

DFT calculations on conjugated organic molecules based on thienothiophene for electronic applications

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ABSTRACT. We report theoretical studies on the optoelectronic structural properties of five thienothiophene (T) conjugated π conjugates. The geometries, the prediction of the optoelectronic structural properties of the five compounds are studied by calculations of functional density theory (DFT). The absorption properties (λ_{max} , E_{tr} , f) of molecules are gained by the (DFT) B3LYP / 6-31G (d) ZINDO method, so that the most occupied molecular orbitals (HOMO), the least molecular orbitals occupied (LUMO), the energy deficit being calculated using the factor Gaussian 09 and its GaussView 5.0.8 graphical interface.

Keywords: DFT; Structural properties; Optoelectronic properties; Thienothiophene; HOMO; LUMO; Gap.

1. INTRODUCTION

Organic photovoltaic tool have opened up the potential for producing light energy in a simple and economical way. The bilayer technology typically uses organic semiconductor cables intercalated between the anode and cathode electrodes, the first is an electron acceptor and the second is an electron donor [1-2]. In this work, we have based on unsubstituted thienothiophene (fig.1a) as a π -conjugated organic semiconductor. We mainly used DFT to study the optoelectronic and structural properties of the four molecules.

Thienothiophene often refers to all the structurally related thiophene derivatives with the given formula $C_6H_4S_2$. As for importance, they are: thiophene thieno (3,2-b), thieno (2,3-b) thiophene and thieno (3,4-b) thiophene. The other isomers are characterized by S (IV) and are less stable [3]. Thieno (2,3-b) thiophene was the series' first member of the series to be isolated.

The thienothiophene conjugate compounds have extensive delocalization of n electrons along the molecular backbone, making them attractive for various optoelectronic applications [4-5].

Because of this applicative interest and to that these shirt systems can be used as model compounds for the parent polymer, they have been extensively studied [6-7]. Also, because of their controllable and precisely defined structure, physical properties can be correlated with the conjugation length and the

side chains. Therefor implementing these molecular structures by functionalization at the terminal and side positions permit their application as molecular materials in organic field-effect transistors [8-9], light-emitting devices [10, 11, 12,13], photovoltaic cells [14-15], or even as molecular wires for information storage or transfer [16-17].

Polymers and oligomers with low band gap are expected to show not only good intrinsic conductivity but also nonlinear optical properties [18-19]. For their successful design, it is vital to have a complete understanding of the relationship between electronic properties and the chemical structure of polymers [20-21]. Different routes are here followed for designing novel conducting polymers, one is provided by donor-acceptor polymers, based on the approach suggested for the first time by Havinga et al. [22]. The study of conjugated oligomers is very attractive for finite size systems can be achieved with a well-defined chemical structure and high purity. This opens the way for the investigation of electronic properties as a function of chain length and extent of the parent π -electron system.

In this paper, we present a detailed study of DFT (B3LYP / 6-31 (d)) of the four thienothiophene compounds. We focus on the geometric structure of the compounds and the electronic properties. The chemical structure and optimized structures of the compounds studied are illustrated in FIG. 1

