n*-BuLi (2 mol.amt.), THF, −78°C to rt, 4 h. (b) I_2 (2.5 mol. amt.), THF, rt, 17 h. c) *n*-BuLi (2 mol.amt.), Et_2O, −78°C, 1 h. d) $(MeO)_4Si$ (1 mol. amt.), Et_2O, −78°C to rt, 16 h.

Reported herein are the synthesis of a series of 1,1-disubstituted-3,4-dimethyl-2,5-bis(trimethylsilyl)siloles **1** and the effect of the 1,1-substituents on their UV absorption spectra. Theoretical studies by ab initio calculations on a series of 1,1-disubstituted-*C*-unsubstituted siloles will also be discussed.



1a (X = Y = H)
1b (X = Y = *i*-Pr)
1c (X = Y = Ph)
1d (X = Y = OMe)
1e (X = OH, Y = F)
1f (X = Y = F)

2. Results and discussion

2.1. Synthesis of a series of 1,1-disubstituted-3,4-dimethyl-2,5-bis(trimethylsilyl)siloles

Since the stability of the silole mostly depends on the bulkiness of the 2,5-substituents [6]a, in this study, we selected the trimethylsilyl groups as the substituents at the 2,5-positions together with 3,4-dimethyl groups because of their facile handling even in the case of 1,1-dihalosiloles. Thus, a series of 1,1-disubstituted-3,4-dimethyl-2,5-bis(trimethylsilyl)siloles **1** have been prepared.

1,1-Dimethoxy-3,4-dimethyl-2,5-bis(trimethylsilyl)silole **1d** was first prepared based on the procedure reported by Ashe [7]a–c, West [7]d, and Tilley [7]e, as shown in Scheme 1. Thus, 2,3-dimethyl-1,4-bis(trimethylsilyl)-1,4-diiodobutadiene **2** ([7]a–b), prepared from trimethylsilylpropyne via zirconacyclopentadiene, was lithiated by butyllithium to form a dilithiated butadiene **3**, which was further reacted with tetramethoxysilane[1] to give **1d** in 73% yield. While West reported the coupling reaction of 1,2,3,4-tetramethyl-1,4-dilithio-1,3-butadiene with silicon tetrachloride to give 1,1-dichloro-2,3,4,5-tetramethylsilole in good yield [7], our 1,4-bis(trimethylsilyl) analog **3** only gave a complex mixture upon treatment with silicon tetrachloride.

The dimethoxysilole **1d** was derivatized to a series of siloles using conventional procedures, as shown in Scheme 2 [6]. Thus, the reduction of **1d** using $LiAlH_4$ afforded 1,1-dihydrosilole **1a** in 73% yield. The reaction of **1d** with isopropylmagnesium bromide in the presence of a catalytic amount of CuCN [9] afforded 1,1-diisopropylsilole **1b** in 62% yield. The compound **1d** was also treated with pyridinium poly(hydrogen fluoride) to give 1,1-difluorosilole **1f** in 80% yield. 1,1-Diphenylsilole **1c** and 1-fluoro-1-hydroxysilole **1e** were obtained from difluorosilole **1f** by the reaction with phenyllithium and the hydrolysis in 67 and 63% yields, respectively. All of these siloles are stable in the air and can be handled without special care.

2.2. Crystal structure of 1,1-diphenylsilole **1c**

The X-ray crystal structure of 1,1-diphenylsilole **1c** has been determined in order to compare its structure with its calculated geometry; the comparison will be discussed later in the section about calculation results. The crystal data and the atomic coordinates and isotropic temperature factors of **1c** are listed in Tables 1 and 2, respectively. Its ORTEP drawing is shown in Fig. 2 with selected bond lengths and angles. All the bond lengths and angles are in the normal range.

