



## Semiconducting Oligomers of 1,4-dimethoxybenzene, Thiophene and Thiazole: A Theoretical Study

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### Authors' contributions

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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### ABSTRACT

Organic semiconducting oligomers containing three to nine heterocyclic units and based on 1,4-dimethoxybenzene, thiophene and thiazole have been studied by DFT and TDDFT at the B3LYP/6-31G(d,p) level. The energy of each molecule, those of the frontier orbitals HOMO and LUMO, the width of the band gaps and the optical properties have been calculated. The inter-ring distances, dihedral angles and torsional angles have been elucidated. These molecules are planar  $\pi$ -conjugated systems. The band gaps of the longer oligomers studied range from 2.53 to 2.72 eV and their excitation energies calculated by TDDFT vary from 2.22 to 2.36 eV. Wavelengths of absorption bands of 524 to 556 nm are also obtained by TDDFT. The results of this theoretical study show that these organic molecules have interesting properties and can potentially be used as components in solar cells.

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## 1. INTRODUCTION

Organic semiconductors are  $\pi$ -conjugated polycyclic and heterocyclic systems which have a certain degree of electrical conductivity. There are several varieties of these compounds such as molecular crystals, amorphous molecular films and polymer films [1-3]. They have moderately low-lying frontier orbitals (the HOMO and the LUMO) with weak energy gap of the order of 1.5 to 3 eV. Early investigations on these systems were on the elucidation of the mechanism of the charge transport and of their optical properties. In 1977, work on conjugated polymers showed that their conductivity can be greatly increased through controlled doping. These findings were well recognized by the Nobel Prize award in chemistry in 2000 [4]. Since then, numerous semiconducting molecules have been synthesized by methods in which aromatic monomer units undergo coupling reactions such as the Yamamoto or Suzuki couplings. Oxidative polymerization of conjugated monomers has also been used. A great deal of experimental research work has been done to understand their electrical and optical properties and to relate them to their geometric structures. Charge carrier mobility, UV-visible absorption maxima, optical band gaps, thermal stability, stability in ambient oxygen and humidity as well as solubility in common organic solvents have been measured [5-8]. The electrical conductivity is extrinsic and may have an origin in the delocalization of the  $\pi$ -electrons or the movement of charge defects generated by redox reactions under an electric field. Structural and morphological studies have shown the dependence of molecular packing on the electrical conductivity due to its effect on charge mobility. Thiophene units in oligomers or polymers were found to give more planar structures, increase in the  $\pi$ -bonds conjugation and better  $\pi$ -electrons delocalization. P-type conductivity was observed with most compounds that contained thiophene or thiazole groups [9].

The aim of both fundamental and industrial material research on organic semiconductors is to develop new molecules that give good performances in electronic low cost devices. Either in the form of molecular crystals or in the form of polymer films, these compounds play nowadays an important role in microelectronics and are used as components in the manufacture

of materials such as flexible light sources, plastic solar cells and organic field effect transistors [10-12].

Theoretical studies have also been carried out on these compounds to enlighten experimental findings with descriptions of the electronic structures and other properties [13, 14]. Bouachrine M. and coworkers [15] have reported the optimized structures, electronic and optical properties of oligomers based on N-substituted carbazole, thiophene, bipyridine and phenylene rings bearing donor and acceptor groups. These studies were done at the Density Functional Theory (DFT) and the Time Dependent Density Functional Theory (TDDFT) levels and their results showed that these oligomers may be used in association with fullerene [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PC60BM) in solar cells. In general, theoretical results are useful guidelines for experiments and for understanding observed chemical properties. Our present work is a contribution to the fundamental research on new molecules and reports a theoretical study on the structural, electronic and optical properties of oligomers based on 1,4-dimethoxybenzene, thiophene and thiazole.

## 2. COMPUTATIONAL METHODOLOGY

The oligomers of interest in the present study are based on units of 1,4-dimethoxybenzene, thiophene and thiazole. The molecule of 1,4-dimethoxybenzene is at the center of each oligomer chain. The combinations of these units can lead to several conformational isomers. In fact, depending on the relative position of the heteroatoms (oxygen, sulfur or nitrogen) in the chain, one can obtain several conformers. We search for conformers that have interesting electronic and optical properties, mainly those which have weak band gaps. Our theoretical study is therefore focused on the optimized geometries and optoelectronic properties of these compounds and is carried out in the gas phase.

