J. Mater. Environ. Sci. 3 (2) (2012) 286-293
ISSN : 2028-2508
CODEN: JMESCN

Density Functional Theory Study of new materials based on thiophene and oxathiazole in their neutral and doped states.

H. Toufik [1], S.M. Bouzzine [2], F. Lamchouri [4], M. Nawdali [1], M. Hamidi [2], M. Bouachrine [1]*

[1]*UMIM, Faculté Polydisciplinaire de TAZA, BP. 1223, Place de la gare Taza Maroc*
[2]*UCTA, Faculté des Sciences et Techniques, B. P. 509 Boutalamine, Errachidia, Maroc;*
[3]*LIMAO, Faculté Polydisciplinaire de Taza BP. 1223, Place de la gare Taza Maroc*
[4] *Equipe de Recherche « Substances Naturelles & Environnement » Faculté Polydisciplinaire de Taza BP. 1223, Taza Maroc*

Received 28 Oct 2011, Revised 4 Jan 2012, Accepted 4 Jan 2012

*Corresponding authors. Email: bouachrine@gmail.com

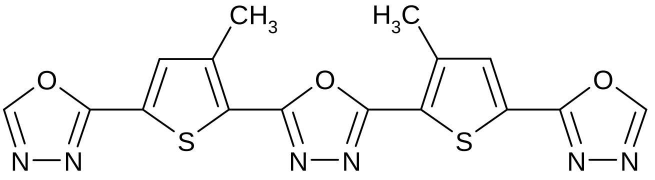
Abstract

We have investigated the effect of doping in new conjugated compounds based on thiophene and oxathiazole with the DFT method at UB3LYP level with 6-31G(d) basis set. Our attention focused on the study on the geometries and electronic properties in neutral and doped state. The absorption properties were determined by ZINDO/s, CIS/6-31G(d) and TD//B3LYP/6-31G(d) calculations. The effects of doping, the ring structure and the substituent on the geometries and electronic properties of these materials are discussed. 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. The results suggest these compounds as good candidates for opto-electronic applications.

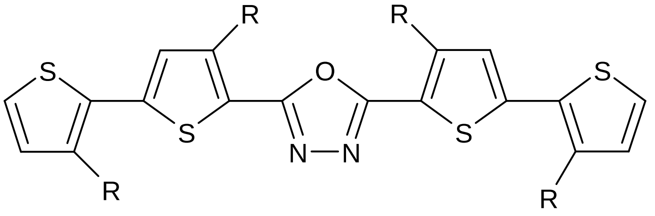
Key Words: Conjugated polymers, thiophene, oxadiazole neutral and doped states, DFT, electronic properties.

I. Introduction

Organic π-conjugated polymers and 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 du to their electronic and photonic properties [2]. Whereas polymers obtained as highly amorphous, small oligomers are not amorphous and can be synthesized as well defined compounds. Moreover, theses oligomers provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in parent polymers [3]. On the other hand oligomers based on mixed heterocyclic compounds in which electron-donating units coexist with electron- withdrawing ones in the polymer main chain were studied [4]. 1.4.4-oxadiaozole considered as important five-membred compound among the large heterocyclic families, has been studied as excellent candidate for material applications during the past years due to its excellent thermal, chemical stabilities and high photoluminescence quantum yields [5]. However, the processing of these materials is limited by their insolubility. This problem was resolved by the incorporation of side chains into thiophene. Unlike unsubstituted oligomers, the substituted ones are soluble and this solubility facilitates their characterization and widens their applicability [6]. These materials are currently under intensive investigation for many applications in optoelectronic. One of the most important factors of controlling physical properties is the band gap (Eg), which is a current topic of research. In particular, materials with a low band gap are desired in optoelectronic applications [7]. Many ways have been used to modulate this parameter as the modification of chemical structure or doping process. A better understanding of the electronic and optical properties of these new materials requires knowledge of their conformations and electronic structures. More importantly, these properties can be tuned by different substituent in several positions. On the other hand, theoretical calculations provide a lot of useful information that help chemists to build up a good relationship between structure and properties of these materials. In this regard, theoretical studies of oligothiophenes certainly facilitate the knowledge of polymeric structure. Smallest oligomers can play also an important role in 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). In this work, the theoretical analysis on the geometries and electronic properties of conjugated compound based on thiophene and oxadiazole {OxTOxTOx(CH_3); TTOxTT; TTOxTT(OMe); TTOxTT(CN); TTOxTT(F); TTOxTT(CH_3)} is reported, as shown in Fig.1. Some of these new series of organic compounds have been successfully recently synthesized [8]. The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G(d) basis set. The effects of the ring structure and the substituent on the geometries and electronic properties of these materials were cited in details in another work [9]. The results are discussed in comparison with the properties of the doped compounds.