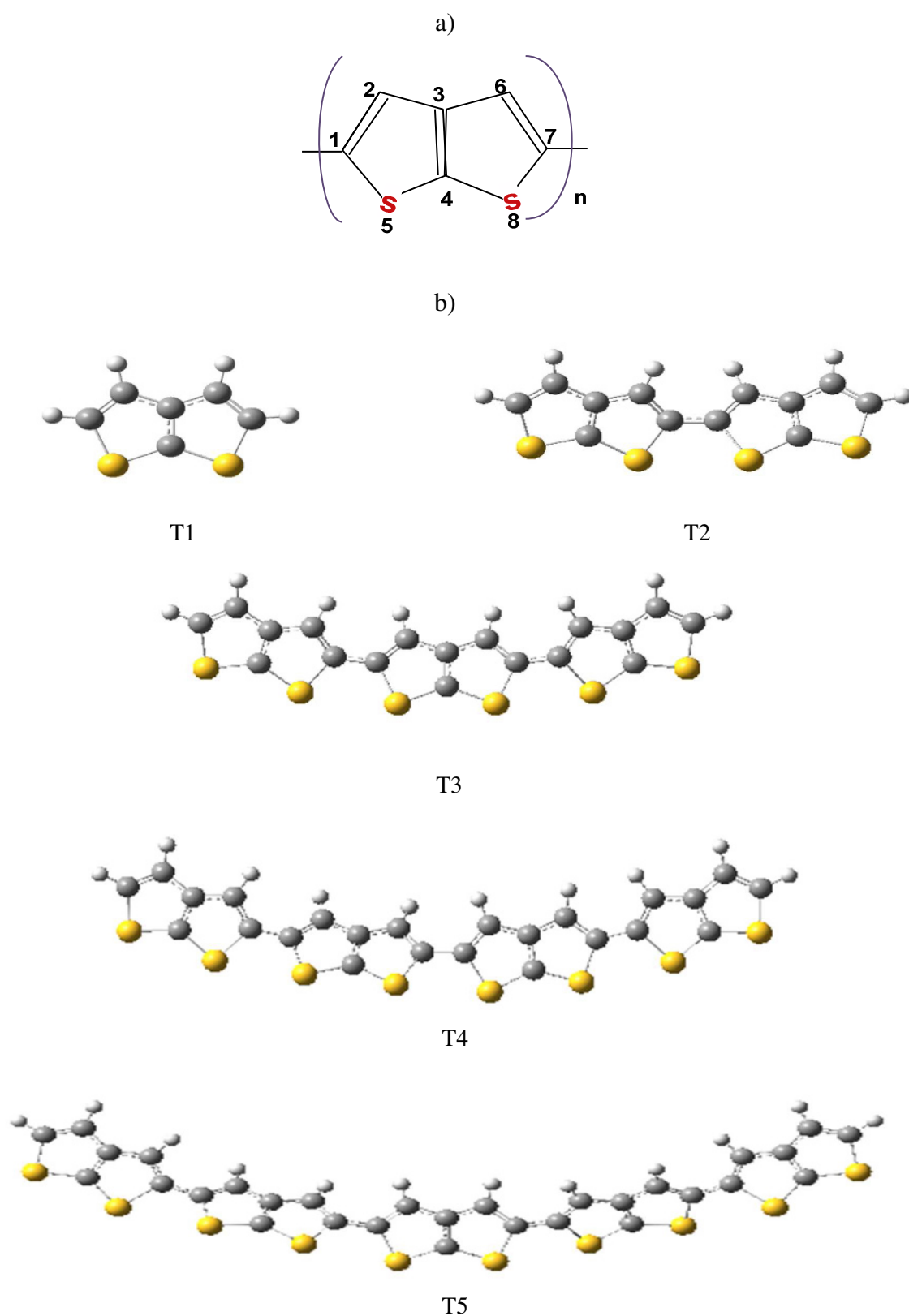


Fig. 1. (a) Compounds chemical structures under investigation. (b) The compounds theoretical geometric structures of optimized by B3LYP/6-31G (d).

The general abbreviation of our studied compounds is T1 (Monothienothiophene), T2 (Dithienothiophene), T3 (Trithienothiophene), T4 (Tetrathienothiophene) and T5 (Pentathienothiophene) thienothiophene, varies between 1 and 5.

2. Calculation methodology

The calculations done on the geometries of the four molecules were carried out under functional density theoretical theory (DFT) B3LYP and the set of bases 6-31G (d) [23]. The notation B3 indicates a parameter with three parameters of Becke [24] and

LYP indicates the function Lee - Yang - Parr [25]. Calculations were given using the Gaussian 09 program. All structures are fully optimized by B3LYP/6-31G (d) without any constraint.

3. Results and discussion

3.1. Geometric structure results

The optimized geometries of the five compounds (T1, T2, T3, T4 and T5) obtained at B3LYP / 6-31G (d) are shown in FIG. 1b.

