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 (λmax, Etr, 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 C6H4S2. 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. Therefore 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 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.
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 di (i = 1 to 29) and the dihedral angles θi (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.](image)

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

| Molecules Inter-atomics distance | T1   | T2   | T3   | T4   | T5   |
|----------------------------------|------|------|------|------|------|
| d1                               | 1.36052 | 1.36002 | 1.35998 | 1.36191 | 1.35994 |
| d2                               | 1.44337 | 1.44391 | 1.44391 | 1.43600 | 1.44389 |
| d3                               | 1.38669 | 1.38756 | 1.38773 | 1.39277 | 1.38773 |
| d4                               | 1.44337 | 1.43647 | 1.43627 | 1.43001 | 1.43611 |
| d5                               | 1.36052 | 1.37118 | 1.37141 | 1.37259 | 1.37142 |
| d6                               | 1.44127 | 1.44098 | 1.45197 | 1.44100 |
| d7                               | 1.37118 | 1.37083 | 1.37220 | 1.37075 |
| d8                               | 1.43647 | 1.43708 | 1.43065 | 1.43709 |
| d9                               | 1.38757 | 1.38837 | 1.39319 | 1.38839 |
| d10                              | 1.44390 | 1.43708 | 1.43042 | 1.43681 |
| d11                              | 1.36002 | 1.37082 | 1.37245 | 1.37091 |
| d12                              | 1.44097 | 1.45163 | 1.44085 |
| d13                              | 1.37140 | 1.37249 | 1.37087 |
| d14                              | 1.43627 | 1.43040 | 1.43686 |
| d15                              | 1.38773 | 1.39323 | 1.38844 |
| d16                              | 1.44391 | 1.43062 | 1.43686 |
| d17                              | 1.35998 | 1.37222 | 1.37087 |
| d18                              | 1.45189 | 1.44085 |
| d19                              | 1.37264 | 1.37091 |
| d20                              | 1.43002 | 1.43681 |
| d21                              | 1.39276 | 1.38839 |
| d22                              | 1.43600 | 1.43708 |
| d23                              | 1.36191 | 1.37077 |
| d24                              | 1.44100 |
| d25                              | 1.37144 |
| d26                              | 1.43610 |
| d27                              | 1.38773 |
| d28                              | 1.44390 |
| d29                              | 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 \( \pi \) electrons.

**Table 2.** The dihedral angles (°) of the compounds examined.

| Molecules | \( \Theta_1 \) | \( \Theta_2 \) | \( \Theta_3 \) | \( \Theta_4 \) |
|-----------|-------------|-------------|-------------|-------------|
| 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 deference in the optimized binding angle (\( \Theta_1 \)) when we add thienothiophene (T) compound, but for T3, T4 and T5 the optimized binding angles (\( \Theta_1 \) and \( \Theta_2 \)) 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): EHOMO, ELUMO and Egap.

| Compound | ELUMO(ev) | EHOMO(ev) | Egap(ev)= ELUMO- EHOMO |
|----------|-----------|-----------|------------------------|
| 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       | ![HOMO contour plot of T1](image) | ![LUMO contour plot of T1](image) |
| T2       | ![HOMO contour plot of T2](image) | ![LUMO contour plot of T2](image) |
| T3       | ![HOMO contour plot of T3](image) | ![LUMO contour plot of T3](image) |
| T4       | ![HOMO contour plot of T4](image) | ![LUMO contour plot of T4](image) |
| T5       | ![HOMO contour plot of T5](image) | ![LUMO contour plot of T5](image) |

**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 $E_{\text{ex}}$ (eV), the maximum absorption $\lambda_{\text{max}}$ (nm), and the oscillator strength ($f$) in all studied molecules. These properties are counted by the DFT-B3LYP/6-31G(d) ZINDO method.

| Compound | $E_{\text{ex}}$(eV) | $\lambda_{\text{max}}$ (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→LUMO+1 (0.67453) |
| T2       | 3.3350           | 371.77          | 0.0118 | HOMO→LUMO+1 (-0.15240), HOMO→LUMO (0.67777) |
|          | 3.8623           | 321.01          | 0.0888 | HOMO→LUMO (-0.37502), HOMO-1→LUMO+2 (-0.17132) |
|          | 4.2448           | 292.08          | 0.5040 | HOMO→LUMO+1 (-0.34244), HOMO-1→LUMO+3 (-0.11824) |
| T3       | 3.2804           | 377.95          | 0.0245 | HOMO→LUMO+2 (0.11121),HOMO→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→LUMO (-0.28946), HOMO→LUMO+2 (0.11835) |
|          | 3.1207           | 397.30          | 0.7974 | HOMO→LUMO (0.12101), HOMO→LUMO+2 (-0.32377) |
|          | 3.2732           | 378.79          | 0.3866 | HOMO→LUMO (-0.17502), HOMO-2→LUMO+1 (-0.12720) |
|          | 3.3141           | 374.11          | 0.6951 | HOMO→LUMO+1 (0.15994),HOMO→LUMO+1 (-0.19999), HOMO→LUMO+2 (0.16608) |
| T4       | 3.2550           | 380.90          | 0.0006 | HOMO→LUMO+3 (-0.13073), HOMO→LUMO (0.10505) |
|          | 3.2902           | 376.83          | 0.0357 | HOMO→LUMO (-0.11026), HOMO→LUMO+1 (-0.12900) |
|          | 3.3027           | 375.40          | 2.3232 | HOMO→LUMO (-0.21785), HOMO→LUMO+1 (0.28140) |

The compounds T1, T2, T3, T4 and T5, have absorption maxima ($\lambda_{\text{max}}$) 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 $S_1$, 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.

![UV-Vis Spectra](image)

**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 \( \pi \)-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. It 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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