

A Unique Siloxane-based Pyridyl Spacer. Preparation and Structure of 1,3-Bis(3-pyridyl)tetraphenyldisiloxane

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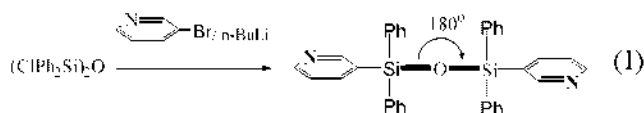
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Much attention has been directed toward the use of multidentate nitrogen donor spacers in supramolecular chemistry.¹⁻⁴ In particular, various polypyridyl ligands that can bridge two or more remote metal centers have been utilized in the construction of abiotic functional supramolecules such as mixed valence, anion exchange, photoinduced electron or energy transfer, sensing, and magnetic exchange between paramagnetic centers.⁵⁻¹⁵ Thus, the design of new tectonic ligand with carefully placed binding site is one of the most important tasks for the construction of tailor-made supramolecular materials. Among such polypyridyl tectonics, some silicon-containing pyridines recently have served as appropriate building blocks for interesting nanoscale molecular materials.¹⁶⁻¹⁸ The silicon-containing pyridines possess characteristic properties such as a potential multidentate, a tetrahedral angle around Si (~109°), a malleable length, conformational nonrigidity, and manageable solubility.^{16,17} In this context, we now describe the synthesis and detailed structural properties of a potential nanoscale spacer, 1,3-bis(3-pyridyl)tetraphenyldisiloxane.

1,3-Bis(3-pyridyl)tetraphenyldisiloxane ((Ph₂(3-Py)Si)₂O) was smoothly synthesized by the reaction of 1,3-dichlorotetraphenyldisiloxane with 3-pyridyl bromide (eq 1). Its composition was confirmed by chemical analysis, NMR, and mass spectrometric data. The product was recrystallized in a mixture of chloroform and *n*-hexane (1 : 1) to obtain single crystals suitable for X-ray crystallography. The colorless crystalline solids are soluble in polar organic solvents and are stable in solution.



X-ray characterization on the single crystal has provided a discrete siloxane molecule. The single molecular unit and packing diagrams are shown in Figure 1. The oxygen atom is situated at a center of symmetry, and consequently the Si-O-Si fragment is strictly linear. The linear Si-O-Si moiety found here is unlikely to be a result of intermolecular forces. The geometry adopted by the Si-O-Si bridge has generally

been discussed in terms of a combination of Si-O π -bond and bulkiness.¹⁹ The overall structure including the linear angle is similar to the structure of bis(triphenylsilane)oxide,²⁰ even though its space group is different from that of bis(triphenylsilane)oxide. This fact indicates that the partial change of heteroatom in the aromatic ring does not have significant influence on the discrete molecular structure. As expected, the Si-O bond (1.6156(7) Å) is median length between those found in O(SiH₃)₂ (1.634(2) Å)²¹ and O(SiCl₃)₂ (1.59(1) Å).²² The local geometry around the Si atom approximates a tetrahedral arrangement (108.57(9)-111.1(1)°), and thus the six aromatic rings lie in a typical staggered conformation as shown in Figure 1. The Si-C distances span in the range 1.849(3)-1.861(3) Å, and the distance involving the pyridyl moiety is the longest 1.861(3) Å. As shown in Table 2, both the steric and electronic effects of organic groups are important factors for the determination of Si-O-Si angle. The more electron withdrawing and bulkier group increases the angle.

The linearity of the siloxane-based pyridine may be one of the interesting angular components in the construction of desirable supramolecules such as molecular boxes, cubes, and strands. The compound has such dual characters: the Si-O-Si moiety is rigid, but the 3-pyridyl moiety is free rotational in contrast to simple bipyridyl moiety with an angular constraint. Thus, the 1,3-bis(3-pyridyl)tetraphenyldisiloxane is a potential *nanoscale* tectonic^{4,27} with a linear Si-O-Si unit. The ligand may contribute to the development of desirable supramolecular-based materials such as sensors, molecular switches, ion exchangers, chemical delivery, and intercalators. Our preliminary experiment indicates that the ligand is a good N-donor spacer. Thus, we believe that this spacer ligand generates various supramolecules.

Experimental Section

Preparation of 1,3-Bis(3-pyridyl)tetraphenyldisiloxane.