All these quantum calculations were done with the Gaussian 09 package [16]. The geometries of the fragments (1,4-dimethoxybenzene, thiophene and thiazole) and those of the oligomers were optimized at the DFT level [17,18] with the hybrid functional B3LYP [19]. C1

symmetry was considered for all these molecular structures. The basis set 6-31G(d,p) of the Gaussian 09 program was also used. The DFT method is convenient for the study of these large molecules because it includes effects of electron correlation. The electronic properties of these systems are deduced from the data of their optimized structures. The band gaps are evaluated as the difference of the Kohn-Sham energies of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO). TDDFT was used to determine the optical properties of the oligomers which include UV-visible maximum absorption wavelengths and the corresponding excitation energies. A Natural Bond Orbital (NBO) analysis of orbital interactions in one of the oligomers was also done by the Gaussian 09 program at the optimized geometry. The molecules were visualized at their minimal energy structures with the Gauss View visualization program included in the Gaussian 09 package.

### 3. RESULTS AND DISCUSSION

#### 3.1 Geometries, Energies and Electronic Properties of the Oligomers

##### 3.1.1 Oligomers based on thiophene and 1,4-dimethoxybenzene

Two conformational isomers of oligomers formed by using thiophene units and 1,4-

dimethoxybenzene have been investigated. They are labeled A1 and A2 and contain a fixed number of thiophene units in addition to the central phenylene unit. Their fully optimized structures are displayed in Figs. 1 and 2. As shown, each of the compounds A1-A and A2-A contain three rings; A1-B and A2-B are those of seven rings while A1-C and A2-C have nine rings. One can observe that the first thiophene molecules are linked to 1,4-dimethoxybenzene at their position 2 and the repeat units are such that the position 2 of one ring is connected to the position 5 of the next one, that is, in a head-to-tail manner. These arrangements lead to shorter S---O distances in compounds of type A1 ( $d_{S\cdots O} = 2.8 \text{ \AA}$ ) than those of type A2 ( $d_{S\cdots O} = 5.2 \text{ \AA}$ ).

The optimization gives minimal geometries with positive vibration frequencies. The geometrical parameters of interest here are the inter-ring C-C distances, the dihedral angle ( $\Phi$ ) that the plane of the phenyl ring of the 1,4-dimethoxybenzene forms with those of the first thiophene units and the torsional angles ( $\theta$ ) between the rings of the oligomers. The calculated values are all collected in Table 1. Table 2 contains the molecular and frontier orbitals (the HOMO and the LUMO) energies, band gaps and optical properties ( $\lambda_{\max}$ ,  $E_{\text{excitation}}$ ) of the studied systems at their optimized structures. Zero-point vibrational energy corrections are included in the molecular energies ( $E_{\text{electronic}} + \text{ZPE}$ ).

