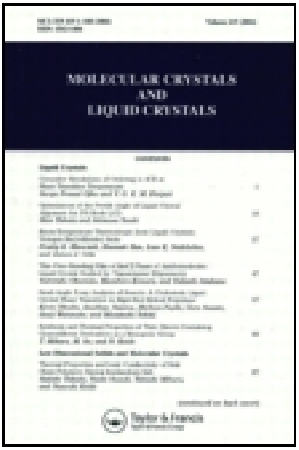

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Stereoelectronic Effects in Polythiophenes

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STEREOELECTRONIC EFFECTS IN POLYTHIOPHENES

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Abstract: Spectroscopic and electrical properties of conformationally *syn*-blocked bithiophene monomers **1-3** and polymers are shown to be strongly dependent on the *inter*-ring torsional angle θ.

INTRODUCTION

Polyheterocycles are organic extrinsic semiconductors: they become conductive when charge defects are produced by doping in their skeleton. Charge carriers are described to hop within the polymer chain if π conjugation between adjacent heteroaromatic units is effective. When structural defects (*e.g.* β junction, chain end, kink, etc.) interrupt this *intra*-chain hopping, the *inter*-chain hopping mechanism becomes active. In these materials charge transport was shown to be strongly dependent upon conjugation[1] and correlations between effective conjugation length and conductivity were found.[2,3]

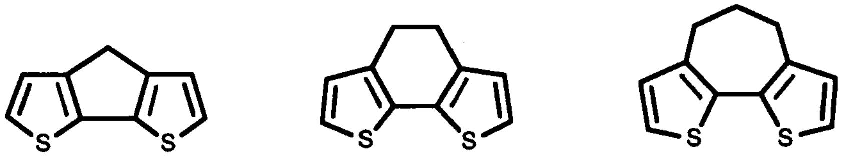
The extent of π conjugation is mainly affected by two factors: the regioselectivity of the *inter*-monomer links and the polymer chain conformation.

Good regioselectivity (high ratio between α-α'and α-β' links) can be obtained[4], for example, by the electroxidation of short chain monomers, in optimized electrical conditions, at low monomer concentrations and for short polymerization times.

Inter-ring conjugation depends upon the conformational arrangement of adjacent thiophene moieties. Till now conformational problems have not been approached systematically; they have been limited to the study of steric effects on the electrical properties of poly(3-alkylthiophenes)[5], poly(3,4-dialkylthiophenes)[4] and poly(dialkylbithiophenes)[6].

We started up a systematic investigation of the effect of conformation on conjugation, and hence on conductivity and spectral properties, of polythiophene-based materials. We planned to electropolymerize bithiophene monomers showing well defined torsional angles at the *inter*-anular bond, in order to have a good control of the conformation of the resulting polymers. Spacers of suitable length between the β and β' positions of bithiophene systems could modulate the *inter*-ring torsional angle θ from *syn*periplanar, to *anti*periplanar conformations.

The complete study of the *syn*-blocked monomers **1-3** (Fig.1) and of their pristine and doped polymers is reported in this paper. The short bridge between β and β' positions fixes the *syn* arrangement of the two thiophene rings in compounds **1-3**: the torsional angle should increase as the number of methylene units increases. The extension to *anti*-blocked systems is planned and will be reported elsewhere[7].



1 **2** **3**

CPBT **DBBT** **CHBT**

FIGURE 1 *Syn*-blocked monomers

EXPERIMENTAL

Synthesis of monomers

4H-Cyclopenta[2,1-b;3,4-b']bithiophene[8] (**1**) (CPBT) and 4,5-dihydrobenzo[2,1-b;3,4-b']bithiophene[9] (**2**) (DBBT) were already known in the literature and were prepared through the known routes.

4H-5,6-dihydrocyclohepta[2,1-b;3,4-b']bithiophene (**3**) (CHBT): 4H-cyclohepta[2,1-b;3,4-b']bithiophen-5-one[10] (0.51 g) and 98% hydrazine hydrate (0.40 ml) were added to a solution of KOH (0.40 g) in diethyleneglicol (35 ml) and the reaction mixture was heated at 230°-240°C for one hour. The mixture was cooled at room temperature, diluted with water and extracted with Et_2O; the organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated to dryness *in vacuo* to give a liquid residue which was distilled under reduced pressure to afford **3** (0.20 g) as pure compound; bp 140°-150°C at 0.5 mmHg. MS 206 (M^+); ^1H NMR ($CDCl_3$) δ 2.03 (2H, m), 2.95 (4H, m), 6.75 (2H, d), 6.98 (2H, d).

