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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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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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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 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.

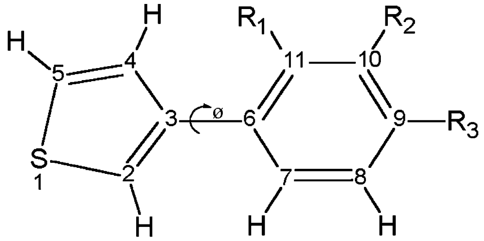

Fig. 1. Chemical configuration and atom numberings of PT (R_1, R2, R3 = H), 2-FPT (R_1 = F, R_2, R_3 = H), 3-FPT (R_1,R_3 = H, R_2 = F) and 4-FPT (R_1, R_2 = H, R_3 = F). The syn-form ($\theta = 0$) is shown.

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° [$\Delta E_0 = \mathrm{E}\ (\theta = 0°) - E$ (equilibrium)], at 90° [$\Delta E_{90} = \mathrm{E}\ (\theta = 90°)$-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

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