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A comparative study of homological series of oligothiophenes: the influence of oligomer length and conformation on some structural, chemical, physical properties

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Abstract

Two homological series of oligothiophenes were studied with the aid of DFT (B3P86, PBE0 and B3LYP) in the aim of exploring the influence of the conformation and conjugation length of oligomers on a number of properties. From the geometrical structure viewpoint, the results have shown that the linear series remains planar, independently on the length of the oligomer, while in the nonlinear series, the planarity is very depend on the number (n) of the thiophene rings: the planarity remains for $n \leq 5$ to give place to a helical conformation for $n \geq 6$. Upon oxidation, the linear series conserve the planarity; the other series, while remaining helical is somehow altered. From the electronic point of view, some of the electronic and physical properties characterizing a good electron-donating (ED) and charge-transporting (CT) capacity such as the frontier molecular orbital energies (E_{HOMO} and E_{LUMO}), the ionization potential (IP) and the intramolecular reorganization energy (λ_h/λ_e for hole/electron) were calculated and comparison made to those of $C_{16}S_8$ and some other already used OFET materials. Some of the studied derivatives were found to display a comparable/much lower λ_h, higher IP and E_{LUMO} than those for some of the already well known organic field-effect transistor (FET) materials such as pentacene, anthracene, and DT-TTF. We recommend a further investigation of these for FET use issue.

Keywords: Homological series, oligothiophenes, DFT, structure, physico-chemical properties

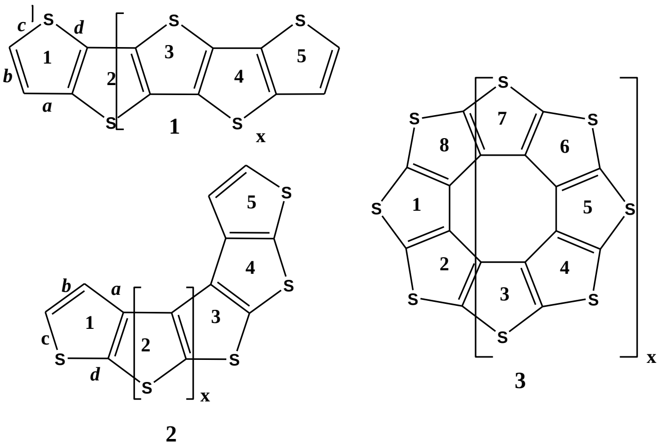
Résumé

Deux séries homologiques d'oligothiophènes ont été étudiées à l'aide des méthodes DFT (B3P86, PBE0 et B3LYP) dans le but d'explorer l'influence de la conformation et de la longueur de conjugaison des oligomères sur un certain nombre de propriétés. Du point de vue structure géométrique, les résultats ont montré que la série linéaire reste plane indépendamment de la longueur de l'oligomère, tandis que dans la série non linéaire, la planéité est très dépendante du nombre (n) des anneaux thiophène: la planéité reste pour $n \leq 5$ pour donner lieu à une conformation hélicoïdale pour $n \geq 6$. Lors de l'oxydation, la série linéaire conserve la planéité, l'autre série étant quelque peu modifiée tout en restant hélicoïdale. Du point de vue électronique, certaines des propriétés électroniques et physiques caractérisant une bonne capacité de donneur d'électrons (ED) et de transport de charge (CT) comme l'énergie des orbitales de frontières (E_{HOMO} et E_{LUMO}), le potentiel d'ionisation (IP) et l'énergie de réorganisation intramoléculaire (λ_h / λ_e pour le trou / l'électron) ont été calculées et comparées à celles du $C_{16}S_8$ et de certains autres matériaux OFET déjà utilisés. Certains des dérivés étudiés des valeurs de λ_h, IP et E_{LUMO} comparables / inférieures à ceux de certains des matériaux déjà connus tels que le pentacène, l'anthracène et le DT-TTF. Nous recommandons une étude plus approfondie sur ceux-ci pour des fins d'utilisation en électronique.

Keywords: Séries homologiques, oligothiophènes, DFT, structure, propriétés physico-chimiques

1. Introduction

In the research field of organic field-effect transistors (OFETs), (Moon M. et al., 2004), thiophene oligomers (Takimiya, 2006) and acene molecules (Chernichenko K. et al. 2006) have been extensively studied for over two decades. With eight thiophene rings, octathio[8]circulene ($C_{16}S_8$) can be considered as a thiophene oligomer with a cyclic structure, which differentiates it from the commonly studied thiophene oligomers. Popularly called sulflower, this molecule was the first fully heterocyclic circulene, recently synthesized by Chernichenko K-Y. et al. 2006). The extremely close packing of the molecules in the solid state suggested strong intermolecular interactions, both within layers and between adjacent layers (Chernichenko K-Y., 2006). Such interactions should be favorable for its future use as an electron donor (ED) in materials science applications. $C_{16}S_8$ was then considered as the first representative of a novel class of heterocyclic circulenes displaying a high structural stability, illustrating a possible development of an efficient synthetic methodology, which should be applicable to new families of Se-, Te-, N-, and P-containing heterocyclic circulenes, with the success in the preparation of a mixed thiophene-selenophene circulene ($C_{16}S_4Se_4$) being announced already. Since the synthesis of $C_{16}S_8$ only four years ago, a number of works have been reported on it (Gahungu G. et al.. 2009; Oleksandr I. et al.., 2009). One of them was on fabrication of field-effect transistors using the new organic semiconductors $C_{16}S_8$ and $C_{16}S_4Se_4$; the maximum hole mobility of 9×10^{-3} $cm^2\ V^{-1}\ s^{-1}$ was found to be, most likely, limited by one-dimensional growth of the two compounds in thin films (Fujimoto T et al., 2008). Efforts have been directed toward enhancing intramolecular π conjugation in oligothiophenes by bridging adjacent β-carbon atoms with a sulfur linkage, thereby fusing the rings; this is the case, for example, in bisdithienothiophene (quaterthiophene with two bridges) (Li X-C. et al., 1998) and oligothienoacenes (nTA: fully fused oligothiophenes) (Zhang, X. et al., 2005). In our recent works, comparing an oligothienoacene with 8 thiophene rings (8TA: $C_{16}S_8H_4$ in the linear conformation), $C_{16}S_8$ and a number of its plate-like derivatives, we identified a number of differences, most of them being ascribed to their different conformations (Gahungu G. and Zhang J-P., 2008; Gahungu G. et al., 2009). By only comparing the two oligothiophenes, this was not sufficiently representative, so that effective conclusions can be drawn, relatively to the influence of the cyclic/linear conformation on any of the studied properties. In previous reports on octathio[8]circulene and a number of its plate like derivatives, (Gahungu G. and Zhang J.-P., 2008 & Gahungu G. et al., 2009) the influence of the S/Se substitution and the cyclic structure over the linear conformation on a number of properties including λ (one of the commonly used properties to evaluate and explain the mobility of FET materials such as pentacene: (Gruhn N-E. et al., 2002), and dithiophene-tetrathiafulvalene (Kahn A. & Brédas J.-L., 2002), were studied. In this study, we were interested in the impact of the conjugation length (number of thiophene rings) and conformation (linear, cyclic and helical) on a number of properties, including the molecular structure, the reorganization energy (λ), the frontier molecular orbital (FMO) energies, the ionization potential (IPs) energies, and the second hyperpolarizability (α). Analogously to benzene, thiophene can create three homological series (see Figure 1 for the chemical structures) of regular structures (Valentine G.N, 2008). Regular [3,2-b] junction results in linear structures, the most famous of them being dithieno[3,2-b:2',3'-d] thiophene. The compound 1 and its higher homologues attract much attention recently as potential candidates for material science (Tsuchida E., 2004 & Sato N., 1992).



