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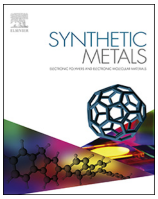

The influence of the position of a chiral substituent on undecathiophene chain. A DFT study

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ABSTRACT

Undecathiophenes substituted by chiral and achiral groups were studied using DFT method. The substituent shift from one end to the other was monitored for: relative energy, the ^{SR}CM chirality measure, the chiral Wiener index, the HOMO-LUMO gap, HOMA and NICS aromaticity indices, and theoretical VCD spectrum. For both, all-*trans* and one-*cis* conformations, structures substituted at the end were ca. 10 kJ/mol more stable than the other isomers. The ^{SR}CMs fluctuations with the conformation made this parameter not useful, but, the topological chiral Wiener index displayed regular yet non-linear changes with the substituent position enabling differentiation of the chiral systems. The HOMO-LUMO gap increased with the substituent shift towards the central ring. It varies regularly with the Wiener index for all-*trans* but irregularly for one-*cis* conformers, indicating strong response of the gap on slight conformational changes. The aromaticity indices adopted to linear systems indicated the all-*trans* to be a bit less delocalized than the one-*cis* isomers. Finally, the calculated VCD spectra were indicated possibility to monitor the position of the chiral substituent along the all-*trans* and one-*cis* structures.

1. Introduction

Polythiophenes were among the first studied conjugated polymers and they are still among the most investigated polymers for applications in organic electronics [1]. Indeed, they are efficient in charge transport and can be produced at a low cost [2,3]. On the other hand, the role of chirality in modern chemistry and medical chemistry is increasing [4] and in material chemistry has been steadily increasing as well. Chiral polymers are applied, e.g., as enantioselective sensors [5]; fibers, adsorbents, and membranes [1]; phases for resolution of enantiomers [6]; catalysts for asymmetric synthesis [7]; and chiral materials for electro-optic devices [8–11]. A lot has been written about conducting polymers [e.g., 12–14] but chiral conductive polymers have rarely been reviewed [15].

Chiral (conductive) polymers can be chiral either by the presence of chirality elements (a center or an axis), by the stabilization of a chiral or helical conformation by the formation of chiral aggregates, by the addition of a chiral additive, or a combination of these factors. They can be obtained either by using chiral monomers, co-polymers, or building blocks [15–20]; by adding a chiral dopant [21–23], by asymmetric polymerization [24–29], or by polymerization in liquid-crystalline media [20]. In chiral polythiophenes, the chiral side chains may induce a chiral (helical) conformation and a chiral superstructure [30]. Thus, the interplay between the chiralities of monomers, chains, and their aggregation determines the chirality-derived properties of a polymer [15,16]. This explains the possibility for an inversion of configuration [31], a change of optical activity with temperature [32] or with solvent [33], and with the kind of aggregation [30]. It has been shown that a change of chiral substituent can change conductivity by 104 S/cm [34].

The aim of this study is to shed some light on how the chiral substitution in undecathiophene system changes the properties of the parent chain. We decided to study undecathiophenes instead of some shorter thiophenes like sexithiophene, because they exhibit well stabilized π-electron delocalization (see plateau in Fig. 5, [35]), which better mimic larger oligothiophenes. However, we are looking for qualitative tendencies rather than for exact values of properties of the model systems. To do this, the all-*trans* undecathiophene was substituted in the 1st, 2nd, … and 11th thiophene molecule by a model chiral $CHF(CH_3)$ moiety (**T(n,m)**, n and $m = 10\text{-}n$ denote the number of rings before and after the substitution, Scheme 1). The $CHF(CH_3)$ substituent was chosen because it is small enough and chiral enough for a computational study. Every substituent with larger alkyl group would introduce a need for

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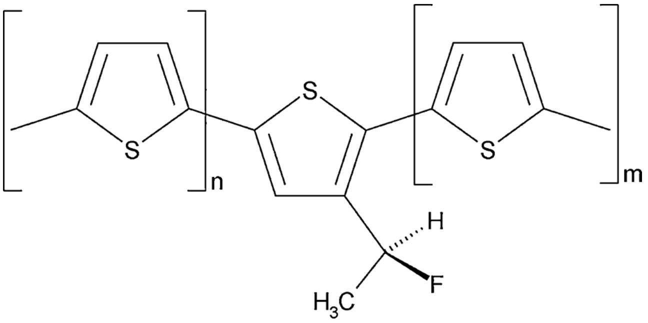


Scheme 1. Model undecathiophene oligomers, **T(n,m)**, with one thiophene ring substituted by the chiral CHF(CH_3) group: **T(n,m)** denotes that the chiral group is substituted in the ring after *n* and before *m* unsubstituted rings ($n = 0$, 1, 2,3, 4, 5; $m = 10\text{-}n$).

additional calculations of the substituent conformation. Use of the −CHFCl chiral substituent would provoke questions about curiosity of such a group, while the −CH(OH)CH_3 group would introduce additional hydrogen bond interactions which would mask the chirality effects. After having scanned the conformational space in substituted ter- and pentathiophenes, we also considered the one-*cis* systems **cT(n,m)** and the systems in which the chiral substituent was replaced by an achiral CF_3 one: $\mathbf{T^{CF3}(n,m)}$ and $\mathbf{cT^{CF3}(n,m)}$ and, in the graph-theoretical section, also by the CH_3, CH_2F and CF_2H groups. We considered both the total energy; the HOMO-LUMO gap; ^{SR}*CM* chirality measures [36–40]; chiral topological indices [41–43]; aromaticity by means of the HOMA and NICS indices; and vibrational dichroism VCD spectra of all studied systems. The former parameters determine physicochemical and structural parameters of the studied molecules, whereas the VCD spectra suggest possible methods for characterizing both the position of the insertion and the influence of the chiral element on the chiroptic behavior of the entire system.

