

Analysis of molecular structures and spectroscopic properties of thiophene molecules

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ABSTRACT

In this research study the substitution effect on the molecular geometries, electronic properties, Raman spectra, force constant and, reduce mass are calculated by using density functional theory (DFT) method with 3-21G bases set for thiophene and derivatives molecules. UV-VIS spectra are computed by using time dependent density functional theory (TD-DFT) at the same level. It was found that the values of energy gap and geometries parameters are in good agreement with experimental values.

KEY WORDS: Electronic properties, Vibrational Spectroscopy, UV-VIS Spectra, thiophene.

1. INTRODUCTION

Thiophene it is aromatic, compound has the formula C_4H_4S and 84.14g/mol, molar mass, and thiophene is melting in $-38^\circ C$ and boiling in $84^\circ C$. Thiophenes are important heterocyclic compounds that are used as building blocks in many pharmaceuticals and agrochemicals (Swanston and Jonathan, 2006). The derivatives of thiophene are used in many applications such as molecular electronic, electromagnetic shielding and displays (Alguno, 2001), and have been used in the new optical devices, such as light emitting diode and surface light emitting diode (Pei, 2003). The simple thiophenes are stable liquids which closely resemble the corresponding benzene compounds in boiling point and even in smell (Mishra, 2011). Previous study has been carried out to calculate electronic properties, UV-VIS spectra and energy gap (E_g) of thiophene and diphenylamine molecules using DFT method with 6-311G (d) basis set (Amine1, 2014). Study the substitution effect on electronic properties by using two methods Hartree-Fock (HF) and DFT and 6-31G* bases sets to pyrrole and thiophene molecules (Adejoro, 2013). Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy gap and UV-VIS are calculated using DFT and TD methods for thiophene and IR dyes (Irfan, 2014), However, DFT method is used to calculate HOMO, LUMO, Raman, IR and UV-VIS spectroscopies for dimethyl phenylphosphonite molecules and compared the values of IR spectra with the experimental value (Bahceli, 2014), in addition, DFT and HF with 6-31G* basis set are used to calculated geometry optimization and electronic properties of Polythiophene and derivatives molecules (Dguigui1, 2012).

The aim of this work is study the influence of substitution effects of hydrogen atom by thiophenes in different positions on the electronic and spectral properties for thiophene and derivative molecules using the B3LYP functional and the 3-21G basis set. Theoretical methods are an efficient method to fine-tune the structural stability and electronic properties of some semiconductor (Jappor, 2011) and nanostructures (Jappor, 2012; 2016; Jappor and Obaid, 2016; Habeeb, 2016).

2. CALCULATIONS

All molecules under the study are carried out by using Gaussian 09 program (Frisch, 2009), the geometric optimization of thiophene and derivatives molecules with substitution effect thiophene molecule in place of hydrogen atom have been performed by using DFT method with 6-321G bases set in gas phase. Fig.1, shows the geometric optimization of (1-4) molecules at phase gas.

