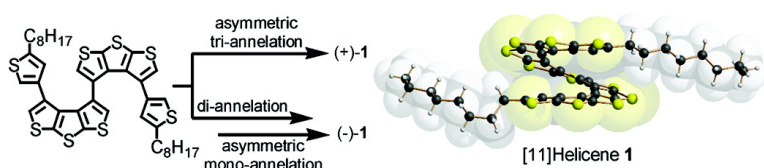## Communication

Cross-Conjugated Oligothiophenes Derived from the (CS) Helix: Asymmetric Synthesis and Structure of Carbon–Sulfur [11]Helicene

Makoto Miyasaka, Andrzej Rajca, Maren Pink, and Suchada Rajca

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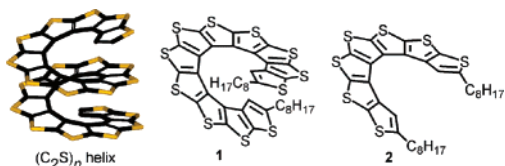
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Cross-Conjugated Oligothiophenes Derived from the (C$_2$S)$_n$ Helix: Asymmetric Synthesis and Structure of Carbon−Sulfur [11]Helicene

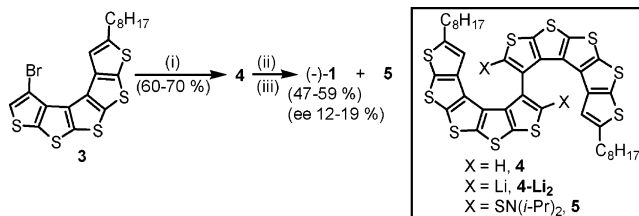Makoto Miyasaka,[†] Andrzej Rajca,*,[†] Maren Pink,[‡] and Suchada Rajca[†]

*Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304, and IUMSC,
Department of Chemistry, Indiana University, Bloomington, Indiana 47405*

Received August 8, 2005; E-mail: arajca1@unl.edu

Carbon−sulfur [n]helicenes correspond to unique β-oligo-thiophenes that are oligomers of (C$_2$S)$_n$ helix, with all sulfur atoms positioned at the molecular periphery.[1−3] The electronic structure of such oligomers is affected by helical curvature and cross-conjugation of the carbon−carbon framework,[4] in contrast to achiral and conjugated α-oligothiophenes, which are widely studied as electronic materials.[1] Such cross-conjugated [n]helicenes with large n may provide materials with extraordinary chiral properties and transparency in the optical region.[2] The recent advances in development of efficient non-photochemical routes to nonracemic [n]helicenes are limited to $n \leq 8$.[2b,c] In particular, asymmetric syntheses of [n]helicenes have been recently extended to [7]-helicenes.[2f,3d]

Herein we describe the asymmetric synthesis and characterization of helical (C$_2$S)$_n$ β-undecathiophene **1**. Using helical β-hep-tathiophene **2** as a reference, the optical band gap (E_g) for the (C$_2$S)$_n$ helix polymer is estimated.

The synthetic approaches to **1** are based upon either mono- or tri-annelation, using (−)-sparteine-mediated asymmetric induction (Schemes 1 and 2).[3d,5]

For the mono-annelation route, Pd-mediated reductive CC-homocoupling of [5]helicene **3**[3c] gives decathiophene **4** (Scheme 1). Treatment of **4** with LDA (2.4 equiv) gives dilithiated intermediate **4-Li$_2$**, showing a ^{1}H NMR spectrum with one singlet at $\delta \approx 4.841$ ppm, assigned to the β-hydrogens; in the presence of (−)-sparteine, two singlets at $\delta \approx 5.656$ and 5.517 ppm with relative integrations of 1:1 are observed (Figure 1).[6] Thus, **4-Li$_2$** is formed in good yield and no asymmetric induction is detected at this stage. Addition of bis(phenylsulfonyl)sulfide ((PhSO$_2$)$_2$S) to **4-Li$_2$**/(−)-sparteine gives [11]helicene (−)-**1** and variable amounts of bypro-duct (−)-**5**. ^{1}H NMR spectra of the crude mixtures indicate that the ratios of **5** to **1** are in the range from negligible to 0.69, with the greater ratios associated with higher ee's for (−)-**1** and lower [α]$_D$ for (−)-**5**.[7,8a,b] Based upon chirooptical data, the predominant enantiomers of nonracemic (−)-**1** and (−)-**5** are derived from **4-Li$_2$** with opposite configurations.[8] Thus, the asymmetric induction leading to (−)-**1** may be viewed as the result of kinetic resolution of **4-Li$_2$**/(−)-sparteine diastereomers via formation of byproduct (−)-**5**.

For the tri-annelation route, octathiophene **7** is prepared by Pd-mediated reductive CC-homocoupling of tetrathiophene **6**[3c] (Scheme

Scheme 1 . Asymmetric Synthesis of (−)-1 via Mono-annelation^a

^{a} Reagents and conditions: (i) Pd(P(t-Bu)$_3$)$_2$ (0.6 equiv), K$_3$PO$_4$ (2.1 equiv), toluene, 75 °C for 3 h, (ii) LDA (2.4 equiv), (−)-sparteine (3.6 equiv), Et$_2$O/hexane (325:1) and 3% benzene-d_6, 0 °C for 5 min, then rt for 20 min, (iii) (PhSO$_2$)$_2$S (∼1.2 equiv).