2.3. UV absorption spectra of a series of siloles

UV absorption spectral data in chloroform for these siloles are summarized in Table 3. Siloles **1** have their absorptions ascribed to the π–π* transitions around 310 nm.[2] Among a series of siloles **1**, the absorption

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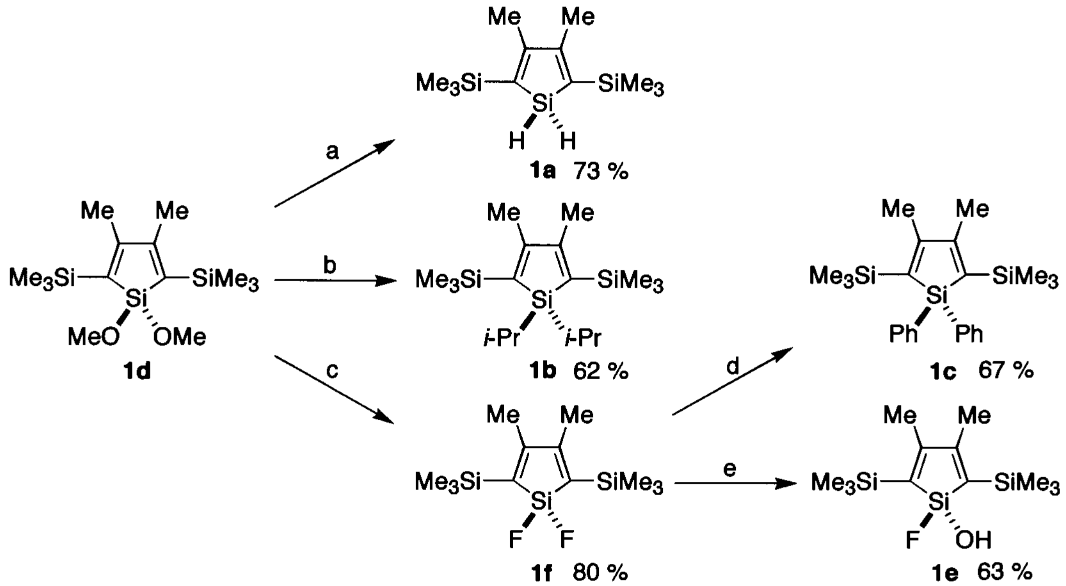
[1] CAUTION: Tetramethoxysilane is a highly toxic compound; its vapor can cause irreversible blindness [8].

[2] 1,1-Dialkyl-2,5-bis(trimethylsilyl)silole **1b** has its absorption maxima at about a 20 nm longer wavelength than 1,1,3,4-tetramethylsilole (λ_{max} 286 nm, log ϵ 3.23) [10], probably due to substituent effects of the 2,5-silyl groups. A similar substituent effect has been observed for silylated oligothiophenes [11].



Scheme 2. Reagents and conditions: (a) $LiAlH_4$ (1 mol. amt.), Et_2O, 0°C to rt, 1 h. (b) *i*-PrMgBr (3 mol. amt.), CuCN (0.2 mol. amt.), THF, reflux, 12 h. (c) $Py(HF)_x$, Et_2O, -78°C, 0.5 h. (d) PhLi (2.2 mol. amt.), THF, rt, 0.5 h. (e) H_2O/THF, rt, 4 h.

maxima steadily shifted to longer wavelengths in the order of H < alkyl < Ph < F from 305 for hydrogen to 318 nm for fluorine. Generally, the more electronegative 1,1-substituents tend to give longer absorption maxima.

Table 1
Crystal and intensity collection data for **1c**

Formula	$C_{24}H_{34}Si_3$
Mol.wt	406.79
Cryst color	Colorless, prismatic
Cryst dimens (mm)	0.50 × 0.50 × 0.10
Cryst syst	Monoclinic
Space group	$P2_1/c$ (no.14)
Cell const	
a (Å)	13.480(1)
b (Å)	9.418(2)
c (Å)	20.132(3)
b (°)	90.79(1)
V (Å^3)	2555.5200
Z	4
D_{calcd} (g cm^{-3})	1.057
Temp (°C)	20
Diffractometer	RAXIS-IV
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71070$ Å)
μ(Mo–K$_\alpha$) (cm^{-1})	1.92
$2\theta_{\max}$ (°)	55.0
No. of collected rflns	5065
No. of unique rflns	3701 ($I > 4\sigma(I)$)
No. of parameters	245
R[a]	0.047
wR[b]	0.074
Goodness-of-fit	1.28

[a] $R = \Sigma \| F_o | - | F_c \| \Sigma | F_o |$.
[b] $wR = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2]^{1/2}$.

