JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

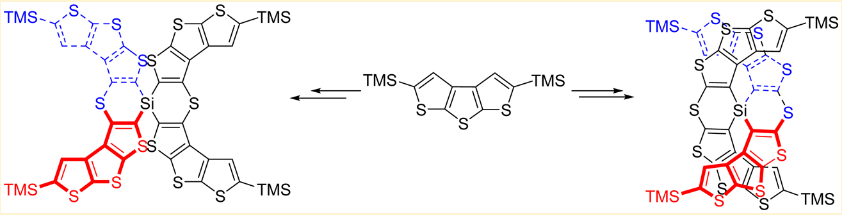
Silicon Spiro Double Helicene-like Compounds Based on Dithieno[2,3-*b*:3′,2′-*d*]thiophene: Syntheses and Crystal Structures

Chunli Li,*[,†] Longlong Wu,[†] Wan Xu,[†] Jinsheng Song,[†] Jianwu Shi,[†] Panpan Yu,[†] Yuhe Kan,[‡] and Hua Wang*[,†]

[†]Engineering Research Center for Nanomaterials, Henan University, Kaifeng, 475004, China

[‡]Jiangsu Province Key Laboratory for Chemistry of Low Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian, 223300, China

Supporting Information



ABSTRACT: Silicon spiro carbon−sulfur double helicene-like compounds **1** and *rac*-**2** were synthesized from 2,5-bis-trimethylsilanyldithieno[2,3-*b*:3′,2′-*d*]thiophene, with total yields of 17% and 7%, respectively. ^{1}H and ^{13}C NMR spectra and X-ray crystallographic analysis showed the predicted 4-fold symmetry for **1** and *rac*-**2** and confirmed their spiro double helicene-like spatial configurations. The absorption behavior of compounds **1** and *rac*-**2** was also investigated.

Helicenes are helically shaped molecules defined as ortho-fused polycyclic aromatic compounds; these molecules possess interesting π-conjugated helical structures and are widely applied in asymmetric catalysis, circularly polarized luminescence materials, and molecular recognition.[1] Helical-fused molecules are generally divided into carbohelicenes and heterohelicenes.[1d,2] Thiahelicenes are typical heterohelicenes that contain all-sulfur atoms along the outer edge of the molecular skeletons, as well as thiophene rings cross-conjugated and annelated into the helix.[1b,3] Rajca et al. have reported a series of synthetic work in preparing carbon−sulfur helicenes, such as carbon−sulfur [5], [7], [9], [11]helicenes.[3,4]

Helicenes with multihelicity have gained considerable attention in recent years.[5−7] Multihelicity provides plural electronic states and molecular dynamics and is characterized by three-dimensional molecular shape and packing in crystalline state.[1a] In our previous work, we prepared carbon−sulfur double helicenes and three helicenes, which bear solubility-supporting groups[3,6b−d,8] from 2,5-bis-trimethylsilanyldithieno-[2,3-*b*:3′,2′-*d*]thiophene. Cyclooctatetrathiophene- and naphthalene-cored carbon−sulfur double helicenes were successfully synthesized, and their absorption behavior was also described.[6b,c] The spacer in cyclooctatetrathiophene-cored carbon−sulfur double helicene exhibits a "saddle" form 8π annulene, which shows two absorption peaks at 247 and 349 nm and a shoulder peak at 354 nm in the UV/vis spectrum.[6c] The spacer in naphthalene-cored carbon−sulfur double helicene is a twisted naphthalene, which exhibits improved planarity compared to that of the "saddle" form 8π annulene. The UV/vis spectrum shows two absorption peaks at 351 and 373 nm and a shoulder peak at 388 nm[6b] and clearly presents a red shift vs the case of cyclooctatetrathiophene-cored carbon−sulfur double helicene.[6b,c]

Spiro-condensed compounds with orthogonal chromophores and a high glass transition temperature (T_g) have been the subject of various studies.[9] Compounds containing silole have been actively investigated because of their unique electronic structures formed by $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the silicon atom and the π^* orbital of the butadiene moiety.[10] As such, developing a single atom-bridged spiro carbon−sulfur double helicene remains a challenging and rewarding endeavor. In the present study, we aim to create new aesthetically pleasing helical molecules and modulate the position of the absorption peaks of a carbon−sulfur double helicene by changing its spacer group. In this paper, we report the facile and efficient synthesis of novel silicon spiro carbon−sulfur double helicene-like compounds and describe their crystal structures. Spectroscopic data are also presented.