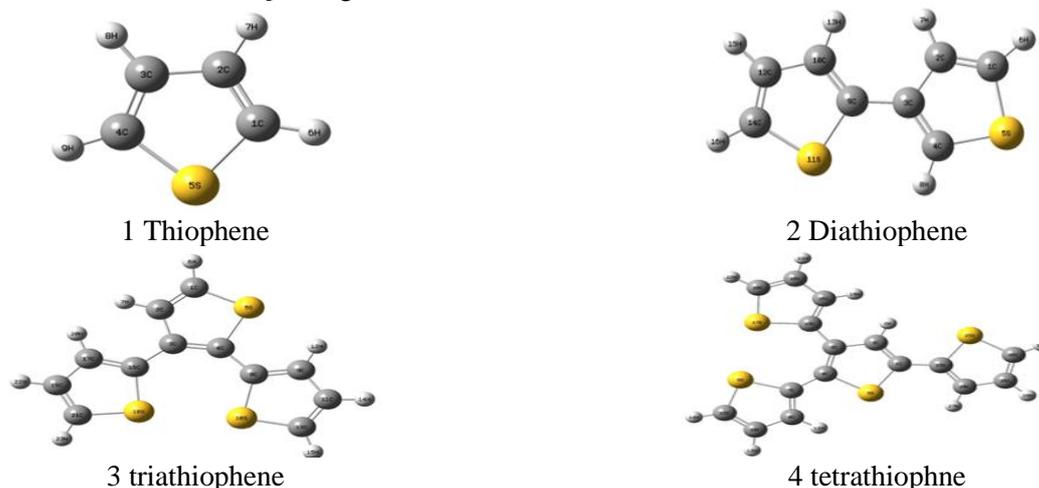


Figure.1. The optimized structures of (1-4) thiophene molecules using B3LYP/3-21G

Ionization potential (IP) and electron affinity (EA) have been calculated by using the following equations.

$$IP = -E_{\text{HOMO}} \dots (1)$$

$$EA = -E_{\text{LUMO}} \dots (2)$$

E_{HOMO} is the energy of the highest occupied molecular orbitals, E_{LUMO} is the energy of the lowest unoccupied molecular orbitals (Shafiee, 2011). While the electronegativity (χ) has been calculated by using the equation (Kumar, 2014).

$$\chi = -(\text{IP} + \text{EA})/2 \dots (3)$$

Whereas the hardness (η) is defined as:

$$\eta = (\text{IP} - \text{EA})/2 \dots (4)$$

The softness (S) by the following equation:

$$S = 1/2\eta \dots (5)$$

3. RESULTS AND DISCUSSION

Electronic properties and Raman spectra: Fig.1, shows the optimized structure parameters calculated by DFT/B3LYP method with the 3-21G basis set. The substitution of thiophene in place of hydrogen atoms and the difference of atomic numbers for the conjugated atoms effects on the bond lengths and bond angles between these atoms, The geometric parameters of (1- 4) thiophene molecules are listed in the Table 1, it is clear from this table that there is small difference between the bond lengths (R) for R(C=C), R(C-C), R(C-H) and R(C-S) bonds. The C-H bond lengths approximately at 1.077Å and 1.081Å, and C=C bond length approximately at 1.345Å and 1.358Å, whereas a C-C bond length varies in the range from 1.43Å to 1.45Å. The C-S bond length for all thiophene and derivatives molecules varies at the range from 1.801Å - to 1.854Å. All angles in molecules under study ring (C-C-C angles) are from (113.811°- 114.1167°). The molecule 3 has higher values of (C-S-C) bond angles compared molecules under study. The bond length (C=C), (C-H), (C-S) and bond angles (C-C-H) and (C-C=C) for thiophene molecule are in good agreement with experimental values.

Table.1. Optimized geometrical parameters of four thiophene molecule, experimental result from ref. (Dguigui1, 2012).

Molecules	Bond length	Our data (Å)	Expt. ⁹	Bond angles	Our data (°)	Expt. ⁹
1	R(C1=C2)	1.3582	1.370	A(C3-C2-H7)	123.0619	124.23
	R(C2-C3)	1.442	1.423	A(C1-S5-C4)	89.3504	
	R(C2-H7)	1.0813	1.078	A(C3-C2=C1)	113.8839	112.65
	R(C4-S5)	1.8076	1.714	A(C4=C3-H8)	123.0541	
2	R(C1=C2)	1.3533		A(C3-C2-H7)	122.8597	
	R(C3-C9)	1.453		A(C1-S5-C4)	89.257	
	R(C4-H8)	1.077		A(C10-C12=C14)	114.1167	
	R(C14-S11)	1.8051		A(C9=C10-H13)	122.698	
3	R(C1=C2)	1.3453		A(C11-C9-H12)	121.6621	
	R(C4-C8)	1.447		A(C8-S10-C13)	90.6727	
	R(C2-H7)	1.0771		A(C17-C19=C21)	113.8343	
	R(C16-S18)	1.8268		A(C16=C17-H20)	123.2659	
4	R(C1=C2)	1.3571		A(C10-C8-H11)	121.657	
	R(C24-C26)	1.4328		A(C15-S17-C20)	90.8751	
	R(C16-H19)	1.0781		A(C8-C10=C12)	113.811	
	R(C4-S5)	1.8542		A(C23=C24-H27)	122.3284	

