



Electroactive Materials Based on Thiophen: Study of the Doping and its Effect

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Abstract

We have theoretically investigated the effect of doping in oligothiophenes (T_n, n=2-8) with the DFT method at UB3LYP level with 6-31G(d) basis set. Our attention focused on the study of the geometrical and electronic properties in the neutral and doped states. We show that the doping process modify both bond lengths and torsion angles and also electronic properties by enhancing the planarity and decreasing the band Gap.

Keywords: *Conjugated oligomers, Doping, Oligothiophene, DFT, Polaron, Bipolaron.*

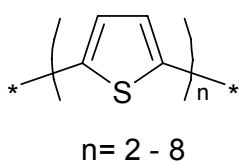
Introduction

Polythiophene and its oligomers are almost the most intensively studied conducting polymers because of their good environmental stability in both the neutral and doped states [1,2], These materials have attracted much interest for potential application in optoelectronic devices to their electronic and photonic properties [2]. Whereas polythiophenes obtained as highly amorphous, oligothiophenes are not amorphous and can be synthesized as well defined compounds. Moreover, these

oligomers provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in parent polymers [3]. These materials are currently under intensive investigation for application in the film transistors [4], electroluminescent diodes [5], lasers [6], sensors [7] and photovoltaic cells [8]. In this regard, theoretical studies of oligothiophenes certainly facilitate the knowledge of the polymeric structure. Smallest oligomers can play also an important role in

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understanding charge transport mechanism and physical properties of polymers. In this work, we are going to carry out the DFT calculations and to discuss the structural and electronic properties of neutral and doped oligothiophenes ($n=2-8$). The results are discussed in comparison with the properties of the doped oligomers.



Scheme 1. Polythiophene structure.

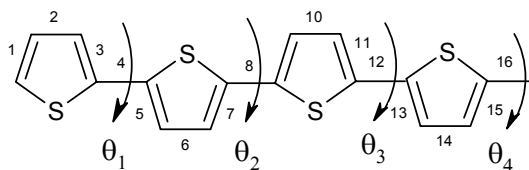
Methodology

DFT method of three-parameter compound of Becke (B3LYP) [9] was used in all the study of the neutral, polaronic and bipolaronic oligothiophene. The 6-31G* basis set was used for all calculations [10–13]. The conformational analysis for the neutral structures was done by changing the torsional angles θ between adjacent thiophene rings by 20 steps in the same direction. To obtain the final torsional angle of the conformation

in each minimum, calculations of these geometries were performed without constraint on the dihedral angles. To obtain the charged oligothiophene structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [14].

Results and discussion

The conformational analysis for all oligomers in their neutral state was done by changing the torsional angles between adjacent thiophene rings by 20 steps in the same direction. The geometries were fully optimized at each point. For each oligomer, the optimised structure at the neutral state was used as a starting file for the optimization of the structure in polaronic state. The HOMO, LUMO and gap energies were also deduced for the stable structure of the neutral and oxidized forms. The results of the torsion potential of the oligothiophene (bithiophene (2T), terthiophene (3T), quaterthiophene (4T), quinquethiophene (5T), sexithiophene (6T), septathiophene (7T) and octathiophene (8T) calculated at B3LYP/6-31G* level are presented in Figure 1.



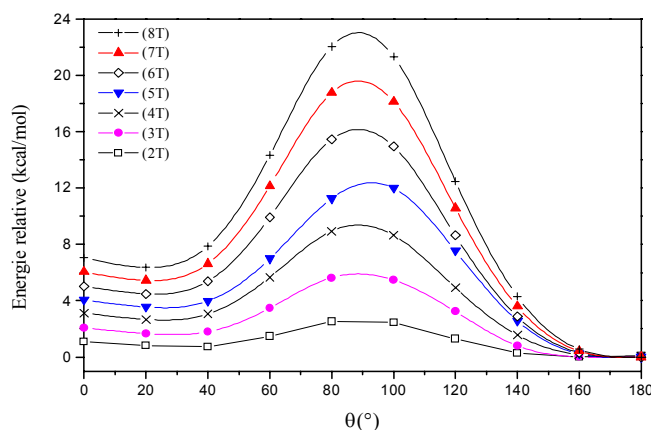


Figure 1. Potential energy curves of oligothiophenes as obtained by B3LYP/6-31G*.

