Conformational Effects on Electrical and Spectroscopic Properties of Bi-, Ter-, and Poly-thiophenes

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Using conformationally constrained bi- and ter-thiophenes, the effects of inter-ring torsional angles on spectroscopic properties of the corresponding polymers are demonstrated; effects on conductivity are complicated by inter-chain contributions.

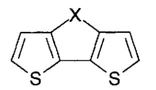
Polyheterocycles represent a growing class of advanced materials for electronics and non-linear optics. Amongst them poly-2,5-thiophene derivatives are particularly interesting due to their outstanding chemical and environmental stability. Recently a lot of effort has been made to establish relationships between the structure of the monomeric thiophene unit and the electrical and spectroscopic properties of the resulting polymer.[1] This communication reports the preliminary results of a systematic search for a quantitative relationship between the conformation, *viz.* the inter-ring torsional angle (θ), and the properties of these materials.

Our approach was to polymerize bithiophene and terthiophene monomers, showing a well defined torsional angle at the inter-ring bond. Stable synperiplanar, (+) synclinal and (+) anticlinal arrangements were expected for 3,3′-bridged bithiophene derivatives **1a–g**, where length and rigidity of the bridge had been tailored to a particular value of θ. A preferred quasi-*anti,anti* conformation should be achieved in the terthiophene system **2**: the bridge is too short to allow stereoisomerization from the *anti,anti* to the *syn,syn* conformer, in which a further, too energetically demanding, 2 Å separation between the 3 and 3″ carbon atoms would be produced.

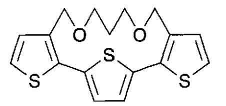
As it is generally assumed that the preferred conformation of a monomer is maintained in the polymer,[2] this strategy allowed us to control the torsional angle of one half and two-thirds of the α–α' junctions in bithiophene and terthiophene polymers respectively.

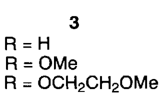
The investigation also included the synthesis of the open chain compounds **3a–c** and **4a**, in order to better evaluate the effect of the bridge.

In all the monomers both the positions involved in the polymerization process are homotopic, thus regioselectivity problems are overcome. The synthesis of **1a–d** was also planned so as to compare the stereochemical and electronic properties of analogously bridged systems in the biphenyl series.[3] 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene **1a** was obtained through a modification of the known route,[4] involving the bis(3-thienyl)glycolic acid as intermediate. The troublesome synthesis reported for the latter was substituted by the benzylic rearrangement of 3,3′-thienyl; this reaction, described[5] as unsuccessful, was found to run smoothly and cleanly when carried out under strictly controlled conditions.

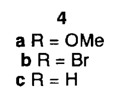

1

a, b, c X = $(CH_2)_n$ n = 1, 2, 3
d, e, f X = $CH_2(OCH_2CH_2)_nOCH_2$ n = 0, 2, 3
g X = $CH_2O(CH_2)_3OCH_2$


2


3

a R = H
b R = OMe
c R = OCH_2CH_2OMe
d R = Br
e R = CN
f R = CO_2Et


4

a R = OMe
b R = Br
c R = H

The key intermediate to the other bithiophene derivatives was the 3,3′-bisbromomethyl-2,2′-bithiophene **3d**, prepared in turn from **3a**.[6] Reaction of **3d** with phenyllithium in Et_2O solution gave **1b** (yield 5%),[7] purified by preparative HPLC. Reaction of **3d** with Ag_2O in aqueous acetone gave **1d** (30%).[8] Reaction of **3d** with the disodium salts of the suitable glycols in DMF solution gave the corresponding cyclic ethers **1e** (yield 15%),[9] **1f** (20%),[9] and **1g** (20%). The reaction of **3d** with an excess of sodium alkoxide under analogous conditions gave ethers **3b–c**. The compound 4*H*-5,6-dihydrocyclohepta[2,1-*b*:3,4-*b*′]dithiophene **1c** was obtained by Wolff–Kishner reduction of cyclohepta[2,1-*b*:3,4-*b*′]dithiophen-5-one, hitherto isolated as 'one yellow crystal' specimen from the Ziegler condensation of dinitrile **3e** followed by hydrolysis and decarboxylation.[6] Dieckmann condensation on the diester **3f** (yield 95% from **3e**) was a definite synthetic improvement.[10] Bridged terthiophene derivative **2** was prepared by reaction of the dibromo compound **4b** with the disodium salt of propane-1,3-diol in DMF solution (yield 4%); **4b** was obtained by HBr cleavage of the diether **4a**. The latter was prepared through the same reaction scheme reported for the synthesis of **4c**, starting from 3-methoxymethylthiophene.[11]