Scheme 2. Asymmetric Synthesis of (+)-1 via Tri-annelation^a
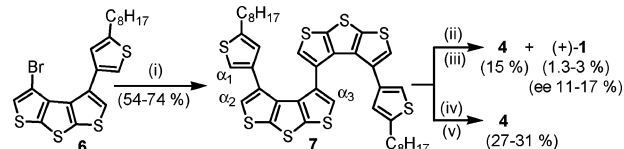
^{a} Reagents and conditions: (i) Pd(P(t-Bu)$_3$)$_2$ (0.45−0.85 equiv), K$_3$PO$_4$ (2.1−2.3 equiv), toluene, 100 °C for 3 h, (ii) LDA (12 equiv), (−)-sparteine (10 equiv), Et$_2$O/hexane (100:1), 40−45 °C for ∼14 h, (iii) (PhSO$_2$)$_2$S (4.2 equiv), (iv) n-BuLi (4.4 equiv), (−)-sparteine (6.6 equiv), Et$_2$O/hexane (13:1), −78 °C for 2 h, then −50 °C for 3 h, (v) (PhSO$_2$)$_2$S (3.6 equiv) at −30 °C.
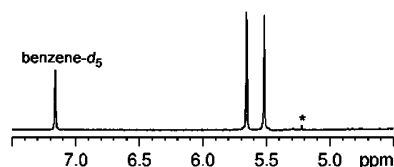

Figure 1. ^{1}H NMR (500 MHz, Et$_2$O/hexane (325:1) and 3% benzene-d_6, 296 K) spectrum for 3 mM **4-Li$_2$**, obtained with LDA (2.4 equiv)/(−)-sparteine (3.6 equiv). Unknown impurity is labeled with asterisk.

2). Treatment of **7** with excess amount of LDA/(−)-sparteine at elevated temperature is followed by quenching with (PhSO$_2$)$_2$S, to give the products of selective di-annelation and tri-annelation, i.e., **4** and (+)-**1**, respectively.[9,10] Notably, the mono-annelation (Scheme 1) and tri-annelation (Scheme 2) produce [11]helicene **1** with opposite configurations.

When n-BuLi/(−)-sparteine is used as a base, the selectivity of the tetralithiation at the α_1- and α_2-positions is greatly improved, as indicated by the deuterium quenching experiments and di-annelation of **7** to give **4** in ∼30% yield.[10b,11] Therefore, the most efficient approach to nonracemic [11]helicene **1** involves a sequence of di-annelation (Scheme 2) and mono-annelation (Scheme 1).

The X-ray structures of racemic crystals of [11]helicene **1** and [7]helicene **2**[12] show that both molecules are helical and possess an approximate two-fold symmetry (Figure 2).

[†] University of Nebraska.
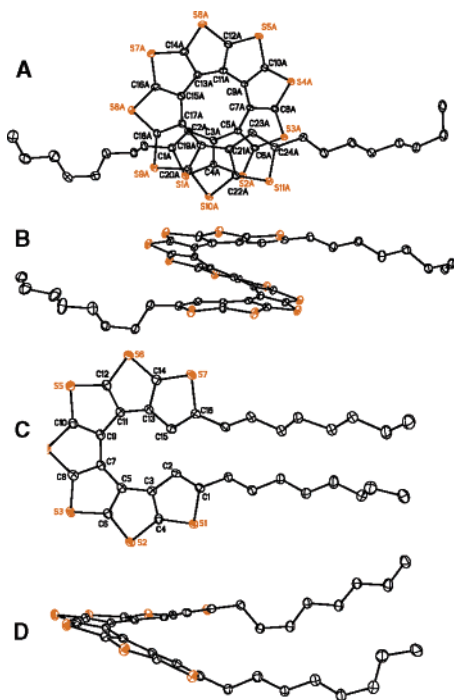[‡] Indiana University.

Figure 2. Molecular structure and conformation for [11]helicene **1** (top view, A; side view, B) and [7]helicene **2** (top view, C; side view, D). Carbon and sulfur atoms are depicted with thermal ellipsoids set at the 50% probability level. Only one of the two unique molecules of **1** (molecule A) is shown; hydrogen atoms are omitted for clarity.
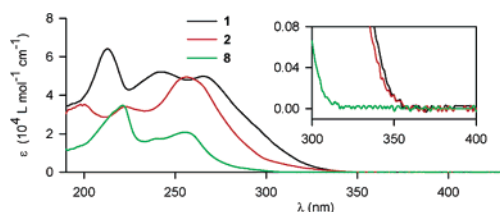

Figure 3. UV–vis electronic absorption spectra for **1**, **2**, and **8** in cyclohexane at room temperature. Inset: absorption onsets.

