A New Chiral Molecular Square with D_4 Symmetry Composed of Enantiomerically Pure Spirosilane

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A cyclic tetramer of optically active spirosilane **1** was prepared as a new chiral molecular square with D_4 symmetry by the Pd-catalyzed cross-coupling reaction, which shows a larger anisotropy factor g_{abs} in the CD spectrum relative to a series of linear oligomers of **1**.

Chiral spiranes[1] with axial chirality are promising chiral angular building units for chiral macromolecules, because of their rigid C_2 symmetry environments provided by the orthogonal arrangements of two planes at the spiro center. In particular, there is an opportunity to construct chiral molecular squares[2-5] with D_4 symmetry from enantiomerically pure chiral spiranes, as schematically shown in Figure 1. However, little attention has been paid to the utilization of chiral spiranes as such a building unit,[5,6] due to the limited availability of enantiomerically pure spiranes. We have recently prepared the 5-silaspiro[4.4]nonane derivative **1**, hereafter abbreviated as spirosilane, as a new chiral spirane by the intramolecular catalytic asymmetric hydrosilation of bis(alkenyl)dihydrosilane using a Rh-SILOP catalyst system.[7,8] We now report the synthesis of oligomers of the optically active spirosilane, which include a cyclic tetramer as a new chiral molecular square.

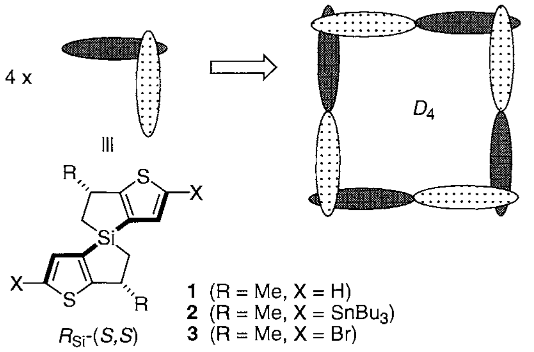
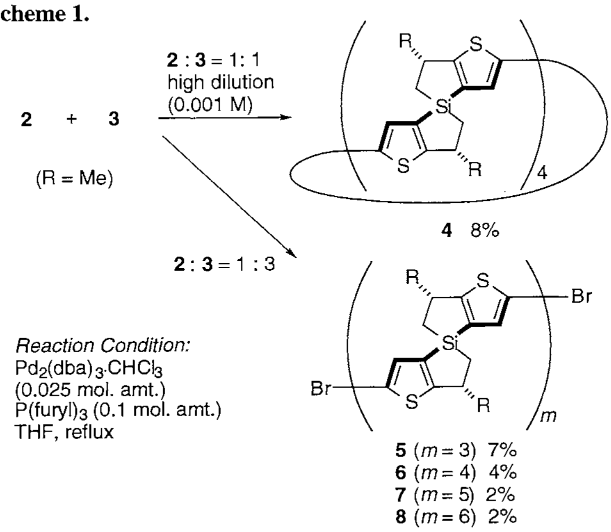


Figure 1. Spirosilane as a building unit of chiral molecular square of D_4 symmetry.

(R)$_{Si}$-(S,S)-spirosilane **1**[9] with 98% diastereomeric purity and >99%ee was used in this study,[10] from which the distannylated derivative **2** and dibromo derivative **3** were prepared as reported in the previous report.[7] The cross-coupling reactions of **2** with **3** using the $Pd_2(dba)_3 \cdot CHCl_3/P(furyl)_3$ catalyst system[11] were carried out in refluxing THF to obtain the spirosilane oligomers, as shown in Scheme 1. Under a high dilution (0.001 M) condition, the coupling using **2** and **3** in a 1:1 ratio indeed produced a spirosilane cyclic tetramer **4**, which was isolated in 8% yield by recycle gel permeation chromatography (GPC), together with other linear higher oligomers. Compound **4** was unequivocally verified by its ^1H and ^{13}C NMR spectra and high resolution mass spectrum (HRMS).[12] For example, the ^1H NMR spectrum of **4** shows one singlet for thienyl protons at 6.74 ppm and one doublet for methyl groups at 1.38 ppm, which are consistent with the D_4 symmetry structure of the cyclic tetramer.

