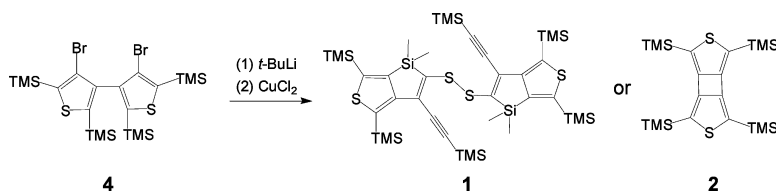


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Organometallics, **2009**, 28 (6), 1961-1964 • DOI: 10.1021/om800994x • Publication Date (Web): 02 March 2009

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Notes

“One-Pot” Reaction Involving Ring Formation of Silole, Thiophene Ring-Opening Alkynylation, and S–S Coupling

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Received October 15, 2008

Summary: With 4,4'-dibromo-2,2',5,5'-tetrakis(trimethylsilyl)[3,3']bithienyl (**4**) as substrate in the presence of *t*-BuLi (4 equiv)/CuCl₂, a compound with a novel structure, a D₂-symmetric derivative of thienosilole (**1**), is prepared in 55–64% yield. Three steps of bond breaking and bond forming are involved in the “one-pot” reaction to form **1**: (1) a C–Si bond forms in the ring formation of silole; (2) a C–S bond breaks in thiophene ring-opening alkynylation; (3) a S–S bond forms in the CuCl₂-promoted coupling. On the other hand, if a short time for Br/Li exchange was used in the process, the intramolecular coupling compound tetrakis(trimethylsilyl)cyclobuta[1,2-*c*:3,4-*c'*]dithiophene (**2**) was obtained instead. **2** could be obtained in 11–20% yield. None of the intermolecular coupling compound octakis(trimethylsilyl)tetrathienylene (**5**) was observed.

In recent years, there has been growing interest in the synthesis of chiral π -conjugated molecules and polymers, directed at the design of organic optoelectronic materials and devices.^{1–5} Especially, the synthesis of helical and double-helical oligomers based upon [n]helicenes⁶ and tetraarylenes^{7–9} by Rajca and Marsella is very challenging as well as being more interesting for many researchers. Double-helical octaphenylene,^{7c} used as a fragment of a double-helical polymer

of tetraphenylenes, was synthesized in 1997; however, the synthesis of a double helix containing the building blocks of tetrathienylenes has not been reported so far.¹⁰ Some methods have been found for the synthesis of tetrathienylenes.^{8,9} In our previous work, we developed an efficient synthesis of tetrakis[2,3-thienylene] in 41% yield with 3-bromothiophene as starting material.⁹ In this paper, we attempted to report the synthesis of octakis(trimethylsilyl)tetrathienylene (**5**) with great steric hindrance; however, we obtained two novel compounds instead, a D₂-symmetric derivative of thienosilole (**1**) and tetrakis(trimethylsilyl)cyclobuta[1,2-*c*:3,4-*c'*]dithiophene (**2**).

The synthetic route to **1** and **2** is shown in Scheme 1. 4,4'-Dibromo[3,3']bithienyl (**3**),^{6,11} made from 3,4-dibromothiophene, was deprotonated with an excess of LDA at –78 °C and then quenched with TMSCl to generate 4,4'-dibromo-2,2',5,5'-tetrakis(trimethylsilyl)[3,3']bithienyl (**4**) in 69–85% yield. Our following attempt was to synthesize the greatly sterically hindered compound **5** in dry ether by using *t*-BuLi for Br/Li exchange and CuCl₂ for oxidation.⁹ None of **5** was obtained; however, D₂-symmetric **1** in good yield (55–64%) or an intramolecular coupling product **2** (11–20%) were generated instead.

The formation of **1** involved three steps of bond breaking and bond forming in the “one-pot” reaction: (1) a C–Si bond formed in the ring formation of silole; (2) a C–S bond broke in thiophene ring-opening alkynylation; (3) a S–S bond formed in the CuCl₂-promoted coupling. The three steps of bond breaking and bond forming in making **1** by such a novel reaction is quite different from the methods of ring formation of silole,^{12,13} thiophene ring-opening alkynylation,^{14,15} and synthesis of disulfides,¹⁶ respectively, in the literature.