2.4. *Calculations on the Electronic Structures of a Series of Siloles*

In order to obtain a deeper insight into the electronic effect by the 1,1-substituents, we performed ab initio

Table 2
Atomic coordinates and B_{iso}/B_{eq} for **1c**

Atom	x	y	z	B_{eq}
Si(1)	0.25251(4)	0.08544(5)	0.16937(3)	3.91(1)
Si(2)	0.33844(5)	−0.17365(7)	0.07001(3)	5.10(2)
Si(3)	0.15426(5)	0.16958(7)	0.31648(3)	5.17(2)
C(1)	0.2870(1)	−0.1027(2)	0.1491(1)	4.42(4)
C(2)	0.2684(2)	−0.1770(2)	0.2055(1)	4.84(5)
C(3)	0.2245(2)	−0.0975(2)	0.2631(1)	4.95(5)
C(4)	0.2120(1)	0.0452(2)	0.25589(10)	4.45(4)
C(5)	0.3597(2)	0.2130(2)	0.1659(1)	4.46(4)
C(6)	0.4074(2)	0.2579(3)	0.2241(1)	5.96(6)
C(7)	0.4874(2)	0.3507(4)	0.2231(2)	7.40(8)
C(8)	0.5217(2)	0.4000(3)	0.1638(2)	6.82(7)
C(9)	0.4766(2)	0.3588(3)	0.1053(2)	6.91(7)
C(10)	0.3964(2)	0.2672(3)	0.1064(1)	5.97(6)
C(11)	0.1467(2)	0.1505(2)	0.11662(9)	4.43(4)
C(12)	0.0651(2)	0.0621(3)	0.1080(1)	6.36(7)
C(13)	−0.0156(2)	0.1039(5)	0.0702(2)	8.44(10)
C(14)	−0.0167(3)	0.2349(5)	0.0408(2)	8.7(1)
C(15)	0.0613(3)	0.3231(4)	0.0488(2)	8.17(10)
C(16)	0.1425(2)	0.2837(3)	0.0867(1)	6.17(6)
C(17)	0.4744(2)	−0.1952(4)	0.0795(2)	8.52(10)
C(18)	0.3080(3)	−0.0497(4)	0.0008(1)	7.89(8)
C(19)	0.2824(3)	−0.3477(3)	0.0445(2)	7.92(9)
C(20)	0.2905(3)	−0.3329(3)	0.2145(2)	7.22(8)
C(21)	0.1955(3)	−0.1808(3)	0.3240(2)	7.29(8)
C(22)	0.2276(3)	0.1745(4)	0.3963(2)	8.9(1)
C(23)	0.0231(3)	0.1220(4)	0.3342(2)	8.8(1)
C(24)	0.1533(3)	0.3513(3)	0.2807(2)	8.93(10)

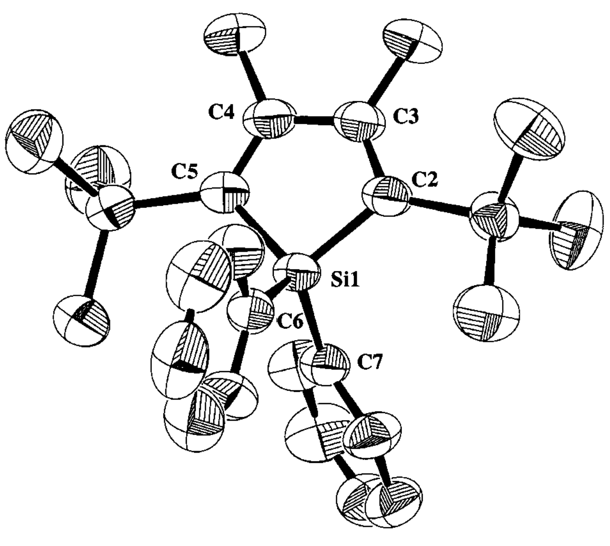
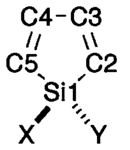


