

A quantum chemical study on structural and electronic properties of new π -conjugated polymer named poly(4-methylthioazole-2,5-diyl)

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ABSTRACT

Organic conjugated polymers based on heterocyclic ring exhibit semiconducting properties associated with the π molecular orbitals delocalized along the polymer chains. These materials have attracted much interest for potential applications in optoelectronic devices due to their unique electronic and photonic properties. Recently, interesting studies have been devoted to the synthesis, characterization, physical and chemical properties and variety of these materials. In this work, a quantum-chemical investigation on the structural and opto-electronic properties of new polymer named poly (4-methylthioazole-2,5-diyl)s is carried out. We present a detailed DFT study of geometrical structures and electronic properties of this organic material. Calculated results are compared with experimental data and based on such comparison we try first, to propose an oligomer model and then, to obtain a qualitative understanding the properties of polymer. We discuss the influence of chain length on structural and optoelectronic properties. The numerical predictions are compared to our experimental results. The ground state optimized structures and energies are obtained using the molecular orbital theory and the DFT (B3LYP/6-31G (d)) calculations. Copyright © 2011 VBRI press.

Keywords: Conjugated polymers; (MTZ) oligomers; DFT; optoelectronic properties; HOMO; LUMO



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concepts of quantum chemistry.

Introduction

Conjugated polymers have attracted considerable attention as a novel class of semi-conductors and are frequently studied because of their interesting optical and electronic properties [1]. The importance and the potentiality of this class were recently recognized by the world scientific community when H. Shirakawa, A.J. Heeger and A.G. MacDiarmid were laureated in 2000 with the Nobel Prize in Chemistry by their research in this field [2]. The high specific capacitance of this type of the polymers in their neutral and oxidized states has stimulated suggestions for a variety of applications such as rechargeable batteries, super-capacitors and electrochromic devices [3-5].

Poly (3-methylthiophene) is an attractive material due to its low cost, easy processability, environmental stability, lower band gap, easy preparation and tunable properties [6]. The research in the novel organic π -conjugated molecules based on thiophene has become one of the most interesting topics in fields of chemistry physics and materials science. Thanks to their specific properties, these compounds become the most promising materials for the optoelectronic device technology, such as LEDs, Transistors (TFTs) and solar cells [3-5]. These materials exhibit interesting electronic and electrochromic properties [7]. One of the most important factors of controlling physical properties is the band gap (E_g), which is a current topic of research. In particular, polymers with a low gap are desired in optoelectronic applications. Many ways have been used to modulate this parameter including the modification of chemical structure through the incorporation of charges carriers in the polymer backbone [8]. Extensive and intensive studies have been devoted to the synthesis, characterization, physical and chemical properties and variety of these materials. The development of novel structures is now being undertaken following the molecular engineering guidelines. In this way, poly (4-methylthioazole-2.5-diyl) and derivatives have been synthesized [9]. Extensive studies on π -stacking of these types of materials have been investigated [10]. However more detailed studies needed for this interesting new class of polymers especially structural and optoelectronic properties. The replacement of the carbone in the position β of thiophene by nitrogen atom will help to minimize and eliminate the default coupling α - β and to obtain a regular polymer.

The present work concerns this novel polymer named poly (4-methylthioazole-2.5-diyl) this material was prepared by Y. Miyazaki et al et al [9]. A better understanding of the electronic and optical properties of this material requires knowledge of their conformations and electronic structures. Besides, theoretical calculations provide a lot of useful information that help chemists to build up a tight relation between structure and properties of these materials. Theoretical analysis on the electronic structures of various conjugated polymers and oligomers has been extensively reported [11]. We have successfully used the DFT method to predict properties of polythiophene and polyparaphenylene [12]. In this regard, theoretical studies of oligo (4-methylthioazole-2.5-diyl) certainly facilitate the knowledge of polymeric structure. Smallest oligomers can play also an important role in

understanding charge transport mechanism and physical properties of polymers. In this work, we are going to carry out the DFT calculations and to discuss the structural and electronic properties of neutral oligo (4-methylthioazole-2.5-diyl) ($n=2-6$) reported in **Fig. 1**.