The possible mechanism for formation of **1** is shown in Scheme 2. After Br/Li exchange for **4** with *t*-BuLi at –78 °C for 0.5–5 h, a dianionic intermediate (**6**) was generated, and during the reaction time, one carbanion in **6** attacked the silicon of neighboring TMS on another thiophene ring to form silole;

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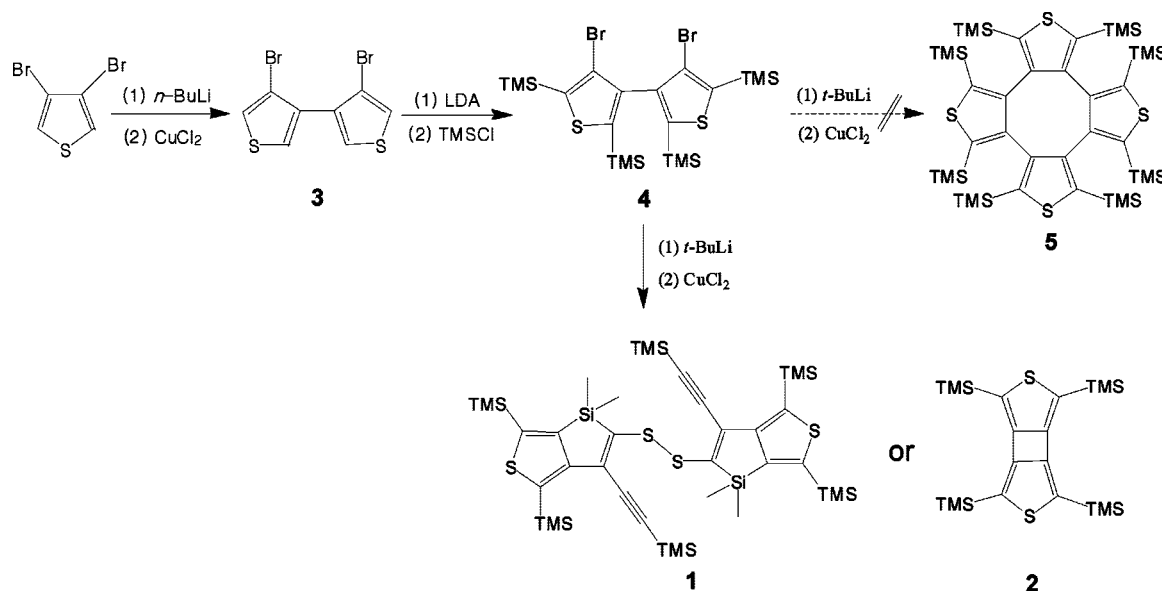
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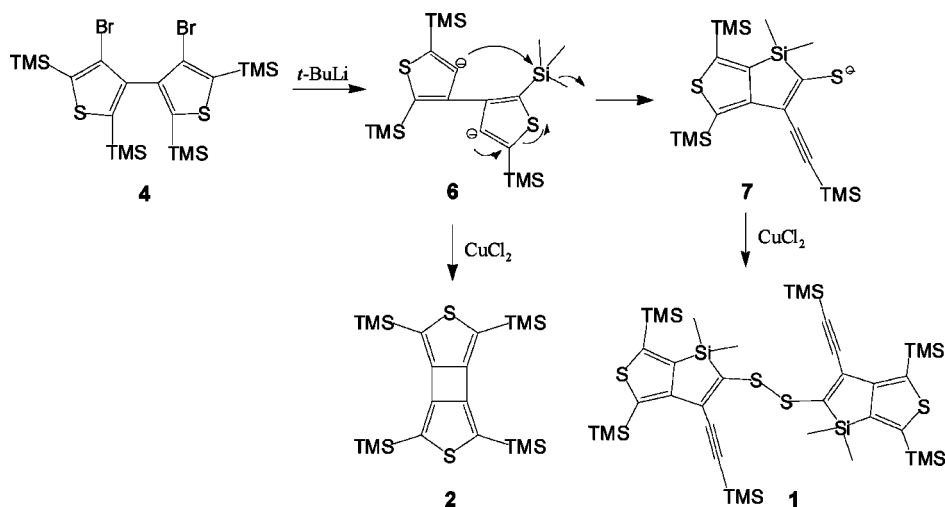
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Scheme 1. Synthetic Route to **1** and **2**^a

^a Abbreviations: LDA = lithium diisopropylamide; TMS = trimethylsilyl.

Scheme 2. Possible Mechanism for the Formation of **1** and **2**

meanwhile, electron transfer from a second carbanion to sulfur occurred to give a thiophene ring opened with alkynylation, and a sulfur anion (**7**) formed at same time. In the presence of CuCl_2 , the sulfur anion (**7**) could be coupled efficiently to form an S–S bond in making **1**. During the period from 0.5 h to 5 h for Br/Li exchange at -78°C , no great change of yields (55–64%) was observed in the formation of **1**.

