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ScienceDirect
Journal of Molecular Structure 834–836 (2007) 508–515
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

A theoretical study of the linear, nonlinear optical properties and conformational analysis of 3-phenylthiophene and its fluoro derivatives with torsional dependence

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Received 25 September 2006; received in revised form 1 November 2006; accepted 6 November 2006
Available online 26 December 2006

Abstract

In this study, we have investigated the energies, dipole moments, HOMO–LUMO energy differences and polarizability values of 3-phenylthiophene and its fluoro-substitued derivatives as a function of the torsional angle. For each molecule, geometrical parameters have obtained using ab initio [Hartree–Fock (HF) and second-order Møller–Plesset (MP2)] and Density Functional Theory (DFT) with the 6-31++G** and 6-311++G** basis sets. The calculated physical quantities, such as electronic energy, dipole moment (μ), HOMO–LUMO energy differences (ΔE), polarizability (α) and hyperpolarizability (β) values are at the ground state geometry. The effect of the position of fluorine substituent on structural parameters, on dipole moments and on torsional potentials have been examined. The frontier molecular orbital calculations clearly show that there is an inverse relationship between HOMO–LUMO energy differences and their polarizabilities. We have also calculated λ_{max} values from the HOMO–LUMO energy differences. Finally we have discussed the trends in the calculated torsional potentials, barrier heights, and energy differences between conformers and correlated them with selected structural parameters.
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Keywords: 3-phenylthiophene and its fluoro-substitued derivatives; Torsional potential; Density functional theory; Hartree–Fock theory

1. Introduction

After the discovery of polyacetylene by Shirakawa and co-workers in 1977 [1], the organic polymers constituted of conjugated monomeric units have been the subject of several studies in new materials science. Heteroaromatic conducting polymers such as polypyrrole, polyaniline, and polythiophene exhibit a wide range of novel electrical and optical properties. The electrical and optical properties of these materials can be manipulated at the molecular level by derivatization of the monomer structure [2,3]. Polythiophene and its derivatives have attracted increasing attentions for their easiness to process, versatility and enhanced stability, which enable them to be used in microelectronic and optoelectronic, etc. [4]. Poly (3-phenylthiophene) has represented such a purpose [5]. The introduction of a phenyl group into the backbone of polythiophene stabilizes the conjugated π-bonds system and makes it an attractive material for the use in super capacitors [6].

The electric conductivity in this kind of polymer is attributed to the overlap between p atomic orbital. The extension of this overlap is associated with the conformation of the chain; thus knowledge of the possible conformations and the energies involved in the conformational equilibrium can be used to understand the electric properties of these compounds [7].

Poly (3-phenylthiophene) which owing to electron delocalization at conjugated π-bonds, the electrical properties originate from a π-conjugation extending over π-bonds.

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0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.11.018

The conformational behavior of phenylthiophene and its fluoro substituents depend on the balance of two interactions; (i) the π-electron conjugation between thiophene and phenyl rings, which tends to keep the molecule planar, (ii) the steric and electrostatic interactions can be either attractive or repulsive, between ortho atoms positions causes the molecule to twist.

The orientation of two rings can be influenced by the environment and different in various phases. As an example, the solid biphenyl has the planar structure [8,9], the dihedral angle about 30° in solution and liquid phase [10–12] and about 44° for the gaseous state [13,14].

The dependence of physical properties of molecules on the twist angle, have been studied by several workers. The twist angle dependence of photoluminescence of 2,2′-bithiophene derivatives has been studied experimentally [15], and the torsional dependence of structure and electronic properties of bithiopenes has been studied theoretically [16].

The conformational behavior of structurally similar molecules with title molecules have been studied theoretically by several authors. Phenylthiophenes has been studied by Hilal and Eittah using CNDO/2 [17], thiophene-phenylene-thiophene has been studied HF/3-21G* level of theory [18], and the para phenylthiophene dimer has been studied using HF, DFT (within B3LYP functional) and MP2 methods with 3-21 G* and 6-31G* basis sets [7].

In this paper, we have reported the electronic structure calculation and torsional potential of 3-phenylthiophene and 3-(fluorophenyl) thiophenes in which the position of the fluorine atom on the phenyl ring were changed systematically. Particularly, our attention will be focused on how the steric interaction, molecular geometry, and electronic energy of the molecule changes according to positional substituent on the phenyl ring.

