[g004]

DFT study of the effect of hidrocarbonated chains on the electronic properties of some oligothiophene derivatives

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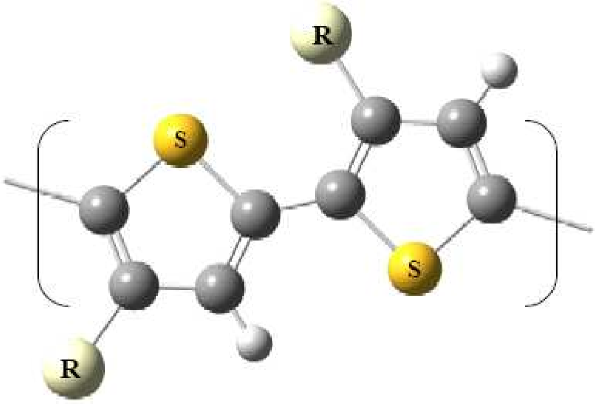
ABSTRACT: In this work, we have studied from a theoretical perspective the electronic properties such as HOMO → LUMO excitation energy, ionization potential and reorganization energy of oligotiophenes and their alkyl and alcoxy derivatives. The effect of charge injection was also studied. The oligomeric approximation was employed in order to calculate the band gap and ionization potential of an ideal polymeric chain for each one of the selected systems. The variation of reorganization energy on the backbone length was also analyzed.

INTRODUCTION

Polythiophenes are ones of the most versatile and studied family of conjugated materials. These compounds often have great possibilities to change and finetune their properties by playing with substituents, molecular weight distribution, regioregularity, doping, etc. An improved understanding and better control of organic semiconductor properties, combined with a fairly simple manipulation, a large-scale and a low-cost deposition from solution make conjugated polymers a promising choice for building electroactive devices such as transistors displays, and solar cells.

The major development of polythiophenes was due to the improved processability achieved when substituted in position 3 (figure 1). Thus, polythiophenes substituted with electron-donating alkyl pendant chains, which display high solubility together with good electrical and optical properties, exhibit a reduced bandgap, as well as lower redox potentials. Other interesting substituents are alcoxylic chains, which display the advantage of an easier dopability and thus a higher stability of the conducting state due to the electron releasing property of the alkoxy group.

Here, we have studied from a theoretical perspective the molecular electronic properties of three families of oligothiophenes i.e native oligothiophene, head-to-tail oligo-3-hexyl-thiophene and head-to-tail oligo-3-hexoxythiophene (see figure 1). The aim of this work is the analysis of the effects that different pendant substituents bring on the electrical properties, aromaticity, π-delocalization and impact of charge injection.



PT: R = H
P3HT: R = Hexyl: $(CH_2)_5CH_3$
P3OHT: R = Hexoxy: $O(CH_2)_5CH_3$
From dimer to hexamer

Figure 1. Three families of selected compounds.

This will allow us to carry out a comparative analysis of the effect of alkylic and alkoxylic chains on polythiophenes. For this challenge, B3LYP method and 6-31G***** and 6-31+G* basis sets have been tested. 6-31+G* basis set was employed for a more precise calculation of the energy-related properties such as HOMO→LUMO excitation energy, ionization potential and intramolecular reorganization energy over the geometry optimized at B3LYP/6-31G*.

All molecules were optimized fixing inter-ring dihedral angles in order to guarantee planarity of the backbone, since it is known that thiophene oligomers are planar in crystal

HOMO → LUMO EXCITATION ENERGY AND BANDGAP

The bandgap was studied through the HOMO → LUMO excitation energy by means of time dependent B3LYP (TD-B3LYP) with 6-31+G* basis set on the corresponding ground state geometry optimised at the B3LYP/6-31G* level. Bandgaps of the ideal polymeric chain were calculated using the oligomeric approximation. Figure 2 shows the bandgap of energy *vs.* the inverse of the number of thiophene rings for the series of studied oligomers. The linear fit of these plots allows calculate the energy bandgap for an ideally infinite polymeric chain. The corresponding values for the oligomer and polymeric chain appear in Table 1.