Electropolymerization

Compounds **1-3** were electropolymerized at 25°C, under nitrogen, in CH_3CN solution with 0.1M tetraethylammonium perchlorate as supporting electrolyte in a three electrode cell. The counterelectrode was platinum and the reference electrode was a silver/ 0.1M silver perchlorate in CH_3CN (0.34 V vs SCE). The voltammetric apparatus (Amel) included a 551 potentiostat, modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a glassy carbon disc (0.2 cm^2). A platinum sheet (15 cm^2) was used in preparative electrolysis.

Spectral characterizations of the materials

The electronic spectra of the monomers were recorded in ethyl alcohol solution with a Perkin Elmer Lambda 6 spectrometer. The electronic spectra of the pristine polymers were recorded in KBr pellets with a Perkin Elmer Lambda 15 (diffuse reflectance) spectrometer. CP MAS ^{13}C NMR were recorded with a CXP Bruker spectrometer. Raman spectra with excitation line in the visible (λ = 514 nm of a Spectra Physics Ar^+ laser) both of the monomers and of the pristine polymers were recorded using a Dylor XY-Raman spectrometer with multichannel detector. FT Raman spectra with excitation in the near infrared (λ = 1064 nm of a Nd^{3+} YAG laser) were recorded with a Brucker FT-Raman interferometer. Infrared spectra of the doped polymers were obtained with a Nicolet mod.7000 FT-IR interferometer.

Conductivity Measurements

Apparatus and procedures for conductivity measurements have been previously described in detail[11]. The working electrode was a two band platinum electrode (0.3 cm x 0.01 cm for each band) with 6 µm *inter*-band spacing, typically polymer-coated with the passage of 20 mC. Poly(3-methylthiophene) (60 S cm^{-1})[12] was used as a conductivity standard.

Conformational Analysis: Calculation Methods

Theoretical conformational analysis was performed with the molecular mechanics MM2(85) program[13]. The literature parameters[14] were tested on the parent compound 2,2'-bithiophene (**4**) (BT). By using the standard parameters we found minima at 0° and 180° with nearly the same energy. These results completely disagreed with *ab-initio* results at the HF-SCF/6-31G*//3-21G* level which found two non planar minima: an *anti*clinal one with θ=146° (absolute minimum) and a *syn*clinal one with θ=44° (relative minimum, 0.7 kcal/mol higher in energy). The estimated barrier to rotation between these two minima was 1.7 kcal/mol. A good fitting with *ab-initio* calculations results could be obtained by modifying the torsional parameters and adding a V_4-term to the Fourier expansion of the torsional potential.

STRUCTURAL CHARACTERIZATION OF THE MONOMERS

Conformational Analysis

With the new parameters discussed above we calculated the conformational behaviour of bridged monomers **1-3** and of 3,3'-dimethyl-2,2'-bithiophene (**5**) (DMBT). In compound **5**, due to methyl interaction, the thiophene rings are twisted to a greater extent than in BT (**4**), the dihedral angles θ in the two minima being 122° and 67° respectively. Moreover both the energy difference between the two minima and the barrier to rotation are reduced to less than 0.5 kcal/mol. As expected, MM2 calculations suggested an increase of the *inter*-ring torsional angle θ from CPBT (**1**) (on which the planar structure is imposed by the five membered ring) to DBBT (**2**) and CHBT (**3**). In fact minima with dihedral angles θ of 18° and 46° (absolute minimum) were found for DBBT (**2**) and CHBT (**3**). For the latter a second minimum, 11 kcal/mol higher in energy, was found with θ=22° and a barrier to rotation of approximately 2 kcal/mol. The planar conformations are saddle points in both compounds **2** and **3** with barriers to rotation of 2.3 and 1.8 kcal/mol respectively.