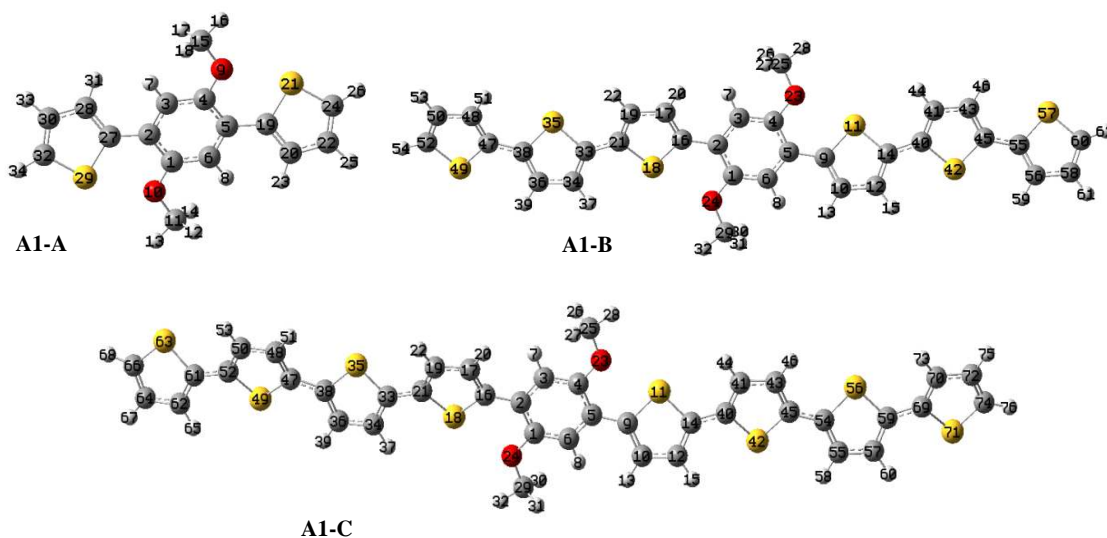


Fig. 1. Optimized geometric structures of oligomers A1-A, A1-B and A1-C

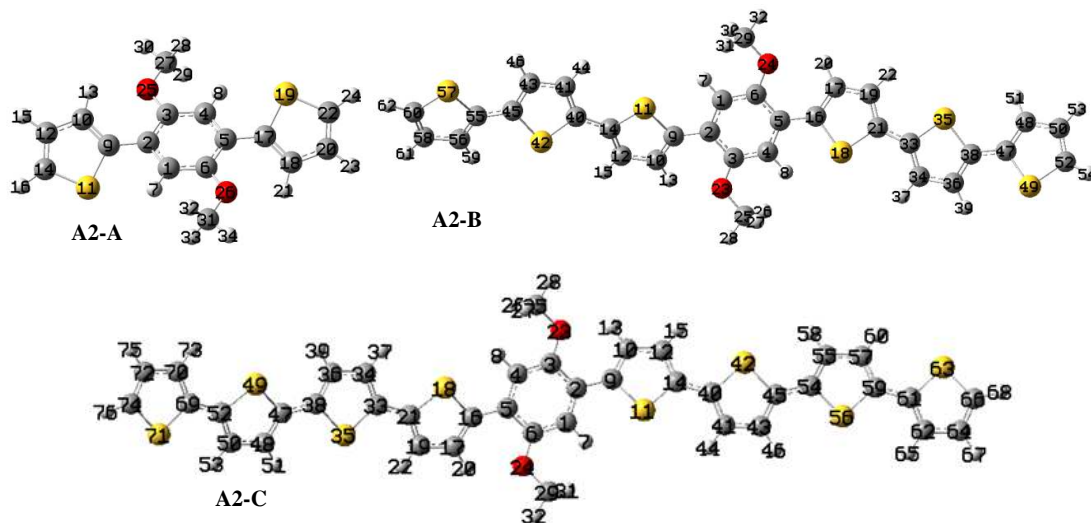


Fig. 2. Optimized geometric structures of oligomers A2-A, A2-B and A2-C

Table 1. Inter-ring C-C distances, dihedral angles ( $\Phi$ ) between the planes of thiophene and of 1,4-dimethoxybenzene and torsional angles ( $\theta$ ) between thiophene rings of the oligomers

Oligomer	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d_3(\text{\AA})$	$d_4(\text{\AA})$	$\Phi(^{\circ})$	$\theta_1(^{\circ})$	$\theta_2(^{\circ})$	$\theta_3(^{\circ})$	$\theta_4(^{\circ})$
A1-A	C5- C19 1.467	.....	.....	.....	C6C5- C19C21 159.40	C4C5- C19C21 -21.77	.....	.....	.....
A1-B	C5- C9 1.462	C14- C40 1.444	C45- C55 1.447	.....	C6C5- C9C11 164.42	C4C5- C9C11 -15.55	C11C14- C40C41 13.13	C43C45- C55C57 -16.70	.....
A1-C	C2- C16 1.462	C21- C33 1.443	C38- C47 1.442	C52- C61 1.447	C3C2- C16C18 164.96	C1C2- C16C18 -15.01	C18C21- C33C34 12.43	C36C38- C47C49 -12.78	C49C52- C61C62 17.69
A2-A	C5- C17 1.466	.....	.....	.....	C6C5- C17C19 154.93	C4C5- C17C19 -23.95	.....	.....	.....
A2-B	C2- C9 1.461	C14- C40 1.443	C45- C55 1.446	.....	C3C2- C9C11 159.51	C1C2- C9C11 -19.82	C11C14- C40C41 13.61	C43C45- C55C57 -17.16	.....
A2-C	C2- C9 1.461	C14- C40 1.442	C45- C54 1.442	C59- C61 1.446	C3C2- C9C11 159.82	C1C2- C9C11 -19.51	C11C14- C40C41 13.28	C43C45- C54C56 -12.89	C56C59- C61C62 17.62