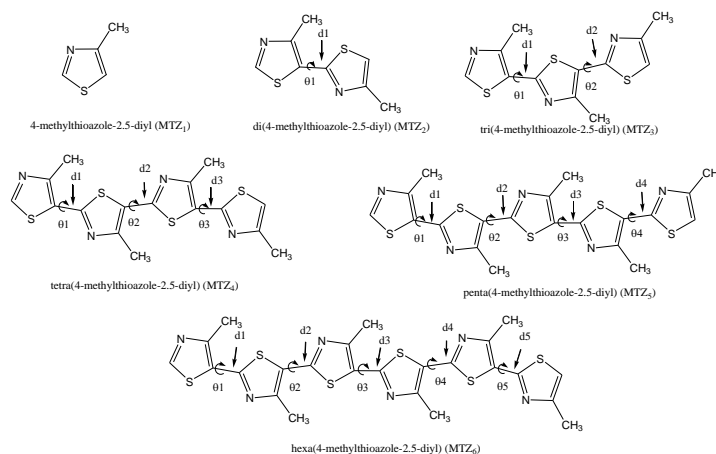


Fig. 1. Studied compounds.

All geometries were fully optimized at the DFT level using the three-parameter compound functional of Becke (B3LYP) [14] and the 6-31G(d) basis set {ref} using the Gaussian 03 computer program [13].

Experimental

All geometries were fully optimized at the DFT level using the three-parameter compound functional of Becke (B3LYP) [13] and the 6-31G(d) basis set [14] using Gaussian03 computer program [15]. We have also examined the energy of HOMO and LUMO levels; this is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using Time Dependent Density Functional Theory (TD-DFT) at B3LYP/6-31G(d) level starting with the fully optimized geometries obtained at B3LYP/6-31G(d) level. In fact, these calculation methods have been successfully applied to other conjugated polymers [12].

Results and discussion

Geometric parameters

The optimized ground state geometries of $(MTZ)_n$ ($n=1, 2, 3, 4, 5$ and 6) obtained at the B3LYP/6-31G(d) level are given in **Fig. 2**. The optimized inter-ring bond lengths and dihedral angles between the subunits are summarized in **Table 1** and **Table 2**.

The results of the optimized structures for the studied molecules show that all molecules possess planar structures. The inter-ring bond lengths and bond angles do not suffer appreciable variation with the oligomer size and it suggests that we can describe the basic structures of the polymers as their oligomers. As shown in **Table 1**, the inter-ring bond lengths (d_i) are in the average of 1.445 Å. The dihedral angles (θ_i , $i = 1 - 5$) are collected in **Table 2**. The inter-ring torsions in the case of the longest oligomer

(MTZ)₆ were evaluated to be about ($\theta_i, i = 1 - 5$) = 180° like as occurs for Octathiophene [17]. It is obvious that the torsion angle constitutes a compromise between the effect of conjugation on crystal packing energy, which favours a planar structure, and the steric repulsion between hydrogens which favours a non planar structure [16]. The π -conjugation across the heterocyclic rings is responsible for this planarity. This agrees very well with experimental results and theoretical results obtained when studying oligothiophenes and derivatives [17].

Table 1. Inter-ring bond lengths (d_i) of (MTZ)_n (n =1-6) obtained at B3LYP/6-31G(d).

distances (Å)	MTZ ₂ (n=2)	MTZ ₃ (n=3)	MTZ ₄ (n=4)	MTZ ₅ (n=5)	MTZ ₆ (n=6)
d_1	1.447	1.444	1.443	1.443	1.443
d_2		1.444	1.440	1.439	1.439
d_3			1.443	1.439	1.439
d_4				1.443	1.439
d_5					1.443

Table 2. Dihedral angles (θ_i) of (MTZ)_n (n =1-6) obtained at B3LYP/6-31G (d).

