ISSN 1984-6428
ONLINE
www.orbital.ufms.br

Orbital: The Electronic Journal of Chemistry

Orbital 2009, *1* (2), 203-214

Full Paper

DFT study of bridged oligo(bithiophene)s. Conformational analysis and opto-electronic properties

Si Mohamed Bouzzine[a], Mohamed Hamidi[a] and Mohammed Bouachrine[a,b*]*

[a]URMM/UCTA, Faculté des Sciences et Techniques, B. P. 509 Boutalamine, 5200, Errachidia, Morocco.
[b]UMIM, Faculté Polydisciplinaire de Taza, B. P. 1223/Taza Gare, Morrocco.

Received: 07 April 2009; revised: 14 July 2009; accepted: 29 July 2009. Available online: 02 August 2009.

***ABSTRACT**: In this paper, we have studied the conformational and opto-electronic properties of several oligomers of bridged oligo(bithiophene)s* $(BTX)_n$ *, n=1 to 4 with (X:* CH_2*,* SiH_2*, C=O, C=S and* $C=C(CN)_2$*). The conformational analysis shows that the most stable conformation is anti-planar conformation. The opto-electronic properties of the octamer (OTX) lead us to suggest that this oligomer is a good model to reflect opto-electronic properties for the parent polymer.*

***Keywords**: oligothiophene, bridging effect, DFT, low band gap, donor acceptor polymer*

---

* *Corresponding author. E-mail: lrmm_fste@yahoo.fr*

Introduction

Polythiophene and its oligomers are almost the most intensively studied conducting polymers because of their good environmental stability [1, 2]. These materials have attracted much interest for potential application in opto-electronic devices due 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 investigations for applications in film transistors [4], electroluminescent diodes [5], lasers [6], sensors [7] and photovoltaic cells [8].

One of the challenges when studying conducting polymers is to investigate new low band gap polymers. This even involves looking for polymers that are intrinsically conducting and thus do not require doping. Although various routes are presently followed for designing novel conducting polymers [9], a very exciting possibility in this direction is provided by the donor-acceptor polymers based on the approach suggested by Havinga et al. [10, 11]. Therefore, in the past decade, many efforts have been devoted to designing and synthesizing new polymer conducting materials, which have low band gap. Recently, a few low band gap polymers based on polyparaphenylene [12], polythiophene [13-15], were synthesized and studied intensively. Moreover, Lambert et al. [16, 17] have synthesized polydicyanomethylene-cyclopenta-dithiophene and poly-4H-cyclopenta-dithiophene-4-one with experimental band gap values of 0.8 and 1.2 eV, respectively.

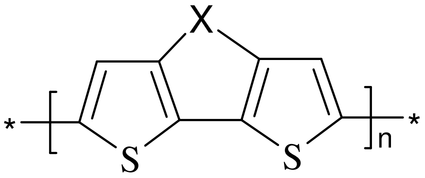
In this regard, we investigated the geometric and electronic structures of some donor-acceptor polymers differing in their electron-donating and electron-accepting moieties. The electron-donating are derived from the bridging groups containing elements carbon C and silicon Si, where the electron-accepting groups are C=O, C=S and $C=C(CN)_2$.

The results of B3LYP/6-31G(d) studies of bridging effects of oligo(bithiophene)s with a variety of bridging groups (CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) (Scheme 1) showed that:

- The important reduction of the energy gap observed for the whole series of bridged compounds is explained on the basis of the orbital interaction analysis;

- The most relevant structural change is the decrease of the inter-rings bond between bridged thiophenes;

- The polymers with C=S and $C=C(CN)_2$ bridged groups are expected to exhibit the very low band gaps suggesting that these compounds can be used in the optoelectronic applications.