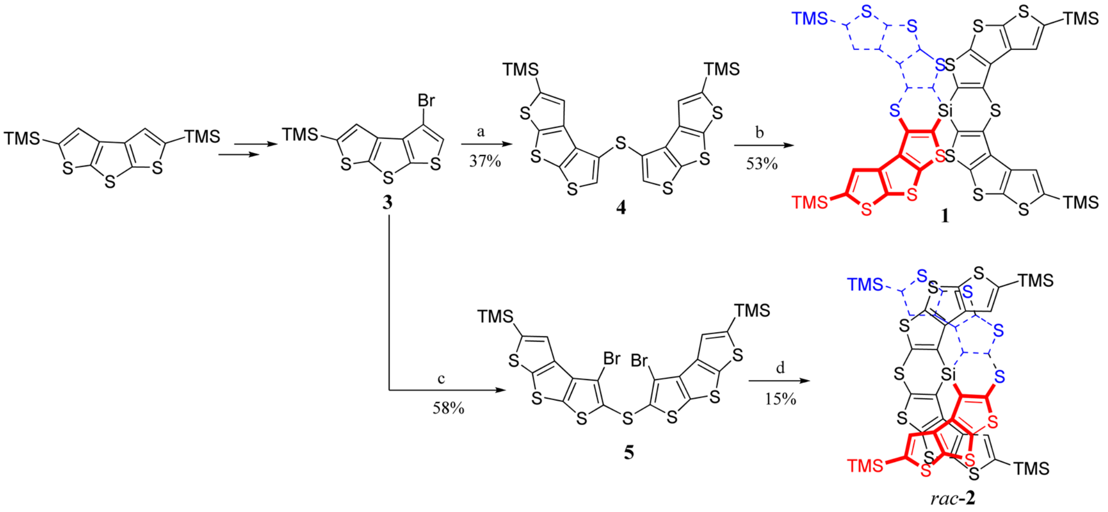
■ SYNTHESIS OF 1 AND *rac*-2

We developed a synthesis route for **1** and *rac*-**2**, which are silicon spiro carbon−sulfur double helicene-like compounds (Scheme 1). 4-Bromo-2-trimethylsilanyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene (**3**) was prepared from 2,5-di(trimethylsilanyl)-dithieno[2,3-*b*:3′,2′-*d*]thiophene through a bromination and bromine dance reaction according to our previous method.[6c] Following the Li/Br exchange on **3** in the presence of *n*-BuLi,

Received: August 17, 2015
Published: October 14, 2015

DOI: 10.1021/acs.joc.5b01910
J. Org. Chem. 2015, 80, 11156−11161

Scheme 1. Synthetic Route to 1 and *rac*-2[a]



[a]Regents and conditions: (a) (i) *n*-BuLi (1.05 equiv), Et_2O, −78 °C/2 h; (ii) $(PhSO_2)_2S$ (0.5 equiv), −78 °C/h, −55 °C/2 h; (b) (i) LDA (2.1 equiv), Et_2O, 0 °C/2 h; (ii) $SiCl_4$ (0.55 equiv), 100 °C/20 h; (c) (i) LDA (1.05 equiv), Et_2O, −78 °C/2 h; (ii) $(PhSO_2)_2S$ (0.5 equiv), −78 °C/2h; (d) (i) *t*-BuLi (4.4 equiv), Et_2O, −78 °C/2 h; (ii) $SiCl_4$ (0.55 equiv), 100 °C/35 h.

$(PhSO_2)_2S$ was added into the reaction mixture to produce bis(5-(trimethylsilyl)dithieno[2,3-*b*:3′,2′-*d*]thiophen-3-yl)-sulfane (**4**), with a yield of 37%. Lithium diisopropylamide (LDA) was introduced to obtain dilithiated **4** by removing protons in the *α* position of **4**. Silicon atom-bridged silicon spiro carbon−sulfur double helicene-like compound **1**, which contains two semicircular moieties, was efficiently developed through the reaction between dilithiated **4** and $SiCl_4$, with a good yield of 53%. Compound **3** was deprotonated with LDA to generate lithiated **3**. Bis(3-bromo-5-(trimethylsilyl)dithieno-[2,3-*b*:3′,2′-*d*]thiophen-2-yl)sulfane (**5**) was obtained via the reaction of lithiated **3** and $(PhSO_2)_2S$, with a yield of 58%. Following the Li/Br exchange on **5** with *t*-BuLi, the resultant aryllithium species were treated with $SiCl_4$ to prepare silicon atom-bridged silicon spiro carbon−sulfur double helicene-like compound *rac*-**2**, in a yield of 15%. ^1H and ^{13}C NMR spectra and X-ray crystallographic analyses show the predicted 4-fold symmetry for **1** and *rac*-**2** (Supporting Information). The ^1H NMR spectra of **1** and *rac*-**2** display a single peak in the aromatic region, namely, 7.88 and 7.17 ppm, respectively. The ^{13}C NMR spectra of **1** and *rac*-**2** demonstrate eight kinds of signal for the moieties of dithieno[2,3-*b*:3′,2′-*d*]thiophene in the aromatic region, namely, 144.8, 143.9, 140.8, 139, 135.9, 129.6, 124.8, and 121.3 ppm and 144, 143.4, 142.5, 142, 141.3, 137.2, 125.5, and 120.1 ppm, respectively.

