2486 *Organometallics* **1997,** *16,* 2486−2488

Silicon-Catenated Silole Oligomers: Oligo(1,1-silole)s

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Received March 31, 1997[⊗]

Summary: Oligo(1,1-silole)s, silole oligomers catenated through silicons, have been synthesized as model compounds of poly(1,1-silole)s. Crystal structures and UV−vis spectra have been determined, in which tersilole and quatersilole have unique absorption maxima around 280−290 nm.

Poly(1,1-silole)s, silole (silacyclopentadiene) polymers catenated through the ring silicons, constitute a new class of polysilanes with $\sigma^*-\pi^*$ conjugation, as shown in Figure 1. In the silole ring itself, there is a significant low-lying LUMO energy level due to the $\sigma^*-\pi^*$ conjugation arising from the interaction of the σ^* orbital of the two exocyclic σ bonds on silicon with the π^* orbital of the *cisoid*-butadiene moiety.[1−3] This type of orbital interaction would also take place in the polymeric system, as schematically shown in Figure 1. Thus, $\sigma^*-\pi^*$ conjugation between the σ^* orbital delocalized over the polysilane main chain and the π^* orbital localized on the *cisoid*-butadiene moiety in every silole ring would lower the LUMO level. In contrast, this type of $\sigma^*-\pi^*$ conjugation is not realized in the conventional aryl-bound polysilanes due to the orbital symmetry; rather, the $\sigma-\pi$ conjugation takes place between σ-orbitals delocalized over the polymer chain with π-orbitals localized on the aryl moieties, resulting in a relative elevation of HOMO energy level in comparison with peralkylpolysilanes.[4−6] Poly(1,1-silole)s are thus interesting target molecules to synthesize, while only a few silole dimers have been synthesized to date.[7−10] We now report the synthesis, structures, and properties of a series of oligo(1,1-silole)s, bisilole **2**, tersilole **3**, and quatersilole **4**, as models of poly(1,1-silole)s.[11] In the course of our study, a theoretical study on poly(1,1-silole)s has been reported by Yamaguchi, suggesting their unique electronic structure due to the $\sigma^*-\pi^*$ conjugation.[12]

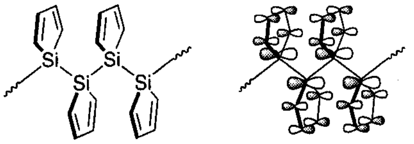
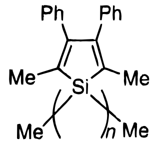


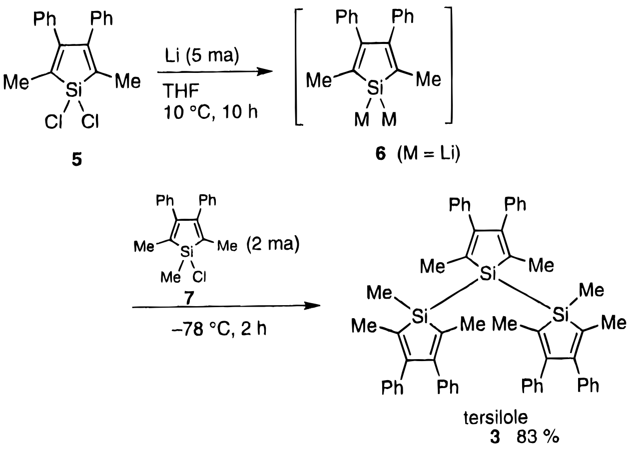
Figure 1. Schematic drawings of poly(1,1-silole) and $\sigma^*-\pi^*$ conjugation in the LUMO.

Chart 1



1 $n = 1$ monosilole
2 $n = 2$ bi(1,1-silole)
3 $n = 3$ ter(1,1-silole)
4 $n = 4$ quater(1,1-silole)

Scheme 1[a]



[a] ma = molar amount.