X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$

Scheme 1: Studied oligo(bithiophene)s

Computational details

DFT method of three-parameter compound functional of Becke (B3LYP) [18] was used to study the bridged oligothiophenes. The 6-31G* basis set was used for all calculations [19–22]. The conformational analysis for the neutral structures was carried out by changing the torsional angle (*θ*, dihedral angle between central two thiophene rings, S—C—C—S) by 20 steps in the same direction between 0 (syn-planar) and 180° (anti-planar). For each conformation, *θi* were held fixed while the remaining variables were fully optimised, i.e., no rigid rotor approximation was adopted. The stable molecular geometries, corresponding to the energy minima on potential energy surface (PES), were separately obtained by releasing the constraints of the torsional angles, *θi*. To obtain the charged oligo(bithiophene)s structures, we started from the optimized structures of the neutral form. The geometric structures of charged structures were optimized independently from the neutral molecules prior to calculation of spin densities. Radical cations were treated as open shell systems by UB3LYP/6-31G* method. All calculations were carried out using the GAUSSIAN 03 program [23].

Results and Discussion

Conformational analysis

The results of the torsion potential of the oligo(bithiophene)s bridged by (X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) calculated at B3LYP/6-31G(d) level are presented in Fig. 1 and Fig. 2. The rotational profiles obtained are similar and both the existence of the syn–gauche conformer corresponding to average values of θ with 28.5° (see Table 1).

The region corresponding to anti-gauche conformer is very flat in both cases, for the both computational level, the difference between the syn-gauche and the anti-gauche region is about 0.89 eV, the rotational barrier present five extrema, three maxima situated at 0°, 90° and 180° and two minima located at about 29° and 160° (see Table 1).

Table 1. Relative energy (Kcal/mol) and torsional angle of bridged quaterthiophene obtained at B3LYP/6-31G(d).

QTX	Syn	Syn-gauche	Perpendicular	Anti-gauche	Anti plane
4T	-	28.8/23.8(0.11)*	-	162.7 (0.00)	-
CH_2	1.23	28.8 (0.93)	3.46	162.0 (0.00)	0.06
SiH_2	1.04	28.1 (0.80)	3.28	166.6 (0.00)	0.01
C=O	1.00	29.9 (0.72)	2.94	159.7 (0.00)	0.07
C=S	1.04	30.8 (0.76)	2.57	161.3 (0.00)	0.04
$C=C(CN)_2$	1.18	34.5 (1.27)	2.97	160.9 (0.00)	0.09

* Relative energies of state

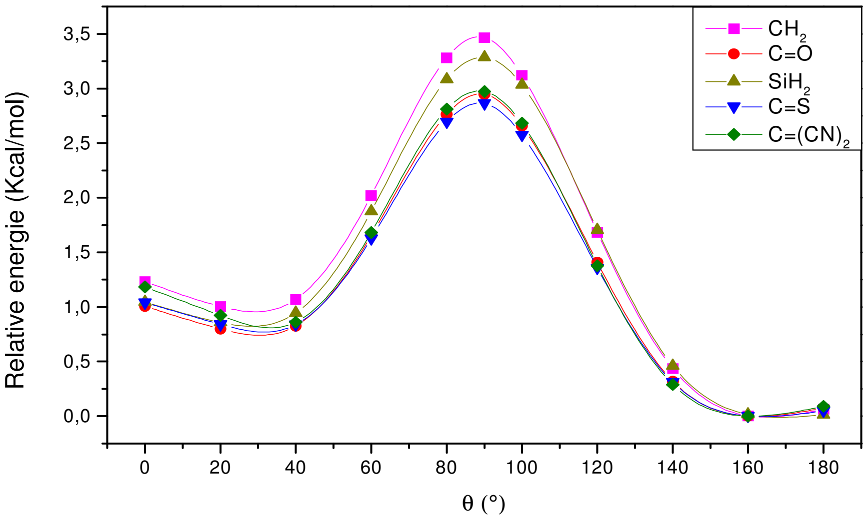


Figure 1: Torsion potential of oligo(bithiophene)s bridged by (X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) obtained by B3LYP/6-31G(d) level.

