

# Helically Annulated and Cross-Conjugated Oligothiophenes: Asymmetric Synthesis, Resolution, and Characterization of a Carbon–Sulfur [7]Helicene

Andrzej Rajca,<sup>\*,†</sup> Makoto Miyasaka,<sup>†</sup> Maren Pink,<sup>‡</sup> Hua Wang,<sup>†</sup> and Suchada Rajca<sup>†</sup>

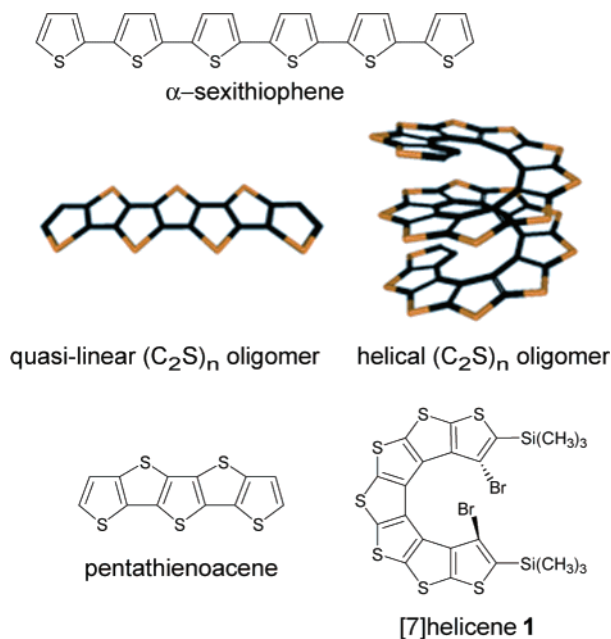
Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304, and IUMSC, Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received June 24, 2004; E-mail: arajca1@unl.edu

**Abstract:** The synthesis and characterization of a novel oligothiophene, in which the thiophene rings are annulated into a [7]helicene with cross-conjugated  $\pi$ -system, are described. Such [7]helicenes may be viewed as fragments of the unprecedented carbon–sulfur ( $C_2S$ )<sub>n</sub> helix, possessing sulfur-rich molecular periphery. Racemic synthesis of [7]helicene is based upon iterative alternation of two steps: C–C bond homocouplings between the  $\beta$ -positions of thiophenes and annelation between the  $\alpha$ -positions of thiophenes. Asymmetric synthesis is carried out using (–)-sparteine-mediated annelation of the axially chiral bis(arylithium) with electrophilic sulfur equivalent. Alternatively, enantiomers of the [7]helicene are obtained via resolution using menthol-based chiral siloxanes. Racemic [7]helicene and four other macrocyclic products of the annelation are characterized by X-ray crystallography. One of the solvent polymorphs of the [7]helicene possesses  $\pi$ -stacked columns of opposite enantiomers and multiple short intermolecular contacts, including both homochiral and heterochiral short S...S contacts, suggesting an effective intermolecular electronic coupling in two-dimensions. The [7]helicene is configurationally stable at room temperature and racemizes at 199 °C with a half-time of about 11 h. Selected physicochemical studies (UV–vis absorption, CD, optical rotation, and cyclic voltammetry) of the [7]helicene are described.

## Introduction

Oligothiophenes are among the most studied  $\pi$ -systems with favorable electrical and optical properties for a wide range of new technologies.<sup>1–8</sup> Current efforts have been focused on  $\alpha$ -oligothiophenes, such as  $\alpha$ -sexithiophene (Figure 1), in which thiophene rings are connected at  $\alpha$ -positions, forming a linearly extended, conjugated  $\pi$ -system.<sup>1–10</sup> However, analogous  $\beta$ -oligothiophenes have received little attention,<sup>11–13</sup> in part due to



**Figure 1.** Oligothiophenes:  $\alpha$ -sexithiophene and annelated carbon–sulfur ( $C_2S$ )<sub>n</sub> oligomers that are quasi-linear and helical.

the lack of efficient synthetic methodologies.<sup>14</sup> Furthermore,  $\beta$ -oligothiophenes are highly twisted at  $\beta$ – $\beta$ -linkages, except for the planar macrocyclic trimer,<sup>12</sup> leading to negligible electron

<sup>†</sup> University of Nebraska.

<sup>‡</sup> Indiana University.

- (1) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359–369.
- (2) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571–588.
- (3) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147–156.
- (4) Tour, J. M. *Acc. Chem. Res.* **2001**, *34*, 791–804.
- (5) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286–5287.
- (6) (a) Krömer, J.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debaerdemaeker, T.; Mena-Osteritz, E.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3481–3486. (b) Gesquiere, A.; Jonkheijm, P.; Schenning, A. P. H. J.; Mena-Osteritz, E.; Bäuerle, P.; de Feyter, S.; de Schryver, F. C.; Meijer, E. W. *J. Mater. Chem.* **2003**, *13*, 2164–2167. (c) Caras-Quintero, D.; Bäuerle, P. *Chem. Commun.* **2004**, 926–927.
- (7) Casado, J.; Pappenfus, T. M.; Miller, L. L.; Mann, K. R.; Orti, E.; Viruela, P. M.; Pou-Amerigo, R.; Hernandez, V.; Navarette, J. T. L. *J. Am. Chem. Soc.* **2003**, *125*, 2524–2534.
- (8) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425–2427.
- (9) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337–1341.
- (10) (a) Murphy, A. R.; Fréchet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597. (b) Liu, J.; Kadnikova, E. N.; Liu, Y.; McGehee, M. D.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9486–9487.
- (11)  $\beta$ -Oligothiophene as a linear tetramer: Ye, X.-S.; Wong, H. N. C. *J. Org. Chem.* **1997**, *62*, 1940–1954.

delocalization. Notably, thiophene-based annulations of linear  $\beta$ -oligothiophenes give helical carbon–sulfur ( $C_2S$ ) $_n$  oligomers for large  $n$ , possessing moderate curvature characteristic of helicenes (Figure 1).<sup>15–17</sup> Such esthetically pleasing structures are also associated with cross-conjugated  $\pi$ -systems for the carbon–carbon frameworks.<sup>18–21</sup> In contrast, analogous carbon–sulfur oligomers derived from  $\alpha$ -oligothiophenes are planar, quasi-linear, with conjugated  $\pi$ -systems (thienoacenes).<sup>22–26</sup>

In these sulfur-rich annelated oligomers, all sulfur atoms are positioned at the molecular periphery, facilitating multiple short intermolecular S $\cdots$ S contacts, which may increase the effective dimensionality of the electronic structure, leading to enhanced transport properties. The relevant examples are improved mobility in organic field effect transistors,<sup>27,28</sup> formation of neutral organic metals,<sup>29</sup> organic conductor-to-semiconductor phase transformations,<sup>30</sup> and increased critical temperatures in organic superconductors.<sup>31</sup> Furthermore, cross-conjugated  $\pi$ -systems have attracted recent attention because of their unusually robust optical properties; however, the studies of their electronic properties are in the early stages.<sup>18–21</sup>

An additional motivation to develop syntheses of such helically annelated  $\beta$ -oligothiophenes stems from the well-known strong chiral, especially chiroptical, properties of

extended  $[n]$ helicenes.<sup>17,32–34</sup> In this aspect, solution-based (rather than photochemical) synthetic methodologies for non-racemic  $[n]$ helicenes and applications of  $[n]$ helicenes as organic materials have become topics of current interest.<sup>35–44</sup>

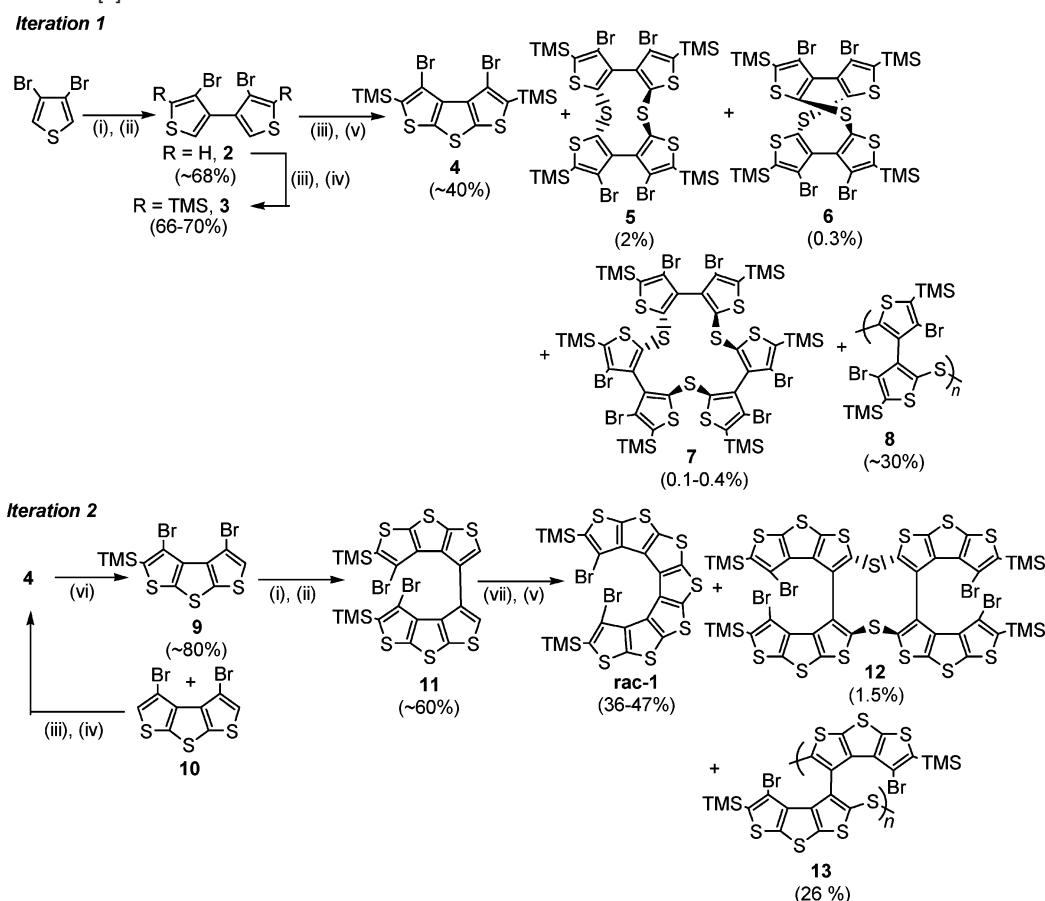
Following the preliminary communication of racemic synthesis of [7]helicene **1** (Figure 1),<sup>45</sup> we now report the improved racemic synthesis, asymmetric synthesis, and resolution of carbon–sulfur [7]helicenes.<sup>14,46–48</sup> Also, crystal structures, determinations of barrier for racemization, and chiroptical and cyclic voltammetric studies for **1** and related compounds are described.