Series	Junction	Termination	Shape
1	[3,2-b]	Open	Linear
2	[2,3-b]	Open	Helical
3	[2,3-b]	Close	Cyclic

Figure 1: Chemical structures of annulated oligothiophenes with regular junction.

Fully thiophenic helicenes (nTH) are a patrimony of the Rajca group since their first report on the synthesis of fully thiophenic helicene 2 (Rajca A., 2000). In all cases, a comparison with already known as good FET materials is made.

2. Material and methods

Calculations were carried out within the density functional theory (DFT) approach using the B03 revision of *Gaussian 03* package (Frisch M. J, 2009). Atomic orbitals contributions to the molecular orbitals are analyzed using the *GaussSum 2.1.6* program (O'Boyle N. M. & Vos, J. G., 2009). Three functionals including the PBE1PBE (also called PBE0) (Ernzerhof M. & Scuseria, 1999). B3LYP, (Becke, A.-D., 1988, Lee C., 1988) and B3P86 (Becke A.-D., 1993) were used with the 6-31G(d,p) (Frisch M.-J. at al., 1984) basis set. Both the PBE0 and B3P86 functionals are recognized to provide reliable predictions and interpretations of molecular geometries, electronic properties (Gahungu G. et al., 2007; Jacquemin D. & Perpète E. A., 2006) and vibrational frequencies in good agreement with experimental data of organic molecules bearing Sulfur and Selenium atoms (Wartelle C., 2003). The radical cations and anions were treated as open-shell systems and were computed by using spinunrestricted DFT wave functions (UB3P86 and UPBE0). The frequency check was done on the optimized structures to confirm that they are true minima. The reorganization energies were calculated as a sum of relaxation energies of a radical cation/anion (from the geometry of a neutral molecule) and of a neutral molecule (from the geometry of a radical cation/anion), as described earlier (Gahungu G. and Zhang J-P., 2008; Gahungu G. et al., 2009). For the sake of comparison, already well known charge transport materials (like pentacene (Anthony, J. E, 2006) and dithiophene-tetrathiafulvalene (DT-TTF) (Mas-Torrent, M., 2004) were considered. It has been shown (Sánchez-Carrera, R. S. et al., 2006) that the DFT estimates of the reorganization energy depend significantly on the amount of "exact" Hartree-Fock exchange included in the hybrid functionals. Among the standard functionals, B3LYP provides the best description of relaxation processes in oligoacenes. Recently, the same functional was successfully used to calculate the charge transport parameters for thiophene oligomers (Kim, E-G. et al., 2007). For these reasons, B3LYP/6-31G(d,p) single point calculations were performed and all the parameters necessary for the calculation of λ_{reorg} recomputed.

3. Results and discussion

Whereas DFT-B3LYP seems to be mostly preferred by Brédas et al. in the calculation of the reorganization energy, (da Silva Filho, D. A. 2007), it has been shown that both PBE0 and B3P86 functionals provide more reliable predictions and interpretations of the molecular geometries, electronic properties (Gahungu, G. et al., 2007), and vibrational frequencies for sulphur bearing compounds, in good agreement with experimental data of organic molecules bearing sulfur and selenium atoms (Wartelle, C., 2003). For comparison and calibration, since no gas-phase electron diffraction (GED) structure is available yet for any of the molecules under consideration, TTF (whose molecular and atomic composition is close to those of the studied compound) was calculated with the same methods and the results compared to its GED structure (Hargittai I., 1994). An excellent agreement was reported previously with both B3P86 and PBE0, with the former being more accurate (Gahungu G. and Zhang J-P., 2008; Gahungu G. et al., 2009). The two methods were then preferred and used for optimization procedures.