OxTOxTOx(CH_3)



R= R_1: TTOxTT(OMe) ; R_2 : TTOxTT(CN); R_3 : TTOxTT(F) ;
R_4 : TTOxTT(CH_3) ; R_5 : TTOxTT

Figure. 1: Studied compound

2. Methodology

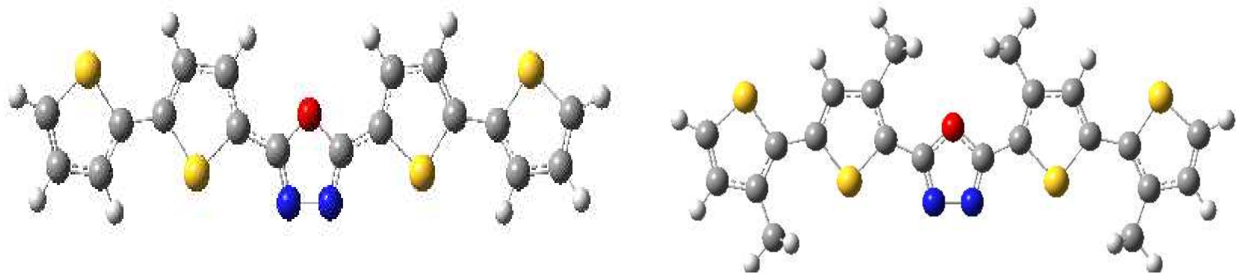
DFT method of three-parameter compound of Becke (B3LYP) [10] was used in all the study of the neutral, polaronic and bipolaronic oligomers. The 6-31G(d) basis set was used for all calculations [11–14]. To obtain the charged oligothiophene structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [15]. The geometries structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the ZINDO/s, CIS/6-31G(d) and TD-DFT(B3LYP/6-31G(d)) calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated polymers [16].

3. Results and discussion

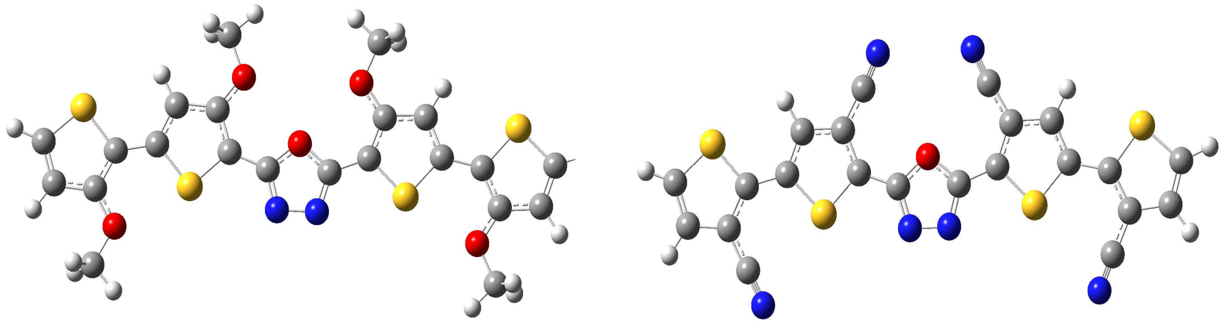
3.1 Geometric properties

For all molecules, geometrical parameters were obtained after total optimization by B3LYP/6-31G (d). It was found that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. To investigate the effect of the substituents on the geometries and electronic properties, the optimized structures of several substituted oligomers built on thiophene and oxadiazole {TTOxTT(Me), TTOxTT(OMe), TTOxTT(CN) and TTOxTT(F)} were compared with the unsubstituted one TTOxTT. On the other hand, to investigate the effect of the ring structure, the optimized structures and the electronic properties of compound TTTTT(Me) were compared with those of TTOxTT(Me). The results of the optimized structures for all studied compounds show that they have similar conformations (quasi planar conformation) (see Fig. 2). We found that the consecutive units have similar dihedral angles (180°) and inter-ring distances (1.443 Å). The incorporation of several groups does not change these parameters.