The torsional angles and barriers to internal rotation depend on the balance of two interactions: as a result of the π-electron conjugation between the thiophene rings, the molecules tend to remain planar, whereas the steric repulsion between hydrogens and groups (X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) causes the molecules to twist. The most significant result found with hybrid B3LYP functional is the presence of two minima. The first in the anti-gauche region corresponding to θ=160°, and the second in the syn-gauche conformer at θ=29° which is less stable than the anti-gauche conformer by about 0.87 Kcal/mol. A schematic representation of the syn- and anti-gauche conformer for all bridged oligomers is given in Fig. 3. These representations were done by the animation option of the GaussView 3.0 graphical interface for Gaussian programs [23]. While the values of the most important geometrical parameters, for the most stable conformer (anti-gauche) structure are collected in Table 2.

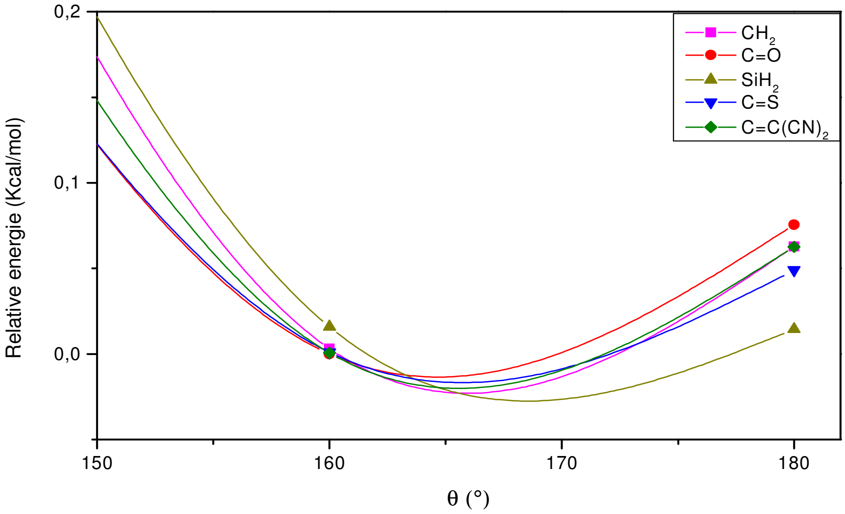


Figure 2: Torsion potential of oligo(bithiophene)s bridged by (X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) obtained by B3LYP/6-31G(d) level, for θ included between 150 and 180°.

The most relevant change observed in the comparison between the geometrical parameters, was more pronounced in the inner thiophene rings and in the terminal rings of the C—S and C=C bonds. This trend is in good agreement with theoretical calculations [24] and experimental results [25]. The structures of these oligomers present a shorting C—S and C=C bonds length in the terminal bonds of the thiophenes rings. In the comparison of the unbridged oligothiophene, the same evolution is noted by the C=C bond, but the bond C=C changes length while passing from the terminal to the inner of the chain. This variation of distance can be caused by the effect of insertion of the grouping X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$ between the two thiophenes rings (see Fig. 3).

The variation of inter-ring bond $C_1—C_{1'}$ as well as the function of θ is showed in Fig. 4. All curves have similar look, and the shorter interring bond corresponds to conformation planar syn and anti, indicating that this conformation holds a larger conjugation between dienic structure what can be also evidenced by enlargement of interring bond between monomer ($C_1—C_1^{'}$) and a shortening of C—C single bond of the ring. As expected, the degree of conjugation changes with oligomers conformations being minimal at θ=90° and maximal at planar conformations (anti-planar conformation) (see Fig. 4).

Table 2. Optimized structural parameters bond length (in Å), angle (in degree) of bridged quaterthiophene obtained at B3LYP/6-31G(d).

