Theoretical studies of structural, optic and electronic properties of polypyrrole (PPy) oligomer

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Abstract: In the present study, first-principles calculations are used to investigate the electronic properties of n-pyrrole oligomers with n = 1–29, and all results were plotted to determine the optimal number of chains (n). The molecules were optimized using the density functional theory (DFT) with the B3LYP method combined with the 6-31G(d,p) basis set. Transition energies and oscillator strengths for the electronic excitation of the first 12 singlet-to-singlet excited states of PPy were calculated using time-dependent (TD) DFT at the same level. In addition, optical properties of PPy were studied as theoretically. It was observed that there is quite compatibility between the calculated and experimental data.

1. Introduction

Since the discovery of polypyrrole (PPy) almost 50 years ago, a myriad of publications is now available, more than 800 this past year alone according to Web of Science. PPy is a prototype conducting polymer [1] that displays unique mechanical, optical, electrical, and biocompatible properties. However, much about the physical properties and structural characteristics of PPy are still not well understood, with data that is often contradictory. With the advent of nanomaterials, today PPy is used as a component at the nanoscale in a variety of sensors, fibers, and coated foams among other nanostructures [2]. In addition, conducting polymer are also used in photovoltaic cells [3], smart windows [4], electrochromic displays [5], gas separation members [6], corrosion protection [7] and electrocatalysis [8].

Due to broad interest in PPy, their application in electronic and optical devices have been investigated and well documented in the literature [9-19]. In addition, it has also been reported that the effect of the doping of different material on electronic and optical properties [20, 21]. Furthermore, the theoretical studies on electronic and optical properties of some substitute or doped

PPy were also performed [22-25]. However, to the best of our knowledge, no theoretical study was present on the structural properties and examination of band gap according to chain length (n = 1-29). The aim of this work is to study the molecular structure of PPy oligomer, optical and spectroscopic characterization of PPy oligomer. For this purpose, density functional theory (DFT) calculations were performed to explain the structural and spectral characteristics of the PPy oligomers (n = 1-29). Molecular structure parameters of the all compounds have been calculated by B3LYP/6-31G(d,p) level of theory. In addition, HOMO, LUMO, band gap and UV spectral analysis have been used to elucidate the electronic transitions within the molecule using TDDFT method and same basis set.

2. Computational Method

In this study, all calculations were conducted using density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP) method [26] as implemented in the GAUSSIAN 03 program package [27]. In the first step of the calculation, to elucidate conformational features of the n-pyrrole oligomers with n = 2, the selected

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degree of torsional freedom, T(N1-C1-C5-N2), was varied from -180º to +180º in every 10º and the the potential energy curve (PES) was obtained with the B3LYP/6-31G(d,p) level of theory in the gas phase. In potential energy curve, the stationary points were confirmed by the frequency analysis as minima with all real frequency and with no imaginary frequency implying no transition state. For the four different conformers, the geometric structure was reoptimized at the DFT level of theory by using 6-31G(d,p) level. For all of the calculations in this study, optimized structural parameters were used. The electronic absorption spectra were calculated using the time dependent density functional theory (TDDFT) in gas phase. The band gaps for all PPy oligomers are defined as the difference between the calculated energies for the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). All molecular structures were visualized with GausView software [28].

3. Results and Discussion
3.1 Conformational analysis and optimized structures

The structure of PPy are flexible molecule, rotates the C2-C5 bond and represents several conformations. To establish the most stable conformation, the PPy was subjected to a conformation analysis around the C2-C5 bond. The potential energy surfaces and the structures of PPy represent several conformations as illustrated in Fig. 1.