We have studied energies dipole moments, polarizabilities and HOMO–LUMO energy differences of 3-phenylthiophene, 3-(2-fluorophenyl) thiophene, 3-(3-fluorophenyl) thiophene and 3-(4-fluorophenyl) thiophene molecules as a function of the twist angle (C_4–C_3–C_6–C_{11}), between thiophene and phenyl rings (see Fig. 1). In this paper, our studies show that, the physical and chemical properties of the partially fluorinated compound are changed. The molecule dipole moments that affect molecular electronic properties have been calculated and the results show that the dipole moments are correlated with the position of fluorine

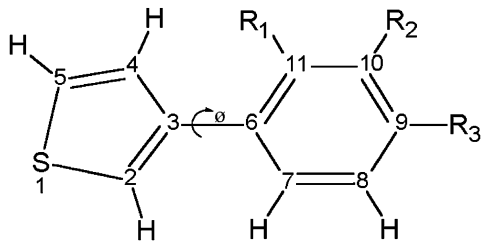

Fig. 1. Chemical configuration and atom numberings of PT (R_1, R2, R3 = H), 2-FPT (R_1 = F, R_2, R_3 = H), 3-FPT (R_1,R_3 = H, R_2 = F) and 4-FPT (R_1, R_2 = H, R_3 = F). The syn-form ($\theta = 0$) is shown.

substituent in the phenyl ring of the molecule. The torsional dependence of energy, dipole moment, polarizabilities and HOMO–LUMO energy differences are investigated for compounds.

2. Computational method

The geometric structure of all molecules have been optimized using DFT with the hybrid Becke's three parameters exchange functional [19] with Lee-Yang-Parr fit for the correlation functional (B3LYP) [20], HF theory [21] using the 6-31++G** and 6-311++G** basis sets and MP2 [22] using only 6-31++G** basis set that contains polarization and diffuse functions on all atoms [23] without any restriction. All the optimized structures have been subjected to vibrational analysis, using the same level of calculations as used in geometry optimization of them, in order to judge their stabilities. The variation of energies against twist angle has been scanned by fixing this angle from 0 to 180° intervals of 10° and optimizing all other structural parameters with HF/6-31++G** and B3LYP/6-31++G** level of theory. In MP2/6-31++G** calculations, to determine the geometry of transition states at 0°, 90°, and 180° we have the molecules optimized by fixing the dihedral angle. The calculated and equilibrium values have been fitted to the torsional potential function, which is a Fourier cosine-based function of the form

$$V(\phi) = V_0 + \sum V_n \cos(n\phi)$$

The calculated potential constants V_n reproduce the mean features of these torsional potentials reasonably accurate and so, to cut calculated time, we did not scan the potential curve between minimum and maximum.

Rotational barriers at 0° [ΔE_0 = E ($\theta = 0°$) − E (equilibrium)], at 90° [ΔE_{90} = E ($\theta = 90°$)-E (equilibrium)] and at 180° [$\Delta E_{180} = E$ ($\theta = 180°$) − E (equilibrium)] have been calculated by using the energies of the respective optimized structures (without any symmetry restriction except the dihedral angle). The global energy minimum of each potential energy surface (PES) has been referred to as zero. The dipole moments, HOMO–LUMO energy differences and polarizability values have been calculated for each molecule as a function of twist angle varying between 0 and 180° in 10° steps with HF/6-31++G** and B3LYP/6-31++G** level of theory. The potential energy calculations have been performed using the GAUSSIAN 03W [24]. Dipole moments, HOMO–LUMO energy differences and polarizability calculations have been performed using the GAUSSIAN 98W program package [25] in the gas-phase.

3. Results and discussion

3.1. Equilibrium structures

The important factor in the geometry of 3-phenylthiophene and its fluoro-substitued derivatives are its torsional

angle. The torsional angle to internal rotation depends on the balance of two interactions. While the interaction between thiophene and phenyl rings causes the molecule tends to remain planar, the steric repulsion between atoms in ortho positions causes the molecule to twist. The molecular configurations of the molecules studied in this work are shown in Fig. 1 and R_1, R_2 and R_3 in the phenyl ring stand for positions of the fluorine substituents, respectively. The molecular configurations of 3-phenylthiophene and its fluoro-substitued derivatives are listed in Table 1. Fully optimized geometric structures of the lowest energy conformer of 3-phenylthiophene and its fluoro-substitued derivatives as obtained by the HF/6-31++G**, 6-311++G**, MP2/6-31++G** and DFT/6-31++G**, 6-311++G** methods are compiled in Table 2.

The ground-state equilibrium geometry of 3-phenylthiophene is not planar. There are a few complete optimization studies in the literature for only PT. The torsion angle obtained at the HF/3-21G* level is 41.5° [18], at the B3LYP/6-31G (d) level is 32° [26], at the CNDO/2 method is 37° [17] and using NMR Spectra of Liquid-Crystalline solution it is 24° [27]. The interring C_3–C_6 bond length obtained at the CNDO/2 method is 1.45Å and using NMR Spectra of Liquid-Crystalline solution it is 1.49Å.