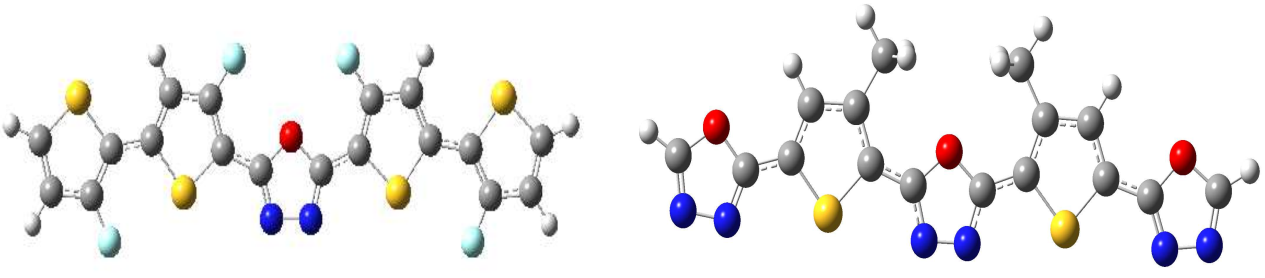
In addition, since the p-doped π-conjugated molecule becomes the ultimate responsible of charged transport, it is interesting to study this phenomenon in our case. As said before, to obtain oxidized optimized structure, we started from the optimized structure of the neutral form.



TTOxTT TTOxTT(CH_3)



TTOxTT(OMe) TTOxTT(CN)



TTOxTT (F) OxTOxTOx(CH_3)

Figure 2 : Optimized structures of studied oligomers.

