

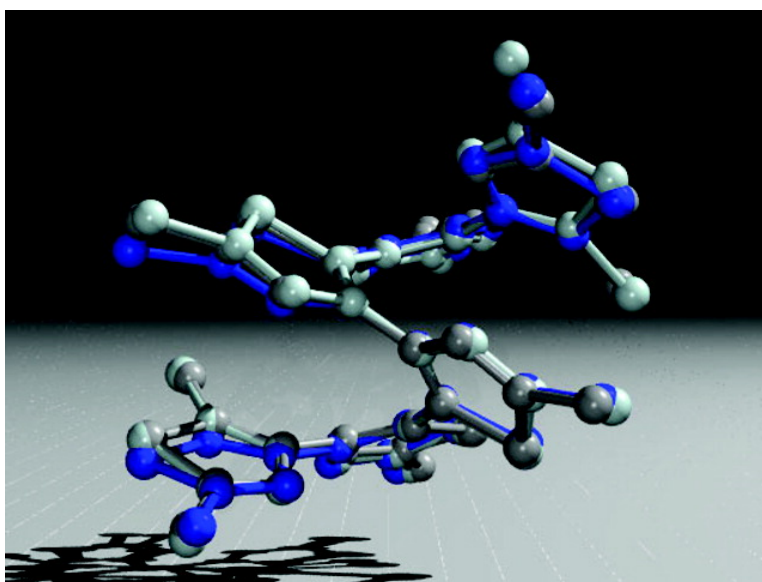
Communication

Helical Sexithiophenes: An Experimental and Theoretical Study Implicating the Alternating 2,2':3,3' Regioisomer as a Reliable Helical Motif

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Helical Sexithiophenes: An Experimental and Theoretical Study Implicating the Alternating 2,2':3,3' Regioisomer as a Reliable Helical Motif

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Helical oligomers and polymers can be broadly classified as having either conformationally rigid or conformationally flexible backbones (i.e., helicenes¹ and poly(isocyanate)s,² respectively). The latter classification requires that an external or internal force bias the conformational dynamics of the molecule to favor a helical conformation over all other possibilities.³ Herein, we report a series of sexithiophenes that utilize internal torsional forces to bias a solid-state helical conformation. The reported sexithiophenes are synthesized in a manner that facilitates end-group modification. It is theoretically predicted and experimentally confirmed that end-group diversity does not affect the helical bias of the system.

In 1988, the X-ray crystal structure of [3,3';2',2'';3'',3''']-quaterthiophene was reported,⁴ revealing a partial helical structure composed of three isomorph conformers (S-C_a disorder in the two terminal thiophenes; see Figure 1a). To date, additional X-ray crystal structures of larger, well-defined oligothiophenes possessing [3,3':2,2'] connectivity have not been reported. Having previously prepared compounds of type **1** as intermediates in the synthesis of cyclic hexachlorohexa(2,3-thienylene),⁵ we decided to prepare compounds **1a–c** (Figure 1b) in an effort to probe conformational preferences. Compounds **1d–i** were not synthesized, but they serve as related structures for theoretical calculations⁶ (vide infra).

Our original synthesis of compound **1a**⁵ was designed such that the terminal α -thienyl positions remained unsubstituted (X = H). The significance of this design is the availability for further chemical transformations to occur exclusively at these two sites (i.e., halogenation or deprotonation). In this regard, note that the chemical reactivity of the thiophene ring toward such synthetic transformations follows the site reactivity trend $\alpha \gg \beta$. Thus, the six α -chlorine atoms act as convenient protecting groups, deactivating reactivity at the corresponding α -thienyl sites. By design, it was possible to convert compound **1a** to **1b** and **1c** via NCS/NBS halogenation. All three products were crystallized from solution to yield colorless samples suitable for X-ray analysis, and all were found to exist in near identical helical conformations, as illustrated by the superimposition of the three X-ray structures⁷ shown in Figure 1c. For each structure, no S-C_a disorder is observed in the terminal A-ring or F-ring, and both substituents X are oriented in the same relative direction.

Figure 1d shows the superimposition of crystal structure **1a** onto its geometry optimized structures (MMFF and BLYP/6-31G(d) levels of theory) and illustrates the utility of making gas-phase theoretical predictions of structure for this particular class of helical oligomers.

Two additional MMFF calculations were performed. First, energy profiles corresponding to complete rotation about the three unique backbone dihedral angles of compound **1a** (C₂ symmetry) were run, and the results were overlaid onto a single plot (Figure 2a) to yield a distinct energy well that coincides with the average of all experimentally determined dihedral angles ϕ_{ab-ef} .

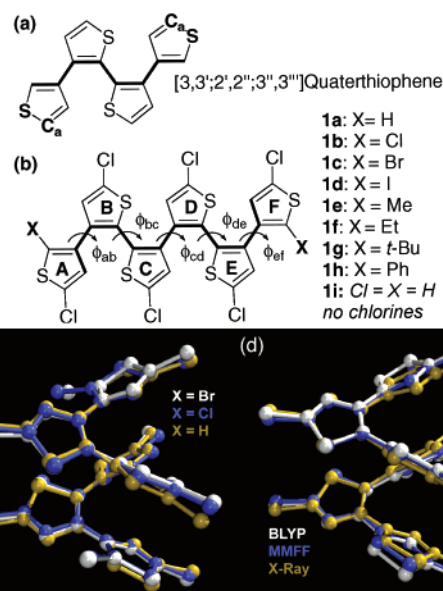


Figure 1. Depicting helical (a) quarter- and (b) sexithiophenes. (c) Overlay of the three X-ray crystal structures corresponding to **1a**, **1b**, and **1c**. (d) Overlay of **1a** as X-ray crystal structure, and as MMFF and BLYP/6-31G(d) minimized structures.