Parameters	$QTCH_2$	$QTSiH_2$	QTC=O	QTC=S	$QTC=C(CN)_2$	4T
C_1C_2	1.386	1.384	1.387	1.385	1.385	1.380
C_2C_3	1.411	1.416	1.408	1.411	1.413	1.419
C_3C_4	1.386	1.390	1.384	1.390	1.391	1.380
C_4C_5	1.440	1.451	1.456	1.451	1.446	1.441
C_5C_6	1.386	1.391	1.385	1.392	1.391	1.379
C_6C_7	1.419	1.424	1.416	1.419	1.420	1.422
C_7C_8	1.372	1.371	1.372	1.372	1.371	1.367
C_6C_{11}	1.516	1.879	1.504	1.419	1.480	-
C_3C_{11}	1.517	1.881	1.509	1.411	1.482	-
C_8S_9	1.750	1.743	1.751	1.754	1.752	1.786
C_5S_9	1.730	1.737	1.719	1.716	1.726	1.758
C_4S_{10}	1.730	1.736	1.719	1.717	1.726	1.757
C_1S_{10}	1.775	1.767	1.776	1.778	1.776	1.758
C_1C_1'	1.441	1.443	1.442	1.442	1.442	1.442
$C_1C_2C_3$	112.9	114.0	112.3	112.4	112.8	113.8
$C_2C_1S_{10}$	110.8	110.4	110.8	110.8	110.9	110.0
$C_2C_3C_4$	113.1	112.0	113.7	113.5	113.0	113.9
$C_1S_{10}C_4$	90.8	91.1	91.0	91.0	90.9	92.1
$C_3C_4S_{10}$	112.2	112.3	111.9	112.0	112.1	110.0
$C_3C_4C_5$	109.2	116.9	109.3	108.6	108.9	129.1
$C_4C_5C_6$	109.2	116.9	109.4	108.6	108.9	129.0
$C_4C_3C_{11}$	109.8	106.8	108.5	109.0	108.7	-
$C_5C_6C_{11}$	109.8	106.8	108.5	109.1	108.8	-
$C_3C_{11}C_6$	101.8	92.3	104.1	104.5	104.6	-
$C_5C_6C_7$	112.8	111.7	113.4	113.1	112.7	113.6
$C_6C_7C_8$	112.0	113.1	111.5	111.6	111.9	112.9
$C_7C_8C_9$	112.5	112.0	112.3	112.4	112.5	111.6
$C_8C_9C_5$	90.5	90.8	90.8	90.8	90.6	91.7
$C_9C_5C_6$	112.1	112.1	111.8	111.9	112.0	110.0

Calculation of band gap (Egap)

The band gap in conjugated oligomers is governed by their chemical structures. There are two theoretical approaches for evaluating the energy gap. One way is based on the ground-state properties, from which the band gap is estimated from the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [24]. The TDDFT, which has been used to study systems of increasing complexity due to its relatively low computational cost and also to include in its formalism the electron correlation effects, this method gives a better account of the excitation energy and even oscillator strength but it is not perfect for determining the gap energy. Many paper in the literature showed that this method is not sufficient for this type of calculation in the case of conjugated molecules and it gives values of gap far from the values of the experience [24-29].