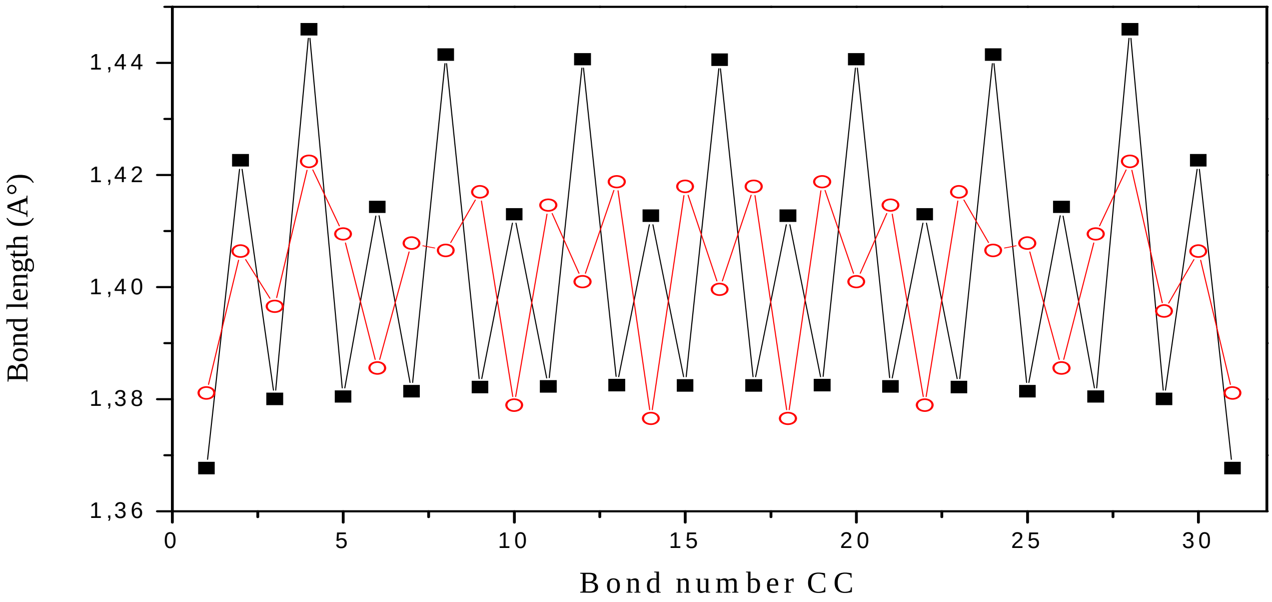


Figure 3: Optimized CC bond lengths of neutral compounds OxTOxTOx(Me) (fille squares) and of its radical cation (open circles) calculated by the B3LYP/6-31G(d).

Table 1 : Geometric parameters of compounds OxTOxTOx(Me) obtained by B3LYP/6-31G(d).

di (Å)	Neutre	Dopé $_1$	Dopé $_2$
d_1	1.29098	1.29967	1.31659
d_2	1.39520	1.37853	1.35394
d_3	1.30233	1.30785	1.32064
d_4	1.44024	1.43175	1.41643
d_5	1.37804	1.39563	1.41670
d_6	1.41930	1.39948	1.38211
d_7	1.38951	1.41623	1.44375
d_8	1.43886	1.40760	1.38047
d_9	1.30595	1.33755	1.37637
d_{10}	1.37782	1.33112	1.28755
d_{11}	1.30595	1.33755	1.37637
d_{12}	1.43886	1.40760	1.38047
d_{13}	1.38951	1.41623	1.44375
d_{14}	1.41930	1.39948	1.38211
d_{15}	1.37804	1.39563	1.41670
d_{16}	1.44024	1.43175	1.41643
d_{17}	1.30233	1.30785	1.32064
d_{18}	1.39520	1.37853	1.35394
d_{19}	1.29098	1.29967	1.31659

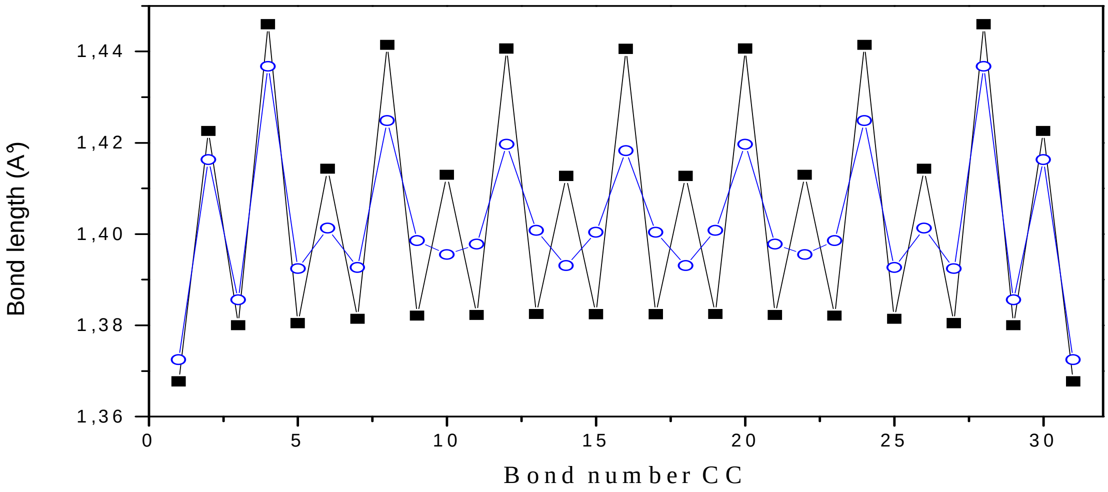


Figure 4: Optimized CC bond lengths of neutral compound OxTOxTOx(Me) (filled squares) and its diradical cation (open circles) calculated by the B3LYP/6-31G(d).