Table.2, shows the calculated values of HOMO, LUMO, IP, EA, η , and S values for (1-4) thiophene molecules, we noticed from Table 2, that the substitution of a thiophene lead to increasing the values of HOMO, EA and S, while the values of LUMO, IP, X and η are decreasing with the substitution, 1-molecule has high IP (6.56eV) and η (3.100eV), while the molecule 4 has small value of η . The thiophene molecule has energy gap 6.2eV which is in good agreement with experimental value 5.23 eV.

Table.2. The calculated electronic properties (in eV) for (1-4) thiophene molecules

Molecules	E_{HOMO}	E_{LUMO}	IP	EA	X	η	S
1	-6.561	-0.360	6.561	0.360	-3.460	3.100	0.161
2	-5.828	-1.185	5.828	1.185	-3.460	2.321	0.215
3	-5.474	-1.786	5.474	1.786	-3.630	1.844	0.271
4	-5.312	-2.053	5.312	2.053	-3.682	1.629	0.307

The Raman spectra of (1-4) thiophene and derivatives molecules are shown in Fig.2, the substitution hydrogen lead to difference vibrational frequencies. For thiophene molecule, the (C-H) stretching studied in the

region (3302.2) cm^{-1} is strong. The (C-C) stretching vibrations occur in the region (1471.7) cm^{-1} . For derivatives molecules, the (C-H) stretches are in the range (3251.3-3301.6) cm^{-1} , the (C=C) occurs in (1482-1509) cm^{-1} , the stretching vibrations of (C-S) are in the region (632.7-706.6) cm^{-1} is weak, the (C-C) appears in (1202-1367) cm^{-1} , the (C=C) stretching appears in the region (1597.4-1625.4) cm^{-1} , the stretching vibration (C-S) for molecules is weak, because (S) atom has high mass and electronegativity compare with hydrogen and carbon atoms.

