Crystallographic Studies of Organosilicon Porphyrins: Stereoelectronic Effects of Axial Groups on the Nonplanarity of the Porphyrin Ring

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Introduction

Conformations of porphyrin macrocycles have attracted attention not only from the fundamental interest in the properties of π-conjugate systems but also in relation to the biological activities of heme-containing enzymes.[1,2] Recently, there have been reported numerous conformationally distorted porphyrins,[1] which include saddled,[3−5] ruffled,[4,6−8] domed,[9] and waved[4,5] conformations (Figure 1). In general, these nonplanar conformations are likely to be caused by electronic and/or steric requirements of the peripheral substituents[3−6] and central elements.[7−9] For some iron porphyrins, however, effects of the axial group on the nonplanarity of the porphyrin ring have been indicated.[10] On the other hand, conformations of porphyrin complexes of nonmetal elements such as phosphorus and silicon have not been explored until very recently,[11−13] despite their unique reactivities and properties.[14,15] Akiba et al. have reported that the porphyrin rings in some phosphorus complexes adopt planar and ruffled conformations depending on the axial group.[11b] More recently, Lemke et al. have investigated difluoride and bis(triflate) complexes of silicon porphyrins, and have demonstrated that their porphyrin rings are significantly ruffled in the crystalline state.[12,13] Herein we report synthesis and results of the first crystallographic studies on a series of organosilicon porphyrins.

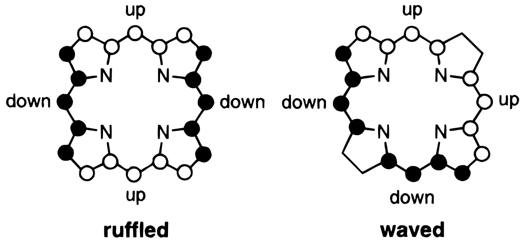
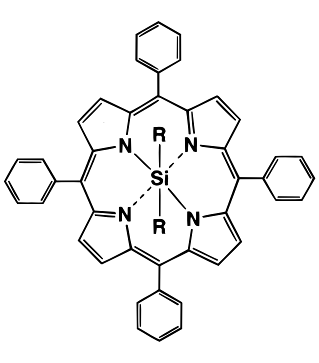


Figure 1. Schematic structures of ruffled and waved porphyrin rings (ref 4a). Circles and filled circles represent the carbon atoms above and below the pyrrole 4N plane, respectively.

Results and Discussion



Si(TPP)R$_2$

1 **R = CH$_2$CH$_2$CH$_3$**
2 **R = CH$_2$Si(CH$_3$)$_3$**
3 **R = CH=CH$_2$**
4 **R = C$_6$H$_5$**
5 **R = C≡CC$_6$H$_5$**

Si(TPP)(CH$_2$CH$_2$CH$_3$)$_2$ (**1**), Si(TPP)(CH$_2$SiMe$_3$)$_2$ (**2**), Si(TPP)(CH=CH$_2$)$_2$ (**3**), and Si(TPP)(C$_6$H$_5$)$_2$ (**4**), and Si(TPP)(C≡CC$_6$H$_5$)$_2$ (**5**) [TPP: 5,10,15,20-tetraphenylporphyrinato] were synthesized in two steps from a lithiated tetraphenylporphyrin (Li$_2$(TPP)).[16] Reaction of Li$_2$(TPP) with Cl$_3$SiH in CH$_2$Cl$_2$ gave dichlorosilicon complex Si(TPP)Cl$_2$,[12] which was

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Table 1. Crystallographic Data of **2**−**5**