The inter-ring C-C distances in these oligomers given in Table 1 range from 1.442 Å to 1.467 Å. They are shorter than those encountered in alkanes ( $d_{C-C} = 1.54$  Å) by approximately 0.1 Å. The interactions of the monomers have therefore induced partial double C-C bonds between the rings leading to elongation of the conjugation and delocalization of the  $\pi$ -electrons along the carbon-heteroatom chains. This double bond character reduces the length of the connectivity and contributes to the rigidity of the conjugated system. The values of the dihedral angles ( $\Phi$ ) vary between 154 and 165°, indicating that the rings of the first

thiophene units and that of the phenyl group of 1,4-dimethoxybenzene are not perfectly coplanar although the short S...O distances in conformer A1 predict non-covalent stabilizing interactions between these atoms. Similar results were obtained at the DFT/B3LYP/6-31G(d) level of theory by Bouachrine M. and coworkers for oligomers based on 1,4-dimethoxybenzene, thiophene and bipyridine. The torsional angles ( $\theta$ ) between thiophene units in our molecules are relatively small for both types of conformers. These low values suggest a flattening of the chains with addition of units of thiophene.

**Table 2. Frontier orbital and molecular energies, band gap and optical parameters of oligomers A1-A, A1-B, A1-C, A2-A, A2-B and A2-C**

Oligomer	$E_{(\text{HOMO})}$ (eV)	$E_{(\text{LUMO})}$ (eV)	$^{(a)}\Delta E_1$ (eV)	$E_{\text{electronic}+\text{ZPE}}$ (au)	$\lambda_{\text{max}}$ (nm)	$E_{\text{excitation}}$ (eV)
A1-A	-5.001	-1.294	3.70	-1564.6746	358.20	3.46
A1-B	-4.685	-1.977	2.70	-3771.7606	512.27	2.42
A1-C	-4.643	-2.106	2.53	-4875.3036	556.24	2.22
A2-A	-5.035	-1.294	3.74	-1564.6743	359.10	3.45
A2-B	-4.728	-2.005	2.72	-3771.7601	510.43	2.42
A2-C	-4.680	-2.132	2.55	-4875.3032	553.82	2.23

$$^{(a)}\Delta E_1 = E_{\text{LUMO}} - E_{\text{HOMO}}$$

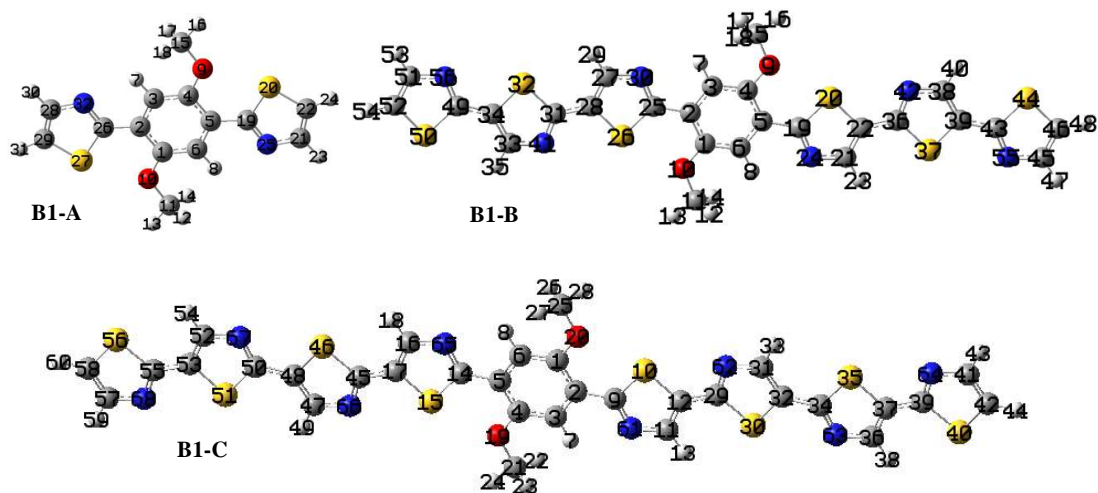
The results in Table 2 indicate that within each series of conformers, the energies of the HOMO increase while those of the LUMO decrease with addition of thiophene units. The band gap narrows by approximately 1.2 eV from the shorter systems to the longer ones. Both A1 and A2 isomers show, for the longer chains, similar values of about 2.50 eV for the energy gaps. These band gaps are well within the range of observed values of organic semiconductors (1.5 to 3 eV). We also found that the HOMO and LUMO have respectively  $\pi$  and  $\pi^*$  character and may be involved in  $\pi \rightarrow \pi^*$  transitions caused by absorption or emission of visible radiation. The molecular energies corrected to take into account zero-point vibrational energies are also given in Table 2. They indicate that these two conformers have similar stabilities, in agreement with their relative geometries and electronic properties.