Scheme 1.



As reference compounds, a series of linear oligomers with bromides as terminal groups were also prepared by a similar coupling reaction using **2** and **3** in a 1:3 ratio (Scheme 1). The isolation by recycle GPC afforded oligomers from trimer **5** to hexamer **8** in several % yield each. The formation of even-number oligomers **6** and **8** suggests that the present reaction involves the oxidative homo-coupling of the stannylated moieties as a side reaction.[13,14] The structures of these linear oligomers were also characterized by ^1H and ^{13}C NMR spectroscopies and HRMS.

Unfortunately, we could not obtain a single crystal of **4** suitable for X-ray crystallographic analysis. Therefore, we examined a theoretical calculation on a model compound **4'** (R = H) to elucidate the structure. Figure 2 represents the structure optimized at the AM1 level.[15] Noticeably, the twisted arrangements of the two thiophene rings in the bithiophene units having the S-C-C-S dihedral angles of about −114° are essential for the construction of the cyclic tetrameric structure of D_4 symmetry. The molecular square has a substantial cavity size. The distance between the two silicons on each side is estimated to be 9.4 Å.

To elucidate the chiral environment of the molecular square, the CD spectrum of **4** was measured as shown in Figure 3. The UV and CD spectral data of **4** are listed in Table 1, together with those of the linear oligomers **5**-**8** for comparison. All the oligomers have their π-π* transition bands, ascribed to the

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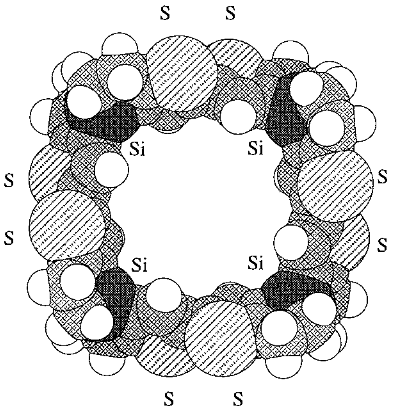

Figure 2. Space filling model of **4'** (R = H), optimized at the AM1 level.

bithiophene moiety, at nearly the same wavelengths around 320 nm and show positive Cotton effects around 340 nm. It should be noted that the degree of circular polarization g_{abs} of **4** is about two times larger than those of the linear oligomers, presumably due to the rigid chiral environment of **4** provided by the cyclic structure.

In summary, a new type of chiral molecular square with D_4 symmetry has been synthesized using spirosilane as a new angular building unit. In the literature, Shea and coworkers[6] and Duhme and coworkers[5] independently reported the molecular squares using spiranes as the angular unit, but they used racemic spiranes. The present report is the first example of the use of enantiomerically pure spiranes for the synthesis of chiral molecular squares as well as chiral macromolecules. To demonstrate the utility of our spirane as the chiral angular building unit, our next interest is directed to the construction of the self-assemblies of spirosilane derivatives having chiral network structures.

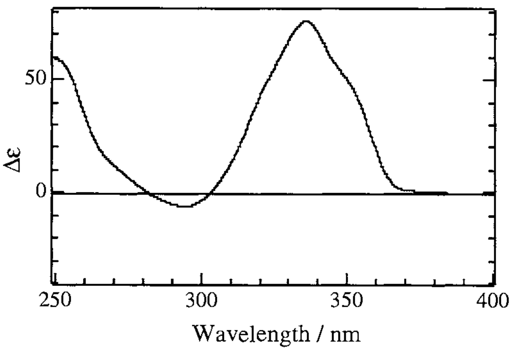

Figure 3. CD spectrum of **4** in chloroform.