	2 (R = $CH_2Si(CH_3)_3$)	**3** (R = $CH{=}CH_2$)	**4** (R = C_6H_5)	**5** (R = $C{\equiv}CC_6H_5$)
empirical formula	$C_{52}H_{50}N_4Si_3$	$C_{48}H_{34}N_4Si$	$C_{56}H_{38}N_4Si$	$C_{60}H_{38}N_4Si$
fw	815.3	694.9	795.0	843.0
space group	$C2/c$	$I4$	$P2_1/c$	$P\bar{1}$
a, Å	12.104(3)	13.783(2)	10.516(1)	11.061(2)
b, Å	18.381(4)	13.783(2)	31.624(4)	11.068(4)
c, Å	20.850(4)	9.909(2)	12.931(2)	10.796(2)
α, deg				116.45(2)
β, deg	100.03(2)		99.41(1)	107.27(2)
γ, deg				73.77(2)
V, Å^3	4568(2)	1882.5(8)	4242(1)	1113.1(5)
Z	4	2	4	1
D_{calc}, g cm^{-3}	1.185	1.226	1.244	1.257
R	0.109	0.062	0.075	0.072
wR	0.137	0.079	0.104	0.098
GOF	2.680	1.114	1.513	1.002

reacted with the corresponding Grignard reagents in C_6H_6 to give **1**−**5** in 50−57% yield based on $TPPH_2$.[14] A difluorosilicon complex ($Si(TPP)F_2$, **6**)[13] could also be used in place of $Si(TPP)Cl_2$ for the above reaction, affording the organosilicon porphyrins in comparable yields.

Crystal structures of **2**−**5** were successfully determined, and the crystal data were summarized in Table 1.[17] All these complexes were found to adopt a trans configuration as for the two axial groups, having a silicon atom at a geometric center of the four pyrrole nitrogen atoms (4N). The divinyl complex (**3**) was virtually “planar” with respect to the porphyrin skeleton (Figure 2a), where the average displacement for the meso carbon atoms from the 4N plane (Δr) was only 0.03(2) Å [Figure 3 (●)], and the average distance between two diagonal meso carbon atoms (trans C_m-C_m) was 6.88 Å (Table 1). Similarly, the porphyrin ring in the dipropyl complex (**1**) was “planar”.[17] On the other hand, the crystal structure of the bis(2-phenylethynyl) complex (**5**) showed that the porphyrin ring is nearly planar but with a slightly “waved”, chairlike conformation (Figures 1 and 2 c) with Δr and trans C_m-C_m, respectively, of 0.13 and 6.85 Å (Table 2). The two adjacent meso carbon atoms [C(15) and C(20)] were located 0.129(2) and 0.123(2) Å above the 4N plane, respectively, while the others [C(5) and C(10)] were below the 4N plane [Figure 3 (◇)]. Furthermore, the β-carbon atoms of the pyrrole rings B and D (Figure 3) were also situated above and below the 4N plane, respectively, with an average displacement of 0.130(2) Å, while the other two pyrrole rings (A and C) were twisted with respect to the 4N plane. Likewise, in the bis(trimethylsilylmethyl) complex (**2**), the porphyrin skeleton was slightly “waved” [Figure 3 (▲)] with Δr and trans C_m-C_m of 0.09 and 6.87 Å, respectively (Table 2). Such a “waved” conformation of the porphyrin ring is quite rare and has been reported only for porphyrins having a steric repulsion between the meso and pyrrole-β substituents.[4,5] In sharp contrast with the above examples, the crystal structure of the diphenyl complex (**4**) clearly showed a nonplanar, ruffled conformation [Figures 1 and 2b], similarly to $Si(TTP)(OSO_2CF_3)_2$[12] and $Si(TTP)F_2$ (TTP: 5,10,15,20-tetra(4-methylphenyl)-porphyrinato),[13] where the meso carbon atoms lie above and below the 4N plane alternately [Figure 3 (□)]. However, the observed Δr value of 0.48 Å is smaller than those reported for $Si(TTP)(OSO_2CF_3)_2$ (0.79 Å)[12] and $Si(TTP)F_2$ (0.63 Å)[13] (Table 2). The pyrrole rings exhibited an average tilt angle of 15.76° relative to the 4N plane, and the trans C_m-C_m value was 6.73 Å.