2. Computations

All structures were calculated using the B3LYP functional [44,45] combined with the Pople-type 6-31G ** basis set [46–48], and Gaussian 09 suite of programs [49]. Although the 6-31G ** basis set was constructed in the early 1970s, it performs fairly well, especially in studies where semi-quantitative answers are adequate [50–53]. The reliability of results obtained with the B3LYP functional has been thoroughly assessed [50,54,55]. All studied systems exhibited real harmonic frequencies indicating that the local minima structures were found. The chiralities of the systems were calculated according to the *Sinister Rectus* chirality measures (^{SR}*CM*) based on a Property Space approach [36–40] and chiral topological indices based on Chiral graph theory [41–43]. The aromaticity analysis was based on HOMA [56–59] and NICS [60–62] aromaticity indices. The Vibrational Circular Dichroism VCD spectra were calculated using the formalism outlined in Ref. [63] implemented in Gaussian 09. SigmaPlot 12.0 software [64] was used for the correlation analysis.

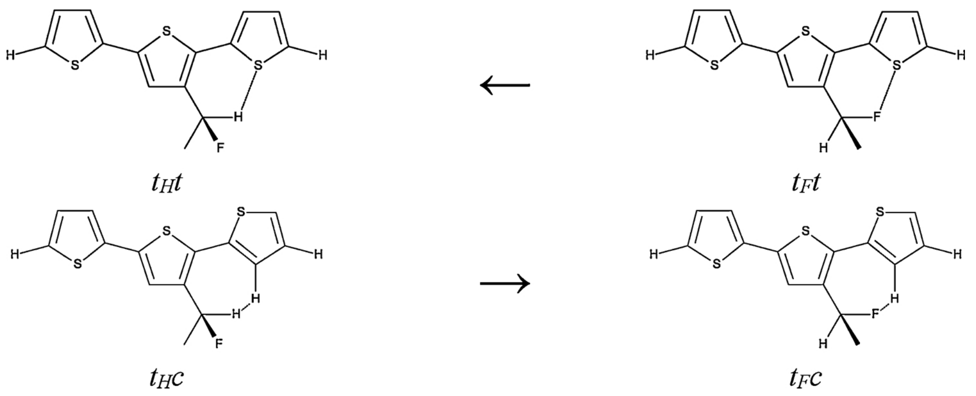
3. Results and discussion

3.1. Geometry, conformation and energetics

The experimental shape of poly- or oligothiophenes depends on many factors including monomer substituent(s), conditions of polymerization, temperature, physical state, solvent, chain length distribution, way of crystallization, etc. The quantum chemical calculations are mostly focused on the properties of single molecules instead of features of bulk polymer phases. Thus, the mentioned factors are either omitted or replaced by some constrains like periodicity, chain planarity, average properties of a surrounding solvent, etc. Here, we put no constraints on the calculated single molecule structures, paying attention only to true local minima structures.

However, for undecathiophenes, there are 10 single bonds between the rings, so the conformation issue is always a problem. Yet here, it seems that it can be easily simplified. The presence of π-electron delocalization across the oligomer chain limits the conformational freedom from as many as 3^{10} structures to nearly planar structures with either more stable *trans*- or less stable *cis*- configurations of the (S)-atoms of the neighboring moieties. Still, 2^{10} conformers can potentially co-exist. Because of higher stability of *trans*- than *cis*-thiophene conformers, we had first considered only the most stable all-*trans* arrangements. However, reviewer of this paper rightly suggested that what is true for the unsubstituted undecathiophene, is not necessarily true for the substituted one. Thus, first we searched for regularity in the substituted ter- and pentathiophenes with substituted central ring. For these we introduced the two- and four-letters codes in which "*t*" and "*c*" denote *trans*- and *cis*-arrangement of the subsequent rings.

In the studied systems, presence of the chiral CHF(CH_3) substituent results in possibility of an additional inter-ring interaction and a need for distinction between different arrangements of the substituted ring within the same code (Scheme 2). Therefore, H and F subscripts were introduced to symbolize interaction with the next unit trough either substituent's H or F atom with either S or H-C moiety (Scheme 2). Nevertheless, it appeared that the $t_{H}t$ and $t_{F}t$ systems converged to the same forms in which the S atom is between H and F, but, ca. 0.1 Å closer to the H. On the other hand the $t_{H}c$ systems converged to the $t_{F}c$ ones. Similar appeared to be true for the considered pentathiophenes (Table 1). As a result the additional subscript is not necessary if one remembers that different possible substituent conformations are stabilized in selected arrangements.



Scheme 2. Example of possible different inter-ring interactions in terthiophene oligomers substituted by the chiral CHF(CH_3) substituent and the letter codes assigned to the conformers and types of the contact.