Angles (°)	MTZ ₂ (n=2)	MTZ ₃ (n=3)	MTZ ₄ (n=4)	MTZ ₅ (n=5)	MTZ ₆ (n=6)
θ_1	180	179	1.79.9	180	180
θ_2		180	180	180	180
θ_3			179.7	180	180
θ_4				179.7	180
θ_5					180

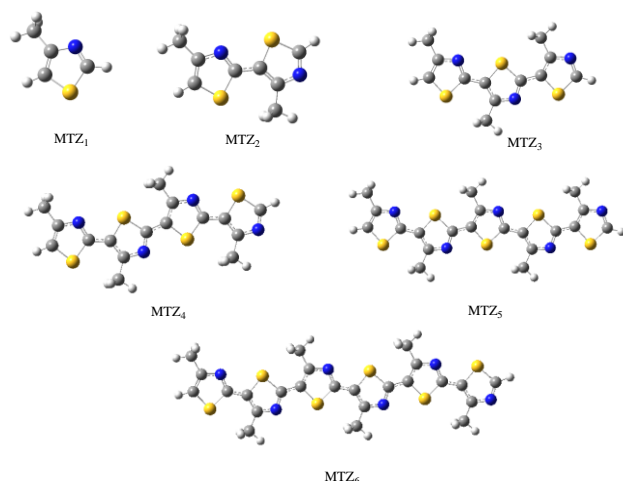


Fig. 2. Optimized structures obtained by the B3LYP/6-31G (d) level for (MTZ)_n (n =1-6)

Electronic properties

The optoelectronic properties depend essentially on the appropriate HOMO and LUMO energy levels and the electron and hole mobilities. It is known that (E_{gap}) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is an important parameter which determines the molecular admittance because it is a measure of the electron density

hardness. The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry [18-19]. But in the theory, the HOMO and LUMO energies can be calculated by DFT calculation. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers [20].

For a better understanding of the electronic properties of the studied oligomers, we present in **Table 3**, the calculated HOMO and LUMO energy levels, the energies $E_{\text{gap}} = E_{n(\text{LUMO})} - E_{n(\text{HOMO})}$ and include experimental data. In theory, the band gap of the polymer is the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) when the repeated unit number is infinite [21]. Band Gap for infinite chains polymer were determined by plotting band gaps oligomers against the inverse of the number n of the monomer units and extrapolating the number of units to infinity (**table 3** and **Fig. 3**).

Table 3. The HOMO, LUMO and $\{E_{n(\text{HOMO})} - E_{n(\text{LUMO})}\}$ gaps energies (eV) of (MTZ)_n obtained at B3LYP/6-31G(d).

	$E_{n(\text{HOMO})}$ (eV)	$E_{n(\text{LUMO})}$ (eV)	E_{gap} (eV)
1MTZ	-6.54	-0.58	5.96
2MTZ (n=2)	-5.92	-1.64	4.28
3MTZ (n=3)	-5.62	-2.06	3.56
4MTZ (n=4)	-5.46	-2.29	3.17
5MTZ (n=5)	-5.36	-2.42	2.94
6MTZ (n=6)	-5.30	-2.52	2.78
PMTZ (n= ∞)			2.24
PMTZ (Exp)			2.48[9]

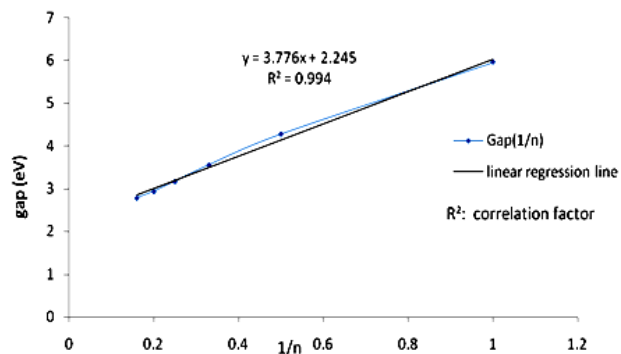


Fig. 3. Progress of the B3LYP/6-31G(d) calculated energy gap as a function of 1/n (n number of monomer).