The structural data in Table 2 show that the average Si−N bond distances in silicon porphyrin complexes, $Si(por)R_2$, increase in the following order: R = CF_3SO_3 (1.87 Å) < F (1.92−1.93 Å) < C_6H_5 (1.97 Å) < $C{\equiv}CC_6H_5$ (1.98 Å) < $(CH_3)_3SiCH_2$ ~ $CH{=}CH_2$ (2.01 Å). Taking into account the observed Δr and trans C_m-C_m values, the above order indicates a correlation between the nonplanarity of the porphyrin ring and the Si−N interaction: electron-withdrawing axial groups such as F^- and $CF_3SO_3^-$ promote the Si−N interaction, resulting in a shortening of the Si−N bond distance and a ruffling of the porphyrin ring. In contrast, for the organosilicon porphyrins, **2**−**5**, the weaker Si−N interaction, due to the more electron-donating axial groups, is accompanied by a less nonplanar or virtually planar conformation for the porphyrin ring. The diphenyl complex (**4**) is an exception, where possible steric interactions between the *ortho*-H of the phenyl ligands and the porphyrin moiety may contribute to the nonplanarity of the porphyrin skeleton (Figure 1b): The two phenyl ligands are staggered by an angle of 67°, which is almost bisected by a $C_{ipso}-Si-N$ plane. The average interatomic contacts for the *ortho*-H atoms (based upon their corrected positions) with the nearest meso carbon, pyrrole-α carbon, and nitrogen atoms are respectively 3.08, 2.76, and 2.52 Å. The shortest van der Waals C−H and N−H contacts, as estimated from the corresponding sums of the respective van der Waals radii for H (1.20 Å), N (1.55 Å), and C (1.70 Å),[18] are respectively 2.90 and 2.75 Å, which are comparable to the observed intraatomic contacts. Thus, the porphyrin ring is ruffled in such a way as to minimize the steric interactions with the phenyl ligands.

Among the organosilicon porphyrins, **2**−**5**, the Si−C bond distances of **3** (Si−C (sp^2); 1.83(2) Å) and **5** (Si−C (sp); 1.819(2) Å) are apparently shorter than those of **2** (Si−C (sp^3); 1.929(6) Å) (Table 2). In contrast, the diphenyl complex (**4**, Si−C (sp^2)) shows notably longer Si−C bond distances (1.943(4) and 1.950(3) Å) than those of **3**. This observation again indicates the steric repulsion between the phenyl ligand and the porphyrin moiety. For comparison with the known examples, the Si−C bond distances of **4** are shorter than the metal−carbon bond distances of planar $Sn(TPP)(C_6H_5)_2$ (2.196(4) and 2.212(4) Å)[19] but almost comparable to that of nonplanar $Fe(TPP)C_6H_5$ (1.955(3) Å).[20]

In the ^1H NMR spectra in C_6D_6 at 25 °C, the diphenyl complex (**4**) having a notably ruffled conformation exhibited a pyrrole-β signal at a higher magnetic field (δ 9.10) than the planar dipropyl and divinyl complexes (**1** [δ 9.28] and **3** [δ 9.28]).[21] On the other hand, such a shift was less significant or not observed for the “waved” organosilicon porphyrins (**5** [δ 9.20] and **2** [δ 9.28]).

Conclusion

Through structural studies on a series of organosilicon tetraphenylporphyrins (**1**−**5**), we have shown that their porphyrin rings generally adopt much less distorted conformations than those of the difluoride and bis(triflate) complexes. This

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(17) The crystal of **1** contained 0.5 molecule of cyclohexane relative to **1**, as evidenced by elemental analysis. Although the structure of **1** was not well-behaved (R down to 13%) due to the presence of a significant disorder of the cyclohexane solvate and to partial decomposition of the crystal during the data collection, the porphyrin core was confirmed to adopt a virtually planar conformation with Δr smaller than 0.04 Å.