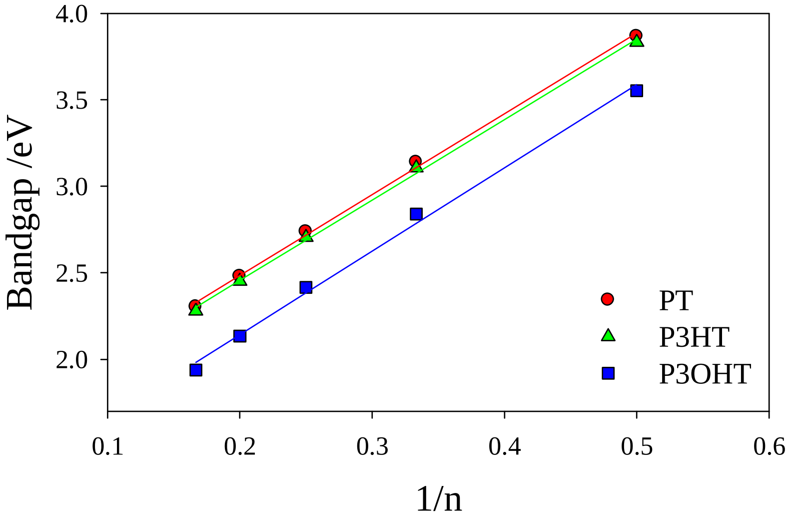


Figure 2. Energy bandgap vs. 1/n (n, number of thiophene rings)

Table 1. Calculated bandgap of energies (eV) in oligomeric approximation.

	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Polymer Chain	R^2
PT	3.87	3.14	2.74	2.48	2.30	1.55	0.99
P3HT	3.83	3.11	2.70	2.45	2.28	1.53	0.99
P3OHT	3.55	2.84	2.42	2.14	1.94	1.18	0.99

The introduction of both, alkylic and alkoxylic chains produce a decrease on the band gap respect to PT being of ~ 0.02eV for P3HT and ~ 0.37eV for P3OHT.

IMPACT OF CHARGE INJECTION

The impact of charge injection (doping) was analyzed by means of the variation in the inter-rings bond length, which are correlated with the aromaticity and π-delocalization along the backbone of the oligomers. The variation of bond length was studied for the hexamer of each system in neutral and cationic (polaronic) states. Table 2 collects inter-rings bond lengths calculated at B3LYP/6-31G* level for neutral and cationic states of different hexamers and their differences; figure 3 shows the bond numbering.

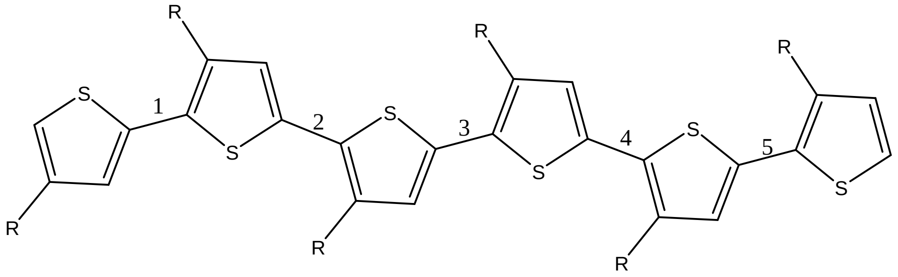


Figure 3.- Hexamer arrangement of thiophene showing inter ring bond numbering.

Table 2. Inter-rings bond lengths and their differences for neutral and polaronic states calculated at B3LYP/6-31G* of each hexamers.

INTER-RING BOND LENGTHS / Angströms						
		1	2	3	4	5
PT	NEUTRAL	1.446	1.441	1.441	1.441	1.446
	POLARONIC	1.432	1.418	1.414	1.418	1.432
	DIFFERENCE	0.014	0.023	0.027	0.023	0.014
P3HT	NEUTRAL	1.451	1.447	1.446	1.447	1.451
	POLARONIC	1.437	1.422	1.418	1.423	1.438
	DIFFERENCE	0.014	0.025	0.028	0.024	0.013
P3OHT	NEUTRAL	1.441	1.435	1.434	1.435	1.441
	POLARONIC	1.420	1.416	1.406	1.416	1.420
	DIFFERENCE	0.021	0.019	0.028	0.019	0.021

The variations of inter-rings bond lengths for neutral and polaronic states of each hexamers are displayed in Figure 4.