Fig. 2. ORTEP drawing of **1c** (50% probability for thermal ellipsoids). Selected bond lengths (Å) and angles (°): Si1–C2 1.878(2), Si1–C6 1.882(2), C2–C3 1.360(3), C3–C4 1.509(3), C2–Si1–C5 95.00(9), Si1–C2–C3 104.8(2), C2–C3–C4 117.7(2), C6–Si1–C7 110.51(10).

calculations on a series of 1,1-disubstituted-*C*-unsubstituted siloles **5** as model compounds of **1** at the HF/6-31G(d) level of theory [12].



5a (X = Y = H)
5b (X = Y = Me)
5c (X = Y = Ph)
5d (X = Y = OMe)
5e (X = OH, Y = F)
5f (X = Y = F)

Geometries of **5** were fully optimized, whose selected bond lengths and angles are summarized in Table 4. Comparison of the optimized geometry of 1,1-diphenylsilole **5c** with the crystal structure of **1c** shows a small difference in the angle C2–Si1–C5, probably due to the substituent effect of the 2,5-silyl groups; electropositive groups on the 2,5-positions tend to enlarge the angle. In a series of siloles **5**, the more electronegative the 1,1-substituents, the shorter the Si1–C2 bond length and the larger the C2–Si1–C5 bond angle.

The calculated HOMO and LUMO energy levels are summarized in Table 5 and plotted as a function of the 1,1-substituents in Fig. 3. These results clearly show the following two points. (1) The nature of substituents on the ring silicon largely affects not only the LUMO energy levels but also the HOMO energy levels to a comparable extent, contrary to our initial expectation. (2) Electronegative 1,1-substituents tend to decrease the HOMO and LUMO levels. Noteworthy is the fact that the HOMO and LUMO levels of 1,1-difluorosilole **5f** are lower than those of 1,1-dimethylsilole **5b** by more than 0.8 eV. These findings imply that the 1,1-substituents predominantly influence the electronic structure of the silole ring by an inductive effect rather than by perturbation through the $\sigma^*-\pi^*$ conjugation. Indeed, coefficients of the 3p orbital of the ring-silicon atom, which is a major part of the σ^* orbital of two exocyclic σ-bonds, is little perturbed by variation of the 1,1-substituents. However, the irregular drop in the LUMO level observed for the 1,1-diphenylsiloles (Fig. 3) is presumably ascribed to the extended $\sigma^*-\pi^*$ conjugation over the phenyl rings on the ring silicon atom[3].

Table 3
UV spectral data for a series of 3,4-dimethyl-2,5-bis(trimethylsilyl)siloles[a]

Compound	λ_{max} (nm)	log ϵ
1a (X = Y = H)	305	3.63
1b (X = Y = *i*-Pr)	308	3.73
1c (X = Y = Ph)	314	3.73
1d (X = Y = OMe)	315	3.69
1e (X = F, Y = OH)	316	3.66
1f (X = Y = F)	318	3.56

[a] In chloroform.

3. Conclusion

Experimentally, it has been observed that more electronegative 1,1-substituents on the ring silicon induce the bathochromic shift of the absorption maxima in the UV absorption spectra from 305 nm for hydrogen to 318 nm for fluorine. Theoretical calculations have shown that the 1,1-substituents largely affect the HOMO and LUMO energy levels of the silole ring mainly due to their inductive effects. The present fundamental data would be useful for the fine-tuning of the electronic structures and properties of silole-based π-conjugated compounds by changing the 1,1-substituents, in addition to the modification by the 2,5- and 3,4-substituents [1]e.