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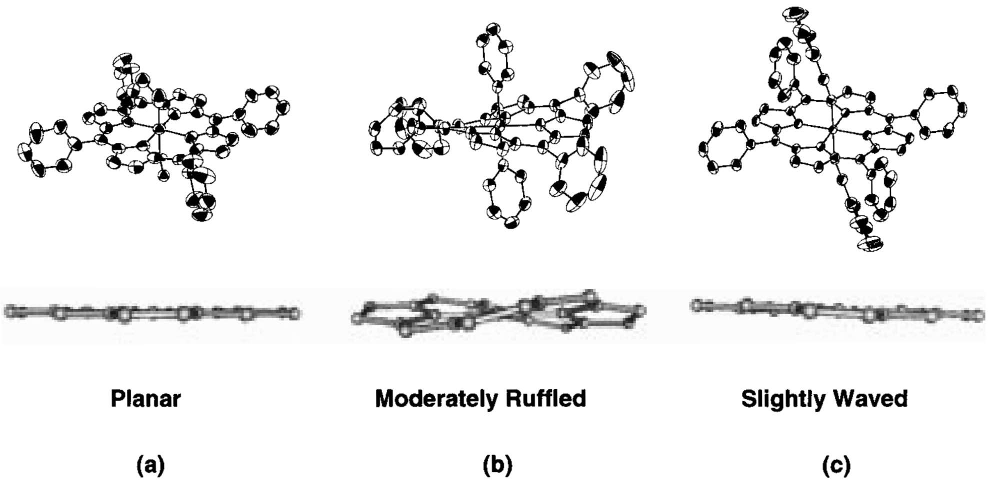

Figure 2. ORTEP views (30% probability ellipsoids with hydrogen atoms omitted for clarity) and schematic side views of the porphyrin skeletons of (a) Si(TPP)($CH{=}CH_2$)$_2$ (**3**), (b) Si(TPP)(C_6H_5)$_2$ (**4**), and (c) Si(TPP)($C{\equiv}CC_6H_5$)$_2$ (**5**).

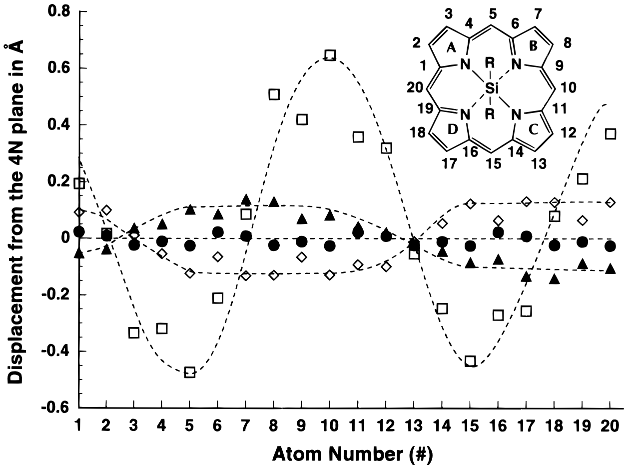

Figure 3. Displacements of the carbon atoms of the porphyrin skeleton from the pyrrole 4N plane; (▲) Si(TPP)(CH_2SiMe_3)$_2$ (**2**), (●) Si(TPP)($CH{=}CH_2$)$_2$ (**3**), (☐) Si(TPP)(C_6H_5)$_2$ (**4**), and (◇) Si(TPP)($C{\equiv}CC_6H_5$)$_2$ (**5**). Atom numbers (#) of the porphyrin skeleton are shown in the schematic structure.

observation indicates that the stereoelectronic features of the axial ligands may influence the conformational structure of the porphyrin ring.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was prepared from pyrrole and benzaldehyde in refluxing propionic acid and recrystallized from $CHCl_3$/MeOH. Grignard reagents in hexane were purchased from Kanto Chemical Co. and used as received. $HSiCl_3$ from Tokyo Kasei was subjected to a trap-to-trap distillation over anhydrous K_2CO_3 just before use.