We can conclude that during the doping process and for all studied compounds the simple 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. These results are consistent with the ab-initio HF and DFT calculations performed by J. Casado et al. [17] and S.M Bouzzine et al [18] for substituted oligothiophenes. The optimized geometry of the dicationic oligomers 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 5).

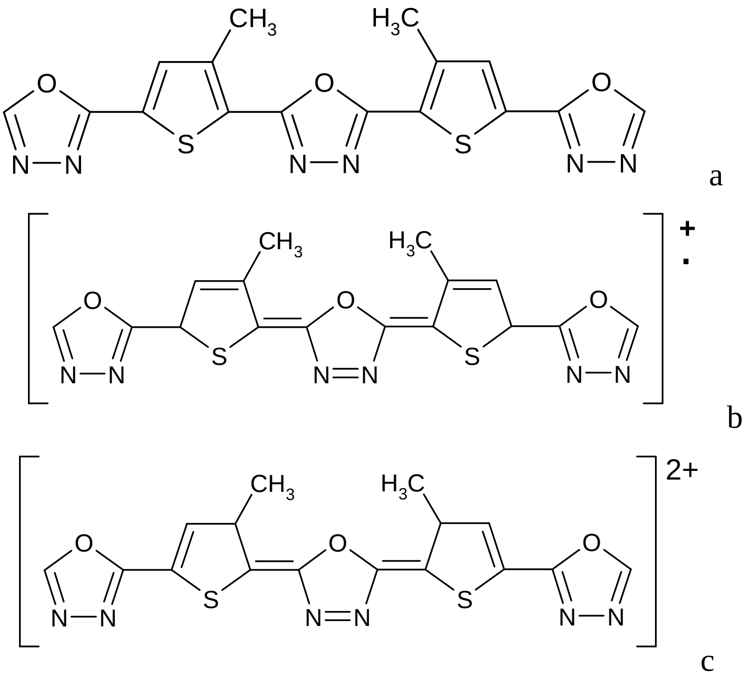


Figure 5: Simplified neutral (a), polaron (b) and bipolaronic (c) structures.

The band gap of TTOxTT(OMe), is much smaller than that of the other substituted compounds. This may be attributed to the number of electron-donating methoxy side groups and also to the Coulombic interaction between sulphur of thiophene and oxygen atoms [19]. Concerning the comparison between the last two compounds TTTTT(Me) and TTOxTT(Me), it suggests that the replacement of thiophene ring in

TTTTT(Me) by oxadiazole leads to the stabilisation of both the HOMO level and LUMO levels with increase in the energy Gap. This is in agreement with what it was found in the cases of TTTTT and TTOxTT and with the experimental results [8].

Table 2 lists the theoretical electronic parameters of the studied conjugated compounds. In the case of compounds TTOxTT(Me) and TTOxTT(OMe), one remark that they exhibit destabilization of the HOMO and LUMO levels in comparison with those of unsubstitued one (TTOxTT) due to electron-donating substitution of methoxy and methyl groups; while in the case of TTOxTT(CN) and TTOxTT(F), there is a net stabilization of the HOMO and LUMO levels. However, these compounds have a smaller energy gap Eg than the unsubstituted one, which is due to the presence of different substituent as described previously [8].

Table 2: Values of HOMO (eV), LUMO (eV) and Eg (eV) energies calculated for, TTTTT TTOxTT, TTTTT(Me), TTOxTT(Me), OxTOxTOx(Me), TTOxTT(OMe), TTOxTT(CN), TTOxTT(F) obtained by B3LYP/6-31G(d).