■ CRYSTALLOGRAPHIC ANALYSIS FOR 1 AND *rac*-2

The molecular structures of **4**, **1**, and *rac*-**2** are confirmed through single-crystal X-ray analysis (Figure 1). As shown in Figure 1A, each moiety is approximately coplanar with torsions of 1.7° (C5−C7−C8−C10) and 1.5° (C12−C15−C16−C18) in **4**. However, two dithieno[2,3-*b*:3′,2′-*d*]thiophene moieties are nonplanar, with an interplanar angle of 72.8°. Meanwhile, the angle of C10−S4−C12 is 101.7°. The torsions of C7−C8−C10−S4 and C16−C15−C12−S4 are 0.3° and 6.5°, respectively. The formation of the spiro-condensed di(dithieno-[2,3-*b*:3′,2′-*d*]thiophene)thiasilines[9] via the reaction of dilithiated **4** and $SiCl_4$ generates silicon atom-bridged silicon spiro carbon−sulfur double helicene-like configuration for compound **1** (Figures 1C and 1D). This compound contains two semicircular, back-to-back moieties, with an interplanar angle of 88.4°, and a perpendicular spatial configuration. Each semicircular moiety is approximately coplanar, with an interplanar angle of 0.6° among the terminal thiophene rings, possibly because the six-membered core possesses minimal strain. The existence of the symmetry center induces the molecule of **1** to be achiral. The distance of the two hydrogen atoms in the terminal thiophene is 3.91 Å, and the angles of C−Si−C are 100.1° and 113.2° inside and outside the six-membered 1,4-thiasilines, respectively.[9a] The crystal packing of **1** (Figure 2A) reveals the existence of intermolecular S···S interaction, with distances of 3.10 and 3.48 Å for S2···S2 and S2···S3, respectively. This interaction confers compound **1** with a cube grid-like packing mode along the *c* axis (Figure 2B), which is a suitable characteristic for potential applications.

The formation of the two 1,4-thiasiline rings from **5** generates the *rac*-**2** molecule, which exhibits double helicene-like spatial configurations (Figure 1E and 1F). *rac*-**2** belongs to the monoclinic space group *P*2(1)/*c* and possesses a spatial configuration of two semicircular structures connected link-by-link. The *rac*-**2** structure shows that the molecule has approximately 4-fold symmetry, including two *rac*-**2** molecules and five chloroform molecules in one cell. These molecules exhibit multiple interactions between two adjacent *rac*-**2** molecules and between *rac*-**2** and chloroform molecules (Figure 2C). Compared with that in **1**, the two 1,4-thiasiline rings are highly distorted, with an interplanar angle of 88.8°. In the semicircular configuration, two terminal thiophene rings are located on one side of the plane of 1,4-thiasiline. In addition, the interplanar angles between two terminal thiophene rings and 1,4-thiasiline ring are 3.9° and 7.7°, respectively. The torsion angles of C10−C8−C6−C5 and C13−C14−C16−C18 are 2.0° and 2.2°, respectively. The distance of the two hydrogen atoms in terminal thiophene is 5.08 Å. In the other configuration, two terminal thiophene rings are located on both sides of the plane of the 1,4-thiasiline ring. The semicircular moiety also presents a helical configuration, which induces the *rac*-**2** molecules to be chiral molecules. Furthermore, the two molecules in the cell are identified as enantiomers. The

