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Impact of the Torsion on the Optoelectronic Properties of Poly(3-alkylthiophene): A Spectroscopic and Theoretical approaches

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The aim of this work is to study the influence of the regioregularity of alkyl substituents on the poly(3-alkylthiophene) properties using UV-vis spectroscopy and theoretical analysis. It is found that the head-to-head sequences produce a steric hindrance and reduce the π-conjugation. Conformationals and optoelectroniques properties are greatly influenced by the type of the polymer's junctions.

Key Words: Regioregularity, 3-Alkylthiophenes, UV-visible spectroscopy, DFT calculations.

INTRODUCTION

Polythiophene derivatives are a class of conjugated materials showing large non-linear optical responses and become conducting when suitable doped[1]. These properties make them good candidates for the electronic and optoelectronic applications[2,3]. However, the processing of these polymers is limited by their insolubility. This problem was resolved by the incorporation of side chains into the polymer backbone. Unlike unsubstituted polythiophenes, the poly(3-alkylthiophene)s are processable. This processability facilitates their characterization and widened their applicability[4]. They show new interesting properties such as solvatochromism and thermochromism[5]. Better understanding of the physical properties of these polymers requires knowledge of their structures.

A characteristic usually associated to these compounds is the planarity which encourages a maximum overlap between the π atomic orbitals. The presence of alkyl groups in the polymer can causes non-planarity, producing "bends" along the polymer backbone which weaken the extent of π-conjugation[6]. It would be interesting to understand the conformation preferences in poly(3-alkylthiophene)s and detail structural parameters. The

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bithiophene and its methyl-substituted derivatives are good models to reflect changes in optoelectroniques properties of the polymer[7].

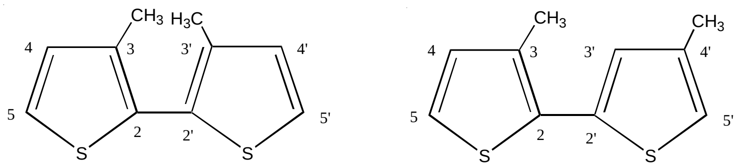
In this work, we aim to study the influence of the substituents in the polymers properties by UV-Vis spectroscopy and theoretical analysis using DFT/B3LYP calculations with the different basis sets (6-31G, 6-31G* and 6-31G**).

EXPERIMENTAL

All calculations were performed using the Gaussian 98 program[8]. The geometries were optimized by B3LYP method with the different basis sets (6-31G, 6-31G*, 6-31G**). The conformational analysis was done by changing the torsional angle θ by 20° steps between the syn-conformation (θ = 0°) and the anti-one (θ = 180°). For each conformation, the dihedral angle was held fixed while the remainder of the molecule was optimized. The energy difference is always done relative to corresponding absolute minimum conformation. The UV-visible spectra have been reported experimentally for solid state and in solution and calculated by the semi-empirical ZINDO method.

RESULTS AND DISCUSSION

If we consider the case of poly(3-methylthiophene), the simplest model can be used to study the conformational properties of this polymer is the dimer. In the polymer, we can recognize two type of α-α' junctions: a head-to-head (HH) and a head-to-tail (HT) which correspond respectively to 3,3'-dimethyl-2,2'-bithiophene and 3,4'-dimethyl-2,2'-bithiophene (Fig. 1). The versatility of the synthetic techniques has been used to prepare a series of polymers with variables degrees of regioregularity. It has been shown that the regioregularity of the alkyl side chains affect the optical properties of the polymer[9].



head-to-head (HH) head-to-tail (HT)

Fig. 1. The two α- α' junctions existing in poly(3-methylthiophene)

UV-visible analysis

Souto Major *et al.*[10] studied the regiochemistry of substitution in the poly(3-hexylthiophene) by comparing the properties of the stereoregular poly(3,3'-dihexyl-2,2'-bithiophene) with those of the conventional polymer obtained from direct chemical polymerization of 3-hexylthiophene. The regiospecific head-to-head polymer showed its maximum absorption at considerably shorter wavelength (417 nm). However, absorption maximum of the non regiospecific polymer was observed at 508 nm. Lère-porte *et al.*[11] developed another regiospecific method producing a poly(3-hexylthiophene) that contains almost exclusively head-to-tail coupling (98%). In the UV-visible, the polymer prepared by this method showed the absorption maximum at 515 nm in solution. Similar results were obtained by Chen *et al.*[12], with the maximum absorption at 460 in solution and 560 nm in the solid state. Other results[11-15] are summarized in Table-1.