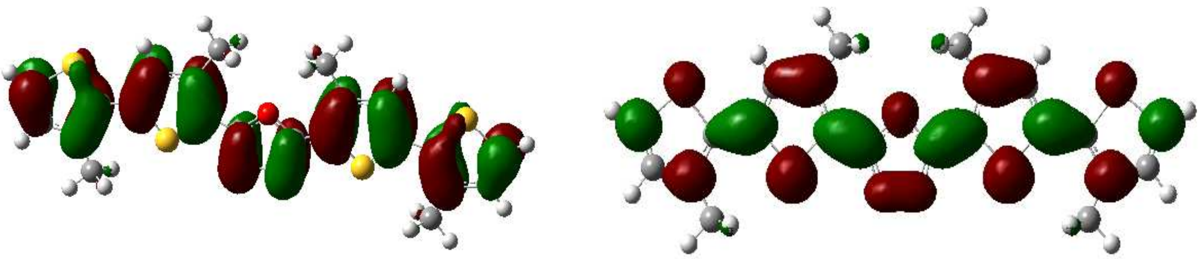
compounds	E_{HOMO}/eV	E_{LUMO}/eV	E_{gap}/eV
TTTTT	-4.860	-2.080	2.78
TTOxTT	-5.414	-2.166	3.24
TTTTT (Me)	-4.626	-1.853	2.72
TTOxTT (Me)	-5.125	-1.980	3.14
OxTOxTOx (Me)	-6.046	-2.638	3.40
TTOxTT (OMe)	-4.540	-1.560	2.98
TTOxTT (CN)	-6.246	-3.255	2.99
TTOxTT (F)	-5.452	-2.212	3.23

On the other hand and since the p-doped π-conjugated molecule becomes the ultimate responsible of charged transport, the values of the energy of the HOMO, LUMO, ΔE_N(HOMO, LUMO) for several compounds in their neutral, polaronic and bipolaronic forms were determinate and presented in table 3. Available values of the gap energy in neural state are presented also in this Table for comparison. Traditionally and until now, charged stated in conjugated molecules have been discussed in terms of one-electron band model. We note that the energy gap decreases when passing from the neutral to the doped form for all oligomers.

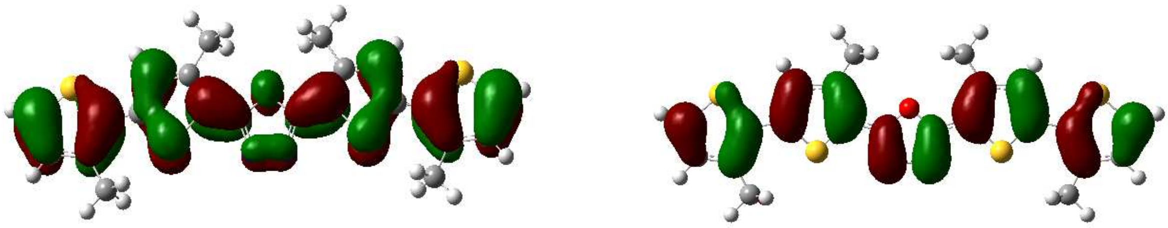
Table 3: Values of Gap energy (eV) of the several oligomers, respectively in their neutral, polaronic and bipolaronic forms.

compouds	Egap (eV) Neutral form	Egap (eV) Polaronic form	Egap (eV) Bipolaronic form
OxTOxTOx(Me)	3,40	3,11	1,56
TTOxTT(CN)	2,99	2,73	1,28
TTOxTT(Me)	3,14	2,87	1,39
TTOxTT(F)	3,23	2,97	1,42
TTOxTT	3,24	2,90	1,25
TTOxTT(OMe)	2,98	2,82	1,53
TTTTT	2,78	2,56	1,65

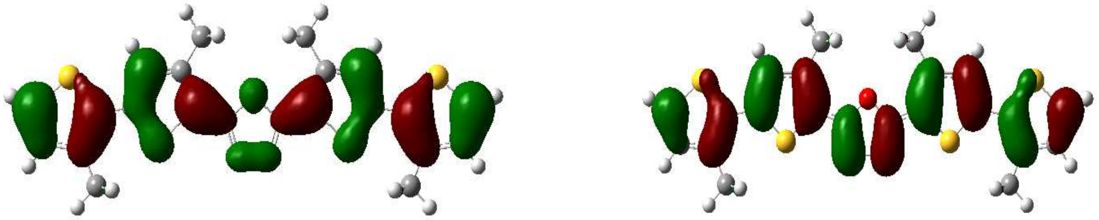
Finally, it is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [21]. In general, as shown in Fig 6 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π-bonding character within subunit and a π-antibonding character between the consecutive subunits while the LUMOs possess a π-antibonding character within subunit and a π-bonding character between the subunits whereas it is the opposite in the case of doped forms