The calculated lengths d_i ($i = 1$ to 29) and the dihedral angles Θ_i ($i = 1$ to 4) of the interatomic bonds are presented in FIG. 2 and their optimized values are summed up in Tables 1 and 2 respectively.

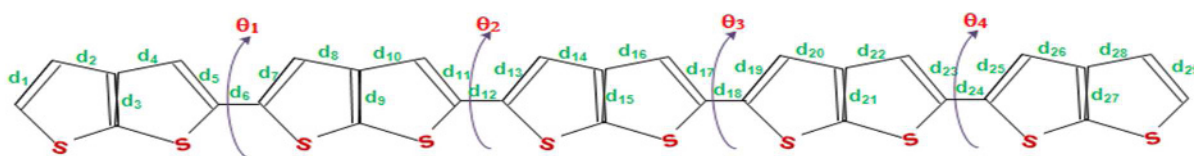


Fig. 2. Marked bond lengths and dihedral angles.

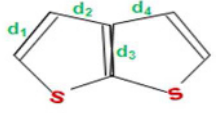
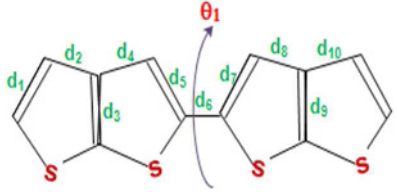
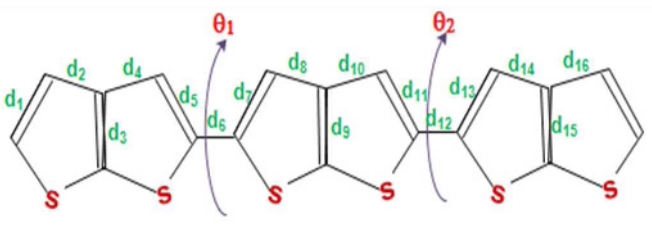
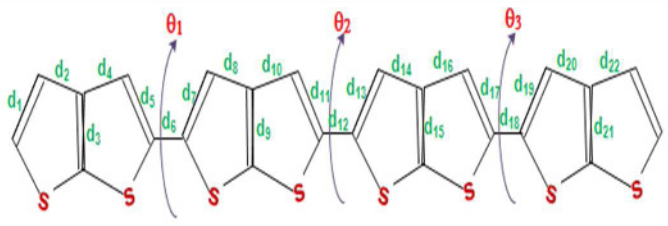
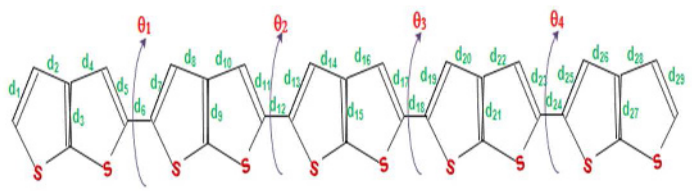
Table 1. The bond length values (Å) of the examined molecules.

Molecules Inter-atomics distance	T1	T2	T3	T4	T5
d ₁	1.36052	1.36002	1.35998	1.36191	1.35994
d ₂	1.44337	1.44391	1.44391	1.43600	1.44389
d ₃	1.38669	1.38756	1.38773	1.39277	1.38773
d ₄	1.44337	1.43647	1.43627	1.43001	1.43611
d ₅	1.36052	1.37118	1.37141	1.37259	1.37142
d ₆		1.44127	1.44098	1.45197	1.44100
d ₇		1.37118	1.37083	1.37220	1.37075
d ₈		1.43647	1.43708	1.43065	1.43709
d ₉		1.38757	1.38837	1.39319	1.38839
d ₁₀		1.44390	1.43708	1.43042	1.43681
d ₁₁		1.36002	1.37082	1.37245	1.37091
d ₁₂			1.44097	1.45163	1.44085
d ₁₃			1.37140	1.37249	1.37087
d ₁₄			1.43627	1.43040	1.43686
d ₁₅			1.38773	1.39323	1.38844
d ₁₆			1.44391	1.43062	1.43686
d ₁₇			1.35998	1.37222	1.37087
d ₁₈				1.45189	1.44085
d ₁₉				1.37264	1.37091
d ₂₀				1.43002	1.43681
d ₂₁				1.39276	1.38839
d ₂₂				1.43600	1.43708
d ₂₃				1.36191	1.37077
d ₂₄					1.44100
d ₂₅					1.37144
d ₂₆					1.43610
d ₂₇					1.38773
d ₂₈					1.44390
d ₂₉					1.35994