If CuCl_2 -promoted coupling took place immediately just after addition of $t\text{-BuLi}$ into the ether solution of **4** was finished at

-78°C , only an intramolecular coupling product, tetrakis(trimethylsilyl)cyclobuta[1,2-*c*:3,4-*c'*]dithiophene (**2**), was afforded in 11–20% yield. **1** was not observed, which means that the step from **6** to **7** is not very fast at -78°C in dry ethyl ether. Totally different from the efficient case in making the tetrakis[2,3-thienylene] derivative in our previous work,⁹ none of the intermolecular coupling product **5** was obtained. This result indicates that the steric hindrance from four TMS groups in **6** prevents the formation of **5**. In addition to **2**, a mixture (about 60% in amount) with weak polarity showing one spot ($R_f = 0.80$) on TLC with hexane as eluent was obtained. With GCMS analysis, the main contents in the mixture include unreacted **4**, and **4** without one and two Br atoms. The peak areas in the

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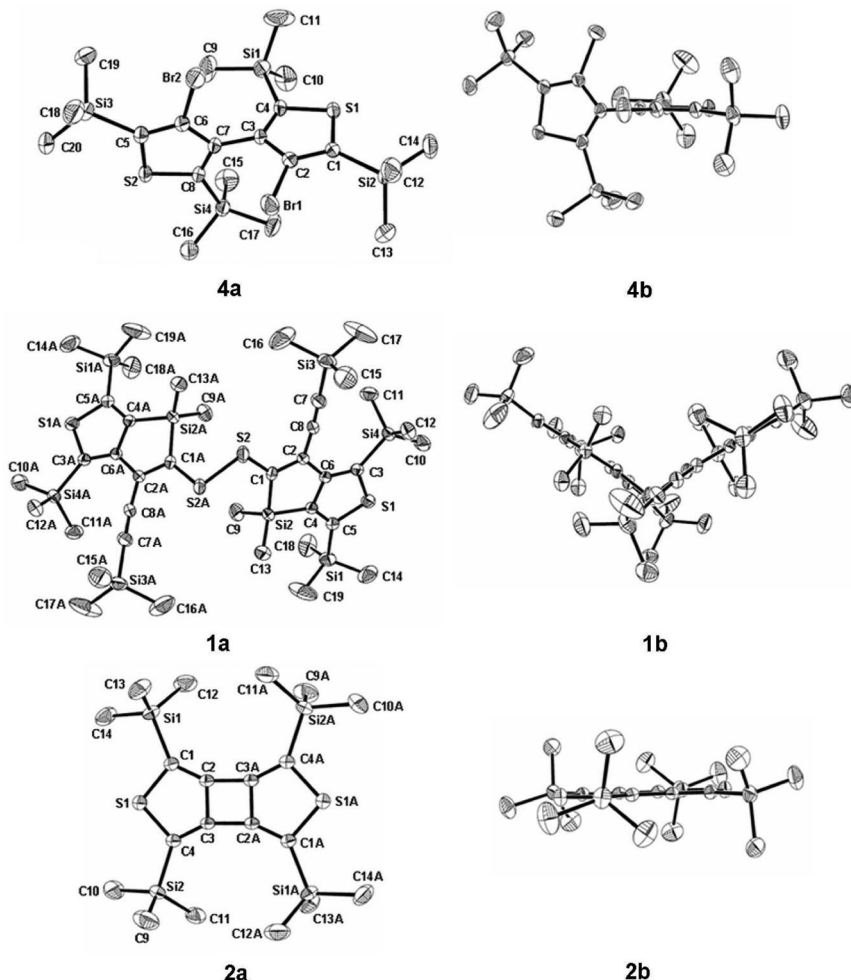


Figure 1. Molecular structures and conformations for compounds **1**, **2**, and **4**: **1a**, top view of **1**; **1b**, side view of **1** through the S–S bond; **2a**, top view of **2**; **2b**, side view of **2**; **4a**, top view of **4**; **4b**, side view of **4**. Carbon, bromine, and sulfur atoms are depicted with thermal ellipsoids set at the 50% probability level.

GCMS spectrum are ca. 15%, 51%, and 14%, respectively (see the Supporting Information).