To a solution of 3-bromopyridine (7 mmol) in dry ethyl ether (20 mL) under nitrogen was added dropwise *n*-butyllithium (7.2 mmol, 2.5 M solution in hexane) at -78 °C. The resulting mixture was stirred at the temperature for 40 min. 1,3-Dichlorotetraphenyldisiloxane (3.2 mmol) was slowly added to the yellow suspension at the temperature. Distilled water (20 mL) was added into the reaction solution, and the

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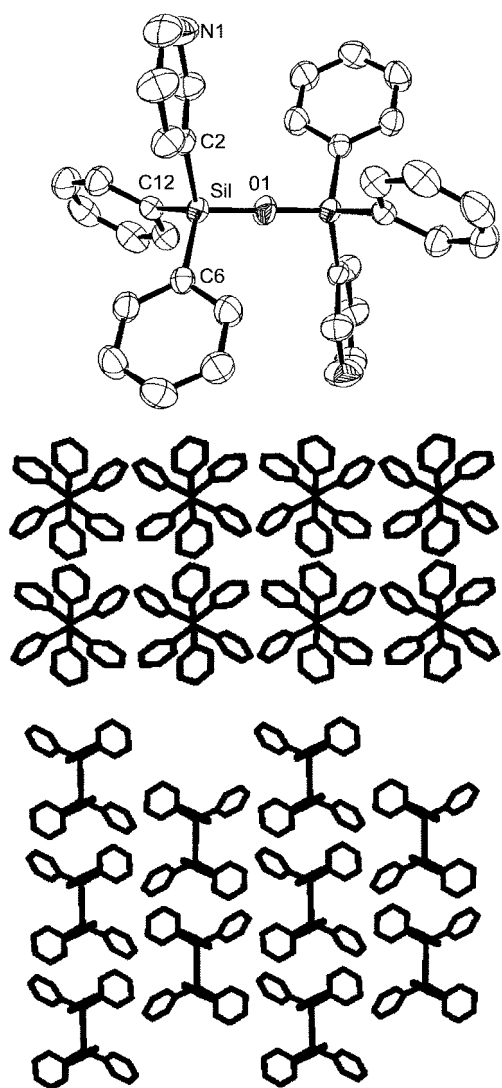


Figure 1. ORTEP view (top), (001) packing view (middle), and (100) packing view (bottom) of 1,3-bis(3-pyridyl)tetraphenyl-disiloxane. The ORTEP is depicted in thermal ellipsoids at the 50% level. The (001) packing view shows the staggered conformation, and the (100) view shows the molecular array of linear Si-O-Si moiety. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Si(1)-O(1) = 1.6156(7), Si(1)-C(2) = 1.861(3), Si(1)-C(6) = 1.856(3), Si(1)-C(12) = 1.849(3), Si(1)-O-Si(1)#1 = 180.00(7), O(1)-Si(1)-C(2) = 108.61(9), O(1)-Si(1)-C(6) = 108.57(9), O(1)-Si(1)-C(12) = 109.34(9), C(2)-Si(1)-C(6) = 111.1(1), C(2)-Si(1)-C(12) = 109.6(1), C(6)-Si(1)-C(12) = 109.58(2). Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$.

organic solution layer was separated. The organic solution was washed with water (2×10 mL), and then was dried over MgSO_4 . The crude product was purified by column chromatography on silica gel with ethyl acetate. Yield, 52%. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{OSi}$: C, 76.08; H, 5.26; N, 5.22. Found: C, 76.10; H, 5.32; N, 5.20. ^1H NMR (300 MHz, CDCl_3 , Me_4Si): δ = 8.75 (s, 1H), 8.70 (dd, J = 5 Hz, J = 2 Hz, 1H), 7.84 (dt, J = 8 Hz, J = 2 Hz, 1H), 7.34 (m, 1H), 7.57-7.45 (m, 10H). EI-MS (80 eV): 536 [M^+].

Crystallographic Structure Determination. A colorless

Table 1. Crystallographic Data for 1,3-Bis(3-pyridyl)tetraphenyl-disiloxane

formula	$\text{C}_{17}\text{H}_{14}\text{NO}_{0.5}\text{Si}$
f.w.	268.38
space group	$P2_1/c$
a , Å	9.163(1)
b , Å	17.062(2)
c , Å	9.729(1)
β , $^{\circ}$	106.492(2)
V , Å 3	1458.4(3)
Z	4
d_{calc} , gcm^{-3}	1.222
μ , mm^{-1}	0.151
R [$I > 2\sigma(I)$]	$R_1 = 0.0575$ $wR_2 = 0.1219$

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum F_o}, \quad wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}^{1/2}$$

Table 2. The Si-O-Si Angles of the Disiloxanes

Compounds	Si-O-Si ($^{\circ}$)	Ref.
$\text{O}(\text{SiH}_3)_2$	142.2(3)	21
$\text{O}(\text{SiCl}_3)_2$	146(4)	22
$\text{O}(\text{SiMe}_3)_2$	148.8(2)	23
$\text{O}(\text{SiF}_3)_2$	156(2)	24
$\text{O}(\text{SiPh}_2\text{H})_2$	160	25
$\text{O}(\text{Si}-t\text{-Bu})_2$	179.11(4)	26
$\text{O}(\text{SiPh}_3)_2$	180	20
$\text{O}(\text{SiPh}_2(3\text{-Py}))_2$	180.00(7)	This work

crystal was wedged in a Lindemann capillary with mother solvent. X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structure was solved by the SHELXS 97 and refined by SHELXL 97.²⁸ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The hydrogen atoms of acetonitrile molecules were not refined. Crystal parameters and procedural information corresponding to data collection and structure refinement were given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-197812). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

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