The identity of all new monomers was fully established by elemental analysis, ^{13}C and ^{1}H NMR and MS spectra; in a few cases the structure was confirmed by X-ray analysis. Interannular torsional angle θ was inferred either from theoretical calculations† or from X-ray diffraction crystal structure determinations.[12] Differences in electronic conjugation were estimated through UV spectra (λ_{max}^{mon}), oxidation peak potential (E_{pa})‡ and Raman spectra (ν_R)[13] (cf. Table 1).

Polymerization was accomplished by anodic oxidation.‡ Bithiophene **1g** did not polymerize, while **1e** and **1f** gave materials which were found to be unstable under electrooxidation conditions. Neutral polymers were obtained by cathodic reduction of oxidized polymers, followed by treatment with 1% $MeCN–H_2O$ hydrazine solution.

Characterization of neutral polymers was based on elemental analysis, IR and, in a few cases, CP MAS ^{13}C NMR spectroscopy. The last technique demonstrated the high regioselectivity of the polymerization. Mean conjugation length was inferred from redox potential (E°_{pol}),‡ UV ($\lambda_{max}^{neutral\ pol}$) and Raman spectra ($\nu_{R'}$).[13] Electronic conjugation in oxidized polymers from **1a–c** was estimated on the basis of IR spectra ($\nu_{R''}$)[13] (cf. Table 1).

The effects of θ are striking in both monomers and polymers. As for the monomers, θ affects the interannular conjugation, and hence the spectral (UV and Raman) properties and the anodic peak potential. The latter reaches its lowest value in synperiplanar arrangement and progressively increases in synclinal conformations: when the θ value approximates 90° polymerization is totally inhibited.

Table 1

Monomer	θ/°	λ_{max}^{mon}/ nm[a]	E_{pa}^{mon}/ V[b]	ν_R/ cm^{-1}[c]	E^0_{pol}/ V[b]	$\lambda_{max}^{neutral\ pol}$/ nm[d]	$\nu_{R'}$/ cm^{-1}[c]	$\nu_{R''}$/ cm^{-1}[c]	σ/S cm^{-1}[e]
1a	0[f]	306	0.65	1480	0.10	545	1510	1275	40
1b	14[g], 16[h]	320	0.70	1526	0.16	525	1546–1513	1320	1.5
1c	22[g], 25[h]	315	0.87	1551	0.28	510	1530	1360	3
1d	8[f], 21[g], 22[h]	315	0.87	1551	0.37	525			0.2
1e	57[f], 85[h]	266	1.10	1563	0.81	392			—
1f	120[h]	271	1.05		0.75	379			—
1g	110[f]	270	1.16		—	—			—
3a	84[g], 122[h]	266	0.90	1568	0.36	420			0.1
3b	110[h]	268	1.00		0.64	420			0.01
3c		271	1.00		0.67	387			0.001
2		348	0.74	1529	0.55	491			0.7
4a		336	0.70		0.58	473			0.15

[a] In EtOH. [b] *vs.* Ag/Ag$^+$. [c] ν_{asym} (C–C). [d] Polymer film on ITO electrode. [e] Ref. 14. [f] X-Ray data. [g] *ab initio*. [h] MM2.

The analysis of calculated θ values (*ab initio* and MM2) and experimental data (UV and Raman) of bridged and open chain monomers suggests the following observations: (*i*) methyl groups in derivative **3a**, structurally matching **1b** and **1c**, force the thiophene rings to strongly deviate from coplanarity; (*ii*) terthiophene **2** shows a red shift of the UV λ_{max} compared with the open chain derivative **4**.

