

Density Functional Theory Calculations of Thiophene - Phenylene Systems And Their Adducts

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Abstract

Density functional theory was employed to investigate the electronic properties of phenylene and thiophene compounds and their adducts, the interaction between the two structures changes to include six systems. Many important electronic properties were studied in two ways, the vertical energy method and vertical orbital method include the chemical potential, chemical molecular hardness, chemical softness, electrophilic index and polarizability. Full geometry optimization was calculated at the same level of theory. The results showed that the new structures have low chemical hardness with large electrophilicity, and they are more reactive .

Introduction

The conjugate polymers have special and interesting electronic properties and they are more extensively studied in the conductivity because they have high capacity of conjugation of atomic orbitals of type p that participate in molecular orbitals. Conjugated polymers can be used in the production of electric devices[1,2]. If the polymers and organic oligomers are doped they can have semiconductor or conductor properties[3,4], this leads to construct a variety of electric devices[5,6]. Oligothiophene and polythiophene have good properties of electronic conductors, and this is a good idea to modify these properties by adding of substituent [7-9]. For example, the addition of phenylene into the polymeric chain[8-15].

The production systems (thiophene-phenylene) have semiconductor properties can be used in molecular systems, photovoltaic cells and logic elements[1-5]. Adding the phenylene leads to decreased the energy gap of the thiophene oligomers[7-10]. In this study, standard 6-31G** basis sets used with B3LYP density functional theory to study the electronic properties for phenylene-phenylene (ph-ph), thiophene-phenylene (th-ph), thiophene-thiophene (th-th), thiophene-phenylene (th-ph), phenylene-thiophene-phenylene (ph-th-ph), thiophene-thiophene-phenylene-phenylene (th-th-ph-ph), thiophene-phenylene-thiophene-phenylene (th-ph-th-ph) and thiophene-phenylene-thiophene (th-ph-th-ph).

Theory and computational details

Figure 1 represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 suite of programs [16]. The molecular properties of the compounds have been computed by DFT using the standard 6-31G** basis set. In the DFT calculations the Lee, Yang and Parr correlation functional [17] is used together with Becke's three parameters [17] exchange functional B3LYP. Conformational analysis of the molecules has been performed to have an idea about the lowest energy structures of the species.

The geometry optimization was performed at the B3LYP density functional theory with the same basis set [17, 18]. Harmonic vibrational frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [19-21].

The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V , and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC} , which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT

dominant over the conventional HF procedure [17].

The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and vibrational analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface [18].

The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer and the respective neutral molecule; $IP_v = E_{cation} - E_n$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_{n+} - E_{anion}$ [19]. The HOMO and LUMO energy was also used to estimate the IP and EA in the framework of Koopmans' theorem [20].

$$IP = -\epsilon_{HOMO} \quad \text{and} \\ EA = -\epsilon_{LUMO}$$

Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential (μ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the Energy versus N(number of electrons) curve at external potential $v(r)$ [21]:

$$\mu = \left[\frac{\partial E}{\partial N} \right]_{v(r)} \quad (1)$$

Finite difference approximation to Chemical Potential gives,

$$\mu \approx -\chi = -(IP + EA)/2 \quad (2)$$

The theoretical definition of chemical hardness has been provided by the density functional theory as the

second derivative of electronic energy with respect to the number of electrons N , for a constant external potential $v(r)$ [21]:

$$\eta = \frac{1}{2} \left[\frac{\partial^2 E}{\partial N^2} \right]_{v(r)} = \frac{1}{2} \left[\frac{\partial \mu}{\partial N} \right]_{v(r)} \quad (3)$$

Finite difference approximation to Chemical hardness gives,

$$\eta = (IP - EA)/2 \quad (4)$$

For Insulator and semiconductor, hardness is half of the energy gap ($\epsilon_{HOMO} - \epsilon_{LUMO}$) [20] :

Electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index (ω) is defined as [17],

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

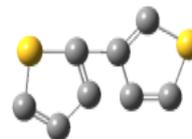
One of the other global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F , and represents a second-order variation in the energy [21] :

$$\alpha = - \left(\frac{\partial^2 E}{\partial F_a \partial F_b} \right)_{a,b=x,y,z} \quad (6)$$

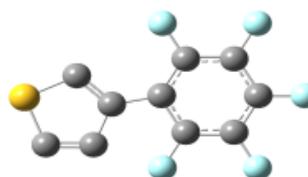
If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability $\langle \alpha \rangle$ is evaluated using the equation [17].

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (7)$$

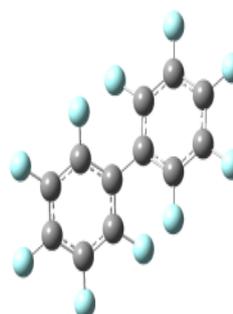
Where $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$ are the eigenvalues of the polarizability tensor.