TABLE-1
EXPERIMENTAL VALUES OF λ_{max} OF POLY(3-*n*-HEXYLTHIOPHENE)

Polymer	λ_{max} (nm) (Chloroform)	λ_{max} (nm) (Solid state)	Head-to-head (%)	Ref. no.
P1	515	-	2	11
P2	460	560	2	12
P3	440	505	20	13
P4	438	504	30	14
P5	425	462	37	14
P6	420	444	40	14
P7	419	430	52	14
P8	390	-	100	14
P9	384	-	100	15

According to these results, disruption of π system conjugation occurs when the polymer contains a significant fraction of head-to-head junctions.

Theoretical study

For better understanding the structure-property relationships of the poly(3-alkylthiophene), we examined the role of the regioregularity of the sequence using a theoretical analysis by B3LYP calculations on two dimethyl-substituted bithiophenes *i.e.*, 3,3'-dimethyl-2,2'-bithiophene (HH) and 3,4'-dimethyl-2,2'-bithiophene (HT). Geometrical parameters and potential energy surfaces were determined for each molecule. The effect of the substituent's position on structural parameters and on torsional potentials is also examined.

Conformational analysis of 3,3'-dimethyl-2,2'-bithiophene: The conformational analysis obtained for 3,3'-dimethyl-2,2'-bithiophene at the B3LYP level shows the correspondence of the most stable conformation (*syn-gauche* conformation) to the torsional angle $\theta = 58.7°$ (6-31 G) and $\theta = 58.2°$ (6-31 G*, 6-31 G**) (Table-2). In agreement with those obtained by MP2 method[16], a local minimum located at $\theta = 110°$ is found by B3LYP with the three basis sets for 3,3'-dimethyl-2,2'-bithiophene.

TABLE-2
RELATIVE ENERGY (Kcal/mol) AND TORSIONAL ANGLE OF 3,3´-DIMETHYL-2,2´-BITHIOPHENE (HH) OBTAINED BY B3LYP METHOD WITH THE DIFFERENT BASIS SETS

Basis set	*Syn* (0°)	*Syn-gauche*	Perpendicular (90°)	Anti-*gauche*	Anti (180°)
6-31G	9.54	0.00 (58.7°)	0.38	0.28 (110°)	1.90
6-31G*	9.39	0.00 (58.2°)	0.46	0.40 (110°)	2.39
6-31G**	9.40	0.00 (58.2°)	0.47	0.41 (110°)	2.39

The obtained torsional angles at these various computational levels for the *syn-gauche* conformation agree very well with the X-ray results of the tetramethyl-quaterthiophenes, characterized by a non coplanar *syn*-conformation[17] at $\theta = 54°$.

The torsional barrier of the coplanar conformation is more important than those of the perpendicular and the anti-planar ones, showing the important steric hindrance generated by methyl groups when the molecule is planar.

Fully optimized geometric structures of the lowest energy conformer of 3,3'-dimethyl-2,2'-bithiophene obtained by the three basis sets are compiled in Table-3. The atomic numbering is indicated in Fig. 1.

TABLE-3
OPTIMIZED GEOMETRY FOR THE LOWEST ENERGY STRUCTURE OF 3,3´-DIMETHYL-2,2´-BITHIOPHENE OBTAINED AT B3LYP LEVEL

Basis set	6-31G	6-31G*	6-31G**
S(1)-C(2)	1.835	1.760	1.760
C(2)-C(3)	1.379	1.382	1.382
C(3)-C(4)	1.443	1.433	1.443
C(4)-S(5)	1.362	1.365	1.365
S(1)-C(5)	1.795	1.731	1.731
C(2)-C(2´)	1.449	1.461	1.461
S(1)-C(2)-C(3)	110.6	110.8	110.8
C(2)-C(3)-C(4)	113.2	112.1	112.1
C(3)-C(4)-C(5)	114.7	113.7	113.7
C(4)-C(5)-S(1)	111.7	111.5	111.5

6-31 G* and 6-31 G** basis sets showed identical geometric parameters with small difference when compared with 6-31 G. The inter-rings bond length [C(2)-C(2')] is in good agreement with the experimental value found by X-ray diffraction studies[17]: 1.456 Å.

Conformational analysis of 3,4'-dimethyl 2,2'-bithiophene: The potential energy curves obtained for 3,4'-dimethyl-2,2'-bithiophene (HT) are summarized in Table-4.