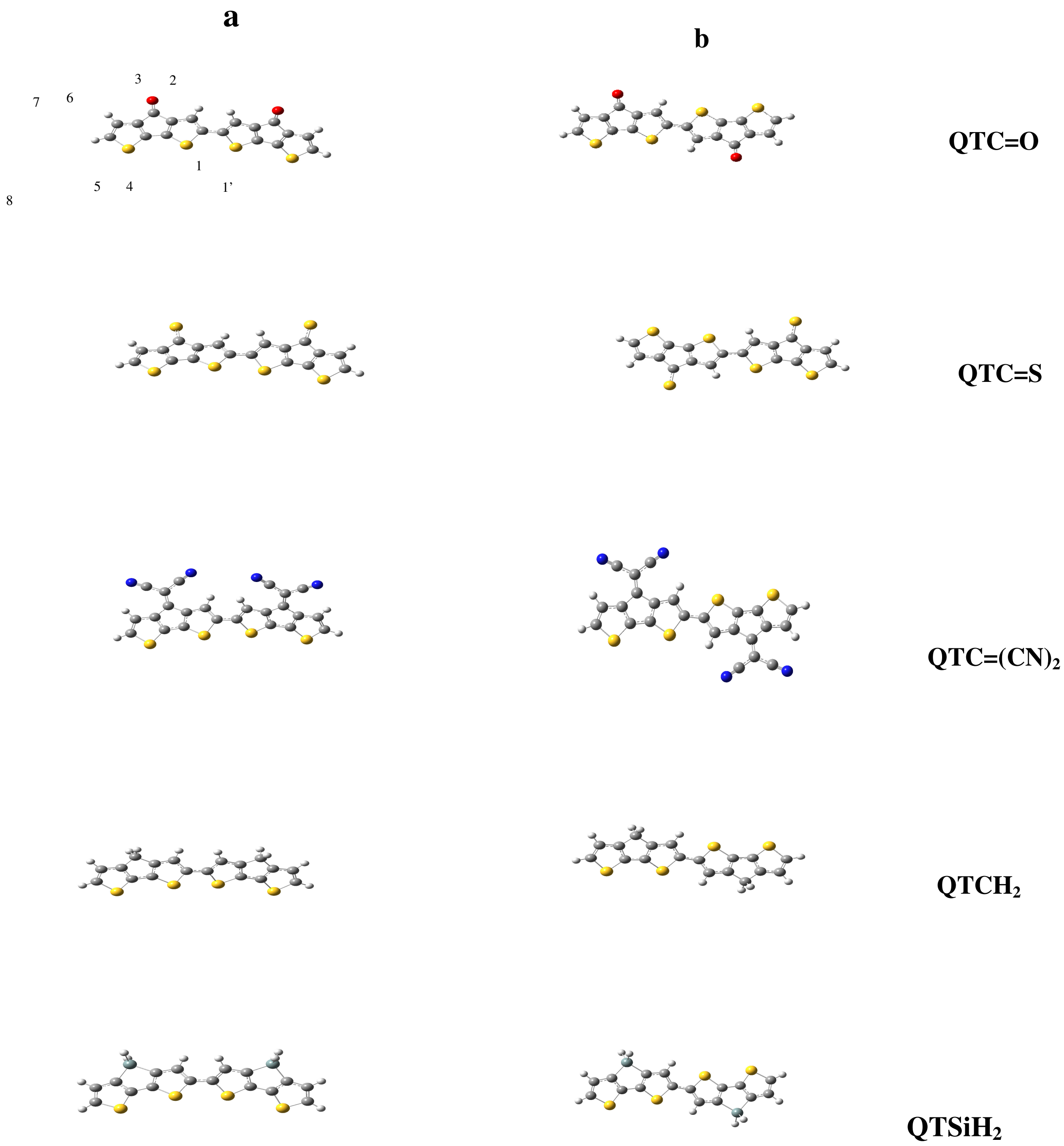


Figure 3: Geometries structural of bridged quaterthiophene: a) conformer syn-gauche b) conformer anti-gauche (stable conformation).

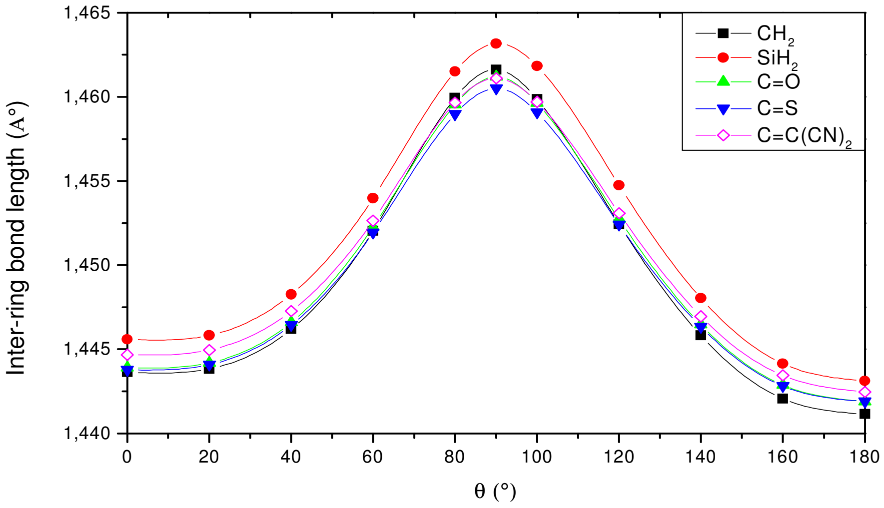


Figure 4: Inter-ring bond length as function of torsional angle θ for the bridged oligo(bithiophene)s QTX (X: CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$).