In our work, between 0 (syn-form) and 180° (anti-form), two non planar conformers have been obtained for ground-state equilibrium geometries of all molecules. These ground-state equilibrium geometries having torsion angle between 0° and 90° (syn-gauche) are represented as θ_{syn} and between 90° and 180° (anti-gauche) are represented as θ_{anti}. The θ_{anti} equilibrium torsion angle values of PT, 3-FPT and 4-FPT molecules can be obtained by the equation of the $\theta_{anti} = 180°$-θ_{syn}. It means that for these molecules, the sum of the θ_{syn} and θ_{anti} equilibrium angles gives 180° as the result ($\theta_{syn} + \theta_{anti} = 180°$). In the other words, the tendency of these molecules to the planarity at the both equilibrium conformation state is the same for three models which we have used in the calculation. For the 2-FPT molecule, the sum of the θ_{syn} and θ_{anti} is larger than 180° ($\theta_{syn} + \theta_{anti} > 180$), and the equilibrium conformation at the anti-gauche state is much closer that is about 10°, to the planarity than the syn-gauche equilibrium conformation state. In the literature, this state has been observed in the 3-phenylfuran molecule [28].

Table 2 shows that inter-ring C_3–C_6 bond length of the molecules which we are studying. For all molecules, calculated equilibrium bond lengths, do not differentiate in the syn-gauche and anti-gauche equilibrium conformation. For the calculated equilibrium bond lengths, we have given only inter-rings C_3–C_6 bond lengths. In the calculations, the value of the inter-rings C_3–C_6 bond length determined in the HF model is longer than that of B3LYP model, and the value of the inter-rings C_3–C_6 bond length determined in the B3LYP model is longer than that of MP2 model. The value for the equilibrium angle in the MP2 model was calculated larger than that of HF model, and the value in the HF model was calculated larger than that of B3LYP model. For PT molecule, we calculated equilibrium dihedral angle at the HF/6-31++G** as 41.5° and at the B3LYP/6-31++G** model as 33.5°. These values agree with the literature as at the HF/3-21G* level it is 41.5° [18], at the B3LYP/6-31G (d) level it is 32° [26]. We know that the hyperpolarizability calculations are as important as polarizibility and dipole moment calculations. So in Table 2, from the hyperpolarizability values we conclude that, the results change due to the change in the position of fluorine atom in the phenyl ring. Also it is clear that 2-FPT molecule has the highest hyperpolarizability value within the molecules we study. λ_{max} values in Table 2 have been obtained from the HOMO–LUMO energy differences. These values are in the UV region of the electromagnetic spectrum.

Table 1
Configurations of PT (R_1, R_2, $R_3 = H$), 2-FPT ($R_1 = F$, R_2, $R_3 = H$), 3-FPT (R_1, $R_3 = H$, $R_2 = F$) and 4-FPT (R_1, $R_2 = H$, $R_3 = F$)

Compounds	Acronym	R_1	R_2	R_3
3-Phenylthiophene	PT	H	H	H
3-(2-Fluorophenyl)thiophene	2-FPT	F	H	H
3-(3-Fluorophenyl)thiophene	3-FPT	H	F	H
3-(4-Fluorophenyl)thiophene	4-FPT	H	H	F

3.2. Torsional barriers and dipole moments

With HF/6-31++G** and B3LYP/6-31++G** the conformational analysis were done by changing the torsional angle θ by 10° steps between $\theta = 0°$ (syn form) and $\theta = 180°$ (anti form). MP2/6-31++G** calculations were compiled at two minima and three transition state structures. For each conformer, the dihedral angle was held fixed while the remainder of the molecule was optimized (the rigid rotor approximation was not applied).

In Figs. 2–4, we have calculated the torsional potential surface of all molecules by using various theoretical methods. The calculations show the existence of two well-defined wells separated by relatively energy barrier. Rotational barrier heights at 0° (ΔE_0), 90° (ΔE_{90}) and 180° (ΔE_{180}) were calculated and these results are given in Table 3. In comparison with the torsional barrier (ΔE^*), the relative energy between the syn-gauche and anti-gauche minima ($\Delta E^* = E_{anti} - E_{syn}$) does not change very much except for 2-FPT. Also the largest energy difference between two minima show potential curve of this molecule. This energy difference is 0.26 kcal mol^{-1} at MP2, 0.25 kcal mol^{-1} at HF, and 0.12 kcal mol^{-1} at B3LYP.