TABLE-4
RELATIVE ENERGY (KCAL/MOL) AND TORSIONAL ANGLE OF 3,4´-DIMETHYL 2,2´-BITHIOPHENE (HT) OBTAINED BY B3LYP METHOD WITH DIFFERENT BASIS SET

Basis set	*Syn* (0°)	*Syn-gauche*	Perpendicular (90°)	Anti-*gauche*	Anti (180°)
6-31G	1.20	0.32 (35.5°)	1.57	-	0.00
6-31G*	1.16	0.00 (39.8°)	1.31	0.08 (145.6°)	0.33
6-31G**	1.14	0.00 (39.8°)	1.33	0.08 (145.8°)	0.33

The torsional profiles predicted by B3LYP with the basis sets 6-31 G* and 6-31 G** showed three maxima situated at θ = 0°, 90° and 180° and two minima corresponding to *syn-gauche* and anti-*gauche* conformations situated at 39.8° and ≈145.7°. With the 6-31 G basis set, B3LYP predicted a global minimum at θ = 180° (anti-planar conformation). The co-planar torsional barrier is very low in comparison with that found for 3,3'-disubstitued compound. The steric hindrance created by one methyl group is smaller than that generated by the two methyl groups.

The optimized geometry obtained for the lowest energy structure of 3,4'-dimethyl-2,2'-bithiophene is presented in Table-5.

TABLE-5
OPTIMIZED GEOMETRY FOR THE LOWEST ENERGY STRUCTURE OF 3,4´-DIMETHYL-2,2´-BITHIOPHENE OBTAINED AT B3LYP LEVEL

Basis set	6-31G	6-31G*	6-31G**
S(1)-C(2)	1.834	1.759	1.758
C(2)-C(3)	1.376	1.376	1.376
C(3)-C(4)	1.437	1.432	1.432
C(4)-S(5)	1.367	1.370	1.370
S(1)-C(5)	1.798	1.735	1.735
C(2)-C(2´)	1.441	1.455	1.455
S(1)-C(2)-C(3)	109.2	109.9	109.9
C(2)-C(3)-C(4)	115.7	114.3	114.3
C(3)-C(4)-C(5)	112.6	111.5	111.6
C(4)-C(5)-S(1)	112.5	112.5	112.5

The comparison with the data reported in Tables 3 and 5 shows that the change on the geometrical parameters is negligible when passing from the 3,3'- to 3,4'-isomer. The only significant is a shortening of the inter-ring distance [C(2)-C(2')] in the 3,4'-isomer which is due to the increase of conjugation associated with the degree of co-planarity of the two rings.

Present results are in good accordance with the experimental observations. In particular, the change of the rotational distortion when passing from the 3,3'- to 3,4'-isomer (θ decreases from 58.2° to 39.8° for the *syn-gauche* conformer and increases from 110° to 145.6° for the anti-*gauche* conformer) explains very well the ipsochromic effect theoretically calculated and experimentally observed[18] for the dimethylbithiophenes (Table-6) and for the polymers using the 3-hexylthiophene and the 3,3'-dihexylthiophene-2,2'-bithiophene (Table-1). Similar information has been obtained in a solid state for the poly(3-methylthiophene) formed by 3'-dimethyl-2,2'-bithiophene (λ_{max} = 417 nm) and 3,4'-dimethylbithiophene (λ_{max} = 508 nm)[18].

TABLE-6
CALCULATED AND EXPERIMENTAL UV-VISIBLE FOR DIMETHYLBITHIOPHENES. IPSOCHROMIC EFFECT OF ALKYL SUBSTITUENTS

Compound	Calcd. (ZINDO)			Exp. λ_{max} (solution)
	6-31G	6-31G*	6-31G**	
3,3´-Dimethyl-2,2´-bithiophene	302.44	301.61	301.65	268 nm
3,4´-Dimethyl-2,2´-bithiophene	336.73	317.195	317.21	299 nm

Conclusion

This study shows that the regioregularity of substituted polythiophenes has a great influence on its conformational and optoelectronic properties. The absorption maximum (λ_{max}) decreases as much more the polymer has a big percentage of head-to-head junctions. As indicated by DFT calculations, the backbone of the two dimers is not planar but tilted to a different extent as results of steric effects of substituents. With the 3,3'-dialkyl-2,2'-bithiophene more twisted than the 3,4'-dialky-2,2'-bitiophene. This is accounted for by the greater inter-ring distance of the former compared to that of the latter.

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