For our work, we have used the method HOMO-LUMO because we have showed in preceding works that it is a best method which gives satisfactory results especially in the case of oligothiophenes and oligophenylenes [26].

Therefore, the detailed band gap theoretical calculations are carried out on the bridged oligomers structures. All values of band gaps were obtained by DFT(B3LYP/6-31G(d)). For comparison we have also presented in Table 3 the energy gaps calculated by TD/DFT method. The HOMO, LUMO and E_{gap}=HOMO-LUMO energies of the oligomers $(BTCH_2)_n$, $(BTSiH_2)_n$, $(BTC=O)_n$, $(BTC=S)_n$, $(BTC=C(CN)_2)_n$ with n=1 to 4, are presented in Table 3 and the relationships between the calculated energy gaps (E_{gap}) and the inverse chains length are plotted in Fig. 5. One can see that there is a good linear relation between the energy gap and the inverse chain length. Obviously, the E_{gap} presented in Table 3, yields a better agreement with the experimental data. However, we noted that calculations were performed in isolated state; they are still small variations of the calculated results and experimental values. The first factor responsible for deviations by both methods from experimental is that the predicted band gaps are for the isolated condensed phase chains, while the experimental band gaps are measured in the liquid phase, where the environmental influence may be involved. Additionally, the solid state effects have been neglected in the calculations. The theoretical band gaps calculated for isolated chains are expected to be about 0.2 eV larger than condensed phase values [27]. When taking into consideration this difference, the B3LYP/6-31G(d) method has the particularity to reproduce gap values similar to those of the experiment [28]. The band gaps obtained by DFT (B3LYP/6-31G(d)) is 2.41 eV for unbridged octathiophene (8T)

[29], which are higher than that $OTCH_2$ (2.23 eV),$OTSiH_2$ (2.27 eV), OTC=O (1.86 eV), OTC=S (1.43 eV) and $OTC=C(CN)_2$ (1.56 eV) indicating that the reduced band gap of bridged bithiophene oligomers are due to the effect of insertion of grouping (CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$) between two thiophene rings. The measured values of OTX are very close to values measured experimentally [16, 17]. These results lead us to suggest that these oligomers are good models to reflect optoelectronic properties for corresponding parent polymer.

Table 3. Calculated values of HOMO, LUMO and Egap of bridged octathiophene (OT) derivatives (eV).

Polymers	E_{HOMO}	E_{LUMO}	**Egap**	**Egap exp**
OT (unbridged)	-4.72	-2.31	2.41	2.3-2 [30]
$OTCH_2$	-4.32	-2.09	2.23	
$OTSiH_2$	-4.66	-2.39	2.27	
OTC=O	-4.98	-3.12	1.86	1.2 [16,17]
OTC=S	-4.95	-3.52	1.43	
$OTC=C(CN)_2$	-5.40	-3.84	1.56	0.8 [16,17]