3.1. Molecular structures

The optimized structures are shown in Figure 3. In accordance with a previous report, (Sánchez-Carrera, R. S. et al., 2006), the optimized geometries of the isolated oligothienoacenes (nTA = fully fused oligothiophenes) in the neutral state show that the C-C bonds shorten and the C=C bonds lengthen in going from the periphery to the center. In the other series however, the behavior is different: the C-C bond lengthens in going from the periphery to the center, while the C=C bonds lengthen sharply (by ~ 0.03 Å) from the outer ring to the next, and decreases slightly up to the third one from which, its value remains almost constant to the center while staying greater than in the outer by more than 0.02 Å. The results are shown in Figure 2 for the C-C bonds. On the other hand, the C-S bond length alternates and converges already at the fourth bond from the periphery in the case of the nTA. In the other group however, the C-S bond shortens sharply from the outer to the next ring (by ~ 0.02 Å), and remains almost constant (1.74 ± 0.002 Å) to the center. Turning to the geometric relaxation upon oxidation of an isolated molecule, our results show that, in both the nTH and nTA series, the C=C and C-C bonds undergo geometric changes to a greater extent in the cationic state than in the anionic state

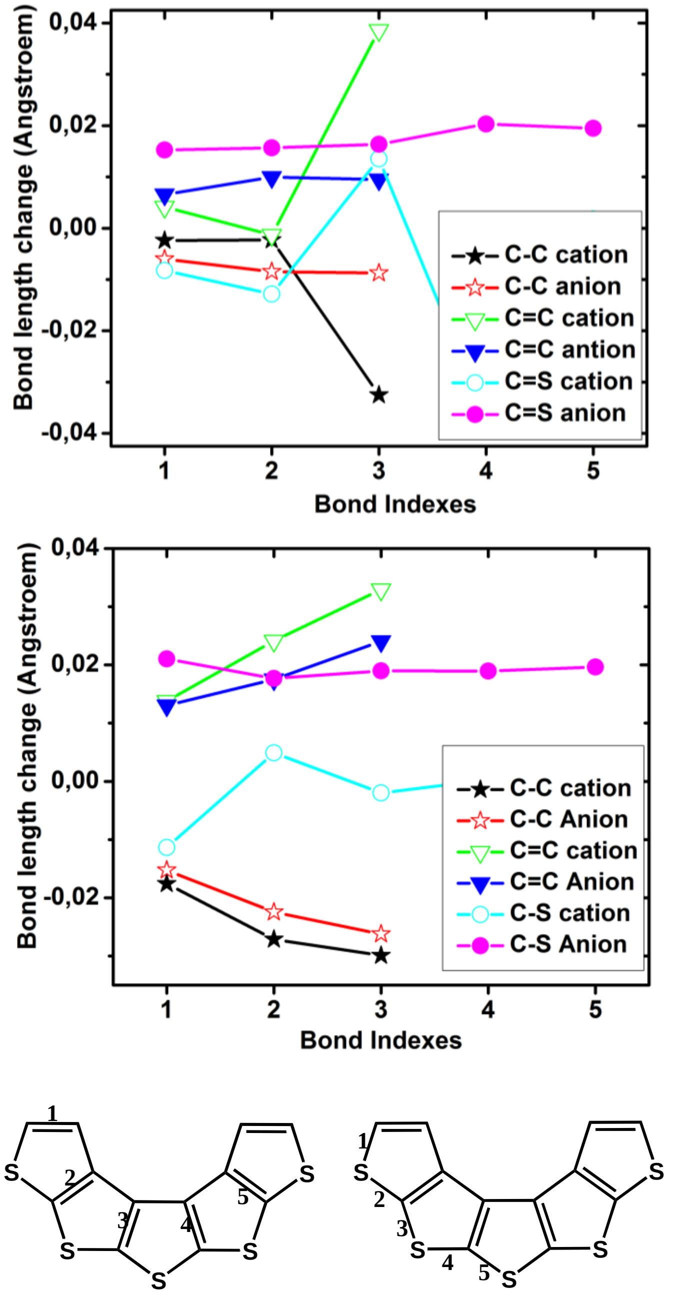


Figure 2. Calculated bond length changes in isolated 5TH (top panel) and 5TA (bottom panel) upon oxidation (open symbols) and reduction (filled symbols).

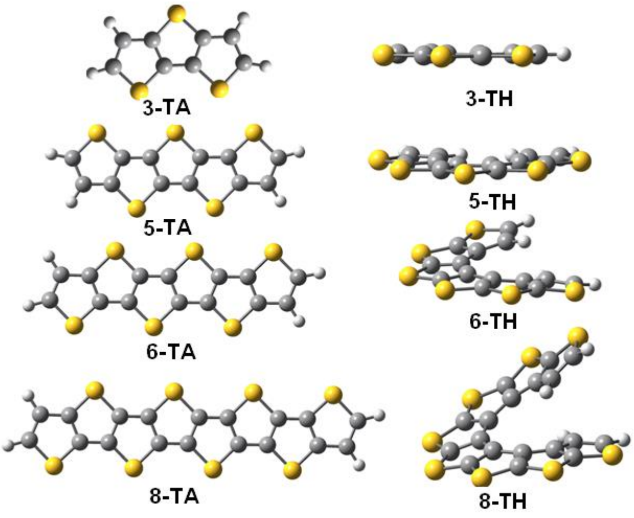


Figure 3: B3P86/6-31G(d,p) optimized structures for representatives of the oligothienoacenes (nTA) and thiophenic helicenes (nTH) studied herein (S, C and H atoms are displayed in Yellow, Gray and White colours respectively).

In general, the bond relaxations occur over the entire molecule but seem to be more pronounced toward the molecular center, especially in the thiophenic helicenes. For the C-S bond on the other hand, the geometric relaxations are in general more pronounced toward the molecular periphery and occur predominantly upon reduction (see Section 3.2.2). The wave functions of the highest occupied molecular orbital (HOMO) have nodes on the sulfur atoms), except for 5TH which shows a more pronounced relaxation towards the center upon oxidation; the weak geometric changes in the cationic state are localized to the molecular ends in the two series. These results are summarized in Figure 2 for nTH and nTA as representatives of each series. As an indicator of aromaticity, which is a useful criterion to judge the nature of a given heterocycle, the nuclear independent chemical shift (NICS) [28] values at the ring centers were calculated for 8TA, 8TH and $C_{16}S_8$. The results plotted in the Figure 4 show that, in comparison with $C_{16}S_8$, the five-member ring in 8TA and 8TH appear to be less aromatic, except for the peripheral rings showing a stronger aromatic character (NICS ≈ - 12 in 8TH and ≈ - 11.7 in 8TA). Similarly to our recent work when comparing $C_{16}S_8$ to 8TA, this feature shows that the helical structure induces some changes in the aromatic character. Comparing 8TH to 8TA, the results show that, although the trend is the same, the helical structure strengthens the aromatic character of the peripheral rings, while slightly weakening that of the internal ones. The results also show that, except for the peripheral thiophene rings in 8TA and 8TH, the aromatic character of the thiophene increases in the order of 8TH < 8TA < $C_{16}S_8$.