Neutral form



Polaronic form



Bipolaronic form

Figure 6: The contour plots of HOMO and LUMO orbitals of TTOxTT (Me),

4. Conclusion

In this study, the theoretical on the geometries and electronic properties of various compound based on thiophene and oxadiazole is performed in order to display the effect of substituted groups, the ring structure and the doping process on the structural and opto-electronic properties of these materials. The concluding remarks are:

- The substitution of electron- donating groups on the thiophene ring destabilizes the HOMO and LUMO levels while the substitution with Fluorine or nitrile groups leads to the stabilization of the HOMO and LUMO levels with a decrease in the energy gap and results in a red shifting in the absorption spectrum. Such theoretical results are in agreement with experimental ones.
- The replacement of thiophene ring by oxadiazole leads to the stabilisation of the HOMO and LUMO levels and increase in the energy gap.
- For polaron and bipolaron oligomers, the obtained structures are completely planar. The gap energy decreases 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 results of this study demonstrate how the electronic properties can be tuned by the backbone ring, side group or doping process and suggest these compounds as good candidates for opto-electronic applications.

Acknowledgements:
This work was supported by Volubilis Program (N° MA/11/248), and the convention CNRST/CNRS (Project chimie1009). We are grateful to the "Association Marocaine des Chimistes Théoriciens" (AMCT) for its pertinent help concerning the programs

5. References

1. Geiger. F., M. Stoldt M, H. Schweizer, P. Bauerle, E. Umbach, *Adv. Mat.* 5 (1993) 922.
2. Garnier. F, Horowitz. G, Peng. X, Fichou. D, Adv. Mat. 2 (1990) 592.
3. Bäurele. P, In: Müllen. Kand Wegner. G, Editors, Electronic Materials : The oligomer Approach, Wiley-VCH, Weinheim, NY (1998)105-197 (and the references therein)
4. Yanagi. H, Okamoto. S; Yanagi. Okamoto. H. S, App. Phys. Lett., 71, 2563 (1997).
5. B. Schultz, M. Bruma, L. Brehmer, Adv. Mater. 9, 601 (1997);
6. Hehre. W.J, Ditchfiesld. R, Pople. J.A, J. Chem. Phys., 56, 643 (1972).
7. Roncali. J, J. Mater. Chem. 9 (1999) 1875.
8. Fisyuk. A.S, Demadrille. R, Querner. C, Zagorska. M, Bleuse. J, Pron. A, *New J. Chem.* 29 (2005) 707.
9. Bouachrine. M, Hamidi. M, Bouzzine. S.M, Taoufik. H, J. Appl Chem. Res, 10, 29 (2009).
10. Becke. A.D, J. Chem. Phys. 98 (1993) 5648..
11. Ditchfield. R, Hehre. W.J, J.A. Pople, J. Chem. Phys., 54, 76 (1971).
12. Hehre. W.J, Ditchfiesld. R, J.A. Pople, J. Chem. Phys., 56, 643 (1972).
13. Hariharan. P.C, J.A. Pople, Mol. Phys., 27, 209 (1974).
14. Gordon. M.S, Chem. Phys. Lett., 76, 33 (1980) .
15. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N., Jr.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN 03, *Revision B. 04; Gaussian: Pittsburgh, PA, 2003*
16. Meille. S. V, Farina. A, Bezziccheri. F and Gallazi. M. C., Adv. Mater., 6, 848 (1994).
17. Casado. J, Hernàndez. V, Ramirez. F.J, López Navarrete J.T, J. Mol. Struct. (Theochem), 463 (1999) 211.
18. Bouzzine. S.M, Bouzakraoui. S, Bouachrine. M, Hamidi. M, J. Mol. Struct. (Theochem), 726, 269 (2005); Bouzzine. S.M, Hamidi. M, Bouachrine. M, J. Appl Chem. Res, 11, 40 (2009).
19. Pan. J-F, Chua. S. L, Huang. W, Chem. Phy. Lett., 363, 18 (2002).
20. Yang. L, Feng. J, A. Ren, Polymer, 46, 10970 (2005).