## Results and Discussion

**Racemic Synthesis of [7]Helicene 1.** The synthesis of [7]helicene rac-**1** consists of two iterations (Scheme 1). Each iteration consists of two key steps, connection of thiophene derivatives at their  $\beta$ -positions and annelation to form a new thiophene ring.<sup>45</sup>

In the first iteration, 4,4'-dibromo-3,3'-bithienyl (**2**) is obtained from 3,4-dibromothiophene, using optimized conditions for the Li/Br exchange, followed by oxidation of the resultant 3-bromo-4-thienyllithium with  $CuCl_2$ .<sup>49</sup> Selective 5,5'-dilithiation ( $\alpha,\alpha'$ -

- (12)  $\beta$ -Oligothiophene as a cyclic trimer: Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326–4327.
- (13)  $\beta$ -Oligothiophene as a cyclic tetramer: (a) Kauffmann, T.; Greving, B.; König, J.; Mitschker, A.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 713–714. (b) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 1–19.
- (14) Miyasaka, M.; Rajca, A. *Synlett* **2004**, 177–182.
- (15) ( $C_2S$ ) $_n$  oligoacetylenic sulfides: Lee, A. W. M.; Yeung, A. B. W.; Yuen, M. S. M.; Zhang, H.; Zhao, X.; Wong, W. Y. *Chem. Commun.* **2000**, 75–76.
- (16) ( $CS_2$ ) $_n$  oligomers and polymers of carbon disulfide: (a) Zmolek, P. B.; Sohn, H.; Gantzel, P. K.; Troglor, W. C. *J. Am. Chem. Soc.* **2001**, *123*, 1199–1207. (b) Frapper, G.; Saillard, J.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 5367–5370. (c) Chou, J.-H.; Rauchfuss, T. B. *Z. Naturforsch., B: Chem. Sci.* **1997**, *52*, 1549–1552. (d) Genin, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 12328–12335. (e) Gompper, R.; Knieler, R.; Polborn, K. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1621–1624.
- (17) Annulations of various aromatic rings were considered in terms of number of rings per helical turn: Meurer, P. P.; Vögtle, F. *Helical Molecules in Organic Chemistry. Top. Curr. Chem.* **1985**, *127*, 1–76.
- (18) Nielsen, M. B.; Schreiber, M.; Baek, Y. G.; Seiler, P.; Lecomte, S.; Boudon, C.; Tykwinski, R. R.; Gisselbrecht, J.-P.; Gramlich, V.; Skinner, P. J.; Bosshard, C.; Günther, P.; Gross, M.; Diederich, F. *Chem.-Eur. J.* **2001**, *7*, 3263–3280.
- (19) (a) Zhao, Y.; Tykwinski, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 458–459. (b) Zhao, Y.; McDonald, R.; Tykwinski, R. R. *J. Org. Chem.* **2002**, *67*, 2805–2812.
- (20) Gaab, K. M.; Thompson, A. L.; Xu, J.; Martinez, T. J.; Bardeen, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9288–9289.
- (21) (a) Londergan, T. M.; You, Y.; Thompson, M. E.; Weber, W. P. *Macromolecules* **1998**, *31*, 2784–2788. (b) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681–8683.
- (22)  $\alpha,\alpha'$ -Bis(thieno[3,2-*b*:2',3'-*d'*]thiophene) as an active layer in organic field effect transistors: Li, X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206–2207.
- (23) Mazaki, Y.; Kobayashi, K. *Tetrahedron Lett.* **1989**, *30*, 3315–3318.
- (24) Sato, V.; Mazaki, Y.; Kobayashi, K.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 765–770.
- (25) Zhang, X.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813–9815.
- (26) Oyaizu, K.; Iwasaki, T.; Tsukahara, Y.; Tsuchida, E. *Macromolecules* **2004**, *37*, 1257–1270.
- (27) Bromley, S. T.; Mas-Torrent, M.; Hadley, P.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 6544–6545.
- (28) Xue, J.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 3714–3716.
- (29) Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. *Science* **2001**, *291*, 285–287.
- (30) Laukhina, E.; Tkacheva, V.; Chekhlov, A.; Yagubskii, E.; Wojciechowski, R.; Ulaniski, J.; Vidal-Gancedo, J.; Veciana, J.; Laukhin, V.; Rovira, C. *Chem. Mater.* **2004**, *16*, 2471–2479.
- (31) (a) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55–58. (b) Williams, J. M.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W.-K.; Whangbo, M.-H.; Schirber, J. E. *Science* **1991**, *252*, 1501–1508.
- (32) (a) Newman, M. S.; Lutz, W. B.; Lednicer, D. *J. Am. Chem. Soc.* **1955**, *77*, 3420–3421. (b) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770. (c) Newman, M. S.; Darlak, R. S.; Tsai, L. *J. Am. Chem. Soc.* **1967**, *89*, 6191–6193.
- (33) (a) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649–659. (b) [11], [12], and [14]helicenes: Martin, R. H.; Bayes, M. *Tetrahedron* **1975**, *31*, 2135–2137. (c) Martin, R. H.; Libert, V. *J. Chem. Res., Synop.* **1980**, 130–131.
- (34) (a) [7], [9], [11], [13], [15]helicenes with alternant thiophene and benzene rings: Yamada, K.; Ogashiwa, S.; Tanaka, H.; Nakagawa, H.; Kawazura, H. *Chem. Lett.* **1981**, 343–346. (b) Racemic [5], [7], [9], [11]helicenes with alternate thiophene and benzene rings: Caronna, T.; Catellani, M.; Luzatti, Malpezzi, L.; Meille, S. V.; Mele, A.; Richter, C.; Sinisi, R. *Chem. Mater.* **2001**, *13*, 3906–3914.
- (35) (a) Urbano, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3986–3989. (b) Schmuck, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2448–2452.
- (36) (a) Katz, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1921–1923. (b) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913–915. (c) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. *J. Am. Chem. Soc.* **1999**, *121*, 79–88. (d) Paruch, K.; Vyklíncký, L.; Katz, T. J.; Incarvito, C. D.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 8774–8782. (e) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. *J. Am. Chem. Soc.* **2001**, *123*, 11899–11907. (f) Vyklíncký, L.; Eichhorn, S. H.; Katz, T. J. *Chem. Mater.* **2003**, *15*, 3594–3601.
- (37) (a) Teplý, F.; Stará, I. G.; Starý, I.; Kollárovič, A.; Šaman, D.; Vyskočil, S.; Fiedler, P. *J. Org. Chem.* **2003**, *68*, 5193–5197. (b) Teplý, F.; Stará, I. G.; Starý, I.; Kollárovič, A.; Šaman, D.; Rulířföek, L.; Fiedler, P. *J. Am. Chem. Soc.* **2002**, *124*, 9175–9180.
- (38) Ogawa, Y.; Toyama, M.; Karikomi, M.; Seki, K.; Haga, K.; Uyehara, T. *Tetrahedron Lett.* **2003**, *44*, 2167–2170.
- (39) Carreño, M. C.; García-Cerrada, S.; Urbano, A. *J. Am. Chem. Soc.* **2001**, *123*, 7929–7930.
- (40) Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465–4470.
- (41) (a) Dubois, F.; Gingras, M. *Tetrahedron Lett.* **1998**, *39*, 5039–5040. (b) Gingras, M.; Dubois, F. *Tetrahedron Lett.* **1999**, *40*, 1309–1312.
- (42) (a) Field, J. E.; Muller, G.; Riehl, J. P.; Venkataraman, D. *J. Am. Chem. Soc.* **2003**, *125*, 11808–11809. (b) Field, J. E.; Hill, T. J.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 6071–6078.
- (43) (a) Larsen, J.; Bechgaard, K. *J. Org. Chem.* **1996**, *61*, 1151–1152. (b) Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 71–76; *Acta Chem. Scand.* **1996**, *50*, 77–82.
- (44) Racemic oligophenylenes with helical connectivity and low barriers for racemization: Han, S.; Bond, A. D.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3223–3227. (b) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3227–3230.
- (45) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481–4483.
- (46) Determination of the absolute configuration of (–)-**1** by vibrational circular dichroism spectroscopy: Friedman, T. B.; Cao, X.; Wang, H.; Rajca, A.; Nafie, L. A. *J. Phys. Chem. A* **2003**, *107*, 7692–7696.
- (47) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *Chem.-Eur. J.*, in press.
- (48) Dithieno[2,3-*b*:3',2'-*d'*]thiophene: de Jong, F.; Janssen, M. *J. J. Org. Chem.* **1971**, *36*, 1645–1648.

**Scheme 1.** Synthesis of [7]Helicene *rac*-1<sup>a</sup>

<sup>a</sup> Conditions: (i) *n*-BuLi (1.05 equiv), ether/hexane,  $-78^{\circ}\text{C}$  for 2 h, then  $-50^{\circ}\text{C}$  for 15–30 min; (ii)  $\text{CuCl}_2$  (1.3–10 equiv),  $-78^{\circ}\text{C}$  to room temperature for 2 d; (iii) LDA (2.3 equiv), ether/hexane,  $0^{\circ}\text{C}$  for 2 h; (iv) TMSCl; (v)  $(\text{PhSO}_2)_2\text{S}$  (1.0 equiv), ether,  $-78^{\circ}\text{C}$  for 3 h, then room temperature for 12+ h; (vi) TFA,  $\text{CHCl}_3$ ; (vii) LDA (2.3 equiv), ether/hexane or toluene/hexane,  $0^{\circ}\text{C}$  for 2 h.

dilithiation) of **2** with LDA, followed by a TMS-quench, provides **3**. Dilithiation of the two TMS-unprotected 2,2'- $\alpha$ -positions in **3** with LDA, followed by the reaction with bis-(phenylsulfonyl) sulfide, gives annelated product **4**.<sup>50</sup> The primary side product is polymer **8**. In addition, small amounts of macrocyclic side products are obtained, such as dimer **5**, chiral dimer **6**, and trimer **7**; the overall yield of the three macrocycles (when isolated as a mixture) is 4–9%.<sup>51</sup>

In the second iteration, one of the TMS groups in **4** is removed to give **9**. The Li/Br exchange on dithienothiophene **9** is followed by oxidation of the intermediate aryllithium, to provide bis(dithienothiophene) **11**. Selectivity for the single Li/Br exchange at the less hindered 4'-position of dithienothiophene **9** is further verified by the protonation and deuteration of the intermediate aryllithium, giving 4-bromo-5-trimethylsilyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**9-H**) and its 4'-D isotopomer (**9-D**), respectively (Supporting Information). In the final step, bis(dithienothiophene) **11** is annelated to give [7]helicene *rac*-1.