3.2. Electronic structures

Table 1 shows the FMO energies (see Figure 7) and IP as computed at different levels of theory. For comparison, experimental values (where available) are also listed. As one may notice, an excellent accuracy is observed between our computed IP values and the first ionization peaks for 3TA, 4TA, 5TA and 7TA based on UPS (Ultra Phase Spectroscopy) data (Table 1).

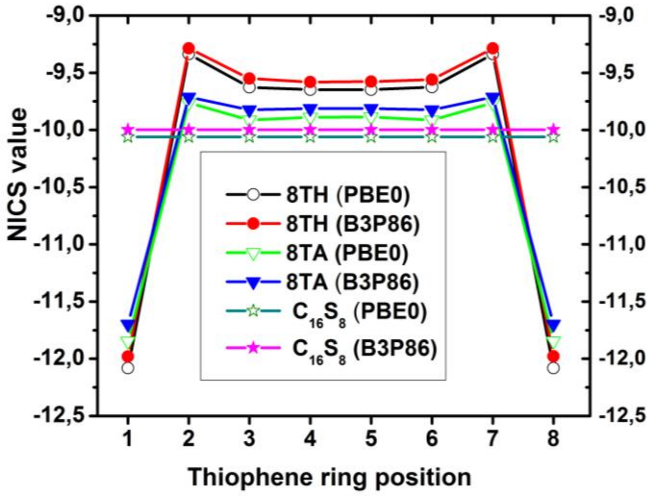


Figure 4. NICS values for 8TA, 8TH and $C_{16}S_8$ as computed at PBE0/6-31G(d,p) and B3P86/6-31G(d,p) levels of theory

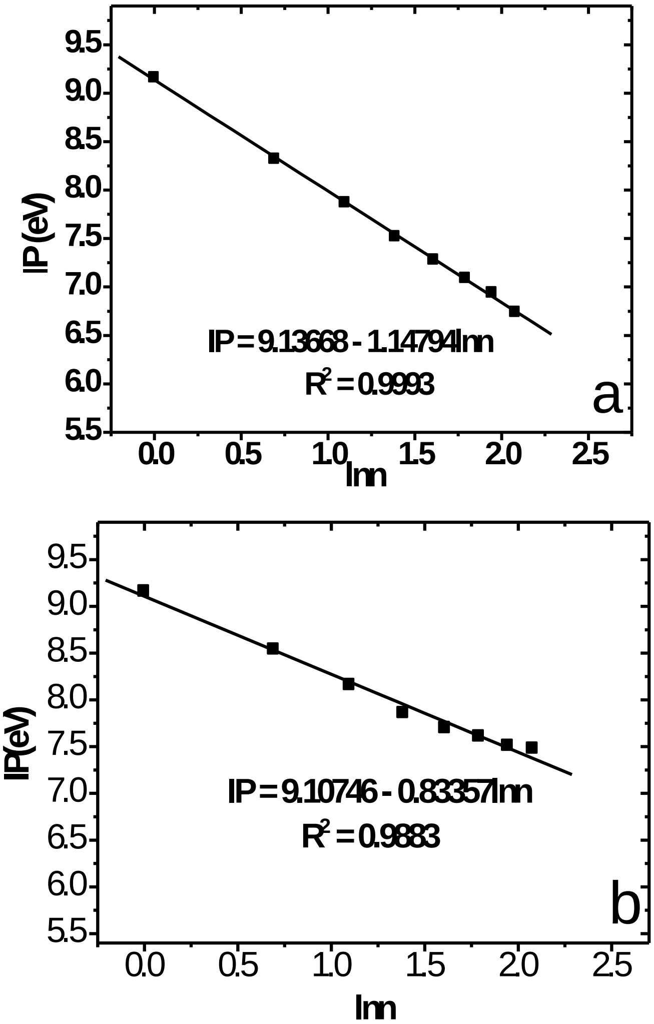


Figure 5. The B3P86/6-31G(d,p) IP values as a function of the number (lnn) of thiophene rings in (a) nTA and (b) nTH series.

Indeed, 7.87, 7.52, 7.28 and 6.98 eV, are the computed IP values *vs* experimental values of 7.78 (Sato N., 1992), 7.52 (Sato N., 1992), 7.25 (Kim E-G. et al., 2007) and 6.97 eV (Kim E-G. et al., 2007) respectively. Experimentally, the ionization energy of 5TA (7.28 eV) as measured at the peak maximum, (Kim E-G. et al., 2007; Bromley S.T., 2004) is significantly larger than that of pentacene (6.589 eV) (Coropceanu V. et al.. 2002). This feature, which is also well predicted by B3P86/6-31G(d,p) also holds for 3TA, whose predicted IP (7.38 eV) is greater than that of 5TA (da Silva Filho D. A. et al, 2007). In general, based on both PBE0 and B3P86, our results show that the IP in nTA decreases with oligomer length, as in oligoacenes (Sánchez-Carrera R. S., 2006). This feature agrees well with recent reports (Kim E-G.; 2007), for nTA series of compounds on the basis of UPS data.

