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Ground and Excited State Properties of 3-Methyl-pyrrole-1-carboxylic acid: Spin-Flip Time Density Functional Theory (SF-TDDFT) Method

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ABSTRACT

Polymers that efficiently interrelate with biological systems have fascinated a lot of curiosity in biosensor application. In order to determine their suitability and conducting abilities, the nature of ground state, excited states properties and binding affinities of such systems must be known. The vertical singlet-triplet gap, electronic transitions of 3-methyl-pyrrole-1-carboxylic acid has been studied using Spin-Flip Time density Functional Theory (SF-TDDFT) method with 6-311++G(d,p) basis set. All calculations were carried out using quantum mechanical softwares. Results revealed the Highest Occupied Molecular Orbital (HOMO) energies vary within the range of -5.22 to -6.24, while Lowest Occupied Molecular Orbital (LUMO) energies vary (from -0.62 to -1.84). Result revealed that the singlet-singlet transition for 3, 4 and 5 rings of MPC basically involves four ($|H \rangle$, $|H-1 \rangle$, $|L \rangle$ and $|L+1 \rangle$) transitions. Result show a non-zero transition dipole moment (d_{nm}) for MPC monomer and tetramer (Allowed transition), while d_{nm} decreases for trimer, dimer and pentmer, due to the triple integral returning an ungerade (odd) product and redistribute electrons within the same orbital and will return a zero product.

Keywords: Transition dipole moment, HOMO-LUMO energies, Quantum mechanical calculations, SF-TDDFT, DFT, Ground state

INTRODUCTION

Conducting polymers due to the amplification by a total system response are sensitive to very minor perturbations and offer an advantage over small-molecule [1]. Currently progresses have been in the controlled synthesis of these polymeric materials, which allow the rational design and preparation of new chemical and biological biosensor systems. To obtain a long operational life of the bio-molecules, the technique of the enzyme-immobilization onto the transducer is a key process to developing a good biosensor device. Generally, the enzyme-immobilization methods [2] include adsorption [3], covalent attachment [4,5]. Conducting polymers have been applied in the fabrication of biosensor devices in various fields, such as health care, immunosensors, DNA sensors, environmental monitoring and food analysis [6]. In recent years, quantum chemistry methods have made great progresses in studies of electronic and structural properties of conjugated polymers. In the beginning semi-empirical methods were the dominant theoretical tool to study conjugated polymers such as unsubstituted and substituted polypyrrole. More theoretical investigations have been carried out on conjugated polymers to study the electronic and structural properties. These have provided more insight into different forms of oligomers and their repeating units containing different functional groups and substituents [6]. Ab initio quantum mechanical calculations at the MP2 level were used for an extensive study concerning the stability of hydrogen-bonded complexes formed by pyrrole and thiophene, which are the most common building blocks of conducting polymers, and DNA bases [7]. Standard TDDFT also does not yield a good description of static correlation effects, because it is based on a single reference configuration of Kohn-Sham orbitals. Recently, a new variation of TDDFT called Spin-Flip Density Functional Theory (SF-DFT) was developed by Shao et al. [8] to address this issue.

Despite intense theoretical work on polypyrrole concerning structural and electronic properties, the nature of ground and excited state of 3-methyl-pyrrole-1-carboxylic acid are yet to be completely understood. Therefore it is important to understand the nature of electronic transitions and to establish the possibility of intermolecular charge transfer.

COMPUTATIONAL METHODS

Quantum mechanical calculations of the ground state molecular structures of pyrrole and its derivatives were carried out using Spartan 10 software package and Q-Chem 4.2, a 2.50 GHz personal computer and HP cluster machine of 132 GB, at National Chemical Laboratory (NCI), Pune, India. The detailed electronic transitions, including excitation energies, oscillator strength, MO/character (Configurations for the main S_0 to S_1 electronic transitions) and maximum absorption in UV-Visible spectrum (denoted as λ_{max}) are presented in this work. For UV-Visible calculations, TDDFT calculations have been used vertical excitation energies and first excited dipole moments using SF-TDDFT methods.