The interatomic distances (d_i) take small values for d_i ($i = 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29$) and high values for d_i ($i = 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28$). The inter-ring distances

d_i ($i = 6, 12, 18$) take the highest value which is close to 1.45 Å. This implies that these links are sometimes simple and sometimes double, thus favoring a good delocalization and combination of π electrons.

Table 2. The dihedral angles ($^\circ$) of the compounds examined.

Molecules	Θ_1	Θ_2	Θ_3	Θ_4
 T1				
 T2	36.36610			
 T3	35.44174	35.43358		
 T4	35.08110	34.31442	34.91680	
 T5	35.47490	35.78527	35.79901	35.42736

For the two systems (T2 and T3), we observe a great difference in the optimized binding angle (Θ_1) when we add thienothiophene (T) compound, but for T3,

T4 and T5 the optimized binding angles (Θ_1 and Θ_2) since they remain constant.

3.2. Electronic properties of the compounds examined

The electronic properties depend essentially on the fundamental and excited states. The lowest unoccupied molecular orbital (LUMO) and the

highest occupied molecular orbital (HOMO). The gap energy is calculated by the difference between the LUMO and HOMO levels, their values for all the molecules examined are shown in Table 3. Calculations have been achieved by the method B3LYP / 6-31 (d).

Table 3. The energies of the compounds examined in (eV): E_{HOMO} , E_{LUMO} and E_{gap} .

Compound	$E_{LUMO}(eV)$	$E_{HOMO}(eV)$	$E_{gap}(eV) = E_{LUMO} - E_{HOMO}$
T1	-0.624	-6.180	5.556
T2	-1.399	-5.688	4.289
T3	-1.514	-5.585	4.071
T4	-1.300	-5.355	4.055
T5	-1.594	-5.538	3.944