Comparison of θ values and enantiomerization barriers (calculated[†] and experimentally evaluated by low-temperature ^{1}H NMR spectroscopy) of **1b–d** with those of biphenyl systems, having the same bridge,[3] indicates that both of these parameters are lower in the bithiophene series; twist angles being equal, biphenyls show greater rigidity than bithienyls.[3a]

As for the polymers, Table 1 clearly shows that the absorption maximum wavelength ($\lambda_{max}^{neutral\ pol}$) and redox potential ($E^0_{pol}$) can be modulated through the torsional angle of the starting monomer. These data are in agreement with the calculated evolution of electronic properties as a function of the torsional angle in bithiophene systems.[2]

Conductivity dependence upon θ values suggests the importance of intrachain coplanarity for controlling conduction properties. A modest deviation from coplanarity (10–15°) produces a dramatic drop in conductivity of about one order of magnitude (cf. **1a–d**). The synperiplanar cyclopentadithiophene **1a** is anodically oxidized to produce the poly(bithiophene) with the highest conductivity (σ = 40 S cm^{-1}) and the most effective conjugation length ($\lambda_{max}^{neutral\ pol}$ = 545 nm with band edge near 1.8 eV). The apparently meagre conductivity value of poly(**1a**) is significant when compared with that shown by poly(2,2′-bithiophene)[15] (σ = 2.8 S cm^{-1}). Moreover the conductivity can be easily enhanced by the well known alkyl substitution effect: the introduction of long-chain alkyl substituents in position 4 of **1a** gives materials with conductivity higher than 300 S cm^{-1}.[16] It must be observed that the first optical absorption band of poly(**1a**) lies in the same range of highly regioselective poly(3-alkylthiophenes).[17]

The bridged terthiophene **2**, which seems to prefer a quasi-antiperiplanar conformation, polymerizes to give a material similar to that obtained from the corresponding unbridged monomer **4a**. This confirms that the preferred *S-trans* arrangement of sulfur atoms in polythiophenes is not such a crucial parameter as is inter-ring coplanarity.

A good linear correlation[§] was found between the energy of the first electronic band in the polymers (E_g^{pol}) and θ in the monomers. This result highlights that θ is an essential parameter in determining the effective conjugation length in polybithiophenes, thus giving a quantitative support to a hitherto qualitative knowledge.[1] As for conductivity the actual number of significant data is too low for a statistical treatment; however a preliminary multivariate analysis of the data seems to indicate lack of a quantitative σ/θ relationship. This may be due to the interchain contribution to the bulk mobility of charge carriers. However, tuning of optical properties and redox potentials of polybithiophenes by controlling θ in the monomers can be exploited to prepare materials for specific applications in the field of molecular electronics.

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Footnotes

[†] Torsional parameters for the molecular mechanics force fields (MM2, QCPE program no. 501) were optimized by fitting the *ab initio* MP2/6-31G*//HF/6-31G* results for the parent compound 2,2′-bithiophene. Reliability was tested with the *ab initio* SCF-HF results obtained for **1b–d** and **3a**: the obtained MM2 θ values are in good agreement with the *ab initio* ones, with the apparent exception of compound **3a**. For **3a** SCF-HF calculations predict an energy minimum at 84° in a very flat region (< 1.2 kJ mol^{-1}) between 60 and 110°; MM2 calculations find two minima at 122 and 67°, 1.2 kJ mol^{-1} apart, with a rotation barrier of 1.6 kJ mol^{-1}. The conformational behaviour of **1e,f** and **3b** was investigated by the MM2 method using these new torsional parameters.

[‡] Polymerization was performed at 0.1 V beyond the peak potential, under the same conditions as described in ref. 10.

[§] $E_g^{pol} = 2.24 + 9.27 \times 10^{-3}\,\theta$; standard error = 0.089, R^2 = 0.969, R^2_{CV} = 0.885. R^2_{CV} is the cross-validated squared correlation coefficient calculated with the leave-one-out technique.

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