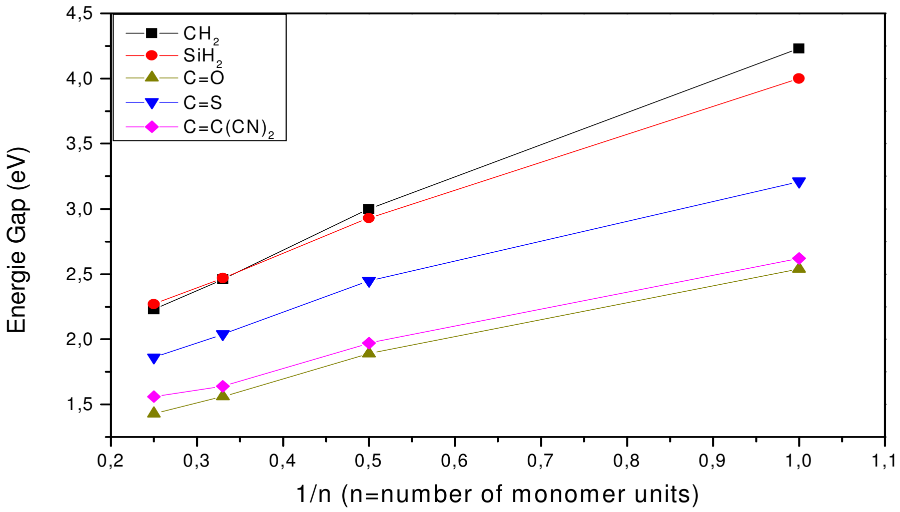


Figure 5: The band gap as a function of reciprocal chain length (n) in bridged oligo(bithiophene)s.

Conclusion

The calculation performed at the B3LYP/6-31G(d) level for bridged oligo(bithiophene)s gives torsional potentials. The most stable conformation is the anti-planar conformation. The calculated gap energy 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 obtained energy band gap for the octamer is very close to those of polythiophene as measured experimentally. This octamer seems to be a useful model to understand electronic properties of the parent polymer. The calculation appears to be reliable for the estimation of the band gap of the conjugated polymers; the effects of bridging on the electronic properties of the octamer entities (OTX) have been examined. The insertion of CH_2, SiH_2, C=O, C=S and $C=C(CN)_2$ groups between two thiophene rings leads to a reduction of the energy gaps. Concerning the $C=C(CN)_2$ derivative the lowing of the HOMO-LUMO energy gap observed certainly indicates a possible reduction of the band gap in corresponding polymer.

Acknowledgments

This work has been supported by the convention CNRST/CNRS (Project chimie1009). We are grateful to the "Association Marocaine des Chimistes Théoriciens" (AMCT) for its pertinent help concerning the programs**.**

References and Notes

[1] Geiger, F.; Stoldt, M.; Schweizer, H.; Bauerle, P.; Umbach, E. *Adv. Mat.* **1993**, *5* 922.

[2] Garnier, F.; Horowitz, G.; Peng, X.; Fichou, D. *Adv. Mat.* **1990***, 2*, 592.

[3] Bäurele P. In: Electronic Materials: The Oligomer Approach. Müllen, K. and Wegner, G., eds. New York: Wiley-VCH, 1998, p. 105-197 (and the references therein).

[4] Horowitz, G.; Hajlaoui, M. E. *Adv. Mater.* **2000***, 12*, 1046; Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B. C.; Van Patten, P. G.; Bao, Z. *Chem. Mater*. **2003**, 1*5*, 1778; Mushrush, M.; Facchetti, A.; Lefenfeld, M.; Katz, H. E.; Marks T. J. *J. Am. Chem. Soc.* **2003***, 125*, 9414.

[5] Pasini, M.; Destri, S.; Porzio, W.; Botta, C.; Giovanella, U. *J. Mater. Chem*. **2003**, *13*, 807; Suzuki, M.; Fukuyama, M.; Hori, Y.; Hotta, S. *J. Appl. Phys*. **2002**, *91*, 5706.

[6] Pisignano, D.; Anni, M.; Gigli, G.; Cingolani, R.; Zavelani-Rossi, M.; Lanzani, G.; Barbarella, G.; Favaretto, L. *Appl. Phys. Lett*. **2002**, *81*, 3534.

[7] Torsi, L.; Lovinger, A. J.; Crone, B.; Someya, T.; Dodabalapur, A.; Katz H. E.; Gelperin, A. *J. Phys. Chem.* B **2002**, *106*, 12563; Roncali, J. *J. Mater. Chem.* **1999***, 9*, 1875.

[8] Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater.* **1995**, *7*, 647; Videlot, C.; El Kassmi, A.; Fichou, D. *Solar Energy Mater. Solar Cells*. **2000**, *63*, 69; Hara, K.;

Kurashige, M.; Dan-Oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New J. Chem.* **2003**, *27*, 783; Ackermann, J.; Videlot, C.; El Kassmi, A.; Guglielmetti, R.; Fages, F. *Adv. Mater.* **2004**, *16*, 1709.