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Table 1. The FMO energies E_{HOMO} and E_{LUMO} (eV) and Ionization Potential (IP in eV) in the thiophenic helicenes as provided by the two levels of theory.*

	B3P86/6-31G(d,p)				PBE0/6-31G(d,p)		
	E_{HOMO}	E_{LUMO}	$IP_{\Delta SCF}$	IP_{FIT}	E_{HOMO}	E_{LUMO}	$IP_{\Delta SCF}$
nTA							
1TA	-7.02	-0.83	9.16	9.11	-6.65	-0.05	8.57
2TA	-6.51	-1.35	8.32	8.32	-6.14	-0.58	7.75
3TA	-6.29	-1.71	7.87 (7.78) [b]	7.85	-5.89	-0.96	7.31
4TA	-6.10	-1.96	7.52 (7.52) b	7.52	-5.70	-1.22	6.97
5TA	-5.97	-2.15	7.28 (7.25) c	7.27	-5.57	-1.41	6.74
6TA	-5.88	-2.29	7.09	7.06	-5.48	-1.57	6.55
7TA	-5.81	-2.41	6.94 (6.97) c	6.88	-5.41	-1.69	6.41
8TA [a]	-5.76	-2.50	6.74	6.73	-5.36	-1.78	6.29
nTH							
2TH	-6.71	-1.02	8.54		-6.32	-0.25	7.97
3TH	-6.50	-1.17	8.16		-6.10	-0.41	7.62
4TH	-6.38	-1.29	7.86		-5.98	-0.53	7.31
5TH	-6.31	-1.38	7.70		-5.91	-0.62	7.16
6TH	-6.30	-1.46	7.61		-5.90	-0.71	7.08
7TH	-6.26	-1.53	7.51		-5.87	-0.78	7.00
8TH	-6.27	-1.61	7.48		-5.88	-0.85	6.97
Reference							
C16S8 [a]	-6.40	-1.68	7.67		-6.02	-0.94	7.17
Tetracene [a]	-5.54	-2.76	6.95		-5.10	-2.03	6.38
Pentacene [a]	-5.28	-3.08	6.57 (6.589) [d]		-4.83	-2.03	5.99
DT-TTF [a]	-5.52	-1.79	6.69		-5.10	-1.01	6.33

* $IP_{\Delta SCF}$ is calculated according to Eq. (3); IP_{FIT} was calculated using the linear fit equation (Figure 5); 1TA = 1TH. [a] From Ref. (Gahungu G. et al., 2009). [b] From Ref. (Sato, N. et al., 1992); [c] From Ref (Kim E-G. et al., 2007). [d] From Ref. (da Silva Filho D. A.;. 2007) and (Coropceanu V. et al., 2002).

Table 2. Atomic orbital contributions (%) from Sulfur (S) and non Sulfur (NS) atoms to the 6 frontier molecular orbitals (FMO) in 8TA and 8TH as compared to their structurally closed homologue ($C_{16}S_8$).

	8TA				8TH				$C_{16}S_8$			
	PBE0		B3P86		PBE0		B3P86		PBE0		B3P86	
FMO*	NS	S	NS	S	NS	S	NS	S	NS	S	NS	S
L+2	23	77	24	76	73	27	73	27	71	29	71	29
L+1	79	21	79	21	66	34	66	34	58	42	58	42
L	75	25	75	25	69	31	68	32	66	34	65	35
H	97	3	97	3	58	42	58	42	61	39	61	39
H-1	24	76	24	76	61	39	61	39	61	39	61	39
H-2	79	21	79	21	61	39	62	38	47	53	47	53

* H = HOMO and L = LUMO.

On the basis of the present results, the same observation stands for the nTH series as well. The experimental oligomer length dependence of the IP is very accurately reproduced by the calculations using both the Koopmans theorem (Koopmans, 1934; Richards W. G.. 1969) and self-consistent field [especially at the B3P86/6-31(d,p) level], with the latter being in a better quantitative agreement with experiment. The Figure 5a shows the linear fit of the B3P86 IP values as a function of Lnn (n = the number of thiophene rings). Using the corresponding linear fit equation (showing a very good linearity, with $R^2 = 0.9993$), the IP (IP_{FIT}) was recalculated (Table 1 and Figure 3). Again, the results agree very well with experimental results where available. Indeed, 7.85, 7.52, 7.27, and 6.88 eV were the computed IP_{FIT} values (using the linear fit equation) for 3TA, 4TA, 5TA, and 7TA respectively, implying an excellent agreement with experimental data. Therefore, IP values may be predicted with acceptable accuracy for n ≥ 8. An additional feature revealed by the same results is that, the IP decreases more rapidly in nTA than in nTH. However, the linear fit equation of the IP as function of lnn shows a bad linearity (see figure 5b; $R^2 = 0.9883$); this was probably ascribed to the very different influence of the oligomer length when n ≤ 5 and n ≥ 6.

HOMO-1 appears to be mainly made of S atomic orbitals for 8TA (76 %) *vs* 39 % for 8TH and **$C_{16}S_8$**. In reverse, the LUMO+1 in all the three cases, is mainly composed of atomic orbitals from the NS atoms (76, 66 and 58% respectively for 8TA, 8TH and **$C_{16}S_8$**). These features suggest a significant difference in electronic structures between the two thiophene oligomers, implying that the helical (and cyclic) structures of 8TH **(**and **$C_{16}S_8$**) induce a significant influence on the electronic structure. From the FMO energy viewpoint, it appears clearly that the E_{HOMO} behaves in the opposite direction of that described for the IP values: it increases with the length of the oligothiophene, while the E_{LUMO} decreases with the length. Consequently, the HOMO-LUMO gap decreases with the length of the oligomer. From the FMO viewpoint (see Figure 6), the general trend is that the HOMO is predominantly composed of delocalized pz atomic orbitals which are symmetric along the nodal plane, and this along with the planarity in the nTA series and nTH (for n≤5) is also suggestive of aromaticity (see NICS values: figure 4).