DOI: 10.1021/acs.joc.5b01910
J. Org. Chem. 2015, 80, 11156−11161

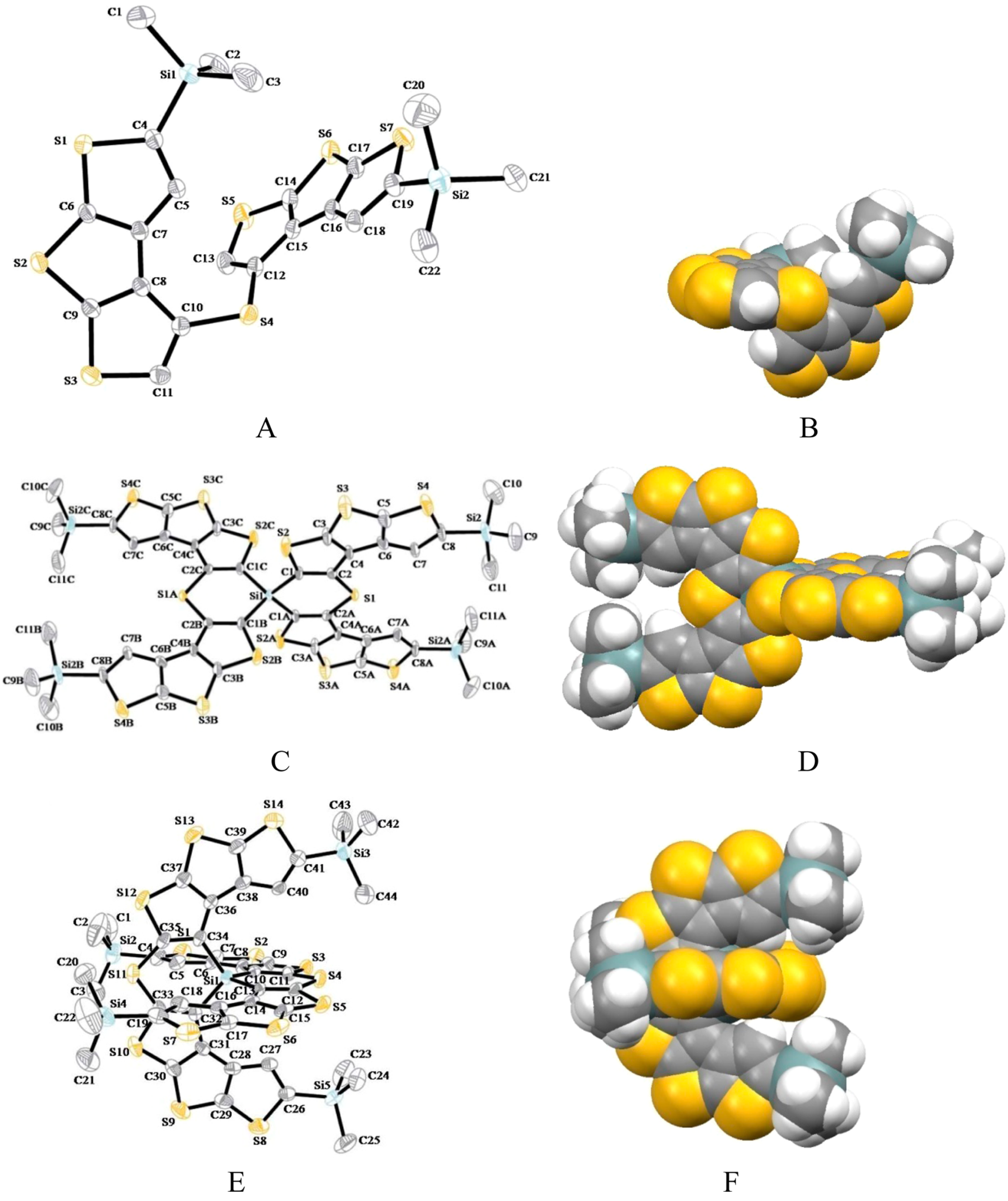


Figure 1. Molcular structures and space fill mode for compounds **4**, **1**, and ***rac*-2**. (A) molcular structure for **4**, (B) space fill mode for **4**, (C) molcular structure for **1**, (D) space fill mode for **1**, (E) molcular structure for *rac*-**2**, (F) space fill mode for *rac*-**2**. Carbon, sulfur, and silicon atoms are depicted with thermal ellipsoids set at the 30% probability level, and all hydrogen atoms are omitted for clarity.

interplanar angles between the two terminal thiophene rings and that between thiophene and 1,4-thiasiline rings are 10.6° and 4.1°, respectively. The torsion angles of C34−C36−C38−C40 and C32−C31−C28−C27 are 2.2° and 0.6°, respectively. The distance of the two hydrogen atoms in terminal thiophene is 5.19 Å. In *rac*-**2**, the angles of C−Si−C in the outside and inner side of 1,4-thiasilines with an average are 104.5° and 112.0°, respectively. The repulsion of the two semicircular