Si(TPP)($CH_2CH_2CH_3$)$_2$ (1). To a THF (120 mL) solution of $TPPH_2$ (1.23 g, 2 mmol) was added a THF solution (8 mL) of Li(N($SiMe_3$)$_2$) (8 mmol), and the mixture was refluxed for 3 h under Ar to afford a green solution of Li_2(TPP). After the solvent was removed under reduced pressure, CH_2Cl_2 (60 mL) and $HSiCl_3$ (0.4 mL, 1.8 mmol) were successively added to this flask at −78 °C under Ar, and the mixture was allowed to warm to room temperature. After the mixture was stirred overnight, the volatile fraction was removed under reduced pressure to leave greenish powdery Si(TPP)Cl_2.[12] Then, to this flask were successively added C_6H_6 (50 mL) and a THF solution (25 mL) of 1-propylmagnesium bromide (25 mmol), and the mixture was stirred at room temperature. After 2 h, silica gel (Kanto Chemical. Co., 60N, 50 g) was added to the reaction mixture, and then the solvent was evaporated. The resulting green powder was placed on a silica gel column, and the first green fraction eluted with CH_2Cl_2 was collected and evaporated to give a green solid, which was washed with cyclohexane to give **1** as dark green crystals (0.83 g, 57% yield). ^{1}H NMR: δ 9.28 (s, 8H, pyrrole-β), 8.37 (d, 8H, *o*-H), 7.62 (m, 12H, *m*- and *p*-H), −1.38 (t, 6H, CH_3), −4.24 (m, 4H, CH_2CH_3), −6.51(m, 4H, $SiCH_2$). UV−vis: λ_{max} 656, 608.5, 558, 453.5, 425.5, 342.5 nm. Anal. Calcd for $C_{50}H_{42}N_4Si{\cdot}0.5\ C_6H_{12}$: C, 82.77; H, 6.29; N, 7.28. Found: C, 82.54; H, 6.51; N, 7.36.

Organosilicon porphyrins **2**−**5** were also synthesized in a manner similar to the above. **2**: ^{1}H NMR: δ 9.28 (s, 8H, pyrrole-β), 8.52 (d, 8H, *o*-H), 7.66 (m, 12H, *m*- and *p*-H), −2.52 (s, 18H, $SiCH_3$), −7.22 (s, 4H, $SiCH_2Si$). UV−vis: λ_{max} 654.5, 607.5, 562.0, 454.5, 345.0 nm. Anal. Calcd for $C_{52}H_{50}N_4Si_3$: C, 75.61; H, 6.18; N, 6.87. Found: C, 75.78; H, 6.32; N, 6.65. **3**: ^{1}H NMR: δ 9.28 (s, 8H, pyrrole-β), 8.28 (d, 8H, *o*-H), 7.64 (m, 12H, *m*, *p*-H), 2.08 (m, 4H, $CH{=}CH_2$), −0.44 (m, 2H, $CH{=}CH_2$). UV−vis: λ_{max} 648, 603, 451, 340 nm. FAB-MS: *m*/*z* 667 [$M^+ - CH{=}CH_2$]. **4**: ^{1}H NMR: δ 9.10 (s, 8H, pyrrole-β), 7.93 (d, 8H, *o*-H in *meso*-Ph), 7.40 (m, 12H, *m*, *p*-H in *meso*-Ph), 5.74 (t, 2H, *p*-H in axial Ph), 5.34 (t, 4H, *m*-H in axial Ph), 1.62 (d, 4H, *o*-H in axial Ph). UV−vis: λ_{max} 645.5, 600, 454.5, 343 nm. Anal. Calcd for $C_{56}H_{38}N_4Si$: C,84.60; H, 4.82; N, 7.05. Found: C, 84.00; H, 5.14; N, 7.18. **5**: ^{1}H NMR: δ 9.20 (s, 8H, pyrrole-β), 8.14 (d, 8H, *o*-H in *meso*-Ph), 7.59 (m, 12H, *m*, *p*-H in *meso*-Ph), 6.36 (t, 2H, *p*-H in axial Ph), 6.26 (t, 4H, *m*-H in axial Ph), 5.67 (d, 4H, *o*-H in axial Ph). UV−vis: λ_{max} 638, 594, 451, 329.5 nm. FAB-MS: *m*/*z* 842 [M^+], 741 [$M^+ - C{\equiv}CC_6H_5$].