The preparation yield in making **2** is not as high; however, the synthesis of cyclobuta[1,2-*c*:3,4-*c'*]dithiophene and its derivatives has not been developed until now. Only 4% yield in preparation of cyclobuta[1,2-*c*:3,4-*c'*]dithiophene¹⁷ and 3% yield for tetraphenyl-cyclobuta[1,2-*c*:3,4-*c'*]dithiophene¹⁸ were reported. In addition, the theoretical search for low-gap polymers based on polythiophenes including the derivative of cyclobuta[1,2-*c*:3,4-*c'*]dithiophene was reported.¹⁹

The structures of **1**, **2**, and **4** were confirmed by single-crystal X-ray analysis (Figure 1). In **4**, repulsion between the two bromine atoms and the two neighboring trimethylsilyl groups generates a twisted locked structure with a large dihedral angle of 86.4° between the two thiophene rings. The Br1–C2–C6–Br2 torsion angle is 99.5°, and the two Br atoms point away from each other with a distance of 4.39 Å (Br1...Br2).

From the side view through the S2–S2A bond, **1** shows a V-shaped conformation (**1b** in Figure 1) and the dihedral angle between the two planar thienosilole moieties is 62.1°. In the top view, **1** shows 2-fold symmetry, which is also confirmed by ¹H NMR and ¹³C NMR. The C1–S2–S2A–C1A torsion angle is 106.2°. The alkynyl group on the silole ring in **1** is not

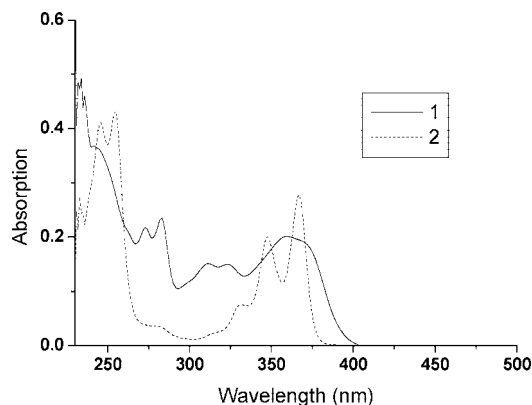


Figure 2. UV spectra of **1** and **2** in chloroform ([C] = 1.0E-5 M).

very linear. The C2–C8–C7 angle is 172.9°, and the C2–C8–C7–Si3 torsion angle is 37.2°. Such deviation is due to the repulsion of the alkynyl group with the neighboring TMS group. In **2**, the two fused thiophene rings are approximately coplanar. The C1–C2–C3A–C4A torsion angle is 3.2°.

The UV/vis spectra for **1** and **2** in chloroform are shown in Figure 2. **1** shows a broad absorption band with the maximum absorption peak at 360 nm, due to the π -electron delocalization between the substituted groups and thienosilole. The π -electron delocalization includes p– π conjugation from the S atom to

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thienosilole and π - π conjugation from the alkynyl group to thienosilole. The molar extinction coefficient (ϵ) of **1** at the peak maximum position (360 nm) is 2.01×10^4 . Different from the case of **1**, **2** shows a long-wavelength absorption band with fine structure containing three peaks at 332, 348, and 367 nm. The molar extinction coefficient (ϵ) of **2** at the peak maximum position (367 nm) is 2.78×10^4 .

In summary, the ring formation of a silole, thiophene ring-opening alkynylation, and S-S coupling are important in organic synthesis, especially in heterocyclic chemistry. These three reactions in a "one-pot" synthesis of D_2 -symmetric **1** were developed. **2** is a novel dithiophene derivative with a planar π -conjugated structure, which might show special properties in organic functional materials.

Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. The chemical shift references were as follows: (^1H) CDCl_3 , 7.26 ppm (CHCl_3); (^{13}C) CDCl_3 , 77.00 ppm (CDCl_3). IR spectra were obtained using an FT-IR instrument (Nicolet, AVATAR 360). MS analysis was carried out at 70 eV on a Finnigan TraceDSQII instrument using a direct insertion technique or GC insertion. HRMS analysis was carried out with a Micromass GCT (TOF MS EI^+). Reagents were used as purchased from various commercial sources.

Synthesis of Compound 4. *n*-BuLi (2.18 M in hexane, 17.0 mL, 37.02 mmol, 6 equiv) was added dropwise to diisopropylamine (5.8 mL, 40.72 mmol, 6.6 equiv) in dry ethyl ether (20 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **3** (1.999 g, 6.17 mmol) with 80 mL of dry ethyl ether. After it was kept at 0 °C for 1 h, the reaction mixture was cooled to -78 °C, and trimethylchlorosilane (6.32 mL, 49.36 mmol, 8.0 equiv) was added dropwise. The reaction mixture was warmed slowly to ambient temperature overnight. After quenching with water (50 mL), the crude product was extracted with ethyl ether (3 \times 20 mL) and dried over MgSO_4 . After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield **4** (3.284 g, 85%) as a white solid. From two other reactions of **3** on the 1.004 and 0.201 g scales, 1.300 g (69%) and 0.297 g (78%) of **4** were obtained, respectively. Mp: 139–140 °C. ^1H NMR (400 MHz, CDCl_3): δ 0.42 (s, 18H), 0.05 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.86, 144.09, 138.91, 122.07, -0.16, -0.93. IR (KBr): 2957, 2898, 2850, 2788 (C-H) cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{Br}_2\text{S}_2\text{Si}_4$: C, 39.20; S, 10.47; H, 5.92. Found: C, 39.67; S, 10.54; H, 6.29. MS (EI, 70 eV): m/z 610.06 [M^+], 612.05 [$\text{M}^+ + 2$].