**1.** Two side products, dimer **12** and polymer **13**, are isolated (Scheme 1).

Optimization of the reaction conditions for the two key steps (connection and annelation) is carried out, as described in the following paragraphs.

In the connection steps, **2** and **11** are obtained via the C–C homocoupling reactions between the 3-thienyllithium derivatives. Slight modification of the conditions for the Li/Br exchange at  $-78^{\circ}\text{C}$ , that is, by allowing the reaction mixture to attain  $-50^{\circ}\text{C}$  for 15–30 min, prior to the addition of  $\text{CuCl}_2$  at  $-78^{\circ}\text{C}$ , improves the isolated yields of **2** and **11** from 40% to 68% and 30% to 60%, respectively.<sup>52–54</sup>

In the annelation steps, the efficient dilithiations of **3** and **11** are important for the yield of the target products **4** and **1**,

(49) When 4-bromo-3-thienyllithium was prepared at  $-70^{\circ}\text{C}$ , via addition of ethereal solution of 3,4-dibromothiophene to *n*-BuLi in ether, isolation of **2** in 52% yield was reported: (a) Gronovitz, S. *Acta Chem. Scand.* **1961**, *15*, 1393–1395. (b) Gronovitz, S.; Moses, P.; Hornfeldt, A.-B. *Ark. Kemi* **1961**, *17*, 237–247.

(50) The previously reported yield for **4** was 65% (ref 45, based upon three reactions), and yields as high as 73% were obtained; however, after more than 40 reactions carried out by several students, the isolated yields average about 40%.

(51) For chiral dimer **6**, HPLC with chiral column shows two partially resolved peaks of equal intensity (Figure 3s, Supporting Information).

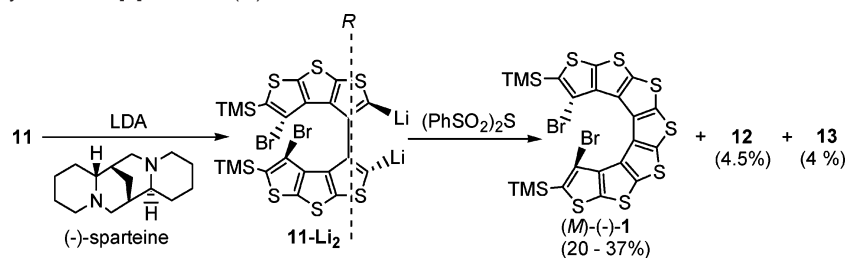
(52) Typical conditions for the formation of 4-bromo-3-thienyllithium or 3-thienyllithium employ BuLi and the corresponding bromothiophene in ether at  $-70^{\circ}\text{C}$ , to affect the Li/Br exchange at the  $\beta$ -position of the thiophene. It has been reported that allowing 3-thienyllithiums to reach room temperature for 5 min (or longer) leads either to the migration of lithium to the more acidic  $\alpha$ -position or to the opening of thiophene ring: (a) Gronovitz, S. *Thienyl-Lithium Derivatives and Their Ring-Opening Reactions*. In *Organic Sulfur Chemistry*; Stirling, C. J. M., Ed.; Butterworths: London, 1975; pp 203–228. (b) Gronovitz, S.; Frejd, T. *Acta Chem. Scand.* **1970**, *24*, 2656–2658.

(53) Bis(dithienothiophene)**11** is obtained in 40% yield from a relatively large-scale reaction.

(54) In CC-homocoupling reactions, using Cu(II) halides, good stirring, which is more difficult with large amounts of relatively heavy Cu(II) halide, was found to be essential for good yields: Rajca, A.; Wang, H.; Bolshov, P.; Rajca, S. *Tetrahedron* **2001**, *57*, 3725–3735.





**Scheme 2.** Asymmetric Synthesis of [7]Helicene (–)-1

In summary, the dilithiated intermediates, **3-Li<sub>2</sub>** and **11-Li<sub>2</sub>**, are formed nearly quantitatively and are moderately persistent.<sup>58</sup> These results indicate that the dilithiations are not limiting factors in the annelation steps. Also, the efficient formation of the dilithiated intermediates is reflected in moderate molecular weights for polymers **8** ( $M_w \approx 4.4$ –13 kDa) and **13** ( $M_w \approx 8$  kDa), for which predominant connectivity is likely derived from **3-Li<sub>2</sub>** and **11-Li<sub>2</sub>**, respectively.

**Asymmetric Synthesis of [7]Helicene (–)-1.** (–)-Sparteine has been shown to be an effective additive for induction of enantiomeric excess (ee) in reactions involving organometallics, and especially organolithiums.<sup>59,60</sup> Because the final annelation leading to [7]helicene **1** involves axially chiral  $\alpha,\alpha'$ -dilithiated **11-Li<sub>2</sub>**, its complexation with (–)-sparteine, followed by the reaction with bis(phenylsulfonyl)sulfide, may provide non-racemic **1**.

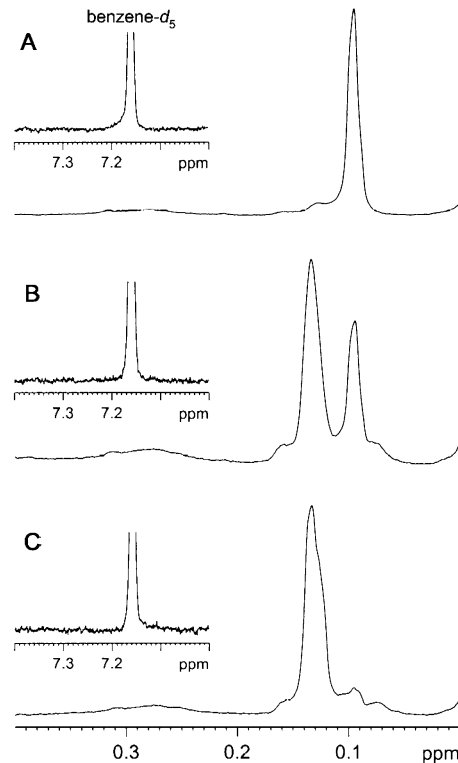
Treatment of bis(dithienothiophene) **11** with LDA (~2.0 or ~2.3 equiv) and (–)-sparteine (3.5 equiv) in ether/hexane at 0 °C is followed by the addition of bis(phenylsulfonyl)sulfide at –78 °C; [7]helicene (–)-**1** is isolated in 20–37% yields and ee's of 19–47% (Scheme 2).<sup>61</sup>

Nonracemic (–)-**1** with high ee's and enantiopure (–)-**1** are obtained by fractional recrystallizations. The absolute configuration of such nonracemic (–)-**1** was determined as (*M*) (left-handed helix) by vibrational circular dichroism study.<sup>46</sup> This implies that  $\alpha,\alpha'$ -dilithiated **11-Li<sub>2</sub>** with axially chiral (*R*) configuration is primarily converted to (*M*)-(–)-**1** (Scheme 2). Such (–)-sparteine-mediated stereinduction involving axial (*R*)-configuration has another precedence in the Cu(II) oxidation of 2,2'-dilithiobiaryls to derivatives of *o*-tetraphenylene.<sup>54</sup> Notably, the higher yields of **1** are associated with the lower ee's and vice versa.

The effect of addition of (–)-sparteine on  $\alpha$ -monolithiated **11-Li<sub>1</sub>** and  $\alpha,\alpha'$ -dilithiated **11-Li<sub>2</sub>**, and the reaction of **11** with LDA, is monitored using <sup>1</sup>H NMR spectroscopy, as illustrated by two experiments (Figures 2 and 3).

In the first experiment, the mixture containing  $\alpha$ -monolithiated **11-Li<sub>1</sub>**,  $\alpha,\alpha'$ -dilithiated **11-Li<sub>2</sub>**, unreacted **11**, and unreacted LDA in Et<sub>2</sub>O/hexane/benzene-*d*<sub>6</sub>, which is obtained via the reaction of **11** with ~1 equiv of LDA (the sample shown in Figure 2A), is further treated with (–)-sparteine (1.5, ~10, and ~80 equiv per LDA). The initial addition of (–)-sparteine (1.5 equiv) leads to the relatively fast increase in concentration of **11-Li<sub>1</sub>** with the corresponding decrease of <sup>1</sup>H integration for **11** and **11-Li<sub>2</sub>** (Figure 2B). Moreover, resonances for **11-Li<sub>1</sub>** in the aromatic region appear as two singlets at  $\delta \approx 7.142$  and 7.105 ppm with the relative integrations of 1:0.8 (Figure 2B); both singlets are downfield-shifted, as compared to the singlet at  $\delta \approx 7.079$  ppm for **11-Li<sub>1</sub>** in the absence of (–)-sparteine in Figure 2A.

The subsequent additions of (–)-sparteine (to a total of ~10 and ~80 equiv) result in slight downfield shifts relative to the benzene-*d*<sub>5</sub> multiplet for all resonances, especially in the aromatic region. However, the relative integration of 1:0.8 for the two singlets for **11-Li<sub>1</sub>** is unchanged (Figure 2C and D). In the TMS-region, the <sup>1</sup>H resonances for **11-Li<sub>1</sub>** are interpreted



**Figure 3.** <sup>1</sup>H NMR (500 MHz, Et<sub>2</sub>O/hexane with 3% of benzene-*d*<sub>6</sub>) spectra for products of lithiation of **11** with LDA (~2.3 equiv). Plots A, B, and C show spectra for consecutive additions of (–)-sparteine, that is, samples with 0, 3.5, and ~10 equiv, respectively, as described in the Experimental Section. The broad resonance at  $\delta \approx 0.27$  ppm is assigned to excess of LDA.