The optimized geometric structures of the neutral oligomers show that all the thiophene rings present the same geometry. They present four extrema, two maxima situated respectively at 0 and 90 and two minima located at about 29° and 180°. The torsional angles and barriers to internal rotation depend on the balance of two interactions: as a consequent of the π -electrons conjugation between the thiophene rings, the molecules tend to remain planar, whereas the

steric repulsion between hydrogen's causes the molecules to twist. For a fixed angle θ , the relative energy for the superior oligomer is greater than that of the inferior one, i.e. the energy-minimal conformation is more stable when the oligomeric chain length increases. The structural modifications progressively decrease away from the center oligomer, illustrated in (Figure 2 and 3).

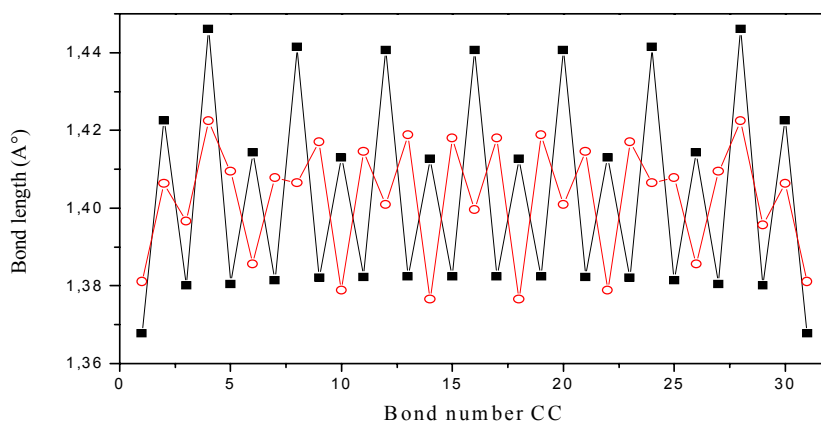


Figure 2. Optimized CC bond lengths of neutral oligothiophene (filled squares) and of oligothiophene as radical cation (open circles) calculated by the B3LYP/6-31G*.

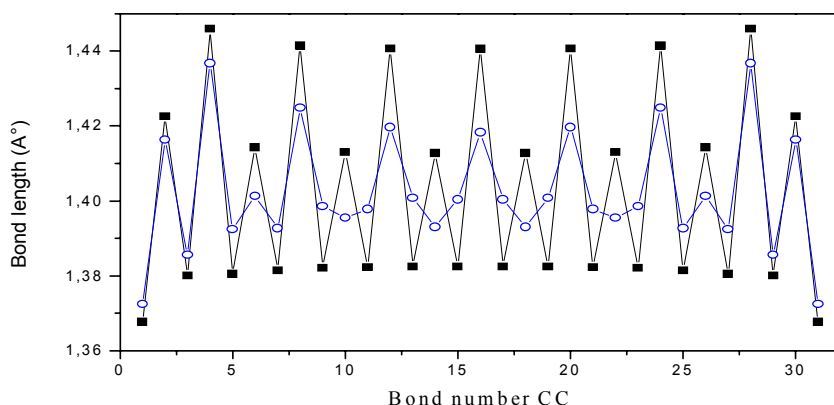


Figure 3. Optimized CC bond lengths of neutral oligothiophene (filled squares) and of oligothiophene as diradical cation (open circles) calculated by the B3LYP/6-31G(d).