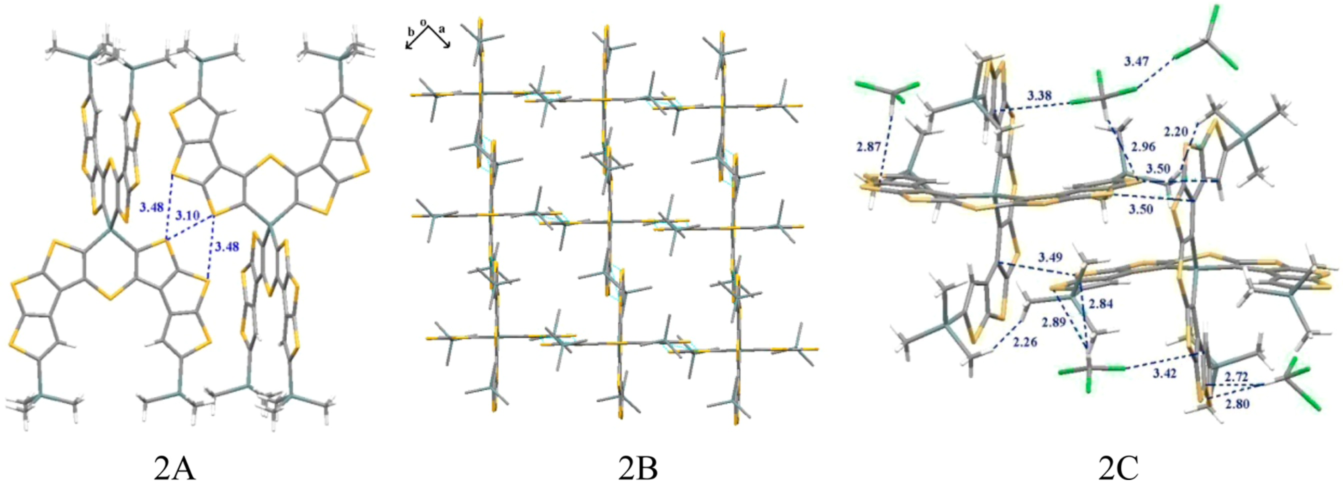


Figure 2. (A) S−S interaction in packing of **1**. (B) cube grid-like packing along *c* axis of **1**. (C) multiple types interaction in the packing of *rac*-**2**.

moieties increases the inner angle of C−Si−C and decreases the outside angle of C−Si−C of the six-membered 1,4-thiasilines compared with those in **1**. Crystal packing of *rac*-**2** exhibits multiple types of interactions (Figure 2C). For example, the distances of C28···Cl4, Cl15···Cl2, S7···C84, S6···C80, S20···C36, and Cl3···C72 are 3.38, 3.47, 3.50, 3.50, 3.49, and 3.42 Å, respectively. The multiple types of interaction stabilize crystal packing and are beneficial for their applications.

The UV/vis spectra for **1** and *rac*-**2** in dichloromethane are shown in Figure 3. The electronic structure and excited-state calculations of these compounds were determined with the Gaussian 09 suite by the TD-DFT/PCM approach at the 6-31G (d,p) level to determine the effects of molecular structure and electron distribution on the spectroscopic properties of the compounds. Visualized HOMO and LUMO distributions and the calculated frontier orbital energies [B3LYP/6-31G(d,p)] for **1** and *rac*-**2** are presented in the Supporting Information (Figure S13). The predicted UV/vis spectra are consistent with the experimental curves shown in Figure S14, and the transition contributions are listed in Table S1. Compound **1** shows two absorption peaks at 233 and 272 nm and two shoulder peaks at 298 and 322 nm. Approximately 233, 272, 298, and 322 nm are characterized mainly by the contributions of HOMO → LUMO + 6, HOMO − 4 → LUMO, HOMO − 2 → LUMO, and HOMO → LUMO + 2, respectively. *rac*-**2** shows three absorption peaks at 230, 256, and 362 nm. Approximately 256 and 362 nm are characterized mainly by the contributions of HOMO − 1 → LUMO + 2 and HOMO − 3 → LUMO, respectively. The blue shift of the UV/vis absorption peaks of compounds **1** and *rac*-**2** was compared with that of cyclooctatetrathiophene- and naphthalene-cored carbon−sulfur double helicene compounds.[6b,c]

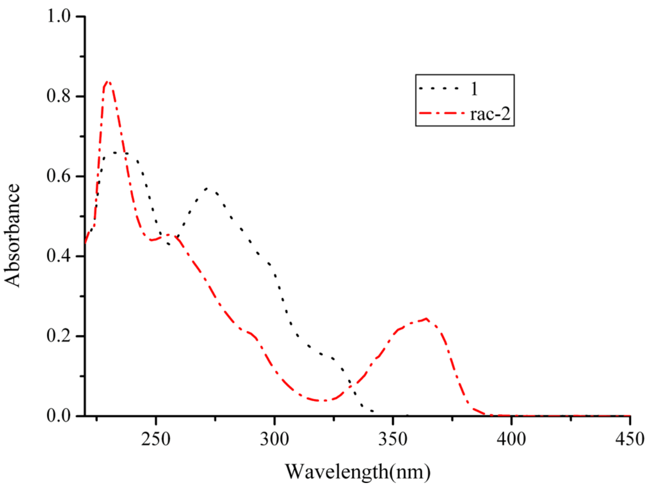


Figure 3. UV/vis absorption spectra of **1** and *rac*-**2** in dichloromethane at room temperature ($C = 1\times 10^{-5}$ M).