The results are shown in Figs. 1–3. All methods produce qualitatively similar form of the torsion potential. While HF and MP2 results are rather close to each other for the orthogonal conformation, and B3LYP results are higher in energy compared to HF and MP2 methods, this situation is reversed in planar conformations where MP2 energy is notably highest, while HF and B3LYP results are closer together. With HF and MP2 methods

Table 2
Selected structural parameters, the energies, dipole moments, HOMO–LUMO energy differences, λ_{max}, polarizabilities and hyperpolarizabilities of the equilibrium conformations of 3-(phenylthiophene) and 3-(monofluorophenyl) thiophene isomers

Molecule	Method/basis set	Structural parameter		Electronic energy (a.u.)	μ (D)	ΔE (eV)	λ_{max} (nm)	α (a.u.)	β (a.u.)
Syn-form		C_4–C_3–C_6– C_{11} (°)	C_3–C_6 (Å)						
PT	HF/6-31++G**	41.5	1.4850	−780.868567577	0.89	9.42	131.80	125.33	89.55
	HF/6-311++G**	41.6	1.4846	−780.94989909	0.88				
	MP2/6-31++G**	43.9	1.4723	−782.326730009	0.74	9.33	133.07	131.46	
	B3LYP/6-31++G**	33.5	1.4796	−784.089549761	0.50	5.10	243.45	136.5	254.85
	B3LYP/6-311++G**	34.9	1.4782	−784.18553994	0.49	5.13	242.02	135.74	254.83
2-FPT	HF/6-31++G**	46.1	1.4846	−879.720543277	1.81	9.62	129.06	124.09	224.77
	HF/6-311++G**	46.7	1.4844	−879.82920252	1.80				
	MP2/6-31++G**	46.3	1.4708	−881.34566795	1.90	9.49	130.83	131.03	
	B3LYP/6-31++G**	37.3	1.4787	−883.328407634	1.42	5.09	243.92	136.1	468.19
	B3LYP/6-311++G**	38.5	1.4773	−883.45270820	1.43	5.12	242.49	135.26	458.57
3-FPT	HF/6-31++G**	40.5	1.4842	−879.722343923	1.33	9.64	128.79	124.13	170.59
	HF/6-311++G**	40.6	1.4839	−879.83097353	1.32				
	MP2/6-31++G**	43.6	1.4719	−881.34678145	1.65	9.58	129.60	131.08	
	B3LYP/6-31++G**	32.2	1.4789	−883.330241062	1.46	5.08	244.40	136.4	309.21
	B3LYP/6-311++G**	33.4	1.4773	−883.45446443	1.49	5.10	243.45	135.65	306.81
4-FPT	HF/6-31++G**	42.8	1.4849	−879.721841746	1.24	9.52	130.42	123.75	276.66
	HF/6-311++G**	42.9	1.4845	−879.83044959	1.24				
	MP2/6-31++G**	44.9	1.4723	−881.34667434	1.59	9.45	131.38	130.70	
	B3LYP/6-31++G**	34.5	1.4794	−883.329790563	1.46	5.11	242.97	135,9	291.03
	B3LYP/6-311++G**	35.6	1.4879	−883.45400824	1.49	5.14	241.55	135.11	250.87
Anti-form									
PT	HF/6-31++G**	138.7	1.4849	−780.868567981	0.89	9.43	131.66	125.39	80.55
	HF/6-311++G**	138.6	1.4846	−780.94989901	0.88				
	MP2/6-31++G**	136.4	1.4725	−782.32703799	0.74				
	B3LYP/6-31++G**	146.5	1.4779	−784.089546068	0.50	5.11	242.97		
	B3LYP/6-311++G**	145.2	1.4781	−784.18553999	0.48	5.13	242.02	135.73	255.18
2-FPT	HF/6-31++G**	143.9	1.4840	−879.720172115	2.18	9.47	131.11	124.63	223.43
	HF/6-311++G**	143.7	1.4837	−879.82880971	2.18				
	MP2/6-31++G**	139.3	1.4707	−881.34608750	2.22				
	B3LYP/6-31++G**	153.8	1.4779	−883.328591889	1.77	5.04	246.34		
	B3LYP/6-311++G**	152.6	1.4764	−883.45286621	1.77	5.06	245.37	136.18	499.96
3-FPT	HF/6-31++G**	139.9	1.4843	−879.722335719	1.98	9.62	129.06	124.33	136.04
	HF/6-311++G**	139.8	1.4839	−879.803096914	1.98				
	MP2/6-31++G**	137.4	1.4720	−881.34730717	2.17				
	B3LYP/6-31++G**	147.5	1.4788	−883.330214237	1.92	5.07	244.89		
	B3LYP/6-311++G**	146.1	1.4774	−883.45445552	1.93	5.10	243.45	135.61	212.28
4-FPT	HF/6-31++G**	137.4	1.4849	−879.721841920	1.24	9.52	130.42	123.75	276.69
	HF/6-311++G**	137.2	1.4845	−879.83044956	1.24				
	MP2/6-31++G**	135.3	1.4725	−881.34691794	1.58				
	B3LYP/6-31++G**	145.7	1.4794	−883.329766294	1.46	5.13	242.02		
	B3LYP/6-311++G**	144.5	1.4780	−883.45400820	1.49	5.14	241.55	135.10	250.89