Fig. 4 displays the evolution of the calculated HOMO and LUMO energies as a function of reciprocal chain length for the series of (MTZ)_n. It is known that in the case of the π -conjugated systems, the HOMO energies destabilized with the increasing of the conjugation length,

whereas the LUMO energies decreased [21]. There is systematical decrease of the electronic calculated E_{gap} of $(\text{MTZ})_n$ oligomers as the number of chain length increased (Fig. 3). These results indicate that the chain length of polymers have more effect on the electronic transition. When we compare the various values of the calculated E_{gap} , we can note that, the in $(\text{MTZ})_6$ (2.78 eV) are higher than that obtained values of in regular $(\text{MT})_6$ (2.58 eV), suggesting that modification of the structure by introducing nitrogen atom in β position of thiophene allow the modulation of the band gaps. Interestingly, when we extrapolate the HOMO–LUMO gaps energies to the infinite chain length, there is a good linear relation (about $r^2 = 0.994$) between the energy gap and the inverse chain length. The obtained value (2.24 eV) is close to the experiment data [9]. The optical band gaps are derived from the absorption edge of a polymer thin film for $(\text{PMTZ})_n$. The observed deviation is not more than 0.03 eV. The principal factor responsible for this deviation is that the predicted band gaps are for the isolated gas-phase chain [23]. It should be noted that this obtained value of band gap is sufficient to consider applications of this material in the optoelectronic field [24].

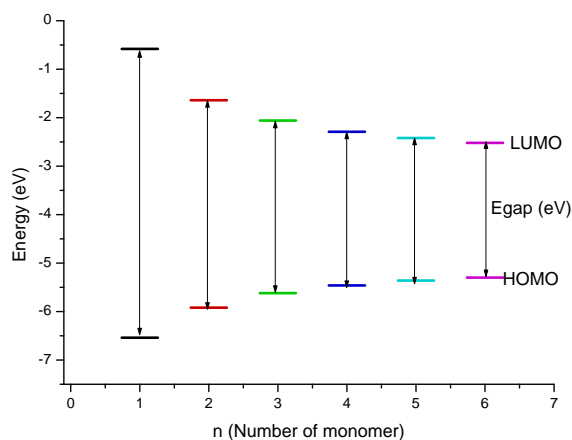


Fig. 4. The evolution of the B3LYP/6-31G(d) calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies as a function of n (number of monomer).

On the other hand, it is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport. In general, as plotted in Fig. 5, the HOMO possesses an antibonding character between the consecutive subunits; whereas the LUMO of all oligomers generally shows a bonding character between the subunits.

Absorption properties

The TD-DFT method has been used on the basis of the optimized geometry to obtain the energy of the singlet–singlet electronic transitions and absorption properties (λ_{max}) of all oligomers $(\text{MTZ})_n$ under study. All electronic transitions are of the π – π^* type and no localized electronic transitions are exhibited among the calculated singlet–

singlet transitions. The maximum absorption wavelength λ_{max} for every oligomer, the corresponding oscillator strength f and the available experimental data of the polymer are exhibited in Table 4.