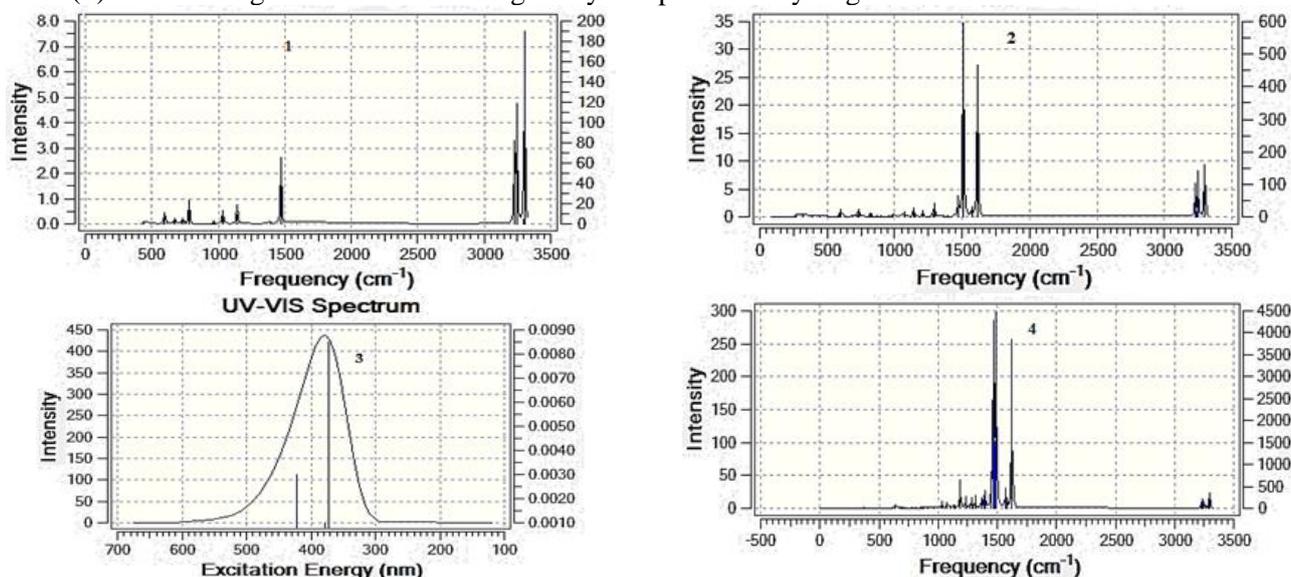


Figure.2. Calculated IR spectra of (1-4) thiophene molecules

UV - VIS Spectra: Fig.3, Shows the vibrational frequencies that calculated for thiophene and derivatives, to study the first three low excited states for investigate the spectral UV and VIS absorption spectra of thiophene and derivatives. We found the bond in (194.73, 252.21, 421.83, and 461.49nm for thiophene, 2-molecule, 3-molecule, and 4-molecule, respectively. The four molecules have high vibrational frequencies compared with derivatives molecules. The values of angles and geometry optimization, which in turn affect the spectral values in excited states.