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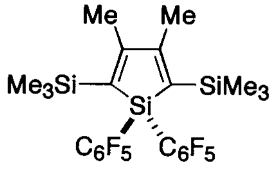
[3] From these results, we anticipated that the introduction of more electronegative aryl groups on the ring-silicon atom causes a decrease in the $\pi-\pi^*$ transition energy by the more effective $\sigma^*-\pi^*$ conjugation. However, 1,1-bis(pentafluorophenyl)silole **1g**, prepared in 87% yield by the reaction of **1f** with C_6F_5Li, has the same absorption maxima (λ_{max} 314 nm; log ϵ 3.60) as that of **1c**, suggesting no significant effect by the nature of aryl groups among the 1,1-diarylsiloles.



1g

Table 4
Selected bond lengths (Å) and bond angles (°) of optimized geometries of **5**[a]

Compound (X, Y)	**5a** H, H	**5b** Me, Me	**5c** Ph, Ph	**5d** OMe, OMe	**5e** F, OH	**5f** F, F
Si1–C2	1.877	1.884	1.884	1.869	1.867	1.856
C2–C3	1.331	1.331	1.331	1.330	1.330	1.330
C3–C4	1.494	1.494	1.495	1.501	1.503	1.505
C2–Si1–C5	92.0	91.3	91.2	93.0	93.0	94.2
Si1–C2–C3	107.1	107.6	107.7	106.4	106.6	105.7
C2–C3–C4	116.9	116.8	116.7	117.1	116.9	117.2
X–Si1–Y	108.0	109.8	110.3	109.5	103.8	104.7

[a] Geometries were fully optimized at HF/6-31G(d) level of theory.

4. Experimental Section

Melting point (mp) determinations were performed by using a Yanaco MP-S3 instrument and are uncorrected. ^{1}H-, ^{13}C-, ^{19}F-, and ^{29}Si-NMR spectra were measured using a JEOL EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, 254 MHz for ^{19}F, and 53.5 MHz for ^{29}Si) spectrometer in appropriate solvents. Chemical shifts are reported in δ ppm with reference relative to the residual protio-solvent peak for ^{1}H and ^{13}C, to $CFCl_3$ for ^{19}F, and to TMS for ^{29}Si, respectively. Thin layer chromatography (TLC) was performed on plates coated with a 0.25 mm thickness of Silica Gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70–230 mesh) (Merck). High-performance liquid chromatography (HPLC) was done using a 20 × 250 mm Wakosil 5Sil column (Wako). Tetrahydrofuran and diethyl ether were freshly distilled before use from sodium/benzophenone. Tetramethoxysilane was purchased from the Shin-Etsu and distilled before use. Pyridinium poly(hydrogen fluoride) was purchased from the Aldrich and used without further purification.

4.1. *1,4-Diiodo-2,3-dimethyl-1,4-bis(trimethylsilyl) butadiene (**2**)*

To a THF (100 ml) solution of Cp_2ZrCl_2 (14.6 g, 50 mmol) and 1-trimethylsilyl-1-propyne (14.8 ml, 100 mmol) was added a hexane solution of *n*-BuLi (67.9 ml, 1.62 M, 110 mmol) at −78°C. After stirring at the same temperature for 30 min, the mixture was allowed to warm to room temperature and stirred for 4 h. A THF (100 ml) solution of iodine (63.5 g, 250 mmol) was added to the resulting mixture at −78°C. After the addition, the mixture was warmed to room temperature and stirred for a further 17 h. A saturated aqueous solution of $Na_2S_2O_3$ was added and the mixture was extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and condensed by rotary evaporation. The resulting mixture was subjected to silica gel column chromatography using hexane as an eluent ($R_f = 0.68$) to afford spectroscopically pure **2** (18.5 g, 38.7 mmol) in 77% yield as a light yellow solid: ^{1}H-NMR ($CDCl_3$) δ 0.30 (s, 18H), 1.97 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ 1.49, 19.39, 103.16, 161.92.