Raman Spectra

The analysis of the Raman spectra (λ_{exc}= 514 and 1064 nm) of compounds **1-5** based on the ECC theory[15-17], is focused on two lines (Table 1):

i) a strong line (S), which corresponds to the ring stretching mode, showing the following peak frequencies: 1435 cm^{-1}(**1**), 1448 cm^{-1}(**2**), 1455 cm^{-1} (**3**), 1444 cm^{-1} (**4**)[17] and 1442 cm^{-1} (**5**). Its frequency depends[18] on the effective electronegativity[19] of the heteroatom included in the aromatic unit: for this reason no relevant frequency dispersion is noticed for this band.

ii) a line (R) showing frequency and intensity dispersions. CPBT: 1480 cm^{-1} very weak; DBBT: 1531 cm^{-1} weak; CHBT: 1552 cm^{-1} medium; BT[17]: 1556 cm^{-1} medium; DMBT: 1567 cm^{-1} medium. This band is identified as the delocalisation dependent Я mode. Its shift towards higher frequencies has been considered [17] to be a spectroscopic evidence for the decrease of π conjugation between adjacent heteroaromatic units. As a consequence, in the series **1-5** the extent of π delocalisation is shown to decrease in passing from CPDT to DMBT, in accordance with the trend suggested by the calculated *inter*-ring torsional angles. Only the general trend can be considered as θ is calculated for isolated molecules in a standard medium, having 1.5 dielectric constant.

TABLE 1 Raman data of compounds **1-5**

Compound	S (cm^{-1})^a	R (cm^{-1})^a	S (cm^{-1})^b	R (cm^{-1})^b
CPBT	1435	1480	1437	1480
DBBT	1448	1531	1446	1526
CHBT	1455	1552	1454	1551
BT	1444	1556		
DMBT	1442	1567	1443	1568

a : λ_{exc} = 514 nm ; b : λ_{exc} = 1064 nm

Electronic Absorption Spectra

It is well accepted [20] that the twist around the "essential single bond" may strongly affect the electronic absorption spectrum of a biaryl system. Two different effects on the *inter*-ring conjugation band, related to the steric hindrance extent, are possible, : 1) Slight hindrance: the conjugation band undergoes a hypochromic effect relative to the spectrum of a planar model. 2) Moderate and severe hindrance: a hypochromic effect is combined with a hypsochromic shift: the extent of the blue shift and of the intensity drop depends on the twist extent.

On this basis the U.V. spectra of **1-5** (Table 2) give notable structural information. A progressive decrease of the conjugation band molar extinction coefficient (at the absorption maximum) is observed in compounds **1-3**. This feature suggests an increasing deviation from planarity, in agreement with calculated θ. Unexpectedly, a 28° θ change in passing from **2** to **3** has only modest influence on the absorption maximum wavelength (λ_{max}). The anomalous value of λ_{max} in CPBT spectrum could be attributed to the fact that some puckering occurs, as in fluorene[21]. The U.V.spectrum of DMBT shows a relevant hypsochromic displacement and drop in the absorption intensity of the conjugation band: the methyl group induced torsion nearly completely inhibits the *inter*-ring π delocalisation.

TABLE 2 U.V. data and calculated θ of compounds **1-5**

Compound	λ_{max} (nm)	ϵ	θ°
CPBT	305	17200	0
DBBT	320	14800	18
CHBT	315	12600	46
BT	302	12100	146
DMBT	265$^{(shd)}$	7400	122

STRUCTURAL CHARACTERIZATION OF THE POLYMERS

Polymers P(CPBT), P(DBBT) and P(CHBT) were obtained both in the pristine and doped state; Table 3 summarizes the electrochemical data for **1-5** monomers and the corresponding polymers.

TABLE 3 Monomer oxidation peak potentials (E_{pa}^{mon}), polymer redox potentials (E^0_{pol}) (vs SCE) and conductivities (σ)

Compound	E_{pa}^{mon}(V)	E^0_{pol}(V)	σ (S cm^{-1})
CPBT	0.99	0.44	40
DBBT	1.04	0.50	1.5
CHBT	1.09	0.62	3
BT[22,23]	1.20	0.83	2.8
DMBT[24]	1.24	0.70	0.1

^{13}C NMR Spectra of the Pristine Polymers

No evidence for irregular structures in P(CPBT) and P(CHBT) is present in the CP MAS ^{13}C NMR spectra. The chemical shift values, corresponding roughly to those of the monomers in solution, support conformational and electronic structures similar to those present in the monomers.