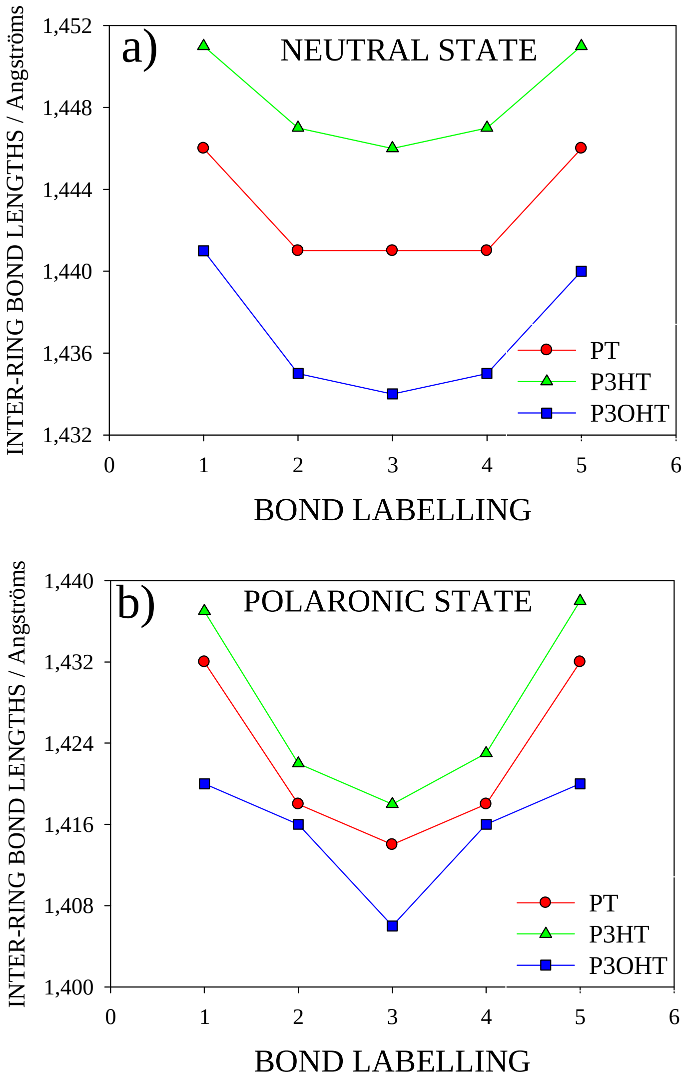


Figure 4. Variation of bond lengths between thiophene rings of neutral (a) and cationic (b) states.

Accordingly, the central, inter-rings bond for the system in the neutral state shows a somewhat higher character of double bond, which is bigger for P3OHT and smaller for P3HT. When the system is oxidized (polaron), the simple bonds become shorter, while the double ones become longer. As it can be seen in figure 4 the increase of partial, double bond character on the central, inter-rings bond is higher in the polaronic state a quinoid-like distortion emerging as a result of the oxidation process.?. All these effects are more remarkable for P3OHT.

IONIZATION POTENCIAL AND REORGANIZATION ENERGY

These conductive materials belong to the so-called *p-type*, wherein the hole-hopping process is generally described as a self-exchange electron-transfer reaction between neighbouring molecules. Ionization potential (IP) and intramolecular reorganization energy (λ_i) are magnitudes that need to be tuned during the design of polymers in order to obtain efficient charge injection and high electron transfer rate according to the semi-classical Marcus equation. One of the key parameters in this process is the reorganization energy (λ_i) that consists of two terms corresponding to the geometry relaxation energies upon going from the neutral-state geometry to the charged-state geometry and *viceversa*:

$$\lambda_i = \lambda_1 + \lambda_2 \tag{1}$$

λ_1 and λ_2 can be calculated directly from the adiabatic potential energy surface as:

$$\lambda_1 = E_0(G_+) - E_0(G_0) \tag{2}$$

$$\lambda_2 = E_+(G_0) - E_+(G_+) \tag{3}$$

where $E_0(G_0)$ and $E_+(G_+)$ are the ground-state energies of the neutral and polaronic states, respectively; $E_0(G_+)$ and $E_+(G_0)$ are the energy of the neutral molecule at the optimal polaronic geometry and the energy of the ion state at the optimal geometry of the neutral molecule. Once calculated λ_2, we can calculate the vertical ionization potential (VIP) as:

$$VIP = AIP + \lambda_2 \tag{4}$$

where AIP (adiabatic ionization potential) defined as:

$$AIP = E_+(G_+) - E_0(G_0) \tag{5}$$

Figure 5 plots the potential energy surfaces for the neutral and charged molecular states.

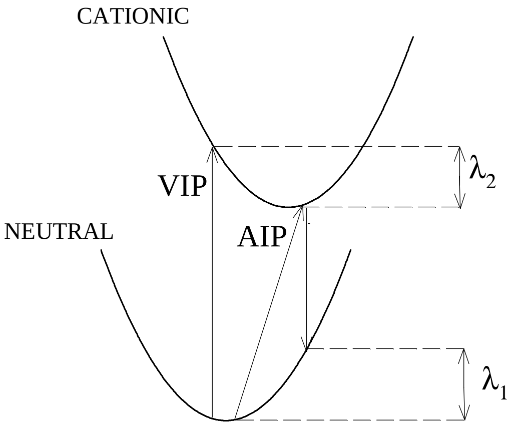


Figure 5: Potential energy surfaces for the neutral and charged molecular states.

Vertical ionization potencial (VIP) and reorganization energy (λ_i) *vs.* number of thiophene rings were plotted to estimate VIP (see figure 6) and λ_i (see figure 7) of an ideal polymeric chain. Table 3 shows the ionization potential and reorganization energy of each oligomer and polymeric calculated at B3LYP/6-31+G*.