Table 5
Calculated HOMO and LUMO energy levels of siloles **5**[a]

Compound	E(HOMO) (eV)	E(LUMO) (eV)
5a	−8.760	2.643
5b	−8.490	2.871
5c	−8.457	2.625
5d	−8.625	2.711
5e	−9.071	2.141
5f	−9.325	1.950

[a] Calculated at HF/6-31G(d) level of theory.

4.2. *1,1-Dimethoxy-3,4-dimethyl-2,5-bis(trimethylsilyl)silole (**1d**)*

To a solution of **2** (39.6 g, 82.8 mmol) in 200 ml of Et_2O was added a hexane solution of *n*-BuLi (106 ml,

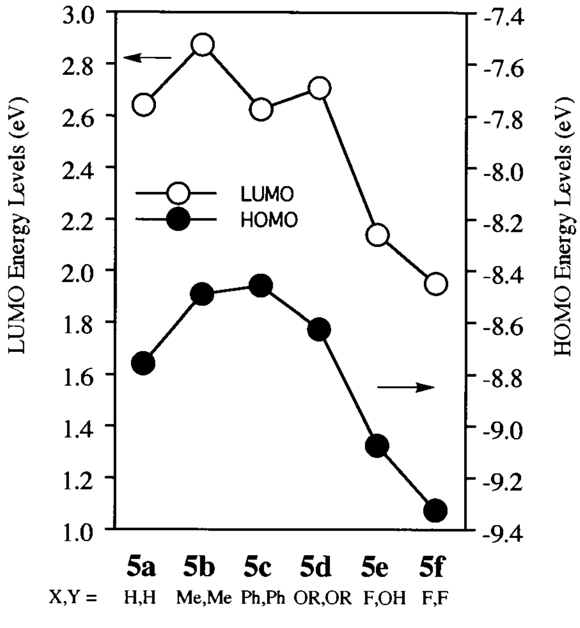


Fig. 3. Change in the HOMO and LUMO energy levels of 1,1-disubstituted siloles **5** as a function of the substituents on the ring silicon.

1.61 M, 170 mmol) at −78°C. The solution was stirred at −78°C for 1 h. Tetramethoxysilane (12.2 ml, 82.8 mmol) was added to the mixture at −78°C. The mixture was gradually warmed to room temperature and stirred for 16 h. The mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and condensed. The resulting mixture was subjected to silica gel column chromatography (hexane/EtOAc = 40/1; $R_f = 0.25$) to afford **1d** (19.1 g, 60.8 mmol) in 73% yield: m.p. 61–63°C. ^{1}H-NMR ($CDCl_3$) δ 0.15 (s, 18H), 2.10 (s, 6H), 3.41 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ −0.07, 20.42, 49.90, 129.92, 167.76. ^{29}Si-NMR ($CDCl_3$) δ −10.95, −5.76. Anal. Calcd for $C_{14}H_{30}O_2Si_3$: C, 53.44; H, 9.61. Found: C, 53.62; H, 9.67.

4.3. 3,4-Dimethyl-2,5-bis(trimethylsilyl)silole (1a)

A solution of **1d** (315 mg, 1 mmol) in Et_2O (2 ml) was added to a vigorously stirred suspension of $LiAlH_4$ (38 mg, 1 mmol) in Et_2O (2 ml) at 0°C. The suspension was allowed to warm to room temperature and then stirred for 1 h. After quenching the excess amount of $LiAlH_4$ by the addition of ethyl acetate (1 ml), the mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was subjected to silica gel column chromatography using hexane as an eluent ($R_f = 0.84$) to afford a colorless oil **1a** (185 mg, 0.73 mmol) in 73% yield: ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, 18H), 2.14 (s, 6H), 4.23 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ 0.45, 21.13, 135.08, 168.52. ^{29}Si-NMR ($CDCl_3$) δ −31.08 (t, $^1J_{Si-H} = 192.4$ Hz), −10.11 (dec, $^2J_{Si-H} = 6.7$ Hz). Anal. Calcd for $C_{12}H_{26}Si_3$: C, 56.61; H, 10.29. Found: C, 56.17; H, 10.47.