■ CONCLUSION

Esthetically pleasing silicon spiro carbon−sulfur double helicene-like compounds **1** and *rac*-**2** were efficiently synthesized from 2,5-bis-trimethylsilanyldithieno[2,3-*b*:3′,2′-*d*]-thiophene, with total yields of 17% and 7%, respectively. X-ray single crystal analysis shows the predicted 4-fold symmetry for **1** and *rac*-**2** and the existence of multiple short contacts, including S···S, C···Cl, Cl···Cl, S···C interactions. The UV/vis absorption peaks of carbon−sulfur double helicene compounds present a red shift as the spacer from the silicon atom changes to the "saddle" form 8*π* annulene and to the twisted naphthalene.[6b,c] This work is a pioneer in the investigations for silicon spiro carbon−sulfur double helicene compounds.

■ EXPERIMENTAL SECTION

General Procedures and Materials. Ether and tetrahydrofuran (THF) for use on vacuum line were freshly distilled from sodium/benzophenone prior to use. 2,5-bis-trimethylsilanyldithieno-[2,3-*b*:3′,2′-*d*]thiophene was prepared according to our previous research work.[11] *t*-BuLi (pentane) and *n*-BuLi (hexane) were obtained from Energy Chemical, prior to use, their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine.[12] Column chromatography was carried out on silica gel (300−400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. Standard techniques for synthesis under an inert atmosphere, using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stopcock, were employed. All starting materials and reagents were commercially available.

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz NMR instrument using $CDCl_3$ and DMSO-d_6 as solvents. IR spectra were obtained using an FT-IR instrument. HRMS analysis was carried out on a mass spectrometer equipped with FTMS and LTQ FT Ultra. Elemental analysis was recorded on an elemental analyzer. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. The X-ray crystallographic analyses were performed using crystals of compounds **4**, **1**, and *rac*-**2** with the size 0.46 × 0.31 × 0.27, 0.46 × 0.23 × 0.05, and 0.50 × 0.46 × 0.07 mm^3, respectively. The intensity data were collected with the ω scan mode (296 K) on a diffractometer with a CCD detector using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using the SADABS program.[13] The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares.[14] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Further details are in the deposited CIFs. Slow evaporation of solutions of **4**, **1**, and *rac*-**2** in $CHCl_3$−CH_3OH (1:3, 1:5, 1:5, v/v) was employed, respectively, for growing single crystals. The predicted absorption spectra were computed in the Linear-Response (LR) formalisms[15,16] within the TD-DFT/PCM approaches based on the hybrid B3LYP level. HOMO and LUMO distributions and the calculated frontier orbital energies were performed using the B3LYP/6-31G(d,p) level of theory.

Synthesis of Bis(5-(trimethylsilyl)dithieno[2,3-*b*:3′,2′-*d*]thiophen-3-yl)sulfane (4). To a solution of **3** (0.4248 g, 1.22 mmol) in dry ethyl ether (15 mL), *n*-BuLi (2.47 M in hexane, 1.28 mmol, 1.05 equiv) was added dropwise at −78 °C. After the temperature was maintained at −78 °C for 2 h, dry $(PhSO_2)_2S$ (0.1921 g, 0.61 mmol, 0.5 equiv) was added at −78 °C, and then the reaction mixture was kept at −78 °C for 1 h and −55 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at 0 °C, extracted with CH_2Cl_2 (3 × 20 mL), and then washed with saturated NaCl (20 mL) and water (2× 20 mL). After the mixture dried over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60−90 °C) as eluent to yield **4** (0.1263 g, 37%) as a light yellow solid. Mp: 115−117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.43 (s, 2H), 7.19 (s, 2H), 0.22(s, 18H), ^{13}C NMR($CDCl_3$, 100 MHz): δ 144.8, 144.5, 140.0, 139.9, 136.8, 127.1, 125.2, 122.6, −0.3. HRMS (MALDI/DHB): *m/z* calcd for [$C_{22}H_{22}S_7Si_2$] 565.9305, found 565.9296. IR(KBr): 3096, 2959, 1432, 1246, 1146, 838, 634 cm^{-1}.