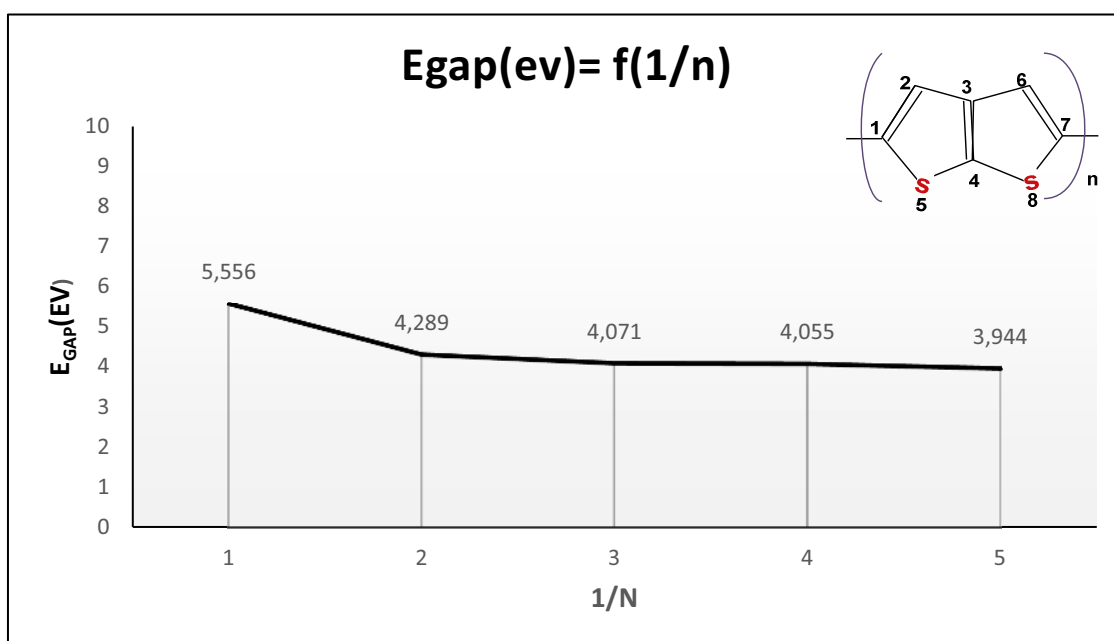


Fig 3. Band structure diagram illustrating the gap energy in function $1/n$ (1 to 5).

In this result, we first observed that the synthesized molecules generally have a high gap energy, especially the molecule (T1) of 5.556 eV, but when we add a base (T) the band gap decreased slightly for

all molecules, then the gap energy gap decrease of the molecule (T1) to (T5) from 5.556 eV to 3.944 eV.

3.3. Electronic structures of the compounds examined

In this section, we study the lowest virtual orbitals LUMO and highest occupied HOMO orbitals for these compounds, because the relative order of occupied and virtual orbitals give a reasonable qualitative indication of the excitation properties [26] and the capacity of electron transitions or whole transport. We plotted the contour curves of the LUMO and HOMO orbitals of five molecules (T1,

T2, T3, T4 and T5) in their fully optimized conformation B3LYP / 6-31G (d) in FIG. 4

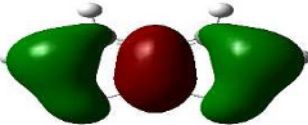









Molecule	HOMO contour plots	LUMO contour plots
T1		
T2		
T3		
T4		
T5		

Fig. 4. The LUMO and HOMO orbitals of the four compounds (T1, T2, T3, T4 and T5) obtained by B3LYP / 6-31G (d).

We observe that in the HOMO orbital the electron density is mainly distributed throughout the chain of compounds. However, it moves completely to the

acceptor unit in the case of LUMO. In the case of T5 the electron cloud are delocalized to the innermost ring in orbit LUMO.

3.4. Absorption spectra

The table 3 shows the vertical excitation energy E_{ex} (eV), the maximum absorption λ_{max} (nm), and the

oscillator strength (f) in all studied molecules. These properties are counted by the DFT-B3LYP/6-31G (d) ZINDO method.

Table 4. Calculated wavelength λ , Transition Energies and Oscillator Strengths (f) of the four compounds (T1, T2, T3, T4 and T5) obtained by (DFT) B3LYP/6-31G (d) ZINDO method.