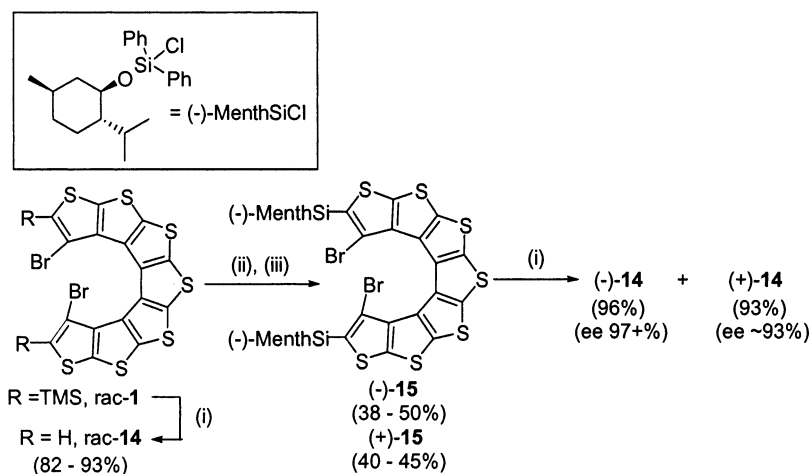
(57) Also, about 10 min at room temperature is required prior to acquisition of the NMR spectrum.

(58) (a) For both **3-Li<sub>2</sub>** and **11-Li<sub>2</sub>** in Et<sub>2</sub>O/hexane/benzene-*d*<sub>6</sub>, no new resonances are found in <sup>1</sup>H NMR spectra over 4 h at ambient temperature. Dilithiated intermediate **11-Li<sub>2</sub>** is studied over a longer period; after 16+ h at room temperature, new <sup>1</sup>H resonances are detectable. Upon quenching with water and usual workup, <sup>1</sup>H NMR spectra and FAB MS indicate **11** and unknown side products, although not simple products of migration of TMS. Migration of TMS is a common reaction for  $\alpha$ -lithiated thiophenes: for example, ref 14. (b) Studies of polymers **8** and **13** and their derivatives will be reported elsewhere.

(59) (a) Beak, P.; Basu, A.; Gallagher, D. J.; Park, Y. S.; Thayumanavan, S. *Acc. Chem. Res.* **1996**, 29, 552–560. (b) Weisenburger, G. A.; Faibish, N. C.; Pippel, D. J.; Beak, P. *J. Am. Chem. Soc.* **1999**, 121, 9522–9530.

(60) (a) Hoppe, D.; Hense, T. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2283–2316. (b) Seppi, M.; Kalkofen, R.; Reupohl, J.; Fröhlich, R.; Hoppe, D. *Angew. Chem., Int. Ed.* **2004**, 43, 1423–1427.

(61) (a) The replacement of (–)-sparteine with [*R*-(*R*\*,*R*\*)]-(+)-bis( $\alpha$ -methylbenzyl)amine gives **1** with negligible ee (0–5% range by NMR). (b) The replacement of ether with hexane, toluene, or tetrahydrofuran for the reactions using (–)-sparteine leads to negligible ee < 5% for **1**.

Scheme 3. Resolution of [7]Helicene **14**<sup>a</sup>

<sup>a</sup> Conditions: (i) TFA,  $\text{CHCl}_3$ , room temperature overnight; (ii) LDA (2.3 equiv), ether/hexane/benzene- $d_6$ , 0 °C for 2 h, then briefly room temperature; (iii) (–)-MenthSiCl (2.5 equiv) in ether at –25 °C, then 0 °C for 0.5 h, and then room temperature overnight.

as two sets of peaks with unequal integrations: a downfield broad singlet (with a shoulder) and two upfield singlets (Figure 2B, C, and D). These results are compatible with the diastereomeric ratio of about 1:0.8 for the observed complexes of **11-Li<sub>1</sub>** with (–)-sparteine.<sup>62</sup>

Notably, the resonances for **11** in the aromatic region appear as two unequal singlets at  $\delta \approx 7.343$  and 7.341 ppm for the sample with ~80 equiv of (–)-sparteine in Figure 2D. Although accurate integration of such closely spaced singlets is problematic, their relative peak heights are clearly different, analogous to those for **11-Li<sub>1</sub>**. The reference sample of **11** with ~80 equiv of (–)-sparteine in the identical solvent mixture shows two singlets at the similar chemical shifts, but their peak heights are equal (right inset in Figure 2D). These results indicate that **11** is configurationally stable on the laboratory time scale (at least 1 h at 300 K); furthermore, the observed diastereomeric ratio for **11-Li<sub>1</sub>** may arise from the partial kinetic resolution, primarily caused by the accelerated reaction of **11** with LDA upon the initial addition of (–)-sparteine.

In another experiment, the solutions of **11-Li<sub>2</sub>** in  $\text{Et}_2\text{O}$ /hexane/benzene- $d_6$ , which are obtained via the reaction of **11** with 2.3 equiv of LDA (the sample shown in Figure 3A), are further treated with (–)-sparteine (3.5 and ~10 equiv). Although the greater degree of lithiation of **11** by the excess amount of LDA leads to significant line broadening, the corresponding  $^1\text{H}$  NMR spectra in Figure 3B and C clearly show formation of a new, upfield-shifted resonance at  $\delta \approx 0.13$  ppm (broad singlet with shoulders), with the concomitant decrease of the  $\delta \approx 0.094$  ppm resonance. This is consistent with the formation of the new species, which is probably a diastereomeric complex of axially chiral **11-Li<sub>2</sub>** with (–)-sparteine.<sup>62,63</sup>

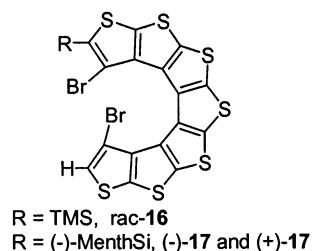
The  $^1\text{H}$  NMR spectroscopic monitoring included the reaction mixtures for which dilithiations of **11** are carried out with LDA in the presence of (–)-sparteine (3.5 equiv). For several reaction mixtures, such as those shown in Figure 3C, the  $^1\text{H}$  NMR monitoring is followed by the addition of bis(phenylsulfonyl)sulfide (Experimental Section).  $^1\text{H}$  NMR analyses of the corresponding crude mixtures suggest that the addition of bis(phenylsulfonyl)sulfide at low temperature (–78 °C) and incomplete dilithiation of **11** (presence of **11-Li<sub>1</sub>**) are associated with higher ee's. Indeed, if axially chiral **11**, **11-Li<sub>1</sub>**, and **11-**

**Li<sub>2</sub>** are configurationally stable, complete conversion of **11** to **11-Li<sub>2</sub>** would annul any kinetic resolution during the reaction of **11** with LDA in the presence of (–)-sparteine. However, further studies would be needed to quantify contributions to ee from the kinetic resolution versus the reaction of the diastereomeric complexes of **11-Li<sub>2</sub>**/(–)-sparteine with bis(phenylsulfonyl)sulfide.

The configurational stability of bis(dithienothiophene) **11** may be discussed in terms of its hindered biaryl structure. Because dithienothiophene **4** is approximately planar, with the nearly parallel C–Br bond axes,<sup>45</sup> bis(dithienothiophene) **11** may be viewed as an analogue of 1,1'-binaphthyl; the Br-substitution in **11**, occupying the “backside” positions, would correspond to the 8,8'-disubstitution in 1,1'-binaphthyl. Notably, the configurational stabilities of 1,1'-binaphthyl-8,8'-dicarboxylic acid and its derivatives are overall only marginally better than that of 1,1'-binaphthyl.<sup>64</sup> Therefore, the thoroughly studied half-time for racemization of 1,1'-binaphthyl, which is about 10 h at 25 °C, may provide a rough estimate for the time scale for racemization of **11**.<sup>64,65</sup> Analogously to 2,2'-dilithio-1,1'-binaphthyl,  $\alpha,\alpha'$ -dilithiated **11-Li<sub>2</sub>** should be configurationally stable as well.<sup>66,67</sup>

**Resolution of [7]Helicene 14.** Because the (–)-sparteine-mediated synthesis gives only a relatively low ee of (–)-**1**,<sup>68</sup> a resolution-based approach to nonracemic carbon–sulfur [7]-helicene is developed. Our approach adopts menthol-derivatized chlorosiloxane, (–)-MenthSiCl (Scheme 3), which has been recently reported as a chiral silylation reagent for the determi-

- (62) For complexes of (–)-sparteine with organolithiums, characterized by X-ray crystallography, see: (a) Papasergio, R. I.; Skelton, B. W.; Twiss, P.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1990**, 1161–1172. (b) Hoppe, I.; Marsch, M.; Harms, K.; Boche, G.; Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2158–2160.
- (63) The presence of (–)-sparteine (3.5 or 10 equiv) has no detectable effect on the persistence of **11-Li<sub>2</sub>**.
- (64) Cooke, A. S.; Harris, M. M. *J. Chem. Soc. B* **1963**, 2365–2373.
- (65) Colter, A. K.; Clemens, L. M. *J. Phys. Chem.* **1964**, *68*, 651–654.
- (66) 2,2'-Dilithio-1,1'-binaphthyl: Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717–4723.
- (67) Cu(II)-mediated oxidation of 2,2'-dilithio-1,1'-binaphthyl at –78 °C to room temperature gives the corresponding dimer without detectable racemization: Rajca, A.; Safronov, A.; Rajca, S.; Wongsiratanakul, J. *J. Am. Chem. Soc.* **2000**, *122*, 3351–3357.
- (68) The enantiomer of (–)-sparteine is not readily available: ref 60a; Smith, B. T.; Wendt, J. A.; Aubé, J. *Org. Lett.* **2002**, *4*, 2577–2579.