Conformations of PPy are feasible depending on the orientation around C2-C5 bond. Conformational analyzes were carried for PPy by potential energy surface scan to find all possible conformers with B3LYP method using 6-31G(d,p) basis set. The most stable conformer was determined that the nitrogen atoms of two PPy are trans position as seen in Fig. 1. All the possible geometries of the conformers were optimized to find out the most stable configuration of PPy, which are presented in Fig. 2. However, the calculation results have shown that the molecule is not planar. Therefore, the dihedral angle, N1-C1-C5-N2 was computed at -153.2º. The energy of this form was more stable than the planer form as 4.340 kJ/mol. The less stable conformer is *cis* form, the energy was calculated at 14.479 kJ/mol. The last suggested conformer is the asymmetric-trans and not planer form as shown in Fig. 2(d) for PPy (n =2). The relative energy of this form was more calculated at 7.577 kJ/mol than the most stable form (*trans* and not planer). The energies of the possible geometries of the conformers are listed in Table 1. The most stable conformer of PPy was then subjected to geometrical optimization by B3LYP method using 6-31G(d,p) basis set to obtained geometrical parameters. In addition, the numbering of atoms of the PPy is shown in Fig. 2.
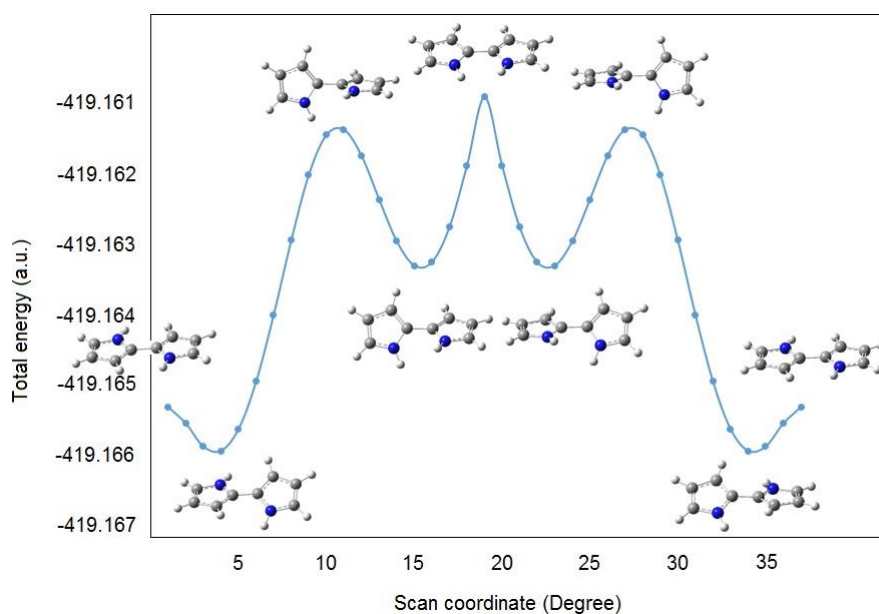

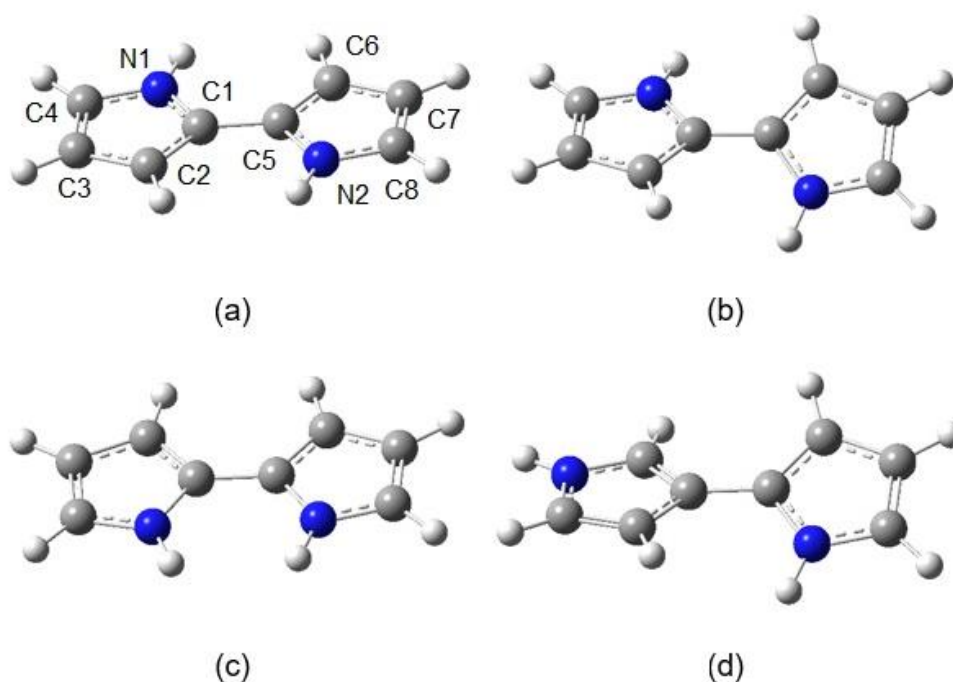**Fig. 1.** Potential energy surfaces of PPy (n =2) calculated by B3LYP/6-31G(d,p)