the torsion angles and the energies corresponding to the minima are produced in good agreement with each other. The B3LYP method predicts the minima to have somewhat more planar conformations. Similarly, the B3LYP method gives few kcal mol^{-1} lower barriers for the planar conformations than the ab initio methods. This is in agreement with earlier studies of conjugated systems, which indicate that B3LYP method somewhat overestimate the delocalization energy [29,30], and therefore, produce more planar structures. From the calculations Figs. 1–3, it is very clear that the position of fluorine atom has a major influence on the rotational barrier of these molecules. We know that the H–F steric interaction is stronger than the H–H steric interaction because of more electronegativeness of fluorine atom due to hydrogen atom. The shape of potential function depends critically on the delicate balance of both steric and conjugative effects.

The dipole moments of all molecules have been calculated as a function dihedral angle, the results are given in Figs. 5 and 6 using HF/6-31++G** and B3LYP/6-31++G** level of theory, respectively. At the both models, the dipole moments of the molecules have same trends with the uniform shape of torsional dependence. The dipole moment of 4-FPT molecule exhibits the uniform shape of torsional dependence with minima at perpendicular and maxima at planar conformations but, PT molecule is vice versa. For 2-FPT and 3-FPT molecules, the increment in interring torsion angles increases the dipole moment values of these molecules. The calculated energy data (a.u.) unit depend on dihedral angle are fitted by Fourier expansion up to six fold and its parameters are given in Table 4. Its values

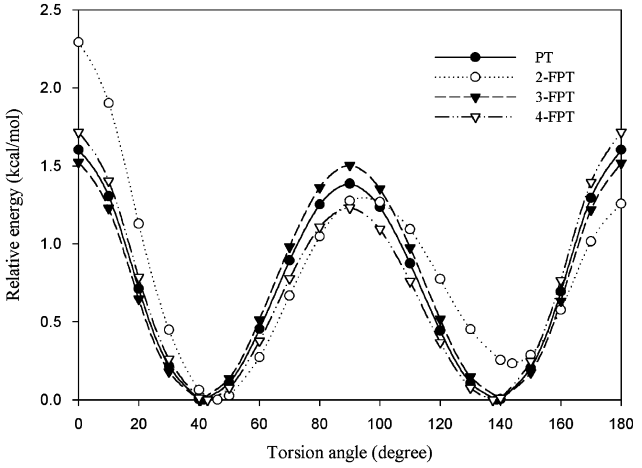

Fig. 2. The dependence of relative energy curves obtain, HF calculations, on the torsion angle for 3-phenylthiophene and 3-(monofluorophenyl)thiophene isomers.

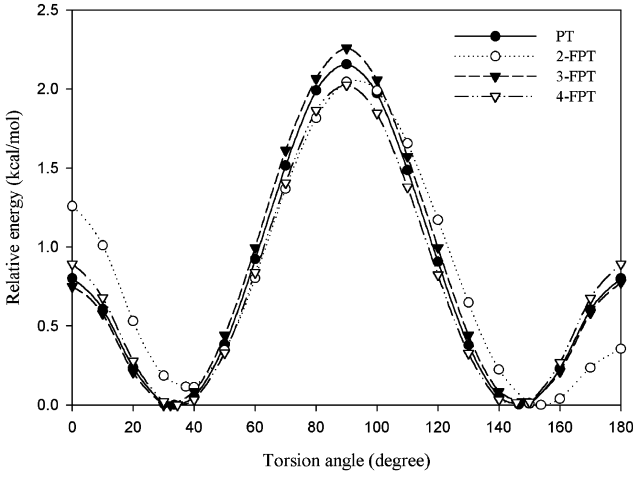

Fig. 3. The dependence of relative energy curves obtain, B3LYP calculations, on the torsion angle for 3-phenylthiophene and 3-(monofluorophenyl) thiophene isomers.