RESULTS AND DISCUSSIONS

The structure of 3-methyl-pyrrole-1-carboxylic acid from monomer to pentamer was optimized and it is given in Figure 1.

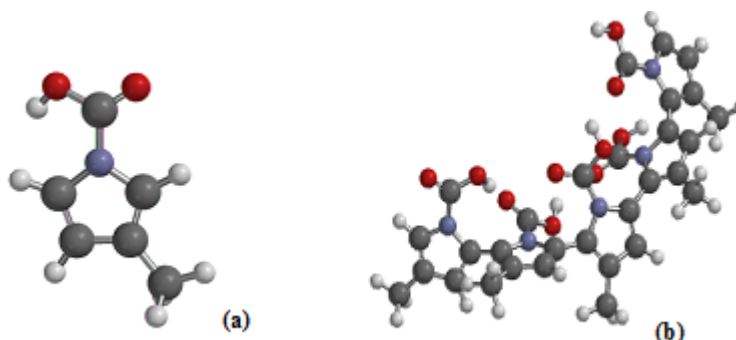


Figure 1: Optimized structure of MPC (a) monomer and (b) pentamer

Molecular energies

Analysis of the results of Ionization Potential (IP) and Electronic Affinity (EA) for MPC in from monomers up to 5 repeating units are positive values. The Highest Occupied Molecular Orbital (HOMO) energies vary within the range of -5.22 to -6.24, while Lowest Occupied Molecular Orbital (LUMO) energies vary from (-0.62 to -1.84). As shown in Figure 2, a linear relationship exist between the direct calculated vertical HOMO energies and $1/n$ calculated from DFT (With a correlation coefficient $r^2=0.76$) and the direct calculated vertical LUMO energies and $1/n$ (With a correlation coefficient $r^2=0.93$). As shown in Plate 4.10, the LUMO of π -nature is delocalized over the C-C bonds of the ring, while the HOMO is located over the C=C bonds.

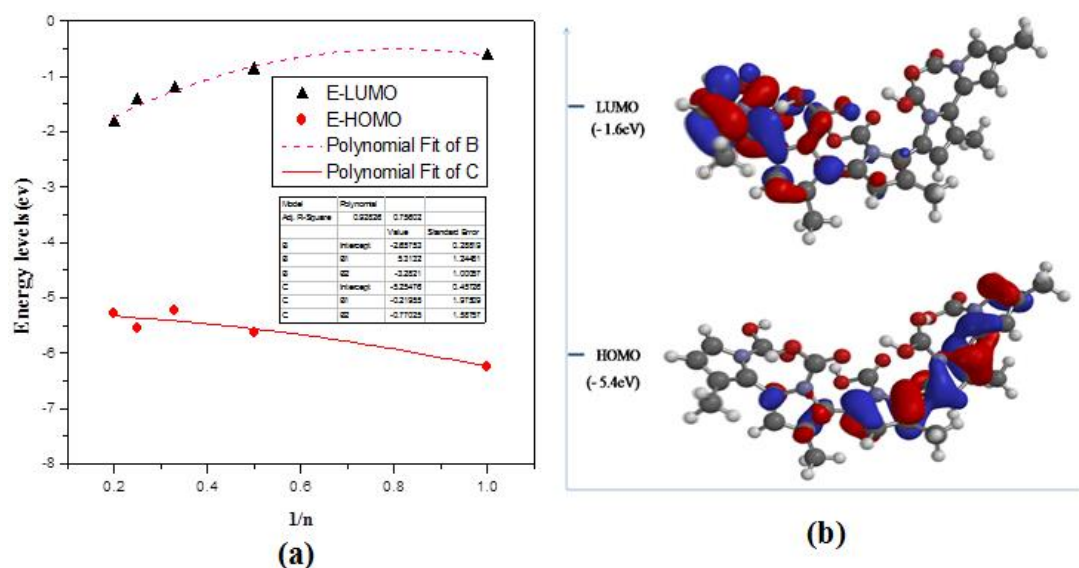


Figure 2: Plot of HOMO, LUMO energy level against $1/n$ and the frontier molecular orbital plot of MPC