Synthesis of Compound 1. To a solution of **4** (301 mg, 0.49 mmol) in dry ethyl ether (60 mL) was added *t*-BuLi (1.48 M, 1.5 mL, 2.21 mmol, 4.5 equiv) dropwise at -78 °C. After the mixture was kept at -78 °C for 2 h, dry CuCl_2 (198 mg, 1.47 mmol, 3.0 equiv) was added. The reaction mixture was kept at -78 °C for 1 h and warmed to -60 °C for 2 h and then warmed slowly to ambient temperature overnight. The reaction mixture was quenched

with water (40 mL), extracted with ethyl ether (2 \times 10 mL), and then finally dried over MgSO_4 . After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield **1** (126 mg, 58%) as a light yellow solid. From three other reactions on scales of 101, 101, and 101 mg of **4** with 5, 5, and 0.5 h for Br/Li exchange at -78 °C, 46 mg (64%), 40 mg (55%), and 40 mg (55%) of **1** were obtained, respectively. Mp: 252.1–253.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 0.52 (s, 12H), 0.46 (s, 18H), 0.32 (s, 18H), 0.29 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.00, 158.09, 150.49, 149.50, 134.72, 126.98, 109.33, 101.27, 1.87, 0.78, -0.09, -1.47. IR (KBr): 2955, 2897 (C-H) cm^{-1} . Anal. Calcd for $\text{C}_{38}\text{H}_{66}\text{S}_4\text{Si}_8$: C, 52.11; S, 14.64; H, 7.60. Found: C, 51.70; S, 14.46; H, 8.04. HRMS (TOF MS EI^+): m/z calcd for $[\text{C}_{38}\text{H}_{66}\text{Si}_8\text{S}_4]$ 874.2202, found 874.2206.

Synthesis of Compound 2. To a solution of **4** (302 mg, 0.49 mmol) in dry ethyl ether (90 mL) was added *t*-BuLi (1.48 M, 1.5 mL, 2.21 mmol, 4.5 equiv) dropwise at -78 °C, and then dry CuCl_2 (198 mg, 1.47 mmol, 3.0 equiv) was added immediately (within 1 min). The reaction mixture was kept at -78 °C for 1 h and warmed to -60 °C for 2 h and then warmed slowly to ambient temperature overnight. The reaction mixture was quenched with water (100 mL), extracted with ethyl ether (2 \times 20 mL), and finally dried over MgSO_4 . After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield **2** (37 mg, 17%) as a white solid. In addition to **2**, a mixture (about 60% in amount) with weak polarity showing one spot ($R_f = 0.80$) on TLC with hexane as eluent was obtained. The GCMS analyses are given in Figure S10 and Table 2 (see the Supporting Information). From two other reactions on scales of 102 and 102 mg of **4** with 10 and 0 min for Br/Li exchange after addition of *t*-BuLi, 15 mg (20%) and 8 mg (11%) of **2** were obtained, respectively. Mp: 209.5–210.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 0.36 (s, 36H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.91, 130.09, 0.40. IR (KBr): 2957, 2897 (C-H) cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{S}_2\text{Si}_4$: C, 53.03; S, 14.16; H, 8.01. Found: C, 52.77; S, 13.99; H, 8.34. HRMS (TOF MS EI^+): m/z calcd for $[\text{C}_{20}\text{H}_{36}\text{Si}_4\text{S}_2]$ 452.1336, found 452.1339.

Acknowledgment. We thank Mr. Pengtao Ma for crystal measurements and discussion. This research was supported by the NSFC (Nos. 20572015, 20672028, 50803015), the Program for NCET-05-0610, the SRF for ROCS-SEM, the Program for Young Excellent Talents in Henan Universities, the Foundation of Henan University (07YB2R006), and the Open Funding from Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences.

Supporting Information Available: Text, figures, tables, and CIF files giving spectral data and crystallographic data for compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM800994X