Synthesis of Silicon Spiro Carbon−Sulfur Double Helicene-like Compound (1). *n*-BuLi (2.0 M in hexane, 0.6 mmol, 6 equiv) was added dropwise to diisopropylamine (0.10 mL, 0.7 mmol, 6.6 equiv) in Et_2O (9 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution (3 mL, 2.1 equiv) was transferred by syringe into a solution of **4** (0.0547 g, 0.1 mmol) in Et_2O (5 mL) at 0 °C, and then the reaction mixture was kept at 0 °C for 2 h. $SiCl_4$ (0.006 mL, 0.055 mmol, 0.55 equiv; namely, 0.3 mL of $SiCl_4$ solution consisting of 0.3 mL of $SiCl_4$ in 15 mL of THF) was added dropwise at 0 °C, and then the reaction mixture was warmed up to 100 °C kept for 20 h. The reaction mixture was quenched with methanol at −78 °C, extracted with CH_2Cl_2 (3 × 25 mL), and then washed with water (3 × 20 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified via ultrasonic washing ($CHCl_3$/CH_3OH = 5/1) yield *rac*-**1** (0.0293 g, 53%) as a milky solid. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.88 (s, 4H), 0.48 (s, 36H), ^{13}C NMR (DMSO-d_6, 100 MHz): δ 144.8, 143.9, 140.8, 139.0, 135.9, 129.6, 124.8, 121.3, −0.5. HRMS (MALDI/DHB): *m/z* calcd for [$C_{44}H_{40}S_{14}Si_5$] 1155.8066, found 1155.8038. Anal. Calcd for $C_{44}H_{40}S_{14}Si_5$ (1155.81): C, 45.63; H, 3.48; S, 38.76. Found: C, 45.25; H, 3.34; S, 38.29. IR (KBr): 3065, 2953, 1480, 1249, 1183, 884, 761 cm^{-1}.

Synthesis of Bis(3-bromo-5-(trimethylsilyl)dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)sulfane (5). *n*-BuLi (2.47 M in hexane, 0.64 mmol, 2.1 equiv) was added dropwise to diisopropylamine (0.11 mL, 0.77 mmol, 2.5 equiv) in Et_2O (10 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution (5 mL, 1.05 equiv) was transferred by syringe into a solution of **3** (0.1056 g, 0.3 mmol) in Et_2O (10 mL) at −78 °C, and then the reaction mixture was kept for 2 h. Dry $(PhSO_2)_2S$ (0.0477 g, 0.15 mmol, 0.5 equiv) was added at −78 °C, and then the reaction mixture was kept at −78 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at 0 °C, extracted with CH_2Cl_2 (3 × 15 mL) and then washed with water (3 × 15 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60−90 °C) as eluent to yield **5** (0.0633g, 57%) as a light yellow solid. Mp: 225−226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.77 (s, 2H), 0.37 (s, 18H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.1, 144.1, 141.6, 140.2, 136.4, 130.1, 124.4, 111.5, −0.1. HRMS (MALDI): *m/z* calcd for [$C_{22}H_{20}Br_2S_7Si_2$] 721.7515, found 721.7509. IR (KBr): 3069, 2954, 1400, 1248, 1066, 834, 629 cm^{-1}.

Synthesis of Silicon Spiro Carbon−Sulfur Double Helicene-like Compound (*rac*-2). To a solution of **5** (0.0495 g, 0.07 mmol) in dry ethyl ether (20 mL), *t*-BuLi (1.58 M in pentane, 0.3 mmol, 4.4 equiv) was added dropwise at −78 °C, and then the reaction mixture was kept at −78 °C for 2 h. $SiCl_4$ (0.0043 mL, 0.037 mmol, 0.55 equiv; namely, 0.2 mL of $SiCl_4$ solution consisting of 0.22 mL of $SiCl_4$ in 10 mL of THF) was added dropwise at −78 °C, and then the reaction mixture was warmed up to 80 °C and kept for about 35 h. The reaction mixture was quenched with methanol at −78 °C, extracted with CH_2Cl_2 (3 × 15 mL), and then washed with water (3× 15 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60−90 °C) as eluent to yield *rac*-**2** (0.0059 g, 15%) as a light green solid. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.17 (s, 4H), 0.36 (s, 36H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 143.4, 142.5, 142.0, 141.3, 137.2, 125.5, 120.1, 0.2. HRMS (MALDI-DHB): *m/z* calcd for [$C_{44}H_{40}S_{14}Si_5$] 1155.8066, found 1155.8052. Anal. Calcd for $C_{44}H_{40}S_{14}Si_5$ (1155.81): C, 45.63; H, 3.48; S, 38.76. Found: C, 45.37; H, 3.33; S, 38.41. IR (KBr): 2955, 1412, 1255, 1087, 839, 631 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01910.