Chart 1.<sup>a</sup>

<sup>a</sup> (-)-MenthSi is defined in Scheme 3.

nation of the absolute configuration of alcohols by NMR spectroscopy.<sup>69</sup>

Starting with rac-1, both TMS groups are removed using TFA in chloroform, to give rac-14; the isolated yields are not nearly quantitative due to the poor solubility of rac-14.<sup>70</sup> LDA-mediated dilithiation of rac-14 at both  $\alpha$ -positions is monitored by <sup>1</sup>H NMR spectroscopy (with double solvent suppression), until no <sup>1</sup>H resonance can be detected in the aromatic region. The resulting suspension of dilithiated rac-14 is quenched with chiral chlorosiloxane (-)-MenthSiCl. The diastereomeric mixture of disiloxanes (-)-15 ( $R_f$  = 0.31) and (+)-15 ( $R_f$  = 0.27) is separated by column or preparative thin-layer chromatography on silica. The removal of the siloxanes using TFA in chloroform gives [7]helicenes (-)-14 and (+)-14 (Scheme 3).

The presence of two chiral auxiliaries, such as in (-)-15 and (+)-15, is essential for good chromatographic separation of diastereomers. The corresponding side products (-)-17 and (+)-17 (Chart 1), in which only one  $\alpha$ -position is functionalized with the chiral auxiliary, have coinciding  $R_f$ -values by TLC. Probably, this precludes the effective resolution based upon the somewhat more soluble [7]helicene rac-16 (Chart 1), which may be readily obtained from rac-1 via selective removal of a single TMS group.

**Crystal Structures.** Structures for [7]helicene rac-1 and selected macrocyclic products of the annelation steps are determined using X-ray crystallography (Table 1, Figure 4, and Figure 5).

For the [7]helicenes, only the racemic crystals, including two solvent polymorphs for rac-1, are studied; although nonracemic [7]helicenes 1 and 14 are crystalline, attempts to obtain data of adequate quality, including an attempt to measure microcrystals with synchrotron radiation for 1, were not successful.

In both solvent polymorphs of rac-1, [7]helicene possesses an approximate  $C_2$  point group. Also, its overall helix structure is nearly identical in both solvent polymorphs; the helix of the chloroform-containing polymorph is similar to that of phenylene-based [6]helicene, as discussed in detail in the preliminary communication.<sup>45,71</sup> However, the local structures for both solvent polymorphs of [7]helicene, as characterized by selected intramolecular distances and angles, are somewhat different; for example, the intramolecular Br $\cdots$ Br distances are 3.90 and 3.72 Å for the chloroform-containing and solvent-free polymorphs, respectively.

The structures of the macrocyclic dimers 5 and 12, and trimer 7 include one solvent molecule per formula unit (chloroform for 5 and 7, and benzene for 12). Chiral dimer 6 crystallizes without inclusion of solvent; however, the crystal is pseudomerohedrally twinned with a twin domain ratio of 70:30 (Supporting Information).

The dimers and the trimer possess two and three biaryl moieties, respectively. These sterically hindered biaryls correspond to bithienyl and bis(dithienothiophene) moieties in 5–7 and 12, respectively; each of such biaryls has a chiral axis. In each of the approximately  $C_{2h}$ -symmetric dimers 5 and 12, the biaryl moieties have opposite configurations (axial  $R$  vs axial  $S$ ); for both dimers, the biaryls adopt cisoid conformations, with the corresponding torsional angles of less than 90° (Table 2s, Supporting Information). The dithienothiophene moieties in dimer 12 are slightly more curved as compared to the dithienothiophene 4; for example, the torsion angles along the inner C–C–C–C backbone of the dithienothiophene moiety (such as the C2–C3–C5–C7 torsion angle in dimer 12) are in the 11.7–13.6° range in dimer 12, as compared to 7.1° in 4. The structure of chiral dimer 6 shows that the molecule has the approximate  $D_2$  point group; one of the three approximate  $C_2$ -axes relates the homochiral bithienyl moieties with transoid conformations (Figure 4 and Table 2s in the Supporting Information). In trimer 7, two of the bithienyl moieties possess the same relative configuration; these two homochiral moieties adopt cisoid conformations, while the third moiety has a transoid conformation. Thus, the molecule has chiral conformation, somewhat distorted from the  $C_2$  point group. The other possible diastereomers of 7 and 12, in which all biaryl moieties are axially homochiral (analogous to 6), have not been isolated.

For all four macrocycles, conformational mobility in solution is expected to be highly restricted, especially due to the highly substituted biaryl moieties. This is consistent with the lack of broadened resonances in the <sup>1</sup>H and <sup>13</sup>C NMR spectra for 5–7 and 12; furthermore, the molecular symmetry in solution on the NMR time scale corresponds to the approximate molecular symmetry found by crystallography. Thus, the NMR spectra at room temperature show only one type of thiophene moiety for the  $C_{2h}$ -symmetric and  $D_2$ -symmetric dimers, and three non-equivalent thiophene moieties for the  $C_2$ -symmetric trimer.

**Crystal Packing.** Because [7]helicene 1 and the macrocyclic side products may be viewed as molecules with sulfur-rich peripheries (e.g., Figure 1), a plethora of short intermolecular S $\cdots$ S (and of S to other atoms) contacts are expected, especially in polymorphs of [7]helicene 1. Both the feasibility of  $\pi$ -stacking and the stereochemistry in 1 are of interest in context of the curvature of the helical  $\pi$ -system.<sup>72,73</sup> (Individual planes of thiophenes in 1, which are nearly planar,<sup>45,74</sup> will be used as reference planes.) Both short intermolecular contacts (especially, S $\cdots$ S) and  $\pi$ -stacking are known to facilitate high carrier mobilities in organic semiconductors.<sup>27,28,75,76</sup>

(69) Chiral silylation reagents for the determination of absolute configuration by NMR spectroscopy: Weibel, D. B.; Walker, T. R.; Schroeder, F. C.; Meinwald, J. *Org. Lett.* **2000**, 2, 2381–2383.

(70) Nonracemic 14 is much more soluble in typical organic solvents as compared to rac-14.

(71) Fits of the (C<sub>2</sub>S)<sub>7</sub>C<sub>2</sub> thiophene-only and the (C<sub>2</sub>S)<sub>7</sub>C<sub>2</sub>Br<sub>2</sub>Si<sub>2</sub> frameworks have weighed rms deviations of 0.145 and 0.192 Å for the atoms, respectively.

(72) For substituent effects on chiroptical properties and analyses of solid-state structures of [6]helicenes, see: Wachsmann, C.; Weber, E.; Czugler, M.; Seichter, W. *Eur. J. Org. Chem.* **2003**, 2863–2876.

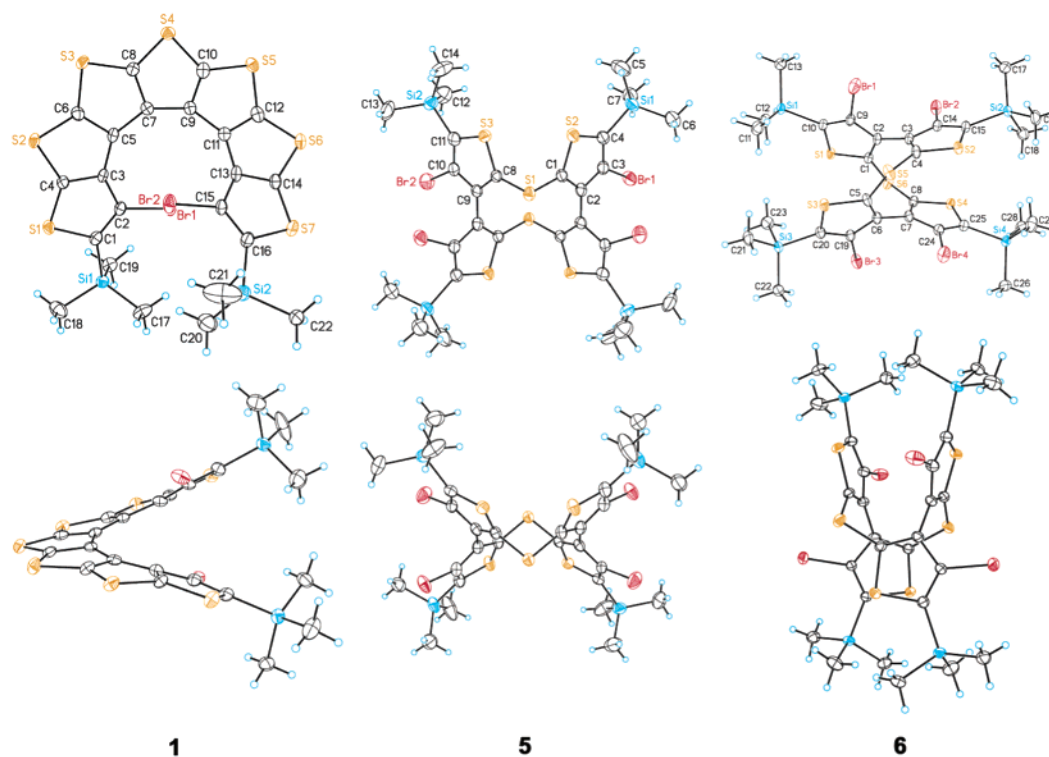
(73) Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, 126, 4318–4328.

(74) For individual thiophene rings in rac-1 (CHCl<sub>3</sub>), mean deviations of the least-squares planes between 0.01 and 0.04 Å are calculated (ref 45). Selected mean deviations in solvent-free polymorph rac-1 are as follows: 0.02–0.03 Å (thiophenes containing S2, S3, and S6) and 0.08 Å (thiophene containing S5).

(75) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, 124, 4184–4185.