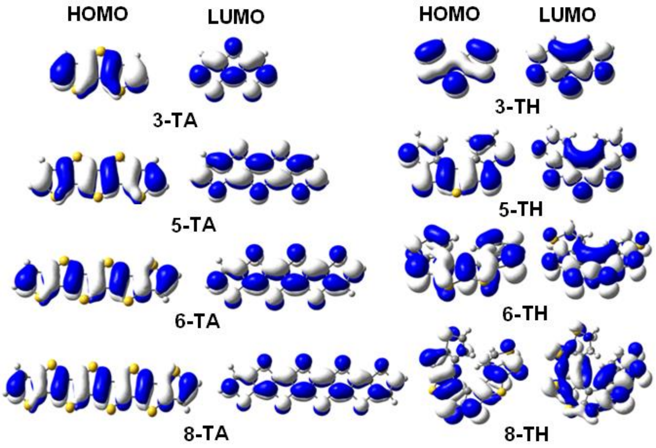

Figure 6: Frontier molecular orbitals for representatives of both the oligothienoacenes (nTA) and thiophenic helicenes (nTH) under investigation.

From the results summarized in Table 2 and Figure 6, one can notice that S atoms contribute more in the HOMO of $C_{16}S_8$ and 8TH than that of 8TA. Both the B3P86/6-31G(d,p) and PBE0/6-31G(d,p) results reveal that S atoms do not contribute for more than 3% to the HOMO of 8TA, while contributing for 42 % to the HOMO of 8TH and 39 % to the HOMO of $C_{16}S_8$. For the LUMO, however, 34±1 and 31±1% of the contributions from S atoms are revealed for $C_{16}S_8$ and 8TH, respectively, *vs* 25% for 8TA. In general, the HOMO-1 appears to be mainly made of S atomic orbitals for 8TA (76 %) *vs* 39 % for 8TH and $C_{16}S_8$. On the other hand, the LUMO+1 in all the three cases, is mainly composed of atomic orbitals from the NS atoms (76, 66 and 58% respectively for 8TA, 8TH and $C_{16}S_8$). These features suggest a significant difference in electronic structures between the two thiophene oligomers, implying that the helical (and cyclic) structures of 8TH **(**and $C_{16}S_8$) induce a significant influence on the electronic structure. From the FMO energy viewpoint, it appears clearly that the E_{HOMO} behaves in the opposite sense of that described for the IP values: it increases with the length of the oligothiophene, while the E_{LUMO} decreases with the length.

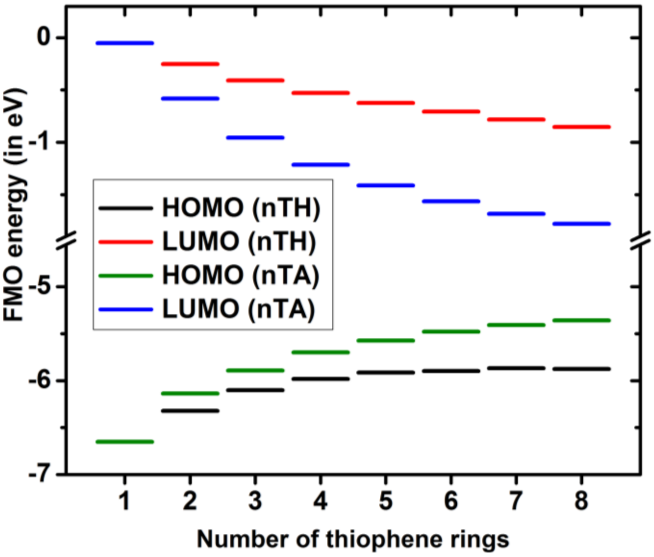

Figure 7: PBE0/6-31G(d,p) evolution of the FMO energies in the two homological series.

Consequently, the HOMO-LUMO gap decreases with the length of the oligomer. From the results shown in Table 1, both the two sets of results (B3P86 and PBE0) are consistent with the fact that most of the oligothiophenes studied herein fulfill the two requirements, comparatively to the materials of reference in this study (also listed). Indeed, one may notice in Table 1 that the highest IP values (9.16 - 6.74 eV with B3P86, and 8.57 - 6.29 eV with PBE0) and the deepest HOMO (in between -7.02 and – 5.76 eV with B3P86, -6.65 and - 5.36 eV with PBE0) in energy correspond to most of them. This suggests a weaker ED strength, comparatively to DT-TTF, pentacene, tetracene, TTF and tetramethylthiofulvalene (TTM-TTF). In comparison with the widely investigated hole-transport materials taken as reference (DT-TTF, pentacene, and tetracene), these results predict a weak reactivity for all the studied oligomers. In both nTA and nTH series, the ED is weak, making them less labile to oxygen. In all the studied cases, the E_{LUMO} is higher than those for tetracene and pentacene, some of them (3TA, 4TA, 5TA, 6TH, 7TH and 8TH) showing a E_{LUMO} value comparable to that of DT-TTF. Assuming that CT can favor the FET use, these properties may allow an improved performance. With reference to λ_h for three of well-studied hole-transport materials, this property was calculated using the same methods for the molecules studied herein, and a comparison was made. The results are summarized in Table 3.

Table 3: Computed intramolecular reorganization energies (in eV) for hole (λh) and electron (λe) in the thiophenic helicenes (for comparison, λh values for tetracene, pentacene, and DT-TTF are listed).