### 3.1.2 Oligomers based on thiazole and 1,4-dimethoxybenzene

The geometry optimization was also done at the B3LYP/6-31G(d,p) level for oligomers resulting

from linking thiazole rings at the positions 2 and 5 of the phenyl ring and then forming 2,5-linked thiazole rings to get molecular chains of 3, 7 or 9 rings. The fully optimized structures of these molecules are labeled B1 and B2 and are shown in Figs. 3 and 4. These conformational isomers differ from the relative position of the heteroatoms N and S of the thiazole units in the molecules. While the B1 molecules have shorter O—S distances, in the B2 the shorter are O—N distances. The geometric parameters are summarized in Table 3. Table 4 contains calculated frontier orbitals and molecular energies, band gaps, and optical properties.

As previously observed for the oligomers of type A1 and A2, the results of the conformers B1 and B2 displayed on Table 3 indicate that the calculated inter-ring C-C bond lengths vary from 1.440 Å to 1,470 Å and are intermediate between double C=C bonds (1.35 Å) and single C-C bonds (1.54 Å). Due to the character of these bonds, one expects delocalization of the  $\pi$ -electrons on all connected rings of these molecules. The data show slight shortening of

**Fig. 3. Optimized geometric structures of oligomers B1-A, B1-B and B1-C**

the inter-ring distances with increase in the number of thiazole units. One may compare the bond length C2-C26 (1.466 Å) in the compound B1-A with that of C5-C14 (1,461 Å) in B1-C. This suggests a strengthening of these bonds with elongation of the chains due probably to a better delocalization of the  $\pi$ -electrons. The calculated values of the dihedral angles ( $\Phi$ ) and those of

the torsional angles ( $\theta$ ) are respectively 180° and 0° for the conformer B1. Therefore, the molecules which have this conformation have planar structures. This may be due to the existence of non-covalent S...O and N...H stabilizing interactions. The geometries of the isomers of type B2 resemble those of compounds A1 and A2.

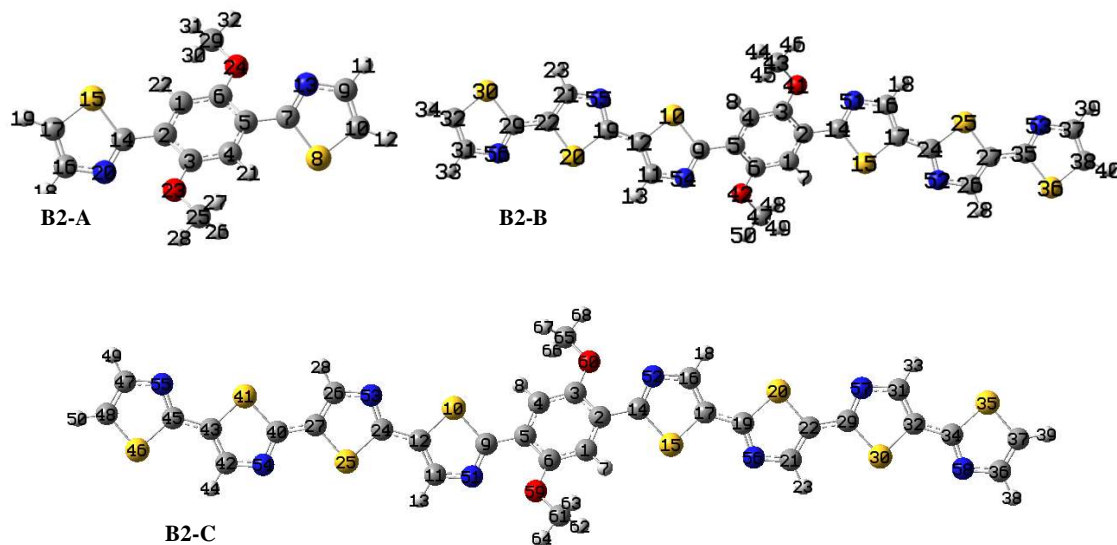


Fig. 4. Optimized geometric structures of oligomers B2-A, B2-B and B2-C

Table 3. Inter-ring distances C-C, dihedral angles ( $\Phi$ ) between the planes of thiazole and of 1,4-dimethoxybenzene and torsional angles ( $\theta$ ) between thiazole rings of the oligomers