**Table 1.** Summary of the X-ray Crystallographic Data

property	rac-1 (CHCl <sub>3</sub> ) <sup>a</sup>	rac-1	5	6	7	12
molecular formula	C <sub>23</sub> H <sub>19</sub> Br <sub>2</sub> Cl <sub>3</sub> S <sub>7</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>18</sub> Br <sub>2</sub> S <sub>7</sub> Si <sub>2</sub>	C <sub>29</sub> H <sub>37</sub> Br <sub>4</sub> Cl <sub>3</sub> S <sub>6</sub> Si <sub>4</sub>	C <sub>28</sub> H <sub>36</sub> Br <sub>4</sub> S <sub>6</sub> Si <sub>4</sub>	C <sub>43</sub> H <sub>55</sub> Br <sub>6</sub> Cl <sub>3</sub> S <sub>9</sub> Si <sub>6</sub>	C <sub>50</sub> H <sub>42</sub> Br <sub>4</sub> S <sub>14</sub> Si <sub>4</sub>
formula weight	842.15	722.78	1116.30	996.93	1614.76	1523.68
temperature, K	173(2)	130(2)	173(2)	112(2)	109(2)	120(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal/color	colorless	colorless	colorless	colorless	colorless	colorless
crystal system	trigonal	orthorhombic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	<i>R</i> -3	<i>Pbca</i>	<i>Pbcn</i>	<i>Pbca</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1
<i>a</i> , Å	36.319(2)	12.471(3)	19.699(2)	18.6063(6)	9.7758(2)	8.1993(3)
<i>b</i> , Å	36.319(2)	13.846(3)	13.0798(15)	23.7325(8)	26.2874(6)	10.5684(4)
<i>c</i> , Å	12.8012(8)	31.152(7)	17.734(2)	18.6074(6)	26.0709(6)	18.3955(7)
$\alpha$ , deg	90	90	90	90	90	91.3400(10)
$\beta$ , deg	90	90	90	90	100.202(1)	92.7710(10)
$\gamma$ , deg	120	90	90	90	90	110.6170(10)
volume, Å <sup>3</sup>	14 623.8(16)	5379(2)	4569.3(9)	8216.5(5)	6593.8(3)	1488.81(10)
<i>Z</i>	18	8	4	8	4	1
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.721	1.785	1.623	1.612	1.627	1.699
reflns collected	50 542	61 201	26 840	203 965	71 707	23 666
unique reflns	7463	6240	4052	13 053	19 254	8712
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0370	0.0678	0.0488	0.0303	0.0326	0.0295
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0857	0.1379	0.1113	0.0676	0.0663	0.0698
GOF	0.965	1.310	1.020	1.031	1.010	1.029

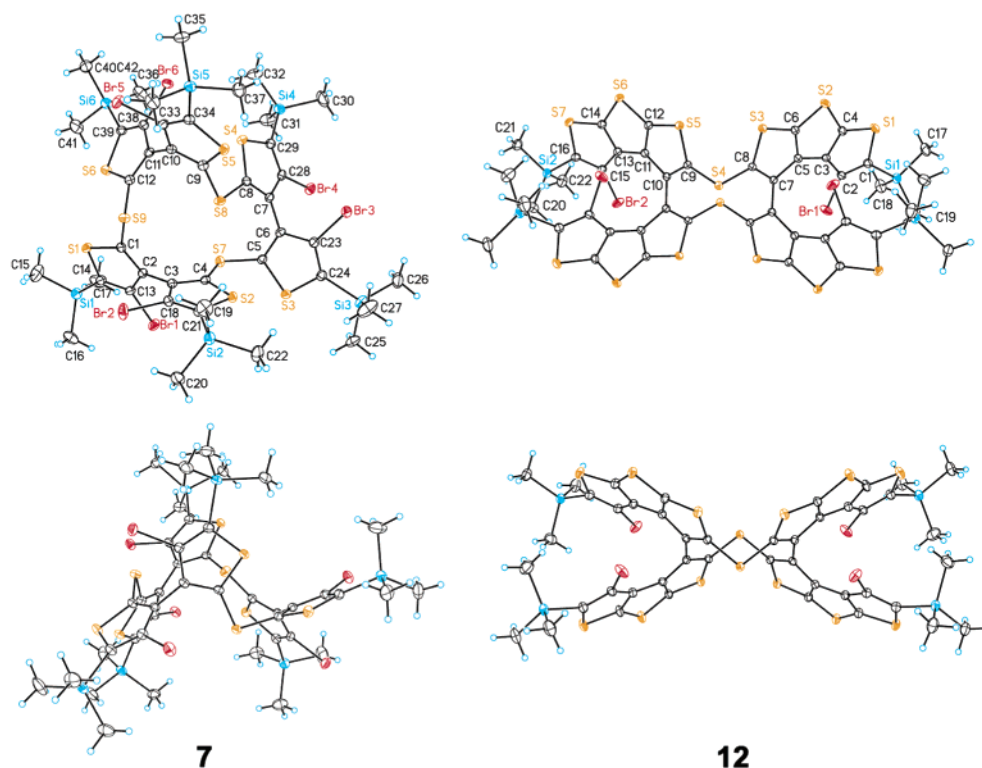
<sup>a</sup> Polymorph rac-1 (CHCl<sub>3</sub>), ref 45.**Figure 4.** Structures of **1** and macrocyclic dimers **5** and **6**. The top and side views of the ORTEP plots at 50% probability levels are shown for each molecule. The molecule of chloroform, included in the crystal of **5**, is omitted for clarity.

The chloroform-containing polymorph, that is, rac-**1** (CHCl<sub>3</sub>), crystallizes in the *R*-3 space group with 18 molecules per unit cell. The crystal packing may be described in terms of the *C*<sub>3</sub>-symmetric “propellers”, consisting of three homochiral [7]-helicenes (Figure 6). The propellers form columns along the crystallographic *c*-axis; the nearest-neighbor propellers, which contain [7]helicenes of opposite handedness, are staggered via an improper rotation (*S*<sub>6</sub>-axis). The [7]helicenes within the

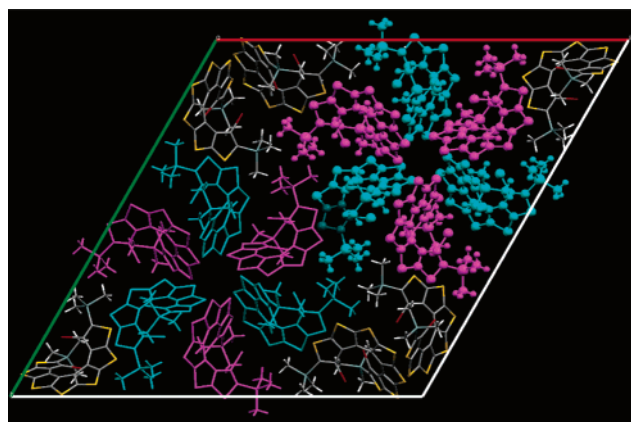
column of propellers are canted with respect to each other; that is,  $\pi$ -stacking is absent. However, close proximity between the sulfur-rich edges and the  $\pi$ -systems of [7]helicenes causes a plethora of short intermolecular contacts involving sulfur atoms, both homochiral (e.g., S3...S3 = 3.520 Å) and heterochiral (e.g., S3...S3 = 3.330 Å, S3...S4 = 3.492 Å, S1...S2 = 3.564 Å, S1...C2 = 3.451 Å, S1...C3 = 3.486 Å, S4...C6 = 3.472 Å). For each pair of the nearest-neighbor heterochiral [7]helicenes, belonging to different columns, the terminal thiophene rings are  $\pi$ -stacked. However, the degree of  $\pi$ -overlap is rather small, involving only sulfur atoms with short contact, S7...S7 = 3.726

(76) High-performance field-effect transistors based upon single crystals of rubrene: Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, *303*, 1644–1646.





**Figure 5.** Structures of macrocyclic trimer **7** and dimer **12**. The top and side views of the ORTEP plots at 50% probability levels are shown for each molecule. The molecules of chloroform and benzene, included in the crystals of **7** and **12**, respectively, are omitted for clarity.

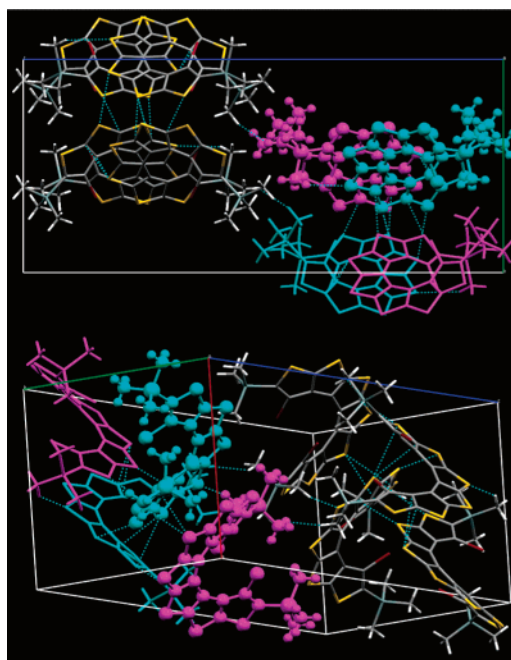


**Figure 6.** Unit cell showing molecular packing of rac-**1** ( $\text{CHCl}_3$ ) as viewed down the crystallographic  $c$ -axis (top plot). The disordered molecules of chloroform are omitted for clarity. Handedness of the highlighted [7]-helicenes is color-coded; the [7]helicenes belonging to two distinct columns of propellers are shown in wire frame and ball-and-stick.

Å. (Also, two  $\text{S} \cdots \text{Br}$  short contacts of about 3.73 Å are present.) Disordered molecules of chloroform fill the voids between the columns.

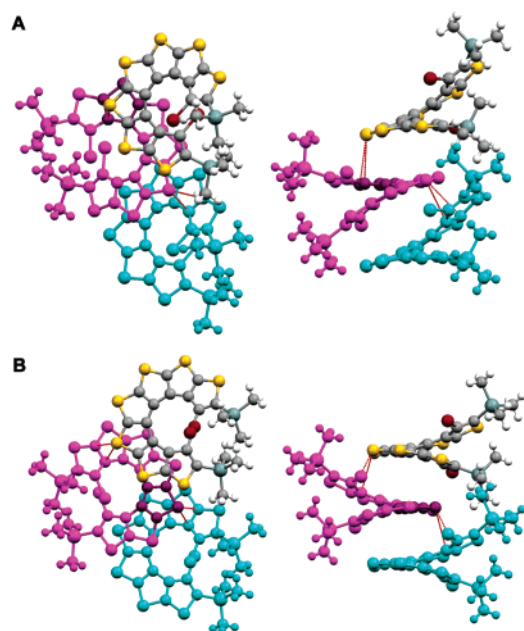
The solvent-free polymorph, rac-**1**, crystallizes in the space group  $Pbca$  with 8 molecules per unit cell. The molecules pack in “ $\pi$ -stacked” columns extending along the crystallographic  $a$ -axis (Figure 7).