[9] Brédas, J. L.; *Adv. Mater.* **1995**, *7*, 263; Bakhshi, A. K. *Ann. Rep. R. Soc. Sect. C* **1992**, *89*, 147.

[10] Havinga, E. E.; ten Hooeve, W.; Wynberg, H. *Polymer Bull*. **1992**, *29*, 119.

[11] Havinga, E. E.; ten Hooeve, W.; Wynberg, H. *Synth. Met*. **1993**, *55*, 299.

[12] Colladet, K.; Nicolas, M.; Goris, L.; Lutsen, L.; Vanderzande, D. *Thin. Solid. Films* **2004***, 7*, 451; Thompson, B. C.; Kim, Y. G.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 5359; Shahid, M.; Ashraf, R. S.; Klemm, E.; Sensfuss, S. *Macromolecules* **2006**, *39*, 7844.

[13] Bundgaard, E.; Krebs, F. C. *Macromolecules* **2006**, *39*, 2823.

[14] Van Duren, J. K. J.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Synth. Met.* **2001**, *121*, 1587; Yoshino, K.; Nakajima, S.; Park, D.H. *Jpn. J. Appl. Phys. Part 2* **2008**, *27*, 716.

[15] Petersen, M. H.; Hagemann, O.; Nielsen, K. T.; Jørgensen, M.; Krebs, F. C. *Sol. Energy. Mater. Sol. Cells* **2007**, *91*, 996; Ashraf, R. S.; Klemm, E. J*. Polym. Sci. Part A* **2005**, *43*, 6445.

[16] Lambert, T.; Ferraris, J. P. *J. Chem. Soc. Chem. Commun*. **1991**,752.

[17] Ferraris, J. P.; Lambert, T. *J. Chem. Soc. Chem. Commun.* **1991**, 1268.

[18] Becke, A. D*. J. Chem. Phys*. **1993**, *98*, 5648.

[19] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys*. **1971**, *54*, 724.

[20] Hehre, W. J.; Ditchfiesld, R.; Pople, J. A. *J. Chem. Phys*. **1972**, *56*, 2257.

[21] Hariharan, P. C.; Pople, J. A. *Mol. Phys*. **1974**, *27*, 209.

[22] Gordon, M. S. Chem. Phys. Lett. 1980, 76, 163.

[23] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin-Jr, K. N.; 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, S.; 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, Inc., Pittsburgh PA, **2003**.

[24] Cornil, J.; Beljonne, D.; Brédas, J. L. *J. Chem. Phys*. **1995**, *103*, 842; Alemán, C. Julia, L. *J. Phys. Chem*. **1996**, *100*, 14661; Moro, G.; Scalmani, G.; Cosentino, U.; Pitea, D. *Synth. Met.* **1998**, *92*, 69.

[25] Kozaki, M.; Yonezawa, Y.; Okada, K. *Org. Lett*. **2002**, *4*, 4535.

[26] Hay, P. J. *J. Phys Chem. A* **2002**, *106*, 1634; Curioni, A.; Andreoni, W.; Treusch, R.; Himpsel, F. J.; Haskal, E.; Seidler, P. *J. Appl. Phys Lett*. **1998**, *72*, 1575; Hong, S. Y.; Kim, D. Y.; Hoffman, R. *Macromolecules* **2001**, *34*, 6474.

[27] Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177.

[28] Bouzakraoui, S.; Bouzzine, S. M.; Bouachrine, M.; Hamidi, M. *Solar Energy Materials Solar Cells* **2006**, *90*, 1393.

[29] Bouzzine, S. M.; Bouzakraoui, S.; Bouachrine, M.; Hamidi, M. *J. Mol. Struct. (Theochem)* **2005**, *726*, 271.

[30] Roncali, J. *Chem. Rev*. **1992**, *92*, 711; Hernandez, V.; Lopez Navarrete, J. T.; Marcos, J. L. *Synth. Met.* **1991**, *41*, 789; Tourillon, G.; Garnier, F. *J. Electroanal. Chem*. **1988**, *246*, 467.