Fig. 2. The optimized structures and the numbering of atoms for the most stable conformers, (a) trans and planer, (b) trans and not planer, (c) cis and planer, (d) asymmetric-trans and not planer.

Table 1. Calculated dihedral angles, energies and dipole moments of 2-PPy.

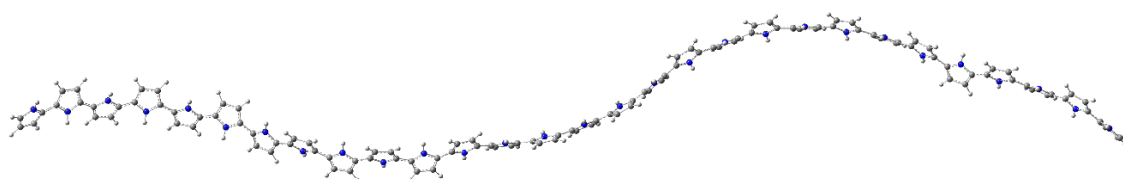| Molecules	Dihedral angles (°) (N1-C1-C5-N2)	E (a.u.)	ΔE (kJ/mol)	Dipol moment (D)
I	180.0	-491.051467	4.340	0.0007
II	-153.2	-419.053120	0.000	0.9496
III	0.0	-419.047567	14.579	3.1207
IV	-153.9 (C1-C2-C5-N2)	-419.050249	7.577	2.7487

Fig. 3. Optimized structure of PPy oligomer (n = 29)

The most stable molecular structure, the *trans* and not planer form for PPy (n = 2) was reoptimized by the DFT/B3LYP method with 6-31G(d,p) basis set. Then, the all PPy oligomers n = 1-29 were optimized same basis set, and the optimized structure of PPy oligomer (n = 29) obtained GausView program is shown in Fig. 3. Generally, the important bonds of PPy are C=N, C=C, C-C and C-H bonds. These bond lengths were calculated at ca. 1.380, 1.390, 1.450 and 1.080 Å respectively. In addition, bond angles, C1-N1-C4, C2-C1-C5 and N1-C1-C2 were performed 110.2, 131.7 and 106.8º respectively. The molecules of straight chain PPy may be linked by N-H······N intermolecular hydrogen bonds. The hydrogen bonds and van der Waals interactions result forms a three-dimensional network in PPy.

3.2 Electronic properties

Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are known as Frontier molecular orbitals (FMOs), which forms band gap (E_g) following equation;

$$E_g = E_{LUMO} - E_{HOMO} \qquad (1)$$

The HOMOs are as electron donors representing the ability to donate an electron and LUMOs are as electron acceptors representing the ability to obtain an electron [29]. It is important to examine the HOMO and the LUMO energies for this oligomer because the relative ordering of the occupied and virtual orbital provides a reasonable qualitative indication of excitation properties. In general, as shown Fig. 4, the HOMO of PPy oligomer possess a π-bonding character within a subunit and a π-antibonding character between the consecutive subunit. On the other hand, the LUMO possess a π-antibonding character within a subunit and a π-bonding character between the subunit. Theoretically, the electronic parameters (E_g, HOMO and LUMO) of PPy oligomer n = 1-29 were calculated at B3LYP/6-31G(d,p) level. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in experimental values compared with an isolated molecule, as considered in the calculations. Even if the calculated energy levels are not accurate, it is possible to use them to obtain the information by effect of chain length (n = 1-29). The calculated electronic parameters (E_g, HOMO and LUMO) of PPy oligomer n = 1-29 are listed in Table 2, while the change of E_g to chain length (n = 1-29) is presented in Fig. 5.