Along the crystallographic  $c$ -axis, the TMS-groups from the neighboring columns are interlocked, forming a lamellar-like structure. Along the crystallographic  $b$ -axis, multiple short contacts are found between the columns, both between the same enantiomers (e.g.,  $\text{S}2 \cdots \text{S}5 = 3.551$  Å,  $\text{S}3 \cdots \text{S}6 = 3.562$  Å,



**Figure 7.** Unit cells showing molecular packing of solvent-free rac-**1** as viewed down the crystallographic  $a$ -axis (top cell) and as viewed from a selected direction (bottom cell). The enantiomers in two  $\pi$ -stacks (out of four for each cell) are color-coded in blue and magenta. Each of the two  $\pi$ -stacks is shown either in stick or in stick-and-ball. Intercepted blue lines correspond to short intermolecular contacts.

$\text{S}3 \cdots \text{C}12 = 3.459$  Å) and opposite enantiomers ( $\text{S}6 \cdots \text{C}8 = 3.436$  Å and  $\text{S}7 \cdots \text{C}6 = 3.436$  Å). These contacts arise from the approximately perpendicular (herringbone-like) relative orientations of the molecules in the adjacent columns; that is,



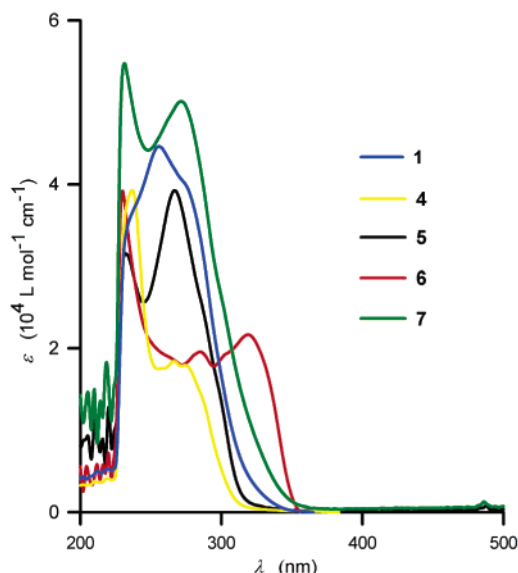
**Figure 8.** Selected  $\pi$ -stacks of solvent-free rac-1 spanning 1.5 unit cells along the  $a$ -axis as viewed normal and parallel to the mean planes of the highlighted thiophene rings (shown in dark magenta color): plots A (S2–C3–C4–C5–C6) and plots B (S5–C9–C10–C11–C12). Short contacts, S5...C3 = 3.442 Å and S5...C4 = 3.413 Å, are indicated with red intercepted lines.

the sulfur-containing edges of [7]helicenes interact with the  $\pi$ -systems of the neighboring [7]helicenes.

In each column, the nearest “ $\pi$ -stacked” neighbors have the opposite handedness. Even in this herringbone-like structure, some  $\pi$ -overlap is retained within the column, as illustrated by the selected views of the three “ $\pi$ -stacked” neighbors (Figure 8). Because of the helical distortions of the  $\pi$ -system of **1**, the point-to-plane distances between selected atoms and the mean planes of the nearly planar thiophene rings are primarily employed to estimate the degree of  $\pi$ -stacking between the neighboring molecules in the column.<sup>74</sup>

The most significant  $\pi$ -overlap is associated with the intra-stack short contacts, such as S5...C3 = 3.442 Å and S5...C4 = 3.413 Å (Figure 8). In the projection on the mean plane of the S2–C3–C4–C5–C6 thiophene (S2-thiophene), S5 is projected inside of the S2-thiophene ring with the atom-to-plane distance of 3.342 Å (Figure 8A). Two other atoms, C10 and C12, which are projected very near the S2-thiophene ring, have atom-to-plane distances of 3.744 and 3.724 Å, respectively (Figure 8A). In the projection on the mean plane of the S5–C9–C10–C11–C12 thiophene (S5-thiophene), C3 and C4 are projected somewhat outside of the S5-thiophene ring but with very short atom-to-plane distances of 3.110 and 3.190 Å, respectively (Figure 8B). The only atom (C6) projecting inside the S5-thiophene ring has an atom-to-plane distance of 3.759 Å (Figure 8B). Because the interplanar angle between the S2- and S5-thiophene rings of the stacked molecules is  $<90^\circ$ , the corresponding  $\pi$ -orbitals are pointing toward each other. In conjunction with the relatively short atom-to-plane distances, this leads to a pronounced  $\pi$ -overlap between the parts of the S2- and S5-thiophenes for each pair of neighboring molecules within the column.

Additional  $\pi$ -overlap within the column may be estimated using projections on the mean planes of the other thiophene



**Figure 9.** Electronic absorption UV–vis spectra for [7]helicene rac-1, dithienothiophene **4**, and macrocycles **5–7** in dichloromethane at room temperature.

rings. The shortest atom-to-plane distances for the atoms projecting inside the S3-, S4-, and S6-thiophene rings are as follows: S3-thiophene (3.794 Å for C12), S4-thiophene (3.872 Å for C14), and S6-thiophene (3.752 Å for C5). Although these distances are relatively long, three atoms projecting near the S4-thiophene ring have rather short atom-to-plane distances: C15 (3.431 Å) and C16 (3.315 Å), and S2 (3.249 Å).

The  $\pi$ -stacking within the columns and multiple short contacts between the columns (especially S...S) may result in an effective electronic coupling in two dimensions in solvent-free polymorph rac-1.

Molecular packing of the sulfur-rich macrocycles **5**, **6**, **7**, and **12** does not lead to any short S...S contacts. Only dimers **6** and **12** possess intermolecular short contacts involving atoms other than hydrogen; that is, 4 short Br...Br contacts for **6** and **12** are in the 3.438–3.497 Å range and 3.576 Å, respectively.

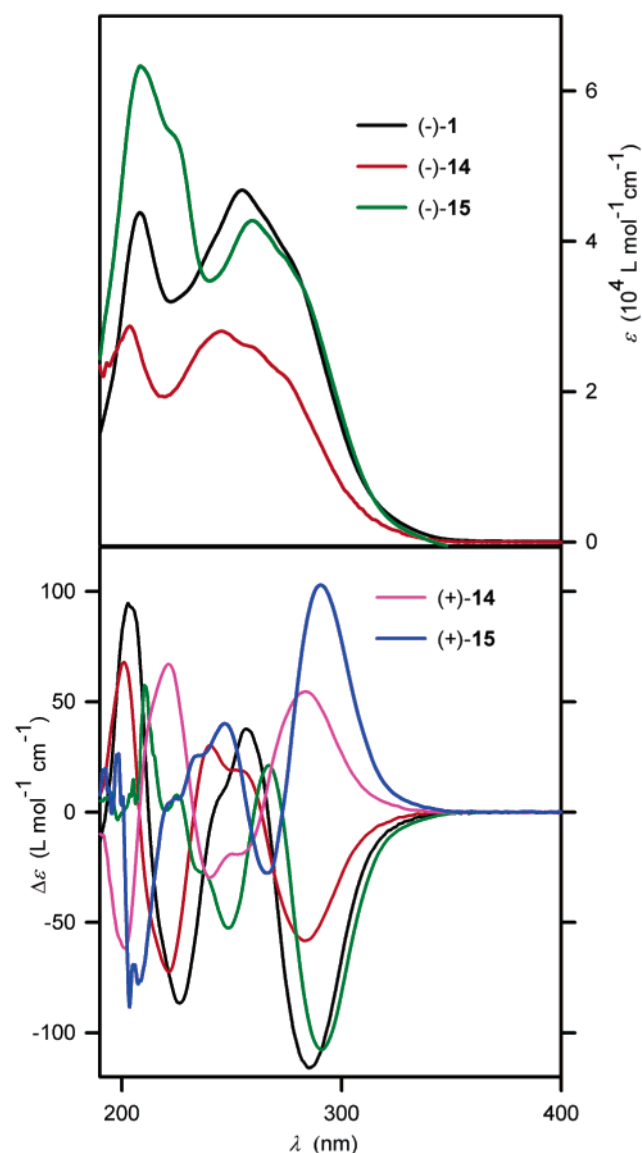
**Barrier for Racemization of 1.** At 199 °C, enantiomerically enriched [7]helicene **1** racemizes in the solid state with a half-life of  $11 \pm 1$  h. This corresponds to a free energy barrier for racemization of  $39.0 \pm 0.2$  kcal/mol at 199 °C (Supporting Information, including Figure 1s). Analogously, the half-life is about 5 h at 203 °C. The propensity of **1** for racemization is similar to that of all-phenylene [6]helicene.<sup>77</sup> This is consistent with the similar helical structures for **1** and all-phenylene [6]helicene.<sup>45,78</sup>

**UV–Vis Spectroscopy, CD Spectroscopy, and Cyclic Voltammetry.** Electronic absorption UV–vis spectra for selected compounds in dichloromethane are shown in Figure 9.

The spectrum for rac-1 with  $\lambda_{\text{max}} = 266$  nm (with shoulder at 274 nm) is significantly blue-shifted, as compared to  $\lambda_{\text{max}} = 390$  nm for  $\alpha$ -quaterthiophene, considering that both  $\pi$ -systems have an equal number of C–C double bonds.<sup>25,79</sup> However, the spectra of [7]helicene rac-1 and dithienothiophene **4** are significantly different, with respect to both a much greater

(77) Racemization of [6]helicene: (a) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 347–349. (b) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031–6035.