Oligomer	$d_1$ (Å)	$d_2$ (Å)	$d_3$ (Å)	$d_4$ (Å)	$\Phi$ (°)	$\theta_1$ (°)	$\theta_2$ (°)	$\theta_3$ (°)	$\theta_4$ (°)
B1-A	C2- C26 1.466	.....	.....	.....	C6C5- C19C20 -180.00	C4C5- C19C20 0.0005	.....	.....	.....
B1-B	C5- C19 1462	C22- C36 1.441	C39- C43 1.443	.....	C6C5- C19C20 -180.00	C4C5- C19C20 0.001	C20C22- C36C42 0.005	C38C39- C43C44 0.004	.....
B1-C	C5- C14 1.461	C17- C45 1.440	C48- C50 1.440	C53- C55 1,442	C3C2- C9C10 -180.00	C1C2- C9C10 0.005	C10C12- C29C62 0.001	C31C32- C34C35 0.001	C35C37- C39C64 0.0006
B2-A	C2- C14 1.470	.....	.....	.....	C6C5- C7C8 144	C4C5- C7C8 -36.6	.....	.....	.....
B2-B	C5- C9 1.466	C12- C19 1.442	C22- C29 1.444	.....	C3C2- C14C15 147.34	C1C2- C14C15 -33.36	C15C17- C24C52 -31.66	C26C27- C35C36 -31.66	.....
B2-C	C2- C14 1.466	C17- C19 1.441	C22- C29 1.441	C32- C34 1.444	C3C2- C14C15 147.19	C1C2- C14C15 -33.57	C15C17- C19C56 1.03	C21C22- C29C30 -0.34	C30C32- C34C58 0.11

One can observe from the molecular energies on Table 4 that the conformers of type B1 are more stable than their isomers of type B2 and this is in good agreement with their relative geometries. The width of the band gap decreases with increase in the number of units of thiazole. They are slightly higher than those of compounds A1 and A2 but are still in the range of semiconductor energy gaps. The energies of their frontier orbitals are much lower than those of their A1 and A2 counterparts due to the presence of the electron donor atom N in these molecules.

### 3.2 Optical Properties

The UV-visible maximum absorption wavelengths and their corresponding excitation energies for the oligomers as determined by TDDFT appear on Tables 2 and 4. One observes an increase of the wavelength upon addition of the thiophene or thiazole units. This suggests an elongation of the conjugation and agrees with the inter-ring distances and the planar structure of these oligomers. As expected, the excitation energies calculated at these wavelengths decrease with increase in the chain length. For the molecules with longer chains, the wavelengths range from 524 nm for compound B2-C to 556 nm for A1-C and fall within the visible region. Their excitation energies vary from 2.22 to 2.36 eV and the lowest are obtained with the thiophene derivatives A1-C and A2-C. Therefore, for these oligomers, the data predict light absorption or emission in the visible region between the ground states and the first excited states. Vanossi D, et al. [20] have shown that DFT energy gaps are in good agreement with experimental band gaps measured by electrochemical methods. These values are higher than excitation energies (optical band gaps) and the negative of the energy difference gives an estimation of the electron-hole binding energy.