4.4. 1,1-Diisopropyl-3,4-dimethyl-2,5-bis(trimethylsilyl)silole (1b)

A THF solution of *i*-PrMgBr (24 ml, 1.25 M, 30 mmol) was added to a mixture of **1d** (3.15 g, 10 mmol) and CuCN (179 mg, 2 mmol) at room temperature. The resulting mixture was refluxed for 12 h. The mixture was cooled to 0°C, hydrolyzed by the slow addition of a saturated aqueous solution of NH_4Cl, and extracted with Et_2O. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was distilled bulb-to-bulb under reduced pressure (125–130°C/0.6 mmHg) to give **1b** (2.1 g, 6.2 mmol) in 62% yield as a viscous oil. The oil slowly solidified upon standing at room temperature to give a colorless solid: m.p. 56–58°C. ^{1}H-NMR ($CDCl_3$) δ 0.15 (s, 18H), 0.94 (d, $J = 7.3$ Hz, 12H), 1.21 (sep, $J = 7.3$ Hz, 2H), 2.10 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ 1.19, 11.79, 18.85, 21.28, 136.44, 167.37. ^{29}Si-NMR ($CDCl_3$) δ −11.07, 30.41. Anal. Calcd for $C_{18}H_{38}Si_3$: C, 63.82; H, 11.31. Found: C, 63.81; H, 11.51.

4.5. 1,1-Difluoro-3,4-dimethyl-2,5-bis(trimethylsilyl)silole (1f)

To an Et_2O (20 ml) solution of **1d** (1.26 g, 4.00 mmol) was added 2 ml of $Py(HF)_x$ (HF content: ~70%) at −78°C. The mixture was stirred at the same temperature for 30 min and condensed under reduced pressure. The residue was twice extracted with dry hexane. The hexane layer was concentrated in vacuo. The residue was distilled bulb-to-bulb at 95–100°C/0.6 mmHg to yield **1f** (0.93 g, 3.20 mmol) in 80% yield as a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 0.17 (s, 18H), 2.12 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ −0.30, 20.49 (t, $^4J_{C-F} = 3.1$ Hz), 125.93 (t, $^2J_{C-F} = 13.8$ Hz), 169.61 (t, $^3J_{C-F} = 7.9$ Hz). ^{29}Si-NMR ($CDCl_3$) δ −10.70 (t, $^1J_{Si-F} = 325.2$ Hz), −9.99. ^{19}F-NMR (C_6D_6) δ −151.10. Anal. Calcd for $C_{12}H_{24}F_2Si_3$: C, 49.60; H, 8.33. Found: C, 49.25; H, 8.49.

4.6. 3,4-Dimethyl-2,5-bis(trimethylsilyl)-1,1-diphenylsilole (1c)

To a THF (4 ml) solution of difluorosilole **1f** (436 mg, 1.50 mmol) was added a pentane solution of PhLi (3.30 ml, 1.03 M, 3.40 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. The mixture was hydrolyzed with water and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was recrystallized from hexane to afford **1c** (406 mg, 1.00 mmol) in 67% yield as colorless crystals: m.p. 129–131°C. ^{1}H-NMR ($CDCl_3$) δ −0.06 (s, 18H), 2.21 (s, 6H), 7.25–7.43 (m, 6H), 7.55–7.68 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ 0.65, 21.06, 127.66, 129.33, 133.59, 135.69, 139.30, 168.09. ^{29}Si-NMR ($CDCl_3$) δ −10.02, 5.09. Anal. Calcd for $C_{24}H_{34}Si_3$: C, 70.86; H, 8.42. Found: C, 70.90; H, 8.57.