When compared too neutral oligomers, the bonds become shorter, while the double ones become longer. The inter-rings bonds are longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation. The region with a clearly distinct quinoid structure extends over four–six thiophene rings, which is consistent with the ab-initio HF and DFT calculations performed by J. Casado et al. [15] for substituted oligothiophenes. The optimized geometry of the dicationic oligothiophene indicates the formation of the positive bipolaron defect localized in the middle of the molecule and extending over the adjacent repeat units. The charged species are characterized by a reversal of the single double C-C bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule (Figure 4).

Structural parameters of the octathiophene

(8T) in its quinoidic form (polaronic and bipolaronic) indicate that the cycles at the ends preserve their aromatic character, whereas the central processing units present a quinoid character. For the oxidized octamer (8T^{••}), the four innermost rings are characterized by quinoidic structure. This is summarized on Figure 4. The values of the energy of the HOMO, LUMO, ΔE_N (HOMO, LUMO) energies are shown in Table 1 for several oligomers in their neutral, polaronic and bipolaronic forms, respectively. Available values of the gap energy of polymer in neural state [17, 18] are presented also in this Table for comparison. The oligomer with eight rings in its aromatic state has the particularity of having a gap (2.41 eV) close to that of the polymer (2.30 eV) [17, 18] we not that the energy gap decrease when passing from the neutral to the doped form for it oligomers.

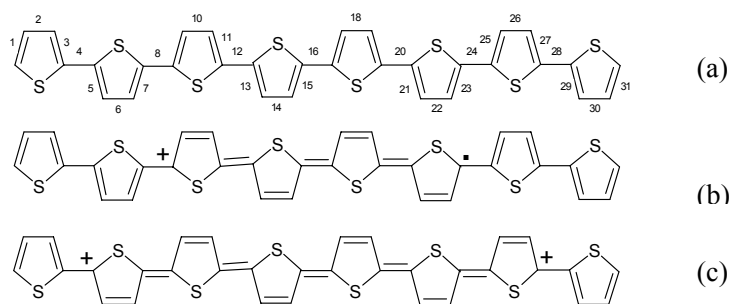


Figure 4. Simplified neutral (a), polaron (b) and bipolaronic (c) structures.

Table 1. The HOMO, LUMO, ΔE_N (HOMO, LUMO); values of energy (eV) of the several oligomers, respectively in their neutral, polaronic and bipolaronic forms.

	HOMO (eV)	LUMO (eV)	Gap (eV)	Gap (eV) exp.
8T	-2.30	-4.71	2.41	(2.3-2) [18-19]
8T+	-7.13	-6.29	0.84	-
8T++	-9.39	-8.56	0.82	-

Comparatively with the work carried out by Diaz et al. [16], the combined systems longest are most stable. Moreover, during oxidation (or doping), a formed radical cation is stable by resonance. After the oxidation of the sexithiophene (6T), one notes the total extinction of the absorption band (2.61eV) at the same time two new bands appear (2.30eV and 0.56eV). These bands allotted to the radical cation of sexithiophene. After the second oxidation a new band appears with 0.91eV. This new band is allotted to the

dication of 6T++. These data compared with the energies of transition obtained by Fichou et al. [17] for neutral, polaronic and bipolaronic sexithiophene are respectively 2,87 eV, (1,59 and 0,84 eV) and 1.24 eV are in concord. The technique of orbital molecular was used to explain the appearance of these new bands since it acts here not of a polymer, but of a molecule of finished size. During oxidation, the molecule undergoes a deformation, which leads to a reorganization of the energy levels of orbital molecular as famous Figure 5.

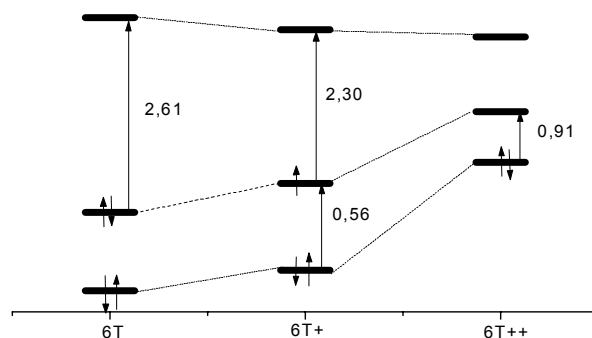


Figure 5. Reorganization of the energy levels of orbital molecular at the time of the oxidation of the hexathiophene (6T), the values of the energy transitions are given in eV.