Organic semiconductors have low intrinsic conductivities due to their relatively large band

gaps compared to those of inorganic semiconductors. Their conductivities may be increased by photogeneration of charge carriers and this process is used in bulk heterojunction solar cells. In these devices, the HOMO and LUMO levels of the donor and acceptor molecules are of great interest in the transfer of photoexcited electrons. Most of these heterojunction solar cells have the fullerene molecule [6, 6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM 60) as an acceptor component. ( $E_{\text{HOMO}} = -6.1$  eV;  $E_{\text{LUMO}} = -3.7$  eV). For an efficient electron injection from the valence band of an electron donor to the conduction band of an electron acceptor, the donor HOMO level should lie between the frontier orbitals of the acceptor and its LUMO should be higher than the LUMO of the acceptor. One may notice that this is indeed observed with all the oligomers studied if PCBM 60 is used as acceptor. The theoretical open circuit voltage  $V_{\text{OC}}$  can be evaluated using expressions (1).

$$V_{\text{OC}} = |E_{\text{HOMO}}^{\text{Donor}}| - |E_{\text{LUMO}}^{\text{Acceptor}}| - 0.3 \quad (1)$$

This expression takes into account the loss of energy that occurs during the photo charge generation.

For Dye-sensitized solar cells (DSSCs), the open circuit voltage is given by expression (2):

$$\alpha = |E_{\text{LUMO}}^{\text{Donor}}| - |E_{\text{LUMO}}^{\text{Acceptor}}| \quad (2)$$

The values of  $V_{\text{OC}}$  calculated from the data on Tables 2 and 4 and the frontier orbital energies of PCBM 60 are respectively 0.64, 0.68, 1.32 and 1.39 eV for A1-C, A2-C, B1-C and B2-C. The values of  $\alpha$  for the same compounds are respectively 1.59, 1.57, 1.01 and 1.04 eV. They are small and suggest that electron transfer from the HOMO levels of these oligomers used as donors to the LUMO of PCBM 60 as acceptor is possible.

**Table 4. Frontier orbital and molecular energies, band gap and optical parameters of oligomers B1-A, B1-B, B1-C, B2-A, B2-B and B1-C**

Oligomer	$E_{\text{(Homo)}}$ (eV)	$E_{\text{(Lumo)}}$ (eV)	$^{(a)}\Delta E_1$ (eV)	$E_{\text{electronic+ ZPE}}$ (au)	$\lambda_{\text{max}}$ (nm)	$E_{\text{excitation}}$ (eV)
B1-A	-5.367	-1.733	3.63	-1596.797401	369.48	3.35
B1-B	-5.316	-2.527	2.78	-3868.110110	389.6	3.18
B1-C	-5.323	-2.674	2.65	-5003.766044	535.67	2.31
B2-A	-5.399	-1.621	3.77	-1596.780261	367.71	3.37
B2-B	-5.383	-2.501	2.88	-3868.091836	492.04	2.51
B2-C	-5.390	-2.662	2.73	-5003.747620	524.03	2.36

$$^{(a)}\Delta E_1 = E_{\text{Lumo}} - E_{\text{Homo}}$$

Table 5. Second order perturbation energies  $E_2$  of NBOs interactions in A1-B

Donor NBO i	Acceptor NBO j	Occupancies NBO i/ NBO j	$E_2$ (kcal/mol)	Donor NBO i	Acceptor NBO j	Occupancies NBO i/ NBO j	$E_2$ (kcal/mol)
<sup>(b)</sup> BD(2)C1-C6	<sup>(c)</sup> BD*(2)C2-C3	1,696/0,445	17,20	BD(2)C43-C45	BD*(2)C40-C41	1,800/0,359	16,07
	BD*(2)C4-C5	1,696/0,462	17,82		BD*(2)C55-C56	1,800/0,350	13,97
BD(2)C2-C3	BD*(2)C1-C6	1,666/0,382	18,95	BD(2)C55-C56	BD*(2)C43-C45	1,815/0,355	13,70
	BD*(2)C4-C5	1,666/0,462	21,51		BD*(2)C58-C60	1,815/0,296	16,75
BD(2)C4-C5	BD*(2)C1-C6	1,590/0,382	19,26	BD(2)C58-C60	BD*(2)C55-C56	1,866/0,350	14,82
	BD*(2)C2-C3	1,590/0,445	21,19	<sup>(d)</sup> LP(2)S11	BD*(2)C9-C10	1,652/0,366	20,97
	BD*(2)C9-C10	1,590/0,366	15,36		BD*(2)C12-C14	1,652/0,371	21,67
BD(2)C9-C10	BD*(2)C4-C5	1,790/0,462	13,37	LP(2)O23	BD*(2)C4-C5	1,847/0,462	25,86
	BD*(2)C12-C14	1,790/0,371	16,51	LP(2)O24	BD*(2)C1-C6	1,847/0,382	29,14
BD(2)C12-C14	BD*(2)C9-C10	1,783/0,366	17,11	LP(2)S42	BD*(2)C40-C41	1,675/0,359	20,37
	BD*(2)C40-C41	1,783/0,359	14,81		BD*(2)C43-C45	1,675/0,355	20,47
BD(2)C40-C41	BD*(2)C12-C14	1,794/0,371	14,16	LP(2)S57	BD*(2)C55-C56	1,653/0,350	20,98
	BD*(2)C43-C45	1,794/0,355	16,47		BD*(2)C58-C60	1,653/0,296	21,24