Second, MMFF conformer searches of compounds **1a–h** revealed all molecules to adopt isostructural lowest energy helical conformers (see Figure 2b). Helical C_a-S isomorphs of compounds **1a–h** lay above the lowest energy conformer by ≤ 1.3 kcal/mol. Despite a small energy difference, recall that only a single conformer is determined from X-ray analysis of compounds **1a–c**. MMFF calculations also suggest that A-ring and F-ring C_a-S conformer preferences in compounds **1a–h** are dictated by steric interactions between substituent and backbone. Specifically, large (X = Et and *t*-Bu) and small (X = Cl, Br, I, Me, Ph) substituents are divided into two unique classes of C_a-S isomorphs (with respect to the A-ring and F-ring; see Figure 2b). Regardless of this fact, the overlay shown in Figure 2b indicates that the helical orientation of the backbone is unaffected by either substituent composition or orientation.

Given the above observations, it is apparent that torsional effects play the major role in biasing the observed (and consistent) helical conformation of compound **1**. Weaker solid-state forces,⁸ such as intramolecular halogen...halogen and halogen...S interactions at less than Van der Waal radii, are not observed in the X-ray structures of compounds **1a–c**. Such intermolecular interactions at less than 3.8 Å are present in the solid state (compounds **1a–c**), but the similitude of the structure from both X-ray data and gas-phase calculations implies that intermolecular forces do not define the helical conformation; hence helical preference should not be restricted to the solid state. Note that the solution-state structure of

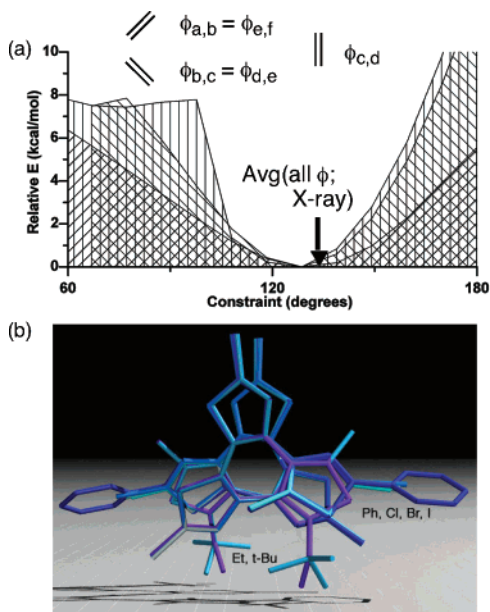


Figure 2. (a) Graph of energy profile (MMFF) corresponding to constraints applied to the three symmetry-unique dihedral angles of compound **1a** (C_2 symmetry). The black arrow corresponds to the average of all five backbone dihedral angles (ϕ_{ab-cf}) observed in the X-ray crystal structure of compound **1a** (C_1 symmetry). (b) An overlay of compounds **1a–h** at MMFF optimized geometries. The only disorder is C_a-S isomerization in rings A and F, as described in the corresponding text.

1 is not yet established, but likely resembles both the gas-phase and the solid-state structures reported herein.

It is instructive to predict the delocalization of electrons in the helical conformer of parent compound, **1**. Thus, an ACID⁹ calculation (B3LYP/6-31G(d)) was performed on compound **1i**, and the corresponding isosurface (reflecting electron delocalization) is displayed as an inset in Figure 3. The isosurface value was selected to illustrate the difference in electron delocalization across 3,3'- and 2,2'-linkages, the latter being the weaker of the two (Figure 3, inset). Regardless, delocalization throughout the helical backbone is predicted for this structure.

The UV–visible spectra of compound **1a** and 5,5'-dichloro-3,3'-bithiophene (THF) are shown in Figure 3. Excited-state calculations (TD-DFT/6-31G[d]) predict a 110 nm ΔE_g between dimer and helical tetramer, but only a 2 nm ΔE_g between helical tetramer and hexamer. Given that a helical structure requires at minimum a tetramer, the broad low-energy absorption shown in Figure 3 may be indicative of helical conformation. More definitive studies are required.

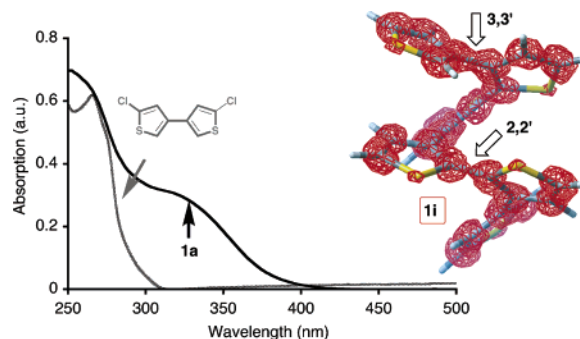


Figure 3. UV–visible spectra of 5,5'-dichloro-3,3'-bithiophene (grey) and compound **1a** in THF. Inset (right) reports the isosurface associated with an ACID calculation performed on compound **1i** at the B3LYP/6-31G(d) level of theory (see text).

As described herein, the reliability of the helical conformation found in type **1** compounds, independent of X substituent diversity, reflects an attractive and synthetically accessible helical and conjugated building block. The synthesis and composition of compound **1a** accommodates substituent diversity at sites X. The synthesis and structure–property relationship among a larger pool of type **1** oligomers and polymers will constitute further studies.

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Supporting Information Available: Details of theoretical calculations, pdb files of calculated structures (PDF), CIF files for compounds **1a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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