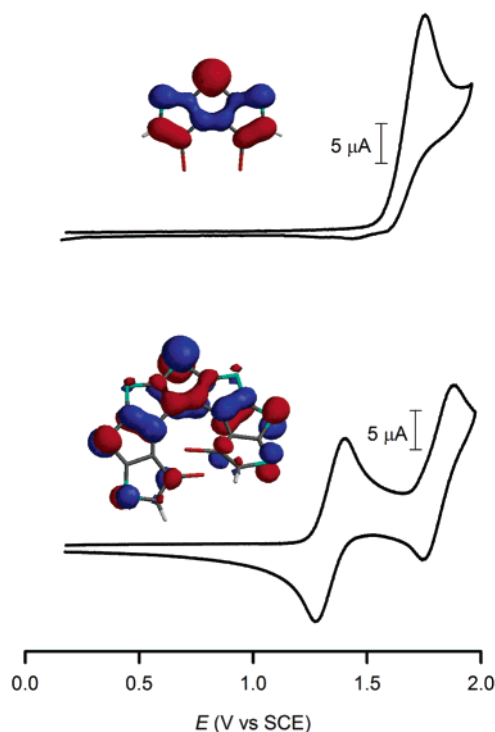
(78) Helical structure of [6]helicene: Navaza, I.; Tsoucaris, G.; Le Bas, G.; Navaza, A.; de Rango, C. *Bull. Soc. Chim. Belg.* **1979**, *88*, 863–870.



**Figure 10.** Top plot: UV-vis electronic absorption spectra for [7]helicenes (–)-**1**, (–)-**14**, and (–)-**15** in cyclohexane. Bottom plot: CD spectra for (–)-**1**, (–)-**14**, (+)-**14**, (+)-**15**, and (–)-**15** in cyclohexane at room temperature.

integrated absorbance and the bathochromic shift in rac-**1**, as compared to those in **4**.<sup>45</sup> These spectral differences for formally cross-conjugated homologues may also be affected by helical distortion in rac-**1**. In addition, the involvement of sulfur atoms in conjugation is feasible;<sup>80</sup> for example, the HOMOs for both dithienothiophene **10** and [7]helicene **14** have significant atomic coefficients at the sulfur atoms (Figure 11). Macrocycles **5–7** may provide further insight on the role of sulfur atoms in conjugation.

Interestingly, the long-wavelength band edges for nonplanar macrocycles **5–7**, in particular for the chiral dimer **6**, show



**Figure 11.** Main plots: cyclic voltammetry for dithienothiophene **4** (top) and [7]helicene **1** (bottom) in dichloromethane (tetrabutylammonium hexafluorophosphate as supporting electrolyte) at room temperature, using 200 mV/s scan rates; potentials are given vs SCE using ferrocene (0.46 V) as the reference.<sup>83</sup> Inset plots: HOMOs for dithienothiophene **10** and [7]helicene **14** at the semiempirical AM1 level of theory.

**Table 2.** Summary of Chiroptical Data for [7]Helicenes (–)-**1**, (–)-**14**, and (–)-**15** in Cyclohexane

compound	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon_{\text{max}}/\text{L mol}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{max}}/\text{nm}$ ( $\Delta\epsilon_{\text{max}}/\text{L mol}^{-1} \text{cm}^{-1}$ )	$[\alpha]_{\text{D}}^{\text{a}}$	$[\Phi]$
(–)- <b>1</b>	256 ( $4.7 \times 10^4$ )	285 (–117)	–1019	–7370
(–)- <b>14</b>	246 ( $2.8 \times 10^4$ )	283 (–61)	–1260	–7280
(–)- <b>15</b>	260 ( $4.2 \times 10^4$ )	290 (–110)	–730	–9140

bathochromic shifts, as compared to those for nearly planar dithienothiophene **4**. Chiral dimer **6** also possesses the most unique conformation, including the smallest torsional angles along the C–S–C–C linkages (40–48°) and the bithienyl moieties with transoid conformations (Table 2s, Supporting Information). However, the torsional angles associated with the bithienyl moieties in **5–7** are too close to 90°, with the smallest torsions of 62–73° for two of the bithienyl moieties in **7**, to have a significant contribution to the bathochromic shifts (Table 2s, Supporting Information). This suggests that the bis( $\alpha$ -thienyl)sulfur chromophore, involving conjugation through sulfur atom, affects absorption at the longest wavelength, especially in **6** with the relatively small torsions along the C–S–C–C linkages.<sup>81</sup>

UV-vis spectra for [7]helicenes (–)-**14**, (–)-**1**, and (–)-**15** in cyclohexane show an intense, long-wavelength, structured band with  $\lambda_{\text{max}} = 246, 256,$  and  $260$  nm, respectively (Figure 10, Table 2). The corresponding CD spectra possess both spectral envelopes and absorbances analogous to typical conjugated helicenes.<sup>17</sup> Based upon the assignment of absolute configuration of (–)-**1** as (*M*),<sup>46</sup> its negative sign of the longest

(79) Qualitative UV-vis spectra for cyclic  $\alpha,\beta$ -quaterthiophene (tetra[2,3-thienylene]) show  $\lambda_{\text{max}} \approx 270$  nm with a relatively weak and broad shoulder extending to about 400 nm: Marsella, M. J.; Reid, R. J.; Estassi, S.; Wang, L.-S. *J. Am. Chem. Soc.* **2002**, *124*, 12507–12510.

(80) Oligo(thio-2,5-thienylenes): Nakayama, J.; Katano, N.; Shimura, Y.; Sugihara, Y.; Ishii, A. *J. Org. Chem.* **1996**, *61*, 7608–7610. Katano, N.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2695–2700. Crystallographic data for one of the structures in the last reference were corrected, see: March, R. E.; Kapon, M.; Hu, S.; Herstein, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 62–77.

(81) Colonna, F. P.; Distefano, G.; Reichenbach, G.; Santini, S. *Z. Naturforsch., A: Phys. Sci.* **1975**, *30*, 1213–1214.



wavelength CD band is consistent with all other known helicenes; that is, the possible cross-conjugation does not significantly impact the CD spectra of (–)-**1** and its derivatives.

As illustrated in Figure 10 and Table 2, silane-, and especially siloxane-, substituted [7]helicenes (–)-**1** and (–)-**15** have relatively enhanced chiroptical properties, as compared to [7]helicene (–)-**14**.<sup>72,82</sup> The CD spectra for [7]helicene (–)-**1** and (–)-**14** possess similar spectral patterns, although the spectrum for (–)-**1** is much more intense and shows bathochromic shifts throughout the recorded wavelength range. The chiral (–)-menthol-based siloxane substituent in (–)-**15** induces a somewhat greater bathochromic shift in the longest wavelength CD band and significantly perturbs spectral shapes of the short wavelength CD bands, as compared to the spectra of (–)-**1** and (–)-**14**. The CD spectra for diastereomers (–)-**15** and (+)-**15** are indistinguishable at  $\lambda > 270$  nm, while they are significantly different at the shorter wavelengths, as expected for a perturbation of the [7]helicene chromophore by the relatively weak and short-wavelength absorbing (–)-menthol-based chromophore. Finally, the CD spectra for (–)-**14** and (+)-**14** are mirror images, as expected for enantiomers.

Cyclic voltammetry of [7]helicene **1** gives two reversible waves at  $E_1^\circ = +1.34$  and  $E_2^\circ = +1.82$  V, most likely corresponding to oxidation to the radical cation and dication, respectively. For **4**, only an irreversible redox process with the anodic peak potential at about +1.8 V is found (Figure 11). Interestingly, chiral dimer **6** shows a reversible wave at  $E_1^\circ = +1.59$ ; also, a second, nearly reversible wave at  $E_2^\circ = +1.89$  V is observed (near the electrolyte solution limit), even at a relatively slow scan rate of 50 mV/s.

The oxidation potentials for [7]helicene **1** may be compared to those obtained under similar conditions for typical  $\alpha$ -oligothiophenes.<sup>83</sup> The potentials for **1** are similar to  $E_1^\circ = +1.35$  and  $E_2^\circ = +1.75$  V reported for a derivative of  $\alpha$ -terthiophene, that is, 3',4'-dibutyl-2,5''-diphenyl-2,2':5',2''-terthiophene.<sup>84</sup> However, these oxidation potentials are significantly higher than

those for alkyl-substituted  $\alpha$ -sexithiophenes ( $E_1^\circ = +0.80$  and  $E_2^\circ = +1.00$  V) or polythiophene ( $E_1^\circ \approx +0.8$  V).<sup>85</sup>

The highest occupied molecular orbitals (HOMOs) for **10** and **14** possess significant atomic contributions from sulfur atoms (Figure 11). Interestingly, the HOMO for [7]helicene **14**, with very low atomic contributions from six carbon and two sulfur atoms, is largely nonbonding.

## Conclusion

The syntheses of racemic and enantiopure carbon–sulfur [7]helicenes, fragments of the  $(C_2S)_n$  helix of annelated thiophenes, provide a novel class of oligothiophenes. Although [7]helicene **1** and its lower planar homologue are both formally cross-conjugated, **1** shows increased electron delocalization as evidenced by both a significant bathochromic shift in the UV–vis absorption spectra and its reversible oxidation at relatively low potentials; both conjugation through sulfur atoms and the helical distortion may play a role. However, the degree of electron delocalization in **1** is significantly less as compared to analogous  $\alpha$ -oligothiophenes. Chiroptical properties of carbon–sulfur [7]helicenes are similar to those of conjugated helicenes. In the solid state,  $\pi$ -stacking and multiple intermolecular short S...S contacts for the solvent-free polymorph of [7]helicene **1** suggest an effective intermolecular electronic coupling in two-dimensions.

**Acknowledgment.** This research was supported by the National Science Foundation (CHE-0107241). MS analyses were carried out at the Nebraska Center for Mass Spectrometry. We thank Dr. Jun Li and Kristin Fulton for assistance with cyclic voltammetry and synthesis. We thank Dr. Victor G. Young, Jr. of the X-ray Crystallographic Laboratory at the Department of Chemistry, University of Minnesota, for X-ray crystallographic determination of dimer **5**.

**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>.

JA0462530

(82) An analogous effect of silicon substitution on chiroptical properties is observed in [7]helicenes, which may be formally derived via the replacement of the center thiophene ring in **1** with a benzene ring. Although for such helicenes, trimethylsilyl-substitution may be associated with flatter helix, with lower helical climb, as determined by X-ray crystallography, the effect of crystal packing on such helical structures is uncertain: ref 47. For the most studied all-phenylene [6]helicenes, the relationship between the crystal structure (substituent-induced helical distortion) and optical rotation could not be established: ref 72.

(83) For dichloromethane with TBAPF<sub>6</sub> as supporting electrolyte, potentials are referenced to ferrocene couple at +0.46 V: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, 96, 877–910.

(84) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, R. R. *J. Am. Chem. Soc.* **1997**, 119, 5888–5899.

(85) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 76–78.