Table 3. Calculated Vertical Ionization Potential (eV) and Reorganization Energy calculated at B3LYP/6-31+G*

	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Polymer Chain	R^2
			Vertical Ionization Potential				
PT	7.46	6.84	6.48	6.23	6.06	5.40	0.99
P3HT	7.07	6.45	6.10	5.86	5.73	5.53	0.99
P3OHT	6.62	5.96	5.56	5.29	5.10	4.78	0.99
			Reorganization energy				
PT	0.36	0.32	0.29	0.27	0.25	0.20	0.99
P3HT	0.37	0.33	0.30	0.28	0.26	0.20	0.99
P3OHT	0.45	0.39	0.36	0.34	0.33	0.31	0.99

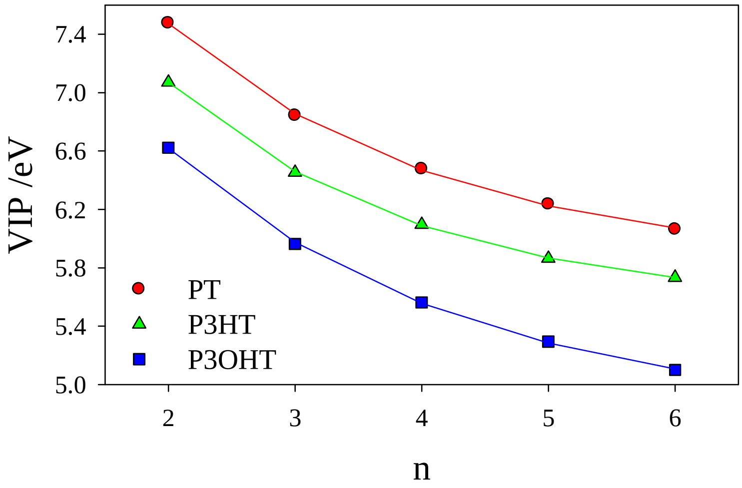


Figure 6. VIP *vs.* n, (n, number of thiophene rings).

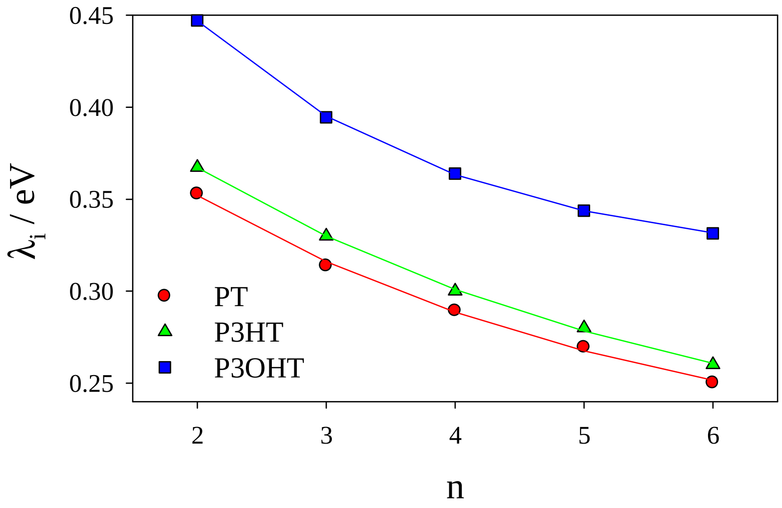


Figure 7. λ_i *vs*. n, (n, number of thiophene rings).

The introduction of alcoxylic chain reduces IPs of polythiophene in a greater extension than alkylic chain. Therefore, it can be expected a more efficient charge injection of the first kind of substituent. This diminution of IP is due to the inductive effect of alkylic chains, which only shows effect along two or three bonds for P3HT. For P3OHT this decrease is also due to the electron-donor effect of the oxygen atom, too. Both kinds of substituents increase λ_i. However P3HT shows a λ_i very close to PT. λ_i is related with the charge transfer rate constant and low values of λ_i are needed in order to get a high electron transfer. In all situations the representation of λ_i or VIP as a function of n can be fitted to a exponential function defined as equation (6) which allows us to calculate λ_i and VIP of ideal polymeric chains (see table 3).

$$y = y_0 + a\exp[-bn] \qquad (6)$$

CONCLUSIONS

Introduction of alcoxylic chains in position 3 produces the same effect that alkylic chain in properties such as solubility or easy processability. Nevertheless, the oxygen atom provides improved electrical properties respect to PT, since P3HOT shows a low band gap and low VIP. However, P3OHT show a λ_i higher than PT and P3HT.

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