As shown Table 2, as the chain length increases in PPy oligomer (n = 1-29), the energy of HOMO molecular orbital decreases, while the energy of LUMO molecular orbital increases. Besides, as shown in Fig. 5, It was observed that the band gap decreased with the increase of the chain length. The band gap (E_g) in 2-PPy oligomer was found to be 5.060 eV, while in the 29-PPy oligomer, it was calculated as 3.101 eV. Band gap (E_g) shows a close to a linear change after chain length twenty (n > 20). Therefore, it is sufficient that the chain length for the band gap is twenty-nine (n = 29). The band gap (E_g) is observed as experimentally at 2.830 eV in the literature [30].
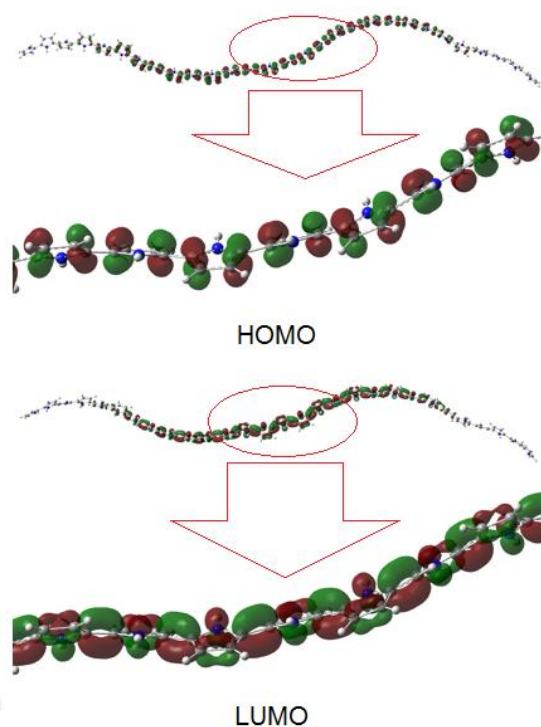

Fig. 4. The counter plots of HOMO and LUMO molecular orbitals of 29-PPy oligomer.

Table 2. HOMO, LUMO molecular orbital energies (a.u.) and band gap (E_g, eV) of PPy oligomers (n = 1-29).

n	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	$\Delta E_{LUMO-HOMO}$ (eV)
1	-0.202	0.049	6.827
2	-0.175	0.011	5.060
3	-0.162	-0.003	4.325
4	-0.156	-0.011	3.944
5	-0.152	-0.016	3.699
6	-0.150	-0.019	3.563
7	-0.149	-0.021	3.482
8	-0.148	-0.022	3.427
9	-0.147	-0.024	3.346
10	-0.146	-0.024	3.318
11	-0.146	-0.025	3.291
14	-0.146	-0.027	3.237
15	-0.146	-0.028	3.210
21	-0.145	-0.029	3.155
25	-0.144	-0.029	3.128
29	-0.144	-0.030	3.101
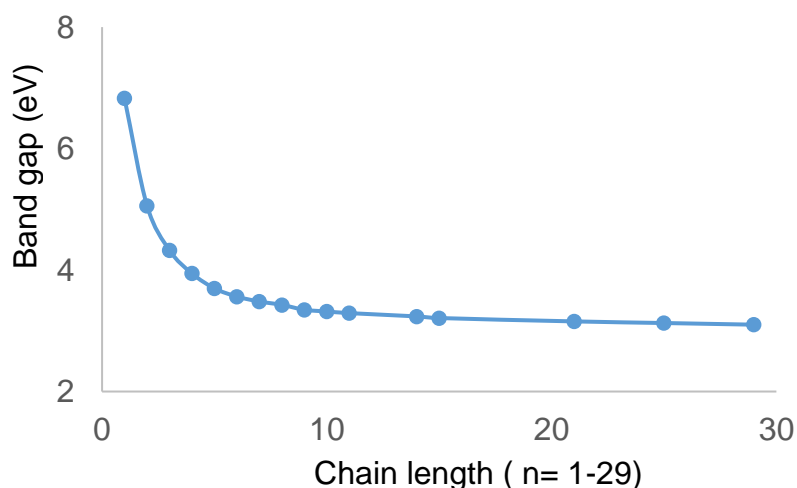
Fig. 5. Change of band gap according to chain length in PPy oligomer.