Characterization of all compounds; predicted UV/vis spectra for **1** and *rac*-**2**; HOMO and LUMO distributions and the calculated frontier orbital energies for **1** and *rac*-**2** (PDF)

Crystallographic data for **4** (CIF)

Crystallographic data for **1** (CIF)

Crystallographic data for *rac*-**2** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: chunli79@126.com.
*E-mail: hwang@henu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge Mr. Pengtao Ma for his assistance in crystal measurements and discussions. This research was financially supported by the NSFC (Nos. U1304207, 51503056, 21270255) and the Foundation for Distinguished Young Scientist of Henan University (No. YQPY20140056).

■ REFERENCES

(1) (a) Fujikawa, T.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 7763. (b) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211. (c) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 1051. (d) Shen, Y.; Chen, C.-F. *Chem. Rev.* **2012**, *112*, 1463. (e) Morrison, D. J.; Trefz, T. K.; Piers, W. E.; McDonald, R.; Parvez, M. *J. Org. Chem.* **2005**, *70*, 5309. (f) Field, J. E.; Muller, G.; Riehl, J. P.; Venkataraman, D. *J. Am. Chem. Soc.* **2003**, *125*, 11808. (g) Shcherbina, M. A.; Zeng, X.; Tadjiev, T.; Ungar, G.; Eichhorn, S. H.; Phillips, K. E. S.; Katz, T. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 7837.

(2) Talele, H. R.; Sahoo, S.; Bedekar, A. V. *Org. Lett.* **2012**, *14* (12), 3166.

(3) Cinar, M. E.; Ozturk, T. *Chem. Rev.* **2015**, *115*, 3036.

(4) (a) Miyasaka, M.; Rajca, A. *Synlett* **2004**, 177. (b) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481. (c) Miyasaka, M.; Pink, M.; Olankitwanit, A.; Rajca, S.; Rajca, A. *Org. Lett.* **2012**, *14*, 3076. (d) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806.

(5) (a) Xiao, S.; Kang, S. J.; Wu, Y.; Ahn, S.; Kim, J. B.; Loo, Y.-L.; Siegrist, T.; Steigerwald, M. L.; Li, H.; Nuckolls, C. *Chem.Sci.* **2013**, *4*, 2018. (b) Zhong, Y.; Kumar, B.; Oh, S.; Trinh, M. T.; Wu, Y.; Elbert, K.; Li, P.; Zhu, X.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2014**, *136*, 8122. (c) Kashihara, H.; Asada, T.; Kamikawa, K. *Chem. - Eur. J.* **2015**, *21*, 6523. (d) Ball, M.; Zhong, Y.; Wu, Y.; Schenck, C.; Ng, F.; Steigerwald, M.; Xiao, S.; Nuckolls, C. *Acc. Chem. Res.* **2015**, *48*, 267.

(6) (a) Shiraishi, K.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 9312. (b) Wang, Z.; Shi, J.; Wang, J.; Li, C.; Tian, X.; Cheng, Y.; Wang, H. *Org. Lett.* **2010**, *12*, 456. (c) Li, C.; Shi, J.; Xu, L.; Wang, Y.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2009**, *74*, 408. (d) Liu, X.; Yu, P.; Xu, L.; Yang, J.; Shi, J.; Wang, Z.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2013**, *78*, 6316. (e) Hashimoto, S.; Nakatsuka, S.; Nakamura, M.; Hatakeyama, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 14074. (f) Nakamura, K.; Furumi, S.; Takeuchi, M.; Shibuya, T.; Tanaka, K. *J. Am. Chem. Soc.* **2014**, *136*, 5555. (g) Sakamaki, D.; Kumano, D.; Yashima, E.; Seki, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 5404.

(7) (a) Hagen, S.; Scott, L. T. *J. Org. Chem.* **1996**, *61*, 7198. (b) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (d) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **2003**, *5*, 1863.

(8) Li, C.; Zhang, Y.; Zhang, S.; Shi, J.; Kan, Y.; Wang, H. *Tetrahedron* **2014**, *70*, 3909.

(9) (a) Lee, K.-H.; Ohshita, J.; Tanaka, D.; Tominaga, Y.; Kunai, A. *J. Organomet. Chem.* **2012**, *710*, 53. (b) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011.

(10) Son, H.-J.; Han, W.-S.; Chun, J.-Y.; Kwon, S.-N.; Ko, J.; Kang, S. O. *Organometallics* **2008**, *27*, 2464.

(11) Wang, Y.; Wang, Z.; Zhao, D.; Wang, Z.; Cheng, Y.; Wang, H. *Synlett* **2007**, *2007*, 2390.

(12) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.

(13) Sheldrick, G. M. *SADABS*; University of Gottingen: Germany, 1996.

(14) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(15) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **2000**, *104*, 5631.

(16) Cossi, M.; Barone, V. *J. Chem. Phys.* **2001**, *115*, 4708.