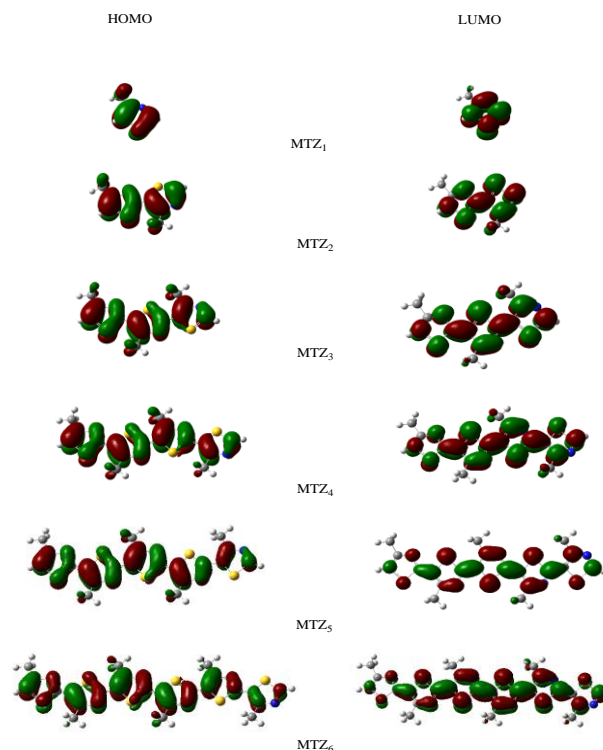


Fig. 5. The HOMO and LUMO orbitals of $(\text{MTZ})_n$ obtained by B3LYP/6-31G(d).

Table 4. Absorption λ_{max} (nm) and the corresponding oscillator strength (f) of oligomers $(\text{MTZ})_n$ obtained by the TD/B3LYP 6-31(d) method and λ_{max} of the PMTZ.

Oligomer	λ_{max} (nm)	E_{ir} (eV)	f
$n = 1$	229.57	5.400	0.0004
$n = 2$	308.14	4.023	0.3586
$n = 3$	373.21	3.322	0.6922
$n = 4$	423.82	2.925	1.0438
$n = 5$	463.70	2.673	1.3826
$n = 6$	495.19	2.503	1.7126
Polymer	500 (in CHCl_3) [9]		

Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO. As in the case of the oscillator strength, the absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO \rightarrow LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition and as analyzed above that with the extending molecular size, the HOMO–LUMO gaps decrease. We typically see that a Maximum absorption wavelength (λ_{max}) increase as the conjugation length increases (Table 4). This is an effect of atomic orbital interacting and creating molecular orbital that are split in

energy. We note that from the oligomer (MTZ)₃ absorption occurs in the visible (380–780 nm).

These values are calculated by TD/DFT method starting with optimized geometry obtained at B3LYP/6-31G (d) level in gas phase. However, we believe that the bulk of intermolecular effect must be taken into account when considering the polymers with long chain. After considering this effect, the λ_{\max} of the longest oligomer (MTZ)₆ is closed to the experimental value of λ_{\max} obtained from the parent polymer PMTZ. The deviation between the calculation and the experimental data is not more than 5 nm. Therefore, the procedures of theoretical calculations give a good description of opto-electronic properties of the studied oligomers and can be employed to predict the electro-luminescence characteristics of other materials.

These results lead us to suggest that the longest oligomer (MTZ)₆ is a good model to reflect optoelectronic properties for the parent polymer.

Conclusions

In this study, theoretical analyses, based mainly on density functional theory (DFT) calculations at B3LYP/6-31G (d) level, are performed to several oligomers (MTZ)_n (n=1-6). Geometrical structures and optoelectronic properties were characterized to investigate the effect of the number of monomers on the structural and opto-electronic properties of these compounds. It was found that calculation results were in good agreement with the reported experimental data. We have observed that there is a systematically change of the HOMO and LUMO energies as the number of monomer unit increased into the backbone causing a destabilisation for HOMO and LUMO levels and lowering the energy band gap. We have also noticed that the calculated values of λ_{abs} shifted in the same direction upon addition of thiophene ring and when the conjugation length is increased. The obtained results lead us to suggest that the longest oligomer (MTZ)₆ is a good model to reflect optoelectronic properties for the parent polymer. This oligomer seems to be suitable for organic electronic applications. It exhibits lower value of (2.58 eV) and high value of absorption (495.19 nm), making it as an attractive candidate for light-emitting diode applications. Joining theoretical studies to experimental ones seems to be a good approach for a deeper comprehension of structural and optoelectronic properties of such electroluminescent materials. Further, theoretical investigations are necessary in order to advance our understanding of the interface phenomena in materials LEDs.

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