	PBE0		B3P86		B3LYP [a]	B3LYP [b]
	λh	λe	λh	λe	λh	λh
Oligothienoacenes (nTA)						
1TA	0.400	0.425	0.400	0.414	0.400	0.395
2TA	0.424	0.380	0.405	0.370	0.408	0.401
3TA	0.365	0.328 (324) [d]	0.347	0. 312	0.354	0.347 (352) [d]
4TA	0.340	0.306 (293) [d]	0.327	0.288	0.327	0.327 (325) [d]
5TA	0.321	0.278 (270) [d]	0.300	0.259	0.310	0.301 (306) [d]
6TA	0.313	0.267 (252) [d]	0.293	0.249	0.294	0.285 (291) [d]
7TA	0.291	0.264 (237) [d]	0.268	0.237	0.280	0.272 (279) [d]
8TA	0.275	0.239	0.257	0.213[c]	0.269	0.261
Thiophenic helicenes (nTH)						
2TH	0.380	0.286	0.359	0.277	0.356	0.367
3TH	0.242	0.278	0.220	0.270	0.229	0.226
4TH	0.350	0.165	0.327	0.159	0.327	0.327
5TH	0.278	0.132	0.248	0.127	0.253	0.248
6TH	0.243	0.137	0.212	0.139	0.218	0.210
7TH	0.216	2.748	0.194	2.706	0.188	0.229
8TH	0.186	2.750	0.182	2.701	0.183	0.180
Compounds for Reference (for comparison)						
C16S8 [c]	0.133		0.125		0.120	0.126
Tetracene [c]	0.118		0.100		0.115	0.112
Pentacene [c]	0.085		0.077		0.094	0.091 (0.098) [d]
DT-TTF [c]	0.253		0.241		0.243	0.242 (0.238) [e]

[a] PBE0/6-31G(d,p) geometries. [b] B3P86/6-31G(d,p) geometries. [c] Theoretical value from (Gahungu G. et at al., 2009). [d] Theoretical value from ref. (da Silva Filho D. A.. 2007) and (Coropceanu V. et al., 2002). [e] Theoretical value from ref. (Mas-Torrent M., 2004)

As shown (in table 3), the B3LYP//PBE0 (B3LYP//B3P86) results provide λ_h range values of 0.400-0.229 eV (0.395-0.180 eV) and 0.400-0.269 eV (0.395-0.261eV) for nTH and nTA respectively *vs* 0.115 eV (0.112 eV), 0.094 eV (0.091 eV), 0.243 eV (0.242 eV) and 0.120 eV (0.126 eV) for Tetracene, Pentacene, DT-TTF and **$C_{16}S_8$** respectively. For 4TH, 5TH, and 6TH, these results predict a comparable λ_h with that of DT-TTF), while the lowest λ_e values [0.132 – 0.165 eV at the PBE0/6-31G(d,p) and 0.127 – 0.159 eV at the B3P86/6-31G(d,p)] were predicted for them. These values were found to be even more smaller than the predicted λ_e for 8TA [0.239 eV at PBE0/6-31G(d,p) and 0.213 eV at B3P86/6-31G(d,p)]. As a general observation in the series considered, a tight relationship between the molecular structure (helical, cyclic, and linear) and λ_h/λ_e was identified. Indeed, the results clearly show a smaller λ_h/λ_e for nTA than nTH. Moreover, the longer the oligomer is, the better the hole mobility is expected to be. The same conclusions are supported by PBE0 and B3P86 results, implying a reliability of this study. In agreement with the trend recently reported by Kim Eung-Gun et al. for a series of thienoacenes,[24] λ_e is smaller than λ_h for nTA (n = 3, 4, 5, 6 and 7). The λ_e values were also found to be smaller than λ_h for nTH series (n = 2, 3, 4, 5 and 6), with surprisingly high λ_e (> 2.7 eV) values being found for 7TH and 8TH. Interestingly, λ_h for 3TH was predicted to be 0.242 eV, 0.220 eV, 0.226 eV and 0.226 eV with PBE0, B3P86,