Electronic absorption properties

The calculated wavelength λ_{\max} (nm) also increases as the number of ring increases. As in the case of the oscillator strength, the absorption wavelength arising from $S_0 \rightarrow S_1$ electronic transition increases progressively with the increase in the conjugation (Table 1). The bands assigned at 236.02, 295.04, 330.59, 337.58 and 372.80 nm correspond to the HOMO-LUMO transition and is of Intramolecular Charge Transfer (ICT) character the singlet-singlet transition for 3, 4 and 5 rings MPC basically involves four ($|H\rangle$, $|H-1\rangle$, $|L\rangle$ and $|L+1\rangle$).

Vertical singlet-triplet gap and first excited state dipole moment

Result in Table 2 shows that studied systems have a singlet ground state, based on the fact that there is no cross over in the singlet-triplet energy gap (From positive value to negative value). Transition dipole moment (d_{nm}) is a transition between two states. For a charged particle it is simply an off-diagonal matrix element of the position operator multiplied by the particle charge. This is useful for determining intermolecular interactions and if the transitions are allowed under the electric dipole interactions. Results in Table 2 show a non-zero d_{nm} for MPC monomer and tetramer (Allowed transition), while d_{nm} decreases for trimer, dimer and pentamer, due to the triple integral returning an ungerade (odd) product and redistribute electrons within the same orbital and will return a zero product.

Table 1: Calculated electronic transition data for MPC

Number of monomers	Electronic transitions	λ_{\max} (nm)	O.S	MO/Characters	Coefficient
1	$S_0 \rightarrow S_1$	236.02	0.0428	HOMO \rightarrow LUMO	0.95
	$S_0 \rightarrow S_2$	212.26	0.0717	HOMO-2 \rightarrow LUMO	0.72
	$S_0 \rightarrow S_3$	205.65	0.0991	HOMO \rightarrow LUMO	0.65
2	$S_0 \rightarrow S_1$	295.04	0.1190	HOMO \rightarrow LUMO	0.99
	$S_0 \rightarrow S_2$	265.72	0.0498	HOMO-1 \rightarrow LUMO	0.35
	$S_0 \rightarrow S_3$	237.96	0.0324	HOMO-1 \rightarrow LUMO	0.86
3	$S_0 \rightarrow S_1$	330.59	0.2110	HOMO \rightarrow LUMO	0.99
	$S_0 \rightarrow S_2$	292.54	0.0493	HOMO \rightarrow LUMO+1	0.92
	$S_0 \rightarrow S_3$	280.34	0.1084	HOMO-1 \rightarrow LUMO	0.90
4	$S_0 \rightarrow S_1$	337.58	0.2465	HOMO \rightarrow LUMO	0.87
	$S_0 \rightarrow S_2$	326.16	0.0139	HOMO-1 \rightarrow LUMO	0.85
	$S_0 \rightarrow S_3$	303.91	0.0552	HOMO \rightarrow LUMO+1	0.88
5	$S_0 \rightarrow S_1$	408.87	0.1508	HOMO \rightarrow LUMO	0.95
	$S_0 \rightarrow S_2$	371.07	0.0927	HOMO-1 \rightarrow LUMO	0.95
	$S_0 \rightarrow S_3$	361.81	0.0941	HOMO \rightarrow LUMO+2	0.92

Table 2: Vertical singlet-triplet gap (eV) and transition dipole moment (Debye) (in parenthesis) for studied system

Number of monomer	MPC ^b
1	4.31
	-0.343
2	3.98
	-0.065
3	3.32
	-0.035
4	3.21
	-0.402
5	3.11
	-0.032

CONCLUSION

It can be concluded that in 3-methyl-pyrrole-1-carboxylic acid, excitation to S_1 state also corresponds to the promotion of an electron from the HOMO to the LUMO and it possesses highest absorption maxima which is attributed to the strong intramolecular charge transfer. Certain transitions are allowed and certain transitions are forbidden due to the symmetry of the ground and excited states, this makes it suitable for biosensor application.

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