Table 1. UV and CD spectral data for spirosilane oligomers[a]

	UV		CD		
compound	λ_{max} / nm	ε	λ_{ext} / nm	Δε	g_{abs}[b]
4	318	44,900	336	+76.0	1.69×10^{-3}
5	322	32,100	337	+12.9	8.05×10^{-4}
6	321	30,800	338	+8.54	8.32×10^{-4}
7	322	55,000	338	+12.5	9.06×10^{-4}
8	322	62,100	338	+11.2	8.97×10^{-4}

[a]In chloroform at 20 °C. [b]$g_{abs} = \Delta\varepsilon/\varepsilon$.

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References and Notes

1 E. L. Eliel and S. H. Wilen, "Stereochemistry of Organic Compounds" John Wiley & Sons, New York (1994), pp. 1138–1142.

2 a) B. Olenyuk, J. A. Whiteford, and P. J. Stang, *J. Am. Chem. Soc.*, **118**, 8221 (1996). b) P. J. Stang and B. Olenyuk, *Angew. Chem., Int. Ed. Engl.*, **35**, 732 (1996). c) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, **30**, 502 (1997). d) P. J. Stang, B. Olenyuk, D. C. Muddiman, and R. D. Smith, *Organometallics*, **16**, 3094 (1997).

3 a) S. Anderson, U. Neidlein, V. Gramlich, and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, **34**, 1596 (1995). b) U. Neidlein and F. Diederich, *J. Chem. Soc., Chem. Commun.*, **1996**, 1493.

4 Y. Zhang, S. Wang, G. D. Enright, and S. R. Breeze, *J. Am. Chem. Soc.*, **120**, 9398 (1998).

5 A.-K. Ouhme, S. C. Davies, and D. L. Hughes, *Inorg. Chem.*, **37**, 5380 (1998).

6 J. H. Small, D. J. McCord, J. Greaves, and K. J. Shea, *J. Am. Chem. Soc.*, **117**, 11588 (1995).

7 K. Tamao, K. Nakamura, H. Ishii, S. Yamaguchi, and M. Shiro, *J. Am. Chem. Soc.*, **118**, 12469 (1996).

8 K. Tamao, K. Nakamura, S. Yamaguchi, M. Shiro, and S. Saito, *Chem. Lett.*, **1996**, 1007.

9 The absolute configuration $(R)_{Si}$ at the silicon atom in **1** is named according to the central chirality notation.[1]

10 The spirosilane **1** of this purity was prepared by the intramolecular hydrosilation described in Ref. 7 using (*R,R*)-TBDM-SILOP[8] as the chiral ligand at 0 °C, followed by several recrystallizations from benzene.

11 V. Farina and B. Krishnan, *J. Am. Chem. Soc.*, **113**, 9585 (1991).

12 **4**: ^{1}H NMR ($CDCl_3$) δ 1.10 (dd, *J* = 3.5 and 15.1 Hz, 8H, CH_2), 1.38 (d, *J* = 7.0 Hz, 24H, CH_3), 1.87 (dd, *J* = 8.1 and 15.1 Hz, 8H, CH_2), 3.51 (m, 8H, C*H*), 6.74 (s, 8H, thiophene). ^{13}C NMR ($CDCl_3$) δ 24.06, 26.62, 35.22, 125.43, 137.92, 140.61, 167.85. HRMS (FAB) Found; 1097.1288. Calcd for $C_{56}H_{57}Si_4S_8$ $[M+H]^+$; 1097.1303. A reliable $[\alpha]_D$ value could not be obtained due to a small quantity of **4** obtained herein.

13 V. Farina, B. Krishnan, D. R. Marshall, and, G. P. Roth, *J. Org. Chem.*, **58**, 5434 (1993). H. A. M. van Mullekom, J. A. J. M. Vekemans, and E. W. Meijer, *Chem. Eur. J.*, **4**, 1235 (1998).

14 An attempt to prepare a linear polymer of the spirosilane by coupling using **2** and **3** in a 1:1 ratio at a normal concentration (0.1 M) resulted in the formation of only an oligomeric mixture (DP = 7), probably due to this side reaction.

15 The geometry optimization of **4'** was performed at the AM1 level using the Spartan Ver. 4.0 program. The heat of formation for the optimized structure is 95.745 kcal mol^{-1}.