We first examined tersilole **3** as shown in Scheme 1. As has been well-documented,[8−10,13] silole dianion **6** can be cleanly prepared from dichlorosilole **5** using a 5 molar amount of Li in THF at room temperature. The coupling reaction of the dianion **6** with 1-chloro-1-methylsilole **7**, which is readily prepared by functional group transformation from the corresponding 1-amino-1-methylsilole,[14] gave tersilole **3** in 83% yield.[15] This is the first example of the synthesis of oligo(1,1-silole)s catenating more than three silole rings.[16]

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) (a) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (b) Tamao, K.; Ohno, S.; Yamaguchi, S. *Chem. Commun.* **1996**, 1873. (c) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327. (d) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974.

(2) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Nefedov, O. M.; Michl. J. *J. Am. Chem. Soc.* **1994**, *116*, 320.

(3) (a) Yamaguchi, Y.; Shioya, J. *Mol. Eng.* **1993**, *2*, 339. (b) Yamaguchi, Y. *Mol. Eng.* **1994**, *2*, 311.

(4) (a) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186. (b) Matsumoto, N.; Takeda, K.; Teramae, H.; Fujino, M. In *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; American Chemical Society: Washington DC, 1990; p 515.

(5) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(6) In contrast, $\sigma-\pi$ conjugation cannot take place in the HOMO of the poly(1,1-silole)s due to the orbital symmetry.

(7) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, *214*, 289.

(8) Joo, W.-C.; Hong, J.-H.; Choi, S.-B. Son, H.-E.; Kim, C. H. *J. Organomet. Chem.* **1990**, *391*, 27.

(9) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387.

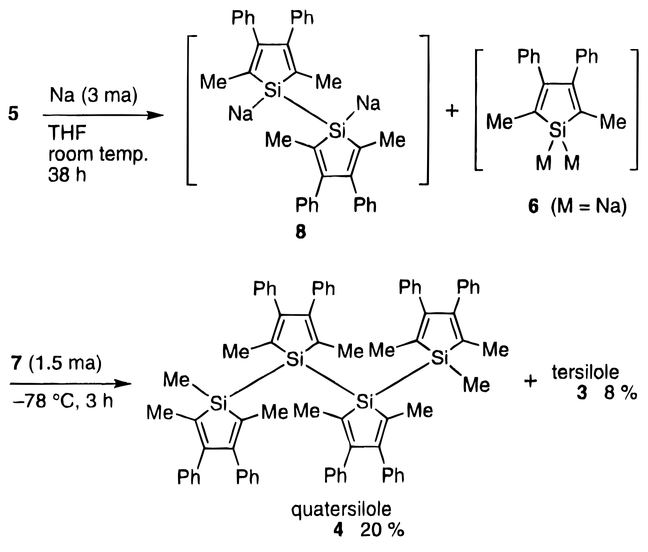
(10) (a) Freeman, W. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882. (b) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(11) Quite recently, some oligo(1,1-silole)s similar to ours have been prepared by Kira and his co-workers: Kanno, K.; Ichinohe, M.; Kira, M. 72nd Annual Meeting of the Chemical Society of Japan, Tokyo, March 1997, Abstract 2E334. A silole-containing polysilane has also been reported by Sakurai and his co-workers in the same meeting: Sakai, T.; Sanji, T.; Sakurai, H. Abstract 3E307.

(12) Yamaguchi, Y. *Synth. Met.* **1996**, *82*, 149.

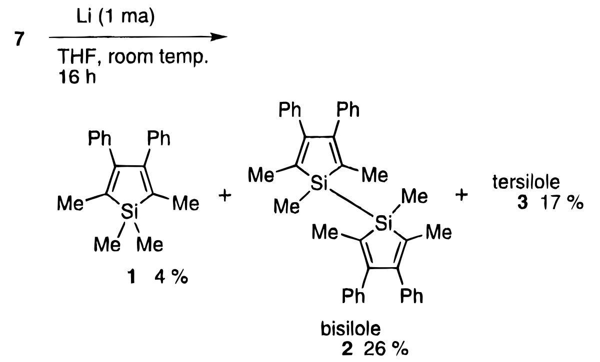
(13) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608.

Scheme 2[a]



[a] ma = molar amount.

Scheme 3[a]



[a] ma = molar amount.