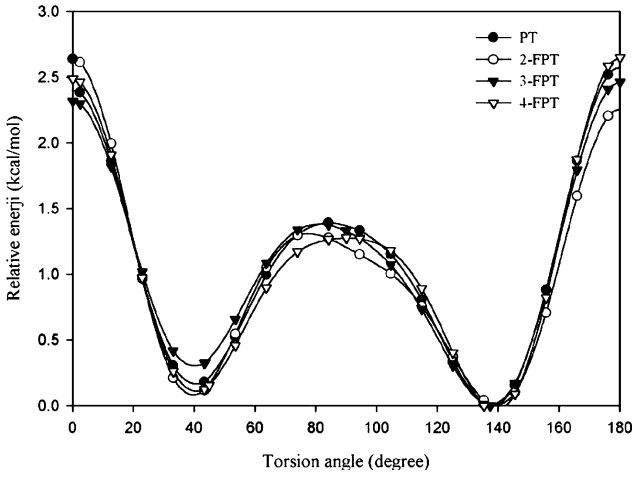

Fig. 4. The dependence of relative energy curves obtain, MP2 calculations, on the torsion angle for 3-phenylthiophene and 3-(monofluorophenyl)thiophene isomers.

Table 3
The rotational barrier heights of 3-(phenylthiophene) and 3-(monofluorophenyl) thiophene isomers

Molecule	Method/ basis set	ΔE_0 (kcal/mol)	ΔE_{90} (kcal/mol)	ΔE_{180} (kcal/mol)
PT	HF/6-31++G**	1.60	1.39	1.60
	MP2/6-31++G**	2.41	1.37	2.58
	B3LYP/6-31++G**	0.80	2.16	0.80
2-FPT	HF/6-31++G**	2.29	1.28	1.26
	MP2/6-31++G**	2.64	1.09	2.26
	B3LYP/6-31++G**	1.26	2.04	0.36
3-FPT	HF/6-31++G**	1.52	1.50	1.52
	MP2/6-31++G**	2.32	1.33	2.46
	B3LYP/6-31++G**	0.75	2.26	0.78
4-FPT	HF/6-31++G**	1.72	1.23	1.72
	MP2/6-31++G**	2.49	1.28	2.65
	B3LYP/6-31++G**	0.89	2.03	0.89

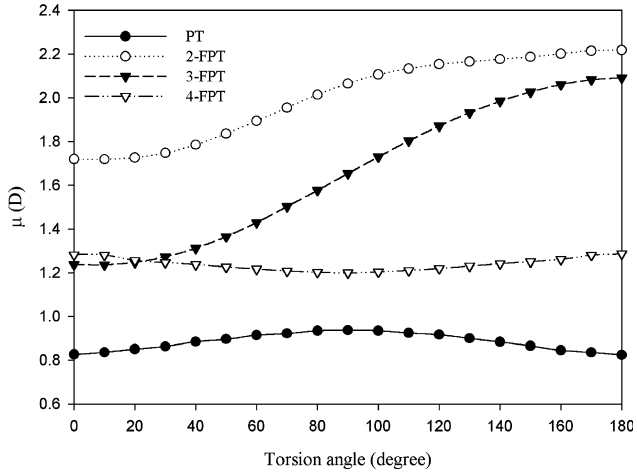

Fig. 5. The dependence of dipole moment curves obtain, HF calculations, on the torsion angle for 3-phenylthiophene, 3-(monofluorophenyl)thiophene isomers.

have the same trends as V_0 term that are dominant in corresponding Fourier expansion at B3LYP as well as HF levels.

3.3. Evolution of HOMO, LUMO and polarizability

HOMO–LUMO energy differences and polarizability values of PT, 2-FPT, 3-FPT and 4-FPT are investigated as a function of the torsional angle using HF/6-31++G** and B3LYP/6-31++G** level of theory. Figs. 7–10 shows the evolution of energy differences ($\Delta E = E_{LUMO}–E_{HOMO}$) between HOMO and LUMO and, polarizability of all molecules as a function of dihedral angle, respectively. For all molecules have the same tendency. It means that these values are symmetric with the orthogonal conformation (90°) of the molecules. The computed results, both models demonstrate that increase with increasing torsion angle from 0° to 90°, decrease with increasing dihedral angle from 90° to 180°. That is, ΔE values increase in the region of syn-gauche (for $0° < \theta < 90°$) and decrease in the anti-gauche