Raman Spectra of Pristine Polymers (Table 4)

The Raman spectra of neutral P(CPBT), P(DBBT) and P(CHBT) are studied on the basis of the ECC theory, taking into account two main spectral features: i) a complex system of strong bands (S') in the range 1450-1100 cm^{-1}, containing the unperturbed ring stretching mode; ii) a system of a few medium or weak lines near 1500 cm^{-1}(R'), including the Я mode. The comparison between Raman spectra recorded at two different excitation frequencies (λ_{exc}=514 and λ_{exc}=1064 nm) gives information about the dispersivity in conjugation length of each polymeric sample. With λ_{exc}=514 nm this group of lines is peaked at 1521 cm^{-1} in P(CPBT), 1534 cm^{-1} in P(DBBT), and 1530-1572 cm^{-1}in P(CHBT). The shift towards higher frequencies of $\nu_{Я}$ indicates a decrease of the effective conjugation length in the polymer chain. With λ_{exc}=1064 nm, the R' group is peaked at 1510 cm^{-1} in P(CPBT), it shows weak lines at about 1546-1513 cm^{-1} in P(DBBT), while it is almost unchanged in P(CHBT). The displacement towards lower frequencies, caused by a longer excitation wavelength, is an evidence that resonance conditions for segments of higher conjugation length are satisfied. The extent of π delocalisation progressively decreases from P(CPBT) to

P(CHBT). P(CPBT) shows the broadest distribution of conjugation length, while P(CHBT) is highly monodispersed.

TABLE 4 Raman data (S' and R') of pristine and i.r. data (S'' and R'') of doped P(CPBT), P(DBBT) and P(CHBT) (frequencies of the strongest peaks in cm^{-1}).

Polymer	S' [a]	R' [a]	S' [b]	R' [b]	S''	R''
P (CPBT)	1396	1521	1387-1341	1510	1085-660	1275
P (DBBT)	1447	1534	1426 -1405	1546-1513	1100-800	1320
P (CHBT)	1464	1530-1572	1464	1530	1100-900	1360

a : λ_{exc} = 514 nm ; b : λ_{exc} = 1064 nm

U.V. Spectra of Pristine Polymers

A good correlation is observed between the mean conjugation length of the pristine polymers, roughly evaluated from the U.V. spectra (P(CPBT): λ_{max}=545 nm; P(DBBT): λ_{max}=525 nm; P(CHBT): λ_{max}=510 nm; P(BT): λ_{max}=480 nm[22]; P(DMBT): λ_{max}=420 nm[6]) and the calculated torsional angles θ of the corresponding monomers: the highest value of λ_{max} is shown by the material prepared from the fully planar CPBT, while P(DMBT) exhibits the shortest λ_{max}.

Infrared Spectra of Doped Polymers (Table 4)

The group of overlapping bands (R'')containing the Я mode is centered at 1275 cm^{-1} in P(CPBT), at about 1320 cm^{-1} in P(DBBT) and at about 1360 cm^{-1} in P(CHBT). This frequency variation indicates that P(CPBT) is able to host longer charge defects than those present in P(DBBT) and P(CHBT). The i.r. spectrum of P(CPBT) gives further evidences of the sample inhomogeneity.

CONCLUSIONS

Spectroscopic and electrical properties of bithiophene- based polymers strongly depend upon the conformational variable parameter θ.

The U.V. and Raman spectra of the pristine polymers correlate with the calculated torsional angles of the corresponding monomers.

The regular increase of the monomer oxidation potential and polymer redox potential (Table 3) can be attributed to a progressive loss in *intra*-monomer π conjugation, since substituent electronic effects are almost the same in **1**-**3** (except for a high hyperconjugation effect in CPBT).

As for conductivity, the polymer resulting from the fully planar CPBT exhibits one of the highest conductivity values shown by polybithiophene materials: σ P(CPBT)= 40 Scm^{-1}, while σ P(BT)[22]= 2.8 Scm^{-1} and σ P(DMBT)[24]= 0.1 Scm^{-1}. P(CHBT) is characterized by a good conductivity (σ= 3 Scm^{-1}), though π conjugated segments were very short in the polymer chain and charge carriers were highly localized in the doped material. *Inter*-chain hopping seems to play the main role in controlling the charge transport in this system.

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