4.7. 1,1-Bis(pentafluorophenyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)silole (1g)

To an Et_2O (10 ml) solution of bromopentafluorobenzene (0.62 g, 2.50 mmol) was added a hexane solution of *n*-BuLi (1.55 ml, 1.61 M, 2.50 mmol) at −78°C. The mixture was stirred at the same temperature for 15 min. An Et_2O (5 ml) solution of **1f** was added dropwise to the mixture at −78°C. The mixture was gradually warmed to room temperature over 6 h followed by hydrolysis with water. After the usual

Table 6
Total SCF energies (Hartree) of siloles **5**

Compound	HF/6-31G(d)
5a	−443.83984
5b	−521.93556
5c	−902.93556
5d	−671.71257
5e	−617.68489
5f	−641.70401

aqueous work-up, the residue was subjected to column chromatography on silica gel (hexane, $R_f = 0.75$) to give **1g** (0.51 g, 0.87 mmol) in 87% yield as a colorless solid: m.p. 77–79°C. ^{1}H-NMR (CDCl$_3$) δ 0.02 (s, 18H), 2.19 (s, 6H). ^{13}C-NMR (CDCl$_3$) δ 0.43, 21.31, 106.09 (m), 133.94, 135.35 (m), 139.14 (m), 140.68 (m), 144.46 (m), 147.35 (m), 150.96 (m), 169.09. ^{29}Si-NMR (CDCl$_3$) δ −15.15, −8.27. Anal. Calcd for $C_{24}H_{24}F_{10}Si_3$: C, 49.13; H, 4.12. Found: C, 49.30; H, 4.18.

*4.8. 1-Fluoro-1-hydroxy-3,4-dimethyl-2,5-bis(trimethylsilyl)silole (**1e**)*

Difluorosilole **1f** (100 mg, 0.34 mmol) was dissolved into 2.5 ml of aqueous THF (THF/H$_2$O = 4/1) and stirred at room temperature 4 h in air. The resulting mixture was extracted with ether. The extract was washed with brine, dried over MgSO$_4$, filtered, and evaporated. The residue was passed through a short silica gel column and then subjected to HPLC on silica gel (hexane/EtOAc = 20/1, $R_f = 0.26$) to give **1e** (62.0 mg, 0.21 mmol) in 63% yield as a colorless solid: m.p. 50–52°C. ^{1}H-NMR (CDCl$_3$) δ 0.16 (s, 18H), 2.10 (d, $^5J_{H-F} = 1.10$ Hz, 6H), 2.35 (s, 1H). ^{13}C-NMR (CDCl$_3$) δ −0.07, 20.36 (d, $^4J_{C-F} = 2.4$ Hz), 128.78 (d, $^2J_{C-F} = 15.9$ Hz), 168.11 (d, $^3J_{C-F} = 6.0$ Hz). ^{29}Si-NMR (CDCl$_3$) δ −10.40, −6.95 (d, $^1J_{Si-F} = 309.7$ Hz). ^{19}F-NMR (C$_6$D$_6$) δ −152.00. Anal. Calcd for $C_{12}H_{25}FOSi_3$: C, 49.94; H, 8.73. Found: C, 49.62; H, 8.77.

4.9. X-ray structure determination

Single crystals of compound **1c** suitable for X-ray crystal analysis were obtained by recrystallization from hexane. The intensity data was collected at 293 K on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo–K$_\alpha$ radiation from a rotating-anode generator operating at 50 kV and 100 mA ($2\theta_{max} = 55°$, 25 3° osillation images each being exposed for 30 min). The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structure was solved by direct methods in SIR92 [13] and full-matrix least squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions but not refined. The crystal data and analytical condition and the final atomic coordinates and isotropic temperature factors are listed in Tables 1 and 2. Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

4.10. Calculations

Ground-state ab initio calculations on the compounds **5** were performed using the Hartree-Fock (HF) approximation with the Gaussian 94 program [14]. The geometries of **5** were fully optimized using 6-31G(d) basis set. Some selected data of the optimized geometries are listed in Table 4 and the final total SCF energies for these compounds are summarized in Table 6.

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