Quatersilole **4** has been obtained by a similar coupling reaction, as shown in Scheme 2. Our procedure is based on the recent results reported independently by Boudjouk and his co-workers[9] and Tilley and his co-workers[10] on the formation of bisilole dianions. Thus, **5** was reduced with a 3 molar amount of Na, resulting in the formation of a mixture of the bisilole dianion **8** and the silole dianion **6**. The mixture was treated with a 1.5 molar amount of 1-chloro-1-methylsilole **7** to afford quatersilole **4** and tersilole **3** in 20% and 8% yields, respectively.[17]

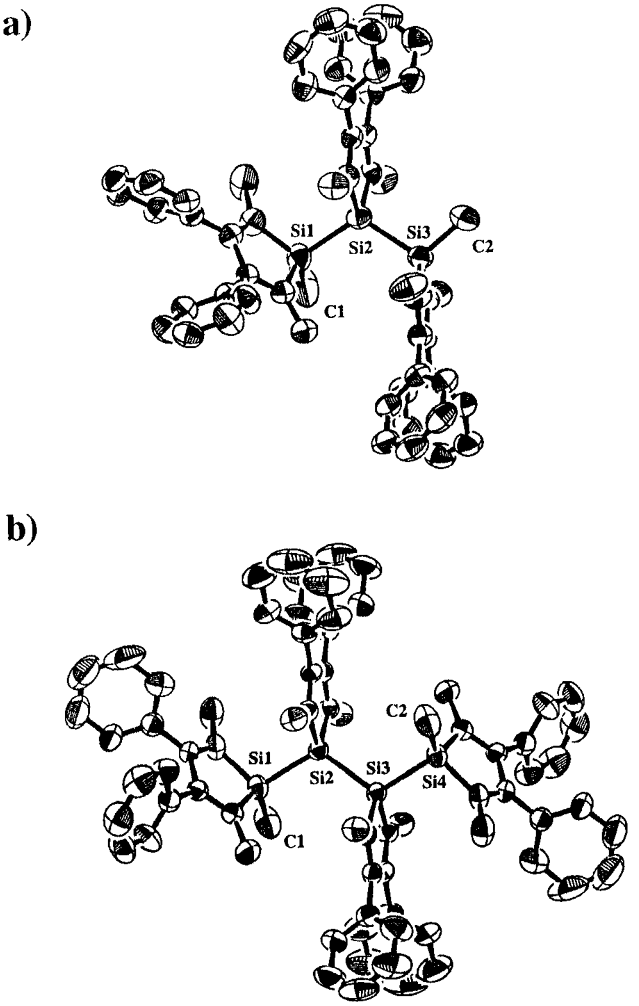


Figure 2. ORTEP drawings (50% thermal ellipsoids) of (a) tersilole **3** and (b) quatersilole **4**. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg) are as follows. **3**: Si1–Si2, 2.330(3); Si2–Si3, 2.341(3); Si1–Si2–Si3, 115.92(9); C1–Si1–Si2–Si3, −64.8(4); Si1–Si2–Si3–C2, 172.0(4). **4**: Si1–Si2, 2.339(2); Si2–Si3, 2.349(2); Si1–Si2–Si3, 115.22(7); C1–Si1–Si2–Si3, −56.7(2); Si1–Si2–Si3–Si4, 180.0.

The silole dimer, bi(1,1-silole) **2**, has also been prepared as a reference compound for comparison of properties with higher oligomers. Thus, as shown in Scheme 3, the reaction of 1-chloro-1-methylsilole **7** with a 1 molar amount of Li afforded the dimer **2** in 26% yield. In addition, unexpectedly, 1,1-dimethylsilole **1** and tersilole **3** were also isolated in 4% and 17% yields, respectively.[18]

Figure 2 provides ORTEP views of the crystal structures of tersilole **3** and quatersilole **4**.[19,20] In the structure of tersilole **3**, three silole rings are arranged as *gauche–anti* conformations along with the Si1–Si2–

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(14) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Shiro, M. *Organometallics*, in press.