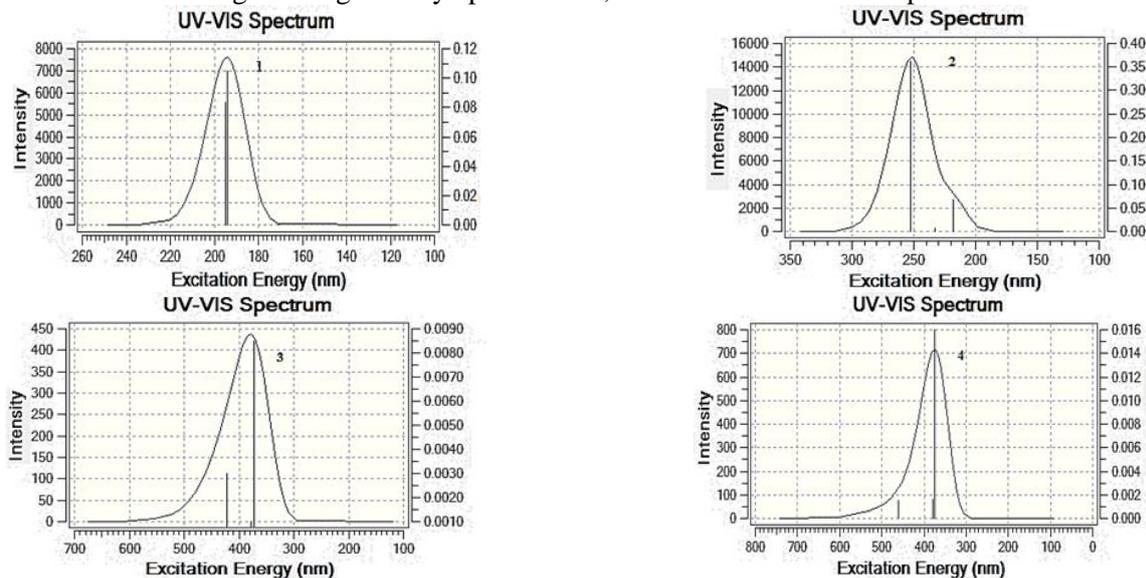


Figure.3. The Calculated UV-VIS spectroscopy of (1-4) thiophene molecules

Figs.4 and 5, are shown the reduce mass and force constant fore thiophene and derivatives molecules, Fig.4, can be divided into two regions of the thiophene molecule, and has highest reduce mass in region is 10.764a.u., also Fig.5, shows two part; the first part is in the range of 0 to 1471.689 cm^{-1} , the 4-molecule has highest force constant in region 11.329 (mDyne/A^0), the second part starts at 1471.68 cm^{-1} and at near 3302.277 cm^{-1} , the values of reduce mass for molecules are decreasing, while the force constant are increasing, because the reduce mass is inversely proportional to frequency while force constant is directly proportional to frequency according to the equation.