In the structures of **1** and **2**, the individual thiophene rings are approximately planar with largest mean deviation of the least-squares $0.007-0.041$ Å and $0.011-0.030$ Å, respectively. The angles between the least-squares planes of the neighboring thiophene rings are $4.8-10.4°$ and $4.5-8.5°$ for **1** and **2**, respectively. With the middle thiophene ring as a reference, the inner (C2, C3, C5, ..., C23) helix climbs 4.20 Å (and 4.36 Å) and turns in-plane by 39.6° (and 40.1°) per thiophene (436° and 441° for the entire helix) for the two unique molecules of **1**. Analogous values for **2** are 1.94 Å and 39.8° (278°). Thus, the helical curvatures of the π-systems are similar in **1** and **2**.

Crystal packing of **1** is characterized by multitude of short intermolecular S- - -S contacts, e.g., for one of the two unique molecules (molecule A), 10 homochiral and 2 heterochiral short S- - -S contacts are found.

UV–vis electronic absorption spectra for homologous di-*n*-octyl oligothiophenes, with 3, 7, and 11 annelated thiophene rings, i.e., trithiophene **8** and helicenes **2** and **1**, are consistent with the approximately linear increase of the integrated absorbance in the 190–400 nm region vs the number of annelated thiophene rings (Figure 3).[13,14] However, the red-shift between two helical oligothiophenes (**1** vs **2**) is small; in fact, the absorption onsets at 355–356 nm are identical for helical undecathiophene **1** and heptathiophene **2**, but significantly red-shifted relative to the onset at ~317 nm for planar trithiophene **8**.

Cyclic voltammetry of **1** and **2** gives reversible waves at the first oxidation potentials, $E_1° = 1.205 \pm 0.01$ and 1.285 ± 0.01 V, respectively, corresponding to oxidation to the radical cations.

The identical electronic absorption onsets and near convergence of the first oxidation potentials for **1** and **2** are consistent with cross-conjugation in helical oligothiophenes **1** and **2**. On the basis of the absorption onsets at 355–356 nm, $E_g \approx 3.5$ eV is estimated for the $(C_2S)_n$ helix polymer.

In summary, asymmetric, atom-efficient, (−)-sparteine-mediated syntheses provided enantiomeric excess of either (+)- or (−)-[11]-helicene **1**. This synthetic method should be applicable to the higher homologues of **1**, as well as other thiophene-based [*n*]helicenes. The electron localization in the $(C_2S)_n$ helix has an onset at $n \leq 7$, with optical band gap $E_g \approx 3.5$ eV.

Supporting Information Available: Experimental section, including X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The ^{1}H NMR spectra are obtained with double solvent (ether) suppression, using samples from the preparative-scale reaction mixtures.

(7) For the limiting ratios of **5** to **1**, the isolated yield (and ee) for (−)-**1** are 67% (ee 3%) and 19% (ee 25%). Determinations of ee are described in the Supporting Information.

(8) (a) (−)-**1** (cyclohexane, corrected for ee 70.6%): $[\alpha]_D \approx -1350$; CD, λ_{max}/nm $(\Delta\epsilon_{max}$/L mol^{-1} cm$^{-1})$ 294 (−122), 266 (−24), 257 (−44), 242 (53), 227 (−101), 212 (73), 200 (−14) (Figure S11). (b) (−)-**5** (cyclohexane): ee's could not be determined, $[\alpha]_D = -320$ (−150); CD, one negative couplet (Figure S12). (c) (−)-Helicenes and their axially chiral derivatives possessing negative couplet are expected to possess opposite configurations: Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *Chem. Eur. J.* **2004**, *10*, 6531–6539.

(9) The only other example of tri-annelation is photochemical cobalt-catalyzed alkyne trimerization to [9]helicenes in 2–3.5% yields, ref 2e.

(10) (a) The product of α_1,α_2-mono-annelation is isolated as well. (b) Selective lithiation at the α_1- and α_2-positions may be due to less steric hindrance, compared to the inner α_3-positions.

(11) Selective α_1,α_2-tetradeuteration of **7** is observed upon lithiation with either near-stoichiometric (4.4 equiv) or excess (6.4 equiv) amount of *n*-BuLi in the presence of (−)-sparteine, followed by addition of MeOD.

(12) Analogous LDA/(−)-sparteine-mediated di-annelation of hexathiophene (obtained by cross-coupling of 4,4′-dibromo-dithieno[2,3-b:3′,2′-d]-thiophene and 2-octyl-5-bromothiophene) gives [7]helicene **2** in ~20% yields. Synthetic details pertaining to **2** and its gelator properties will be reported elsewhere.

(13) UV–vis (cyclohexane), λ_{max}/nm $(\epsilon_{max}$/L mol^{-1} cm$^{-1})$: (a) **1**, 265 (4.98 $\times$ 10^4), 243 (5.21 $\times$ 10^4), 213 (6.41 $\times$ 10^4); (b) **2**, 256 (4.95 $\times$ 10^4), 223 (3.40 $\times$ 10^4); (c) **8**, 255 (2.08 $\times$ 10^4), 240 (1.75 $\times$ 10^4), 221 (3.47 $\times$ 10^4).

(14) The conclusion about the linearity may only be tentative, as only three data points with R^2 of only 0.98 are used.

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