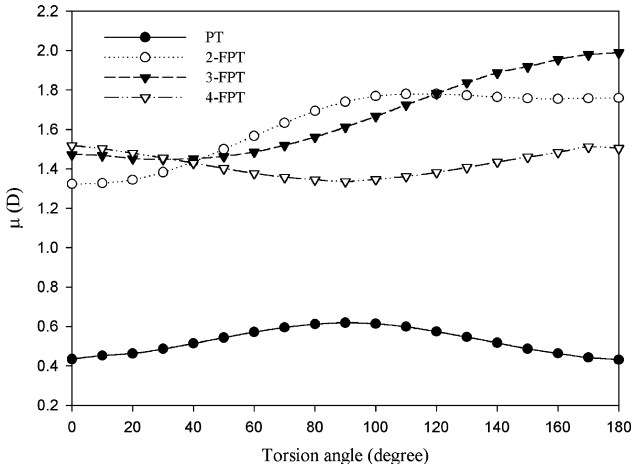

Fig. 6. The dependence of dipole moment curves obtain, B3LYP calculations, on the torsion angle for 3-phenylthiophene and 3-(monofluorophenyl) thiophene isomers.

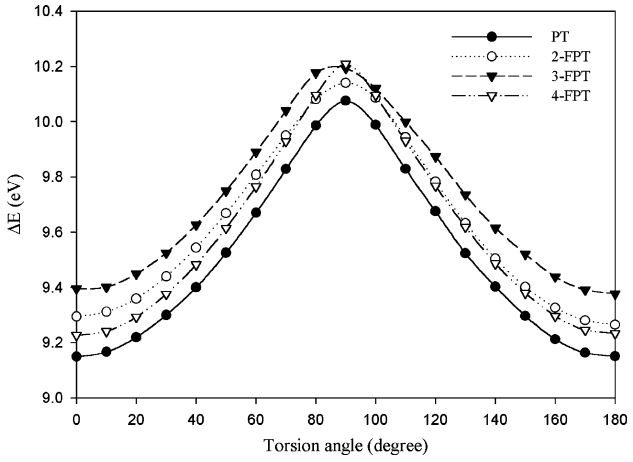

Fig. 7. The dependence of LUMO–HOMO energy differences curves obtain, HF calculations, on the torsion angle for 3-phenylthiophene, 3-(monofluorophenyl)thiophene isomers.

($90° < \theta < 180°$), where as this condition isn't obtained for the polarizability. That is, polarizability values decreas in the region of syn-gauche (for $0° < \theta < 90°$) and increase in the anti-gauche ($90° < \theta < 180°$). As expected, the increment in inter ring torsion angle angles reduces the π-electrons delocalization and consequently increases the energy gap (ΔE) between the HOMO and the LUMO. It can be observed that the increment in ΔE becomes faster at the large torsion angles. This is important for the effect of the torsion angle in different torsion rang, which means that the effect is less at the low torsion angle than at the high ones. We expect that a relationship between the polarizability and the inverse of ΔE might exist over a series of similar molecules.

The energy gap difference calculation of 3-pheylthiophene exist in literature, and energy difference of 3-phenylthiophene (see Table 2) are agree well with the R. Hilal and R. Abu-Eittah [17] using CNDO/2 method and V. Galasso and D. De-Alti [31] which have results as (−0.402 and 0.0684, HOMO and LUMO values at (a.u.), respectively), (−8.935 and 1.146, HOMO and LUMO values at (eV), respectively) using extended Hückel (EH) calculations.

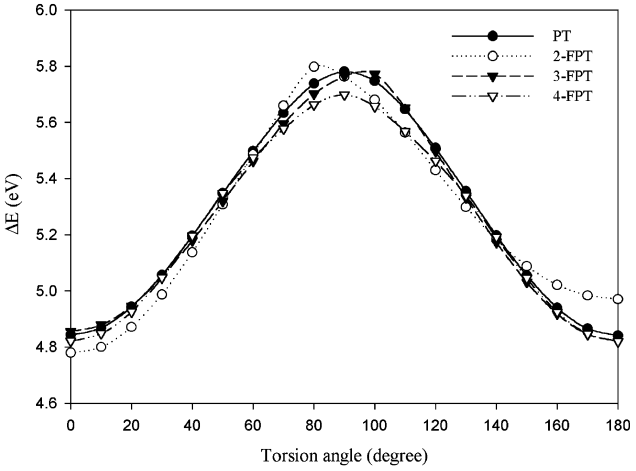

Fig. 8. The dependence of LUMO–HOMO energy differences curves obtain, B3LYP calculations, on the torsion angle for 3-phenylthiophene, 3-(monofluorophenyl)thiophene isomers.

4. Conclusions

We have studied energies, dipole moments, HOMO–LUMO energy gap differences and polarizabilities of

Table 4
Fitted potential parameters to a six-term truncated Fourier series for single-bond torsional potential of 3-(phenylthiophene) and 3-(monofluorophenyl) thiophene isomers (parameters values in a.u.)