Finally and based on the optimized molecular structures with B3LYP/6-31G (d) method, we have calculated the UV-vis spectra of the compound T8 using TD-DFT method (see Figure 6). This method has been used to obtain the energy of the singlet-singlet electronic transitions and absorption properties. All electronic transitions are of the $\pi-\pi^*$ type and no localized electronic transitions are exhibited among the calculated singlet-singlet transitions. Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from the $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO \rightarrow LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition. The absorption spectrum of the studied compound T8 shows a maximum absorption wavelength at 430.10 nm. This value is calculated by TD method starting with optimized geometry obtained at B3LYP/6-31G(d) level. However, we believe that the bulk of intermolecular effect must be taken into account when considering the polymers with long chain. After considering this effect, our calculations are in good agreement with the experimental values

($\lambda_{\max} = 453\text{nm}$). The deviation between the calculation and the experiment data is not more than 35 nm. Therefore, the procedures of theoretical calculations give good descriptions of opto-electronic properties of the proposed oligomer T8 and can be employed to predict the electro-luminescence characteristics of other materials.

On the other hand and in order to study the emission photoluminescence properties of this compound, the TD-DFT/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the TD-DFT level with 6-31G(d) basis set. The normalized photoluminescence (PL) spectrum shows a maximum at 668.65 nm. The observed red-shifted emission of the PL spectra is in reasonable agreement with the obtained results of absorption. We can also note that relatively high value of Stokes Shift (SS) are obtained for this compound (238.55 nm). In fact, the Stokes shift, which is defined as the difference between the absorption and emission maximums, is usually related to the bandwidths of both absorption and emission bands [20]. These results lead us to suggest that the proposed structure is a good model to reflect optoelectronic properties for the parent polymer.

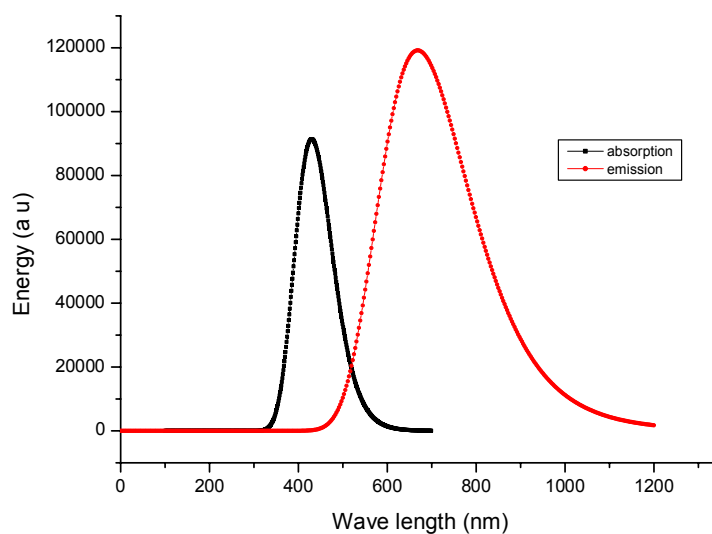


Figure 6. UV visible and emission spectra of polythiophene T8 obtained TD-DFT level.

Conclusion

The most stable conformation in the neutral form is the anti-planar conformation. For polaron and bipolaron oligomers, the obtained structures are completely planar. The gap energy calculated with the same method decreases with the chain length from the dimer to the octamer, and when passing from the neutral to the doped form for each oligomer. The quinoidic character is more accentuated when a second electron is removed. The Gap energy value of the octamer is very close to those of polythiophene as measured experimentally. These results and the calculated absorption and emission properties of the octathiophene (T8) lead us to suggest that this oligomer is a good model to reflect optoelectronic properties for the parent polymer.

Acknowledgements

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