(15) **3** (white powder): mp 213–215 °C; ^{1}H NMR (CDCl$_3$) δ 0.60 (s, 6H), 1.95 (s, 12H), 1.96 (s, 6H), 6.72–6.89 (m, 12H), 6.98–7.17 (m, 18H); ^{13}C NMR (CDCl$_3$) δ −6.99, 15.42, 16.52, 125.77, 125.91, 127.30, 127.42, 129.40, 129.43, 134.95, 135.04, 138.99, 139.66, 154.05, 155.36; ^{29}Si NMR (CDCl$_3$) δ −35.89, −7.92. Anal. Calcd for $C_{56}H_{54}Si_3$: C, 82.91; H, 6.71. Found C, 82.88; H, 6.62.

(16) A germanium analog of ter(1,1-silole) has recently been prepared: Hong, J.-H.; Pan, Y.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186.

(17) **4** (white powder): mp 153–155 °C; ^{1}H NMR (CDCl$_3$) δ 0.63 (s, 6H), 1.90 (s, 12H), 2.11 (s, 12H), 6.68–6.89 (m, 16H), 6.97–7.17 (m, 24H); ^{13}C NMR (CDCl$_3$) δ −7.01, 15.24, 17.02, 125.88, 127.26, 127.39, 129.36, 134.56, 135.44, 138.96, 139.41, 153.89, 155.76; ^{29}Si NMR (CDCl$_3$) δ −34.16, −6.69; found mol wt *m/e* 1071.4626. Anal. Calcd for $C_{74}H_{70}Si_4$: C, 82.93; H, 6.58. Found C, 82.68; H, 6.88.

(18) **2** (white powder): mp 178–180 °C; ^{1}H NMR (CDCl$_3$) δ 0.52 (s, 6H), 1.90 (s, 12H), 6.71–6.86 (m, 8H), 6.94–7.15 (m, 12H); ^{13}C NMR (CDCl$_3$) δ −8.39, 15.40, 125.80, 127.24, 129.43, 135.08, 139.14, 153.94. ^{29}Si NMR (CDCl$_3$) δ −10.70. Anal. Calcd for $C_{38}H_{38}Si_2$: C, 82.85; H, 6.95. Found C, 82.85; H, 6.97.

(19) Crystal data for **3** (instrument Rigaku AFC5R): $C_{56}H_{54}Si_3$, FW = 811.30, crystal size 0.20 × 0.20 × 0.20 mm, orthorhombic, $P2_12_12_1$ (No. 19), $a = 20.676(4)$ Å, $b = 24.291(4)$ Å, $c = 9.458(4)$ Å, V = 4750(1) Å^3, Z = 4, $D_c = 1.134$ g cm^{-3}, μ (Cu Kα) = 11.78 cm^{-1}, number of unique reflections 4012, temperature 25 °C, $R = 0.041$, $R_w = 0.054$, goodness of fit indicator 1.18. Hydrogen atoms were included but not refined.

(20) Crystal data for **4** (instrument Rigaku RAXIS-IV): $C_{80}H_{84}Si_4$, FW = 1157.89, crystal size 0.30 × 0.20 × 0.15 mm, triclinic, $P\bar{1}$ (No. 2), $a = 13.756(1)$ Å, $b = 16.179(1)$ Å, $c = 9.303(1)$ Å, $\alpha = 97.46(1)°$, $\beta = 107.12(1)°$, $\gamma = 114.69(1)°$, $V = 1719.9$ Å^3, $Z = 1$, $D_c = 1.118$ g cm^{-3}, μ(Mo Kα) = 1.28 cm^{-1}, number of unique reflections = 4740, temperature 25 °C, $R = 0.055$, $R_w = 0.085$, and goodness of fit indicator 1.34. Hydrogen atoms were included but not refined. The crystal structure of **4** includes hexane in the ratio of 1:1 in the unit cell.