X-ray Crystallography. The crystal data and details of the data collection for **2**−**5** are given in Table 2. Crystals suitable for the X-ray crystallographic analyses were obtained by slow diffusion of a cyclohexane vapor into concentrated CH_2Cl_2 solutions of **2**−**5**. The crystals were mounted on the top of a glass capillary and placed on a Mac Science MXC 18 four-circle diffractometer, where the diffraction data were measured with a graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) at room temperature. Lattice parameters were determined by least-squares fitting of 20 reflections. No crystal decay was observed during the data collection, as judged from the three representative reflections checked at every 100 data points. The structures were solved by direct methods and refined on F_o by full-matrix least squares by using the CRYSTAN GM packages. For **2**, the crystal structure was constrained by a 2-fold rotation axis passing through the silicon atom and two diagonal pyrrole nitrogens, and the asymmetric unit is comprised of half of the molecule. The crystal structure of **3** was constrained by a crystallographic 4-fold rotation axis passing through the silicon atom and two α-vinyl carbons, and the asymmetric unit is a quarter of the molecule. The crystal structure of **5** involved a crystallographic inversion center at the silicon atom, and the asymmetric unit is comprised of half of the molecule. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included using a riding model with fixed C−H distances of 0.96

Table 2. Degrees of Distortion and Selected Structural Data of Silicon Tetraarylporphyrins

	2 (R = $CH_2Si(CH_3)_3$)	**3** (R = $CH{=}CH_2$)	**4** (R = C_6H_5)	**5** (R = $C{\equiv}CC_6H_5$)	$Si(TTP)(O_3SCF_3)_2$[a]	$Si(TTP)F_2$[b]
Δr (Å)[c]	0.09	0.03	0.48	0.13	0.79	0.63
trans C_m-C_m (Å)[d]	6.87	6.88	6.73	6.85	6.46	6.61
averaged Si−N distance (Å)	2.01	2.01	1.97	1.98	1.87	1.92
axial Si−C distances (Å)[e]	1.929(6)	1.83(2)	1.943(4), 1.950(3)	1.819(2)	–	–

[a] Reference 12. [b] Reference 13. [c] Average displacement for the meso carbon atoms from the pyrrole 4N plane. [d] Average distance between the two diagonal meso carbon atoms. [e] Estimated standard deviations are given in parentheness.

Å and isotropic temperature factors set equal to those of their adjacent carbon atoms. For **3**, the β-vinyl carbon and hydrogen atoms were treated isotropically with a site occupation factor of 0.25.

Measurements. Absorption spectra were recorded in CH_2Cl_2 at 25 °C on a JASCO Type U-best 50 spectrometer. ^1H NMR spectra were recorded in C_6D_6 at 25 °C on a JEOL Type GSX-270 spectrometer operating at 270 MHz. Chemical shifts (ppm) were determined with respect to residual C_6D_5H (δ 7.40) as internal standard. FAB-MS spectra were recorded on a JEOL JMS−HX110 spectrometer using a 3-nitrobenzyl alcohol matrix.

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Supporting Information Available: Tables of displacements for the carbon atoms of the porphyrin ring from the 4N plane with estimated standard deviations (3 pages). X-ray crystallographic files for compounds **2**−**5**, in CIF format, are available on the Internet only. Access and ordering information is given on any current masthead page.

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