<sup>(b)</sup>BD(2)C-C is a  $\pi_{c-c}$  NBO; <sup>(c)</sup>BD\*(2) is a  $\pi_{c-c}^*$ NBO. <sup>(d)</sup>LP: lone pair



### 3.3 Natural Bond Orbital Analysis of the Interactions of Orbitals in Oligomer A1-B

The theory and applications of NBO analysis have been outlined by Reed A. E. and coworkers [21]. The analysis transforms an input basis set into an orthonormal localized basis set consisting of natural atomic orbitals or natural hybrid orbitals. Natural bond orbitals are orthonormal molecular orbitals constructed for an N-electron system by using natural atomic orbitals. They well describe the electron distribution in chemical substances and give their best Lewis structures. An important aspect of NBO analysis is that it can be used to elucidate the presence of intra and intermolecular interactions in chemical species. An occupied NBO of a donor group can interact with an empty one of an acceptor and that can lead to the stabilization of a system. The stabilizing interaction energy is given by the second order perturbation energy  $E^{(2)}$  noted here  $E_2$  obtained by the analysis of the Fock matrix in the NBO basis by using expression (3).

$$E_2 = q_i \frac{F_{ij}^2}{\epsilon_j - \epsilon_i} \quad (3)$$

In which  $q_i$  is the occupancy of the donor NBO,  $F_{ij}$  is an off-diagonal Fock matrix element,  $\epsilon_i$  and  $\epsilon_j$  are respectively the energies of the donor and the acceptor NBOs. The results for the oligomer A1-B are displayed in Table 5. Interactions are similar at both sides of the phenyl ring so that only those on the right side are listed. Moreover, only interaction energies greater than 10 kcal.mol<sup>-1</sup> have been considered. There are many other weaker interactions.

The results indicate that these interactions are between intra and inter-rings NBOs. They involve  $\pi_{C-C}$  donor bonds and  $\pi^*_{C-C}$  acceptors of the phenyl and thiophene rings linked to it. They also occur with NBOs within and between thiophene units. The highest energies (over 20kcal.mol<sup>-1</sup>) are encountered with intra-rings interactions that involve lone pairs of the oxygen and sulfur atoms with  $\pi^*_{C-C}$  orbitals. The relative orientation of the interacting orbitals has an effect on the strength of the interaction and this shows here that one of the lone pair orbitals on the heteroatoms S and O has a  $\pi$  character. Those interactions contribute to delocalize the electronic charge over the entire molecular chain and that is indicated by the occupancies of the acceptor NBOs. This delocalization of the electronic charge of the heteroatoms lone pairs and of the  $\pi$ -electrons

strengthens the bonds between the molecular units and leads to the planar structure of the oligomers.

The calculated natural atomic charges on the oxygen atoms are -0.53a.u and those of their nearest sulfur atoms (S<sub>11</sub> and S<sub>18</sub>) are 0.49a.u. One expects electrostatic interactions between these heteroatoms that will contribute to rigidify the oligomer chain.

### 4. CONCLUSION

In this work, we have done a theoretical investigation on the geometries and optoelectronic properties of oligomers based on 1,4-dimethoxybenzene, thiophene and thiazole. Molecules that contain up to nine rings have been studied. For all these oligomers, the elongation of the molecular chain led to a gradual decrease of the energy gap between the frontier orbitals. This energy splitting varied from 2.5 to 3.7 eV. This indicates that these compounds may exhibit semi-conducting properties. The increase in the molecular chain length also induced a decrease in the excitation energy determined by TDDFT. These oligomers present many intra and inter-unit interactions which contribute to their rigidity and to a better delocalization of the  $\pi$ -electrons. Our results indicate that these molecules have interesting electronic and optical properties which make them potential components of electronic devices such as solar cells.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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