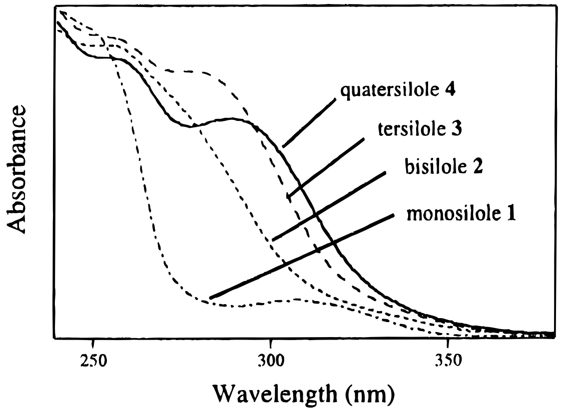

Figure 3. UV−vis spectra of oligo(1,1-silole)s in chloroform, absorbance being normalized per silole unit.

Si3 trisilane skeleton. The dihedral angles ∠C1−Si1−Si2−Si3 and ∠Si1−Si2−Si3−C2 are −64.8(4) and 172.0(4)°, respectively. In the structure of quatersilole **4**, there is a centrosymmetric point at the center of the Si2−Si3 bond. Four silole rings have *gauche*−*anti*−*gauche* conformations along with the Si1−Si2−Si3−Si4 skeleton, having ∠C1−Si1−Si2−Si3 = −56.7(2)° and ∠Si1−Si2−Si3−Si4 = 180.0°. Thus, the partial geometry of the tetrasilane skeleton, from Si1 to Si3, is quite similar to that of tersilole. All the bond lengths and angles in each silole ring and the Si−Si bonds of tersilole and quatersilole are in the normal range.

UV−vis absorption spectra for these oligosiloles are shown in Figure 3 and the data are summarized in Table 1, in which the data of the perphenyl and permethyl trisilanes and tetrasilanes are also given for comparison. The monosilole **1** has two absorption bands around 250 and 310 nm,[21] assignable to the π−π^* transitions of the phenyl and silole moieties, respectively.[22] In comparison with the monosilole **1**, the oligosiloles **2**−**4** show distinct spectra, where the absorption of the silole moieties is hidden by broad bands.

Table 1. UV−Vis Spectral Data for Oligo(1,1-silole)s[a]

compd	λ_{max}/nm	log ϵ
monosilole **1**	307	3.22
bisilole **2**	255	4.42
tersilole **3**	279	4.60
quatersilole **4**	289	4.59
$Ph(Ph_2Si)_3Ph$[b]	255	4.51
$Ph(Ph_2Si)_4Ph$[c]	288	4.36
$Me(Me_2Si)_3Me$[d]	216	3.96
$Me(Me_2Si)_4Me$[d]	235	4.17

[a] In chloroform. [b] Gilman, H.; Atwell, W. H.; Sen, P. K.; Smith, C. L. *J. Organomet. Chem.* **1964**, *4*, 163. [c] Gilman, H.; Atwell, W. H. *J. Organomet. Chem.* **1964**, *4*, 176. [d] Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369.

Remarkably, tersilole **3** and quatersilole **4** have unique absorptions at around 280 and 290 nm, respectively.[23] These absorption maxima are 50−60 nm longer than those of the permethyl oligosilanes, and in comparison with the perphenyl counterparts, **3** has a 20 nm longer λ_{max} value and **4** has a comparable λ_{max} value. As mentioned previously, the unique absorptions of the oligo(1,1-silole)s would have arisen from the orbital interactions. A more detailed theoretical elucidation of the origin is now in progress, as are various synthetic approaches to higher oligomers and polymers.

Acknowledgment. We thank the Ministry of Education, Science, Sports, and Culture of Japan for Grant-in-Aid (No. 07555280).

Supporting Information Available: Text giving experimental procedures for the preparation of oligo(1,1-silole)s and tables giving X-ray crystal structures data for **3** and **4** (27 pages). Ordering information is given on any current masthead page.

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(21) Okinoshima, H.; Yamamto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263.

(22) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215.

(23) In the solid-state UV-vis spectra (KBr pellet), oligo(1,1-silole)s **3** (λ_{max} 279 nm) and **4** (λ_{max} 290 nm) have almost the same absorption maxima as those in solution.