$$\nu = 1/2\pi \sqrt{\frac{k}{\mu}} \quad (6)$$

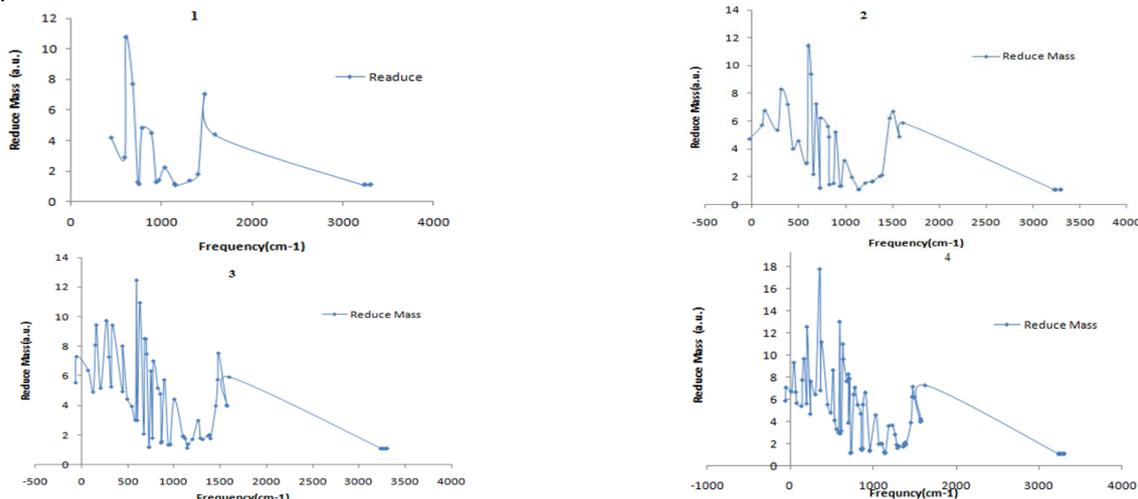


Figure.4. The force constants for (1-4) thiophene molecules

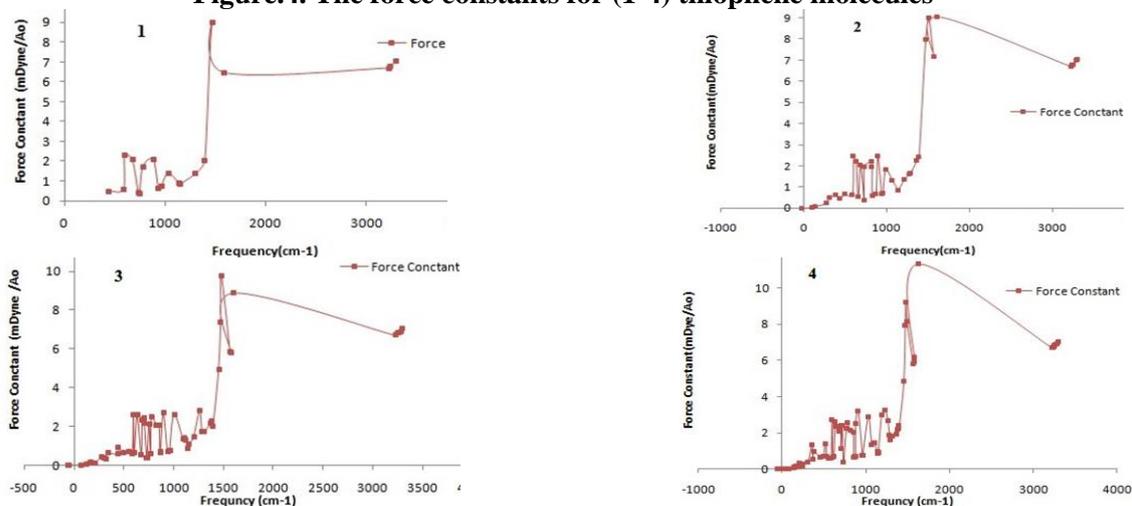


Figure.5. The force constant for (1-4) thiophene molecules

Electrostatic Potential Surface: Fig.6, show the electrostatic potential surfaces for (1-4) thiophene molecules. The electrostatic potential distribution and electron density surfaces depends on the type of substitution, and the negative and positive charges. Fig.6, show the density distribution on (S) atoms, that has high electronegativity therefore attract charge toward them.

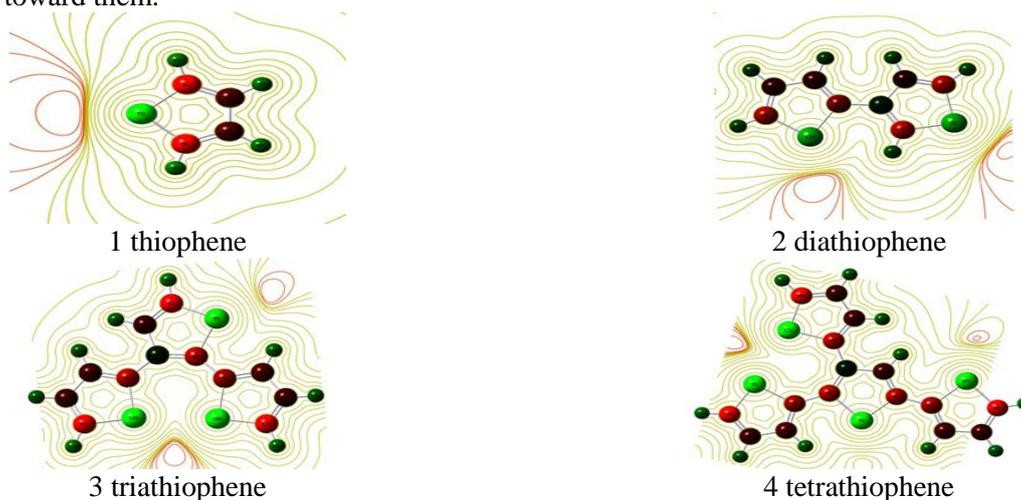


Figure.6. The electrostatic potential surfaces for (1-4) thiophene molecules

4. CONCLUSIONS

- The substitution thiophene in place of hydrogen leads to small difference in the geometric parameters, which are in good agreement with experimental values.
- The values of LUMO are decreasing, and HOMO values are increasing, this refer to corresponds to the more reactive molecule in the reactions with electrophiles.

- The substitution of a thiophene for hydrogen atoms leads to increasing EA and S, and decreasing IP, X and η decreasing.
- The substitution leads to small different of stretching vibration, also, the stretching vibration (C-S) for thiophene and derivatives molecules is weak, because S atom has high mass and electronegativity compare with hydrogen and carbon atoms.
- The substitution of a thiophene lead to increasing the values of UV-VIS spectra, molecule 4 has high vibrational frequencies compared with derivatives molecules.
- The values of reduce mass for all molecules are decreasing, on the other hand, the force constant are increasing because the reduce mass is inversely proportional to the frequency while force constant is directly proportional to the frequency.
- The distribution of electrostatic potential depends on the type of substitution atoms, and on the electronegativity, negative and positive charges.

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