Molecule	Method/basis set	V_0	V_1	V_2	V_3	V_4	V_5	V_6	R-squared
PTT	HF/6-31++G**	−780.867	−0.0002	0.0001	0	0.0012	0.0001	0.0002	0.9954
2-FPT		−879.719	0	0.0009	0.0006	0.0015	0.0001	0.0004	0.9959
3-FPT		−879.721	0.0002	0	0	0.0012	−0.0001	0.0002	0.9968
4-FPT		−879.72	0.0002	0.0004	−0.0001	0.0012	−0.0001	0.0002	0.9978
PTT	B3LYP/6-31++G**	−784.0879	−0.0002	−0.0012	0.0001	0.0010	0.0001	0.0002	0.9983
2-FPT		−883.3266	−0.0001	−0.0009	0.0004	0.0012	0.0001	0.0003	0.9948
3-FPT		−883.3285	0.0002	−0.0013	−0.0001	0.0010	−0.0001	0.0002	0.9980
4-FPT		−883.3282	0.0002	−0.0010	−0.0001	0.0011	−0.0001	0.0002	0.9975

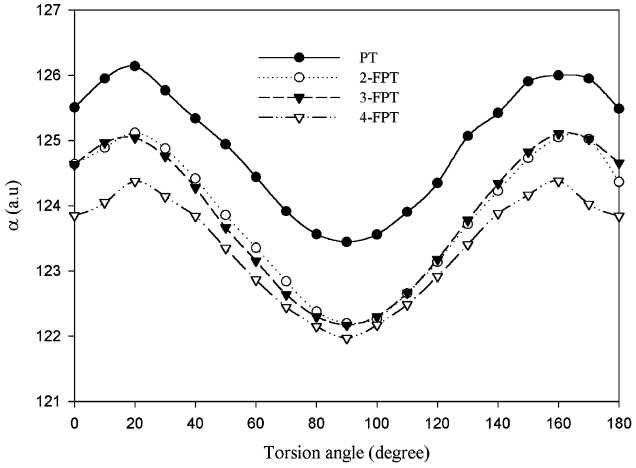

Fig. 9. The dependence of polarizability curves obtain, HF calculations, on the torsion angle for 3-phenylthiophene, 3-(monofluorophenyl) thiophene isomers.

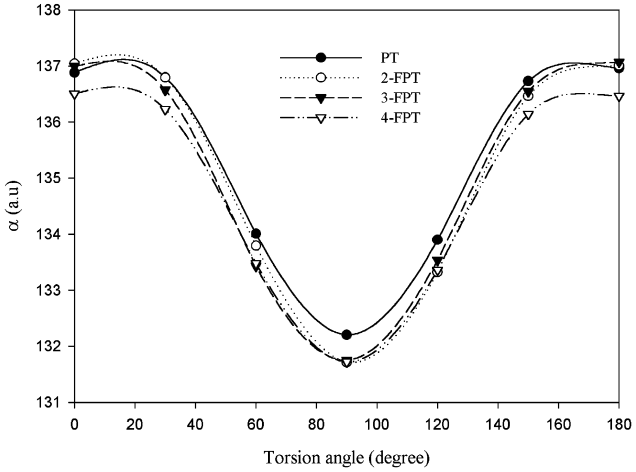

Fig. 10. The dependence of polarizability curves obtain, B3LYP calculations, on the torsion angle for 3-phenylthiophene, 3-(monofluorophenyl)thiophene isomers.

3-phenylthiophene and its fluorine subsistent derivatives a function of the twist angle.

As a result, in models, the internal rotation behavior and MO energy gap of all molecules are very similar. From the calculations, the influence of substituent in the meta and para positions of the 3-(monofluorophenyl) thiophene isomers on the torsional barrier are smaller than the influence of ortho substituents. Thus, fluorination at the ortho-position has a significant influence on the torsion angles. That is, the value of torsional angle increases with ortho fluorine atom. The effect of meta substituent on the torsional angle is much smaller than that of ortho substituent. The works on equilibrium conformation of F ortho-substituted 3-phenylthiophene show that steric effects are very important. As seen from Figs. 7–10, we say that the changes in the HOMO–LUMO differences due to the change in the dihedral angle are opposite. For example the HOMO–LUMO energy differences are maximum at 90° angle, the polarizibility values are minimum for the same angle (Figs. 7 and 8).

The deviations between DFT and HF are obtained for equilibrium conformations, energy, dipole moment and MO energy gap in the region where steric repulsion between lone-pairs or hydrogen and fluorine, π-conjugation and electron correlation became important.

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