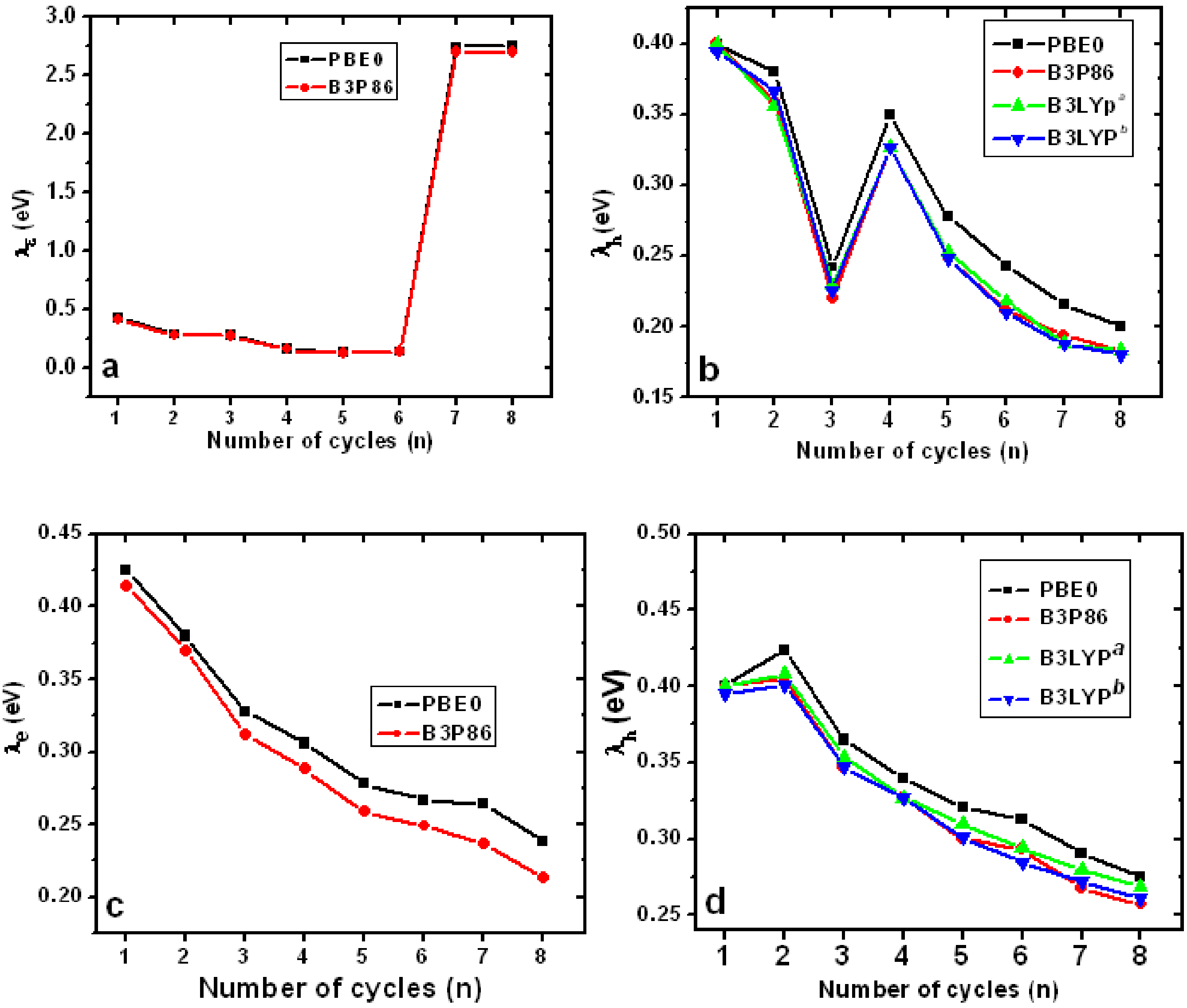

Figure 8. Reorganization for hole (λ_h) and electron (λ_e) as a function of computational method and number of thiophene ring.

B3LYP//PBE0 and B3LYP//B3LYP respectively, well below the λ_h values of both 2TH and 4TH while, in general for the remaining oligomers of the two series, the rule was found to be that both λ_h and λ_e decrease with oligomer length. Accordingly, we suggest further investigation on the OFET use of some of the studied compounds (such as 4TH, 5TH and 6TH) and synthesis of relating derivatives.

3.4. Dipole polarizability

Organosulfur compounds are also attractive in terms of optical properties such as nonlinear optical properties. Some references to these studies will more extend the application of the present results (Nakano, M., 1999 ; Nakano, M., 1999 b & Nakano, M., 2000). Normally, molecules with centrosymmetry have no hyperpolarizability. Probably due to this, all the 27 tensor components mutually cancelled out each other and the first hyperpolarizability becomes zero for $C_{16}S_8$ and some of its plate-like derivatives. The centrosymmetry being broken in the kind of systems of interest in this work, we found interesting the exploration of this property. For the discussion of the second order polarizability (β), examining the physical mechanism concerning the determination of the dipole polarizability (α) is also important. The average polarizability <α> is given by:

$$<\alpha> = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The computed dipole polarizability coefficients for systems under investigation are listed in Table 4. Due to the C_{2V} symmetry for most of the studied systems, only the diagonal dipole polarizability tensors α_{ii} (i = x, y, z) are nonzero. Among the α_{ii}

components, the α_{xx} component is the largest in general, while the α_{yy} and α_{zz} components are the smallest. Hence, the property of the studied compounds (nTA and nTH) is dominantly determined by the z-direction transition.

Table 4. The B3P86/6-31G(d,p) computed dipole polarizabilities (1 × 10-^{24} esu) for systems 1-8 in both the oligothienoacenes (nTA) and thiophenic helicenes (nTH).

Oligomer	α_{xx}	α_{yy}	α_{zz}	α	$\Delta\alpha$
			Oligothienoacenes		
1TA	63.28	24.32	63.09	50.23	38.87
2TA	104.18	39.08	117.57	86.94	72.73
3TA	180.57	53.26	147.83	127.22	114.50
4TA	247.68	67.28	205.13	173.36	163.34
5TA	355.29	81.21	235.77	224.09	238.00
6TA	445.55	95.11	299.13	279.93	304.85
7TA	459.79	108.98	450.74	339.83	346.37
8TA					
			Thiophenic helicenes		
2TH	116.72	38.66	100.86	85.42	71.46
3TH	184.56	52.65	131.84	123.02	115.00
4TH	231.62	66.47	186.50	161.53	147.85
5TH	287.54	80.09	232.21	199.94	186.06
6TH	320.26	98.00	298.24	238.83	212.11
7TH	354.55	127.63	346.10	276.09	222.81
8TH	383.78	158.30	390.89	310.99	229.12

4. Conclusions

A comparative study was made on the homological series nTH and nTA series from different viewpoints by means of quantum chemical methods based on DFT-B3P86 and PBE0. 8TH and 8TA were compared to $C_{16}H_8$, allowing pertinent conclusions on the influence of the helical, linear and cyclic conformation on the molecular structure and a number, chemical / physical properties. The main conclusions are the following: (1) Up to n = 8, the linear conformation does not affect the planarity of the oligomers, while from n = 6, the planarity in the nTH disappears to give place to a helical conformation: although relatively important geometrical parameters changes are identified upon relaxation, this feature was not altered upon redox phenomena. (2) The helical and cyclic conformation induces some changes in the aromatic character: comparing 8TH to 8TA, although the trend is similar, the helical structure strengthens the aromatic character of the peripheral rings, while it slightly weakens that of the internal ones. Except for the peripheral thiophene rings in 8TA and 8TH, the aromatic character of the thiophene increases in the order of 8TH < 8TA < $C_{16}S_8$. (3) Both the HOMO and LUMO are stabilized with the number of thiophene rings, with the former being the least sensitive to this parameter. Consequently, the energy gap decreases with the number of rings. (4) The IP decreases with the number of thiophene rings according to an excellent linearity of the IP as a function of ln*n* (n = number of rings). More interestingly, all these properties change in the same direction for the nTA and nTH series, the quickest variations being revealed in the former. (5) The intramolecular reorganization energy (both λ_h and λ_e) decreases with oligomer length in nTA series, but not within the nTH series with the 3TH being identified as an exception to this rule: its λ_h and λ_e were predicted to be smaller comparatively to those for 3TA, 4TA, 5TA, 4TH, and 5TH. Interestingly, this was also found to be smaller than the one for DT-TTF, an already known OFET material. We strongly recommend a particular attention on some of these compounds for OFET use. (6) Within the two series, the dipole polarizability increases with the oligomer length.

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