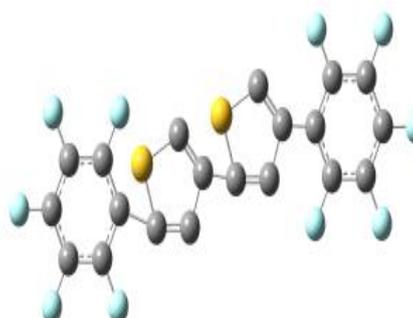
1
Th-Th



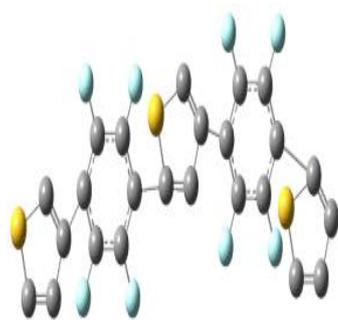
2
Th-Ph



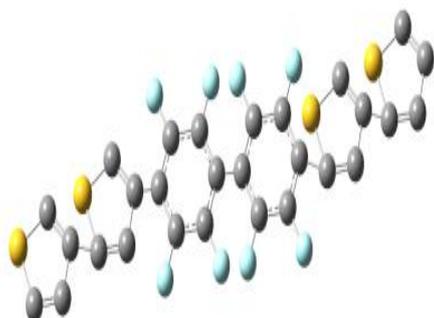
3
Ph-Ph



4
Ph-Th-Th-Ph



5
Th-ph-Th-Ph-Th



6
Th-Th-Ph-Ph-Th-Th

Results and discussion

The geometrical parameters (lengths in \AA and angles in degree) are illustrated in table 1, the length between C-C for the six compounds are the same as they in phynelene and thiophene molecules, and the bonds from the interaction of thiophene-thiophene and the other compounds gave a dihedral angles. The bithiophene is loses its planarity while polythiophene is a planar ring. The dihedral angle in th-ph structure is smaller than that in th-th structure, also in the other structures the dihedral angles are differ from one to the other. The main reason of this result comes from the presence of sulfur and fluorine atoms in the structures. The electrostatic repulsion between the fluorine atoms in ph-ph produces very small dihedral angle. The presence of alternating thiophene and phynelene

rings in the new structures changes the values of dihedral angles, as we see in table 1.

Table 1: Geometrical parameters for molecules under study

Molecule	Bond Length(C-C) \AA	Bond Angle ($^\circ$)	Dihedral Angle($^\circ$)
1	1.451	120.1	180
2	1.465	111.6	154
3	1.480	125.7	120.9
4	1.460, 1.450	125	164, 156
5	1.446, 1.465	112.2	156, 155
6	1.450, 1.460	111.6	155, 160

Table 2 declare the chemical potential, electronic chemical hardness and electrophilic index for studied structures, it is observed that these compounds show few tendency for electrons to escape from the ground or from the equilibrium density associated to the thiophene and phynelene rings. The new compounds constructed by the interactions of thiophenes-phynelenes have small value of chemical hardness in compared with the original phynelene and thiophene systems, as in table 2, and this refer to that these new compounds are more reactive than phynelene and thiophene, small chemical hardness means small energy gap and therefore small excitations from the ground, th-th-ph-th system has the smallest value of hardness comes from the position of phynelene ring in the center of the compound. Table 2 shows the result of electrophilic index, the original rings (thiophene and phynelene) have small value of electrophilicity, they are nucleophiles. While the other new compounds have large value of electrophilicity and they are more reactive because they have large measuring value of the electronic transfer that the compound may accept. The new structures are all of higher

than value of electronic transfer than the origin rings. The electronic properties are calculated by two methods: Vertical-Energy (V-E) which is called the adiabatic method and Vertical-Orbital (V-O), so called Koopman's method.

Table 2: Chemical potential, chemical hardness and electrophilic index for molecules under study

Mol.	Chemical potential(eV)		Chemical hardness(eV)		Electrophilic index(eV)	
	V - E	V - O	V - E	V - O	V - E	V - O
1	-3.615	-3.592	2.110	2.078	3.095	3.102
2	-4.008	-3.994	2.320	2.308	3.475	3.468
3	-4.835	-4.798	2.795	2.784	4.190	4.204
4	-3.993	-3.985	1.590	1.581	4.995	4.982
5	-4.285	-4.301	1.750	1.738	5.260	5.242
6	-4.165	-4.158	1.673	1.665	5.210	5.195

Figure 3 illustrate the values of electric dipole moment and polarizability. Due to the high symmetry of aromatic systems and the high level of delocalization of the electronic density of these systems, the values of electric dipole moment are small, the results showed that the systems have low dipole moment may accept less electronic charge than the systems of high dipole moment. The localized systems have large dipole moment and they are more electrophilic systems, this is a main feature result and refer to that conductivity at these localized systems might be improved through oxidation processes. Table 3 shows that the polarizabilities of all the new compounds are larger than that of the original rings, this refers to that these new systems are more reactive than the original rings, th-ph-th-ph-th has the larger value of polarizability than the others, it is the most polarizable and

this comes from the presence of fluorine atoms. The solubility of the new systems should be enhanced with respect to the solubility of the thiophene and phynelene rings.

Table 3: Electric dipole moment and polarizability for studied molecules

Molecule	Dipole moment (Debye)	Polarizability (a.u)			
		α_{xx}	α_{yy}	α_{zz}	α_{ave}
1	0.000	66.5	94.2	205.3	122
2	0.475	104.3	146.8	174.9	142
3	0.000	93.4	128.6	168	130
4	0.500	285.7	405.8	583.5	425
5	0.460	276.3	290.8	377.9	315
6	0.650	389.8	426.8	683.4	500

Conclusion

One can conclude that the standard basis set used with density functional theory is a suitable for describing the composites under study. The interaction of thiophenes with phynelenes decreased the energy gap of the original molecules and gave the more reactivity for the new composites with small hardness. The new systems are highly electrophilic.

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