Compound	$E_{ex}(ev)$	$\lambda_{max} (nm)$	f	Transition
T1	3.9469	314.13	0.0478	HOMO→LUMO (0.68442)
	4.4539	278.37	0.0155	HOMO→LUMO+2 (0.69993)
	4.7053	263.50	0.1803	HOMO-1→LUMO (-0.15176), HOMO→LUMO+1 (0.67453)
T2	3.3350	371.77	0.4118	HOMO-1→LUMO+1 (-0.15240), HOMO→LUMO (0.66777)
	3.8623	321.01	0.0888	HOMO-1→LUMO (-0.37502), HOMO-1→LUMO+2 (-0.17132) HOMO→LUMO+1 (0.52949)
	4.2448	292.08	0.5040	HOMO-1→LUMO+1 (-0.34244), HOMO-1→LUMO+3 (-0.11824) HOMO→LUMO+2 (0.57217)
T3	3.2804	377.95	0.0245	HOMO-2→LUMO+2(0.11121),HOMO-1→LUMO+1(-0.25489), HOMO→LUMO (0.61551)
	3.3270	372.66	1.0415	HOMO-1→LUMO (-0.38114), HOMO→LUMO+1 (0.54366), HOMO→LUMO+3 (0.11054)
	3.8370	323.13	0.1262	HOMO-2→LUMO (0.28946), HOMO-2→LUMO+2 (0.11835) HOMO-1→LUMO+1 (-0.37007), HOMO-1→LUMO+3 (0.18639) HOMO→LUMO+2 (0.39244), HOMO→LUMO+4 (0.14317)
T4	3.1207	397.30	0.7974	HOMO-2→LUMO (0.12101), HOMO-1→LUMO (-0.32377) HOMO-1→LUMO+1 (0.17478), HOMO→LUMO (0.48842) HOMO→LUMO+1 (-0.19999), HOMO→LUMO+2 (0.16608)
	3.2732	378.79	0.3866	HOMO-2→LUMO (-0.17502), HOMO-2→LUMO+1 (-0.12720) HOMO-2→LUMO+2 (0.17726), HOMO-1→LUMO+1 (0.14429), HOMO→LUMO(0.30685),HOMO→LUMO+1(0.35463), HOMO→LUMO+2 (-0.35077)
	3.3141	374.11	0.6951	HOMO-2→LUMO+1 (0.15994), HOMO-1→LUMO (0.12835) HOMO-1→LUMO+1 (0.40327), HOMO-1→LUMO+2 (0.26868), HOMO→LUMO+1 (0.24586), HOMO→LUMO+2 (0.29916)
T5	3.2550	380.90	0.0006	HOMO-3→LUMO+3 (-0.13073), HOMO-2→LUMO (0.10505) HOMO-2→LUMO+2 (0.20416), HOMO-1→LUMO+1 (-0.30423) HOMO→LUMO (0.52328)
	3.2902	376.83	0.0357	HOMO-3→LUMO (-0.11026), HOMO-2→LUMO+1 (-0.12900) HOMO-2→LUMO+3 (0.15357), HOMO-1→LUMO (-0.37323), HOMO-1→LUMO+2(0.19083),HOMO→LUMO+1(0.43955), HOMO→LUMO+3 (0.12714)
	3.3027	375.40	2.3232	HOMO-3→LUMO (-0.21785), HOMO-2→LUMO+1 (0.28140) HOMO-1→LUMO+2 (-0.34763), HOMO-1→LUMO+6 (0.10028), HOMO→LUMO+3 (0.43624), HOMO→LUMO+5 (-0.10526)

The compounds T1, T2, T3, T4 and T5, have absorption maxima (λ_{max}) respectively at 314.13 nm 371.77 nm, 377.95 nm and 397.30 nm, 380.90 nm reflecting the transition HOMO - LUMO. In addition, the absorption spectra simulated for all studied oligomers have a peak; this can be attributed

to the charge transfer intermolecular band caused by acceptor unit introduced in the molecular structures. This indicates that these organic oligomers could absorbed the maximum amount of incident radiation light, especially T4 and T5 molecules. In the excitation state S1, it corresponds exclusively to the

promotion of an electron from the HOMO to the LUMO. Moreover, the largest oscillation force ($f < 1$) that comes from the S0 to S1 electronic transition.

The simulated absorption spectra of the five compounds (T1, T2, T3, T4 and T5) are illustrated in FIG. 5.

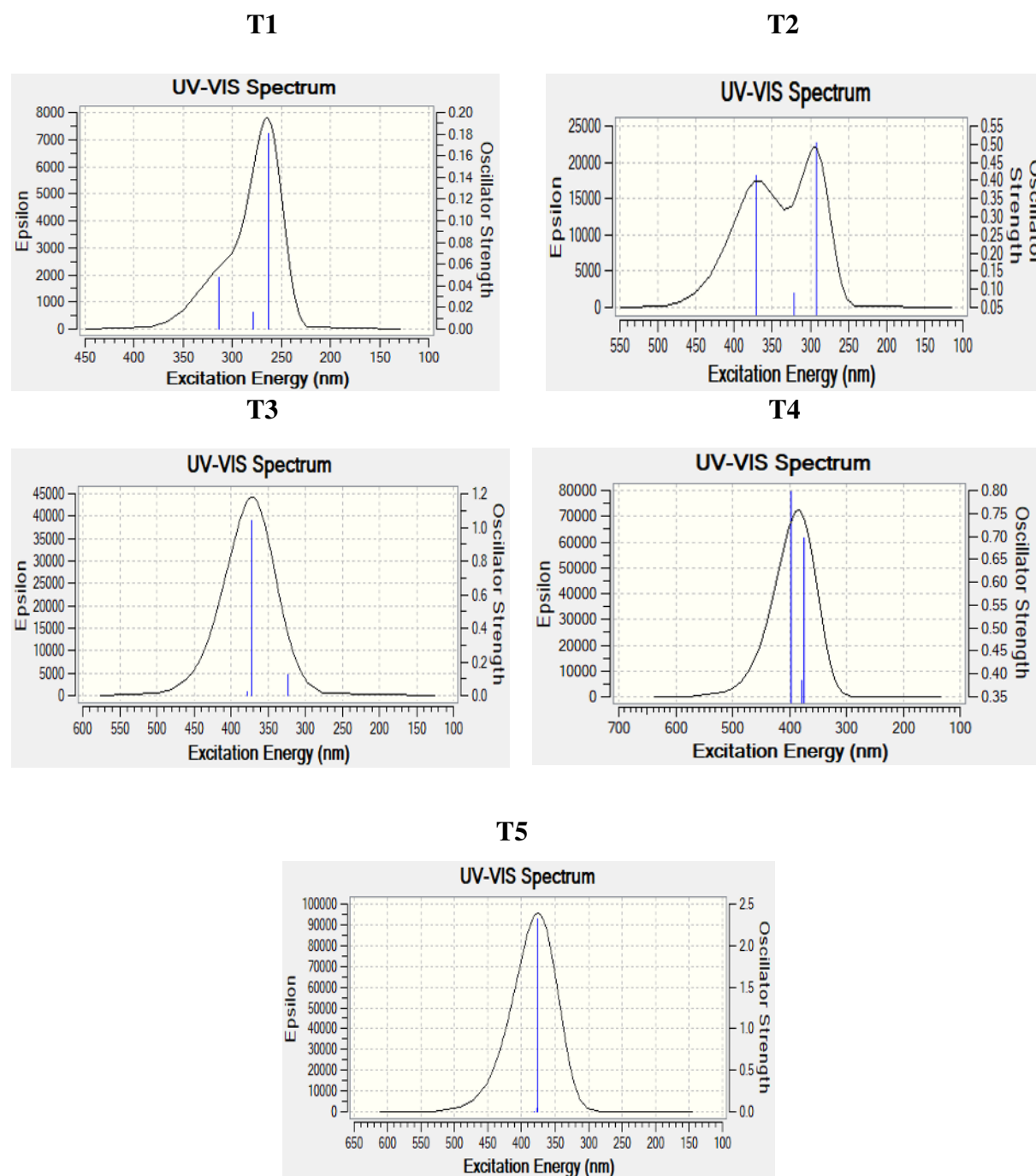


Fig. 5. Computed UV-vis spectra of the examined molecules (T1, T2, T3, T4 and T5) by DFT/B3LYP/6-31(G) ZINDO method.

4. CONCLUSION

The geometric parameters of the four Thienothiophene-based π -conjugated organic compounds (T1, T2, T3, T4 and T5) were obtained by B3LYP / 6-31G (d) calculations. The gap energy calculated with the same method decreases when a

base (thienothiophene) is added for all the molecules. Is basically due to the stabilization of the LUMO level and destabilization of the HOMO level of several compounds leads the reduction of energy gaps HOMO – LUMO. Regarding the T5 the reduction of the observed energy deficit is likely to guarantee the best electronic properties of the

corresponding polymers. These results showed that the T5 is promising material for optoelectronic application.

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