3.3 Optoelectronic properties

For a better understanding of the electronic properties and chain length effects of PPy oligomers (n =3-29), the excitation energy based on the first 12 singlet-singlet electronic transitions has been studied. In recent years, time dependent density functional theory (TDDFT) has emerged as a reliable standard tool for the theoretical treatment of electronic excitation spectra. Transition energies and oscillator strengths for the electronic excitation of the first 12 singlet-to-singlet excited states of PPy oligomers (n = 3-29) were calculated using TDDFT at 6-31G(d,p) basis set, and the absorption spectra of PPy oligomers (n = 3-29) were presented in Fig. 6. The 3-PPy displays an absorption band centered at 306 nm (f_{os} = 0.85). If the chain length is 5, this transition band increases at 376 nm. As the chain length increases, the maximum absorption wavelength shifts to a higher wavelength. Therefore, the absorption band was calculated at 460 nm with an oscillator strength of 8.52 in the 29-PPy oligomer. This absorption is contributed by electron excitation from HOMO to LUMO. Both orbitals, HOMO and LUMO orbitals are mainly located on one of the PPy side, and these orbitals are p character. Therefore, this absorption band assigned to the $\pi \rightarrow \pi^*$ transition. This major absorption band of PPy appears at maximum 472 nm as experimentally [30].
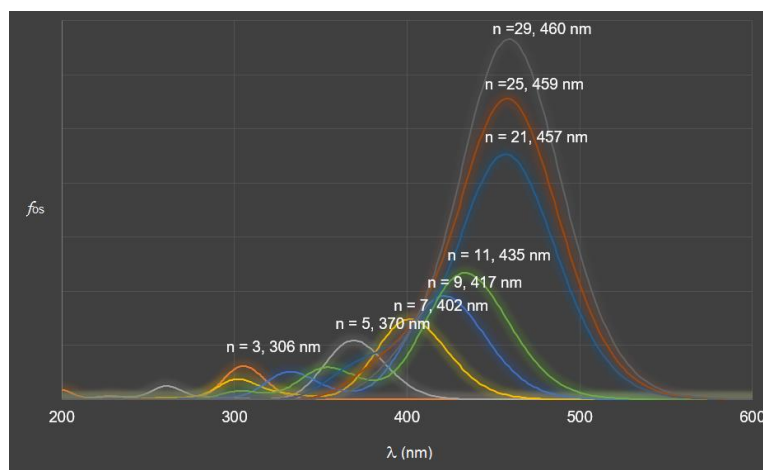
Fig. 6. Calculated electronic spectra of PPy oligomers (n = 3-29)

4. Conclusion

In this work, we have used the DFT/B3LYP method to investigate the theoretical analysis of the geometries, electronic and optic properties of PPy oligomers. The electronic and optic properties of PPy oligomers have been computed using the 6-31G(d,p) basis set. In addition, the effect of chain length was studied as theoretically.

In summary, the conclusions are as follows.

(I) In the first step of the calculation, to elucidate conformational features of the n-pyrrole oligomers with n = 2, the selected degree of torsional freedom, T(N1-C1-C5-N2), was varied from -180º to +180º in every 10º. The calculation results have shown that the 2-PPy molecule is not planar. The dihedral angle, N1-C1-C5-N2 was computed at -153.2º. Therefore, PPy oligomer is not planer.

(II) The conformation studies show that the most stable conformation form is trans and not planer form.

(III) The HOMO level, LUMO level and band gap (E_g) of the PPy oligomers (n = 2-29) were well controlled by the acceptor strength. The band gap (E_g) reduced until the chain length is 20, then the band gap is almost fixed. Therefore, when the chain length is 29, the band gap was calculated as 3.101 eV.

(IV) The UV-vis absorption properties have been obtained by using TDDFT calculations. The obtained absorption maximums of PPy oligomers (n = 3-29) are in the range of 306-460 nm. The absorption band was calculated at 460 nm with an oscillator strength of 8.52 in the 29-PPy oligomer. This absorption is contributed by electron excitation from HOMO to LUMO, assigned to the $\pi \rightarrow \pi^*$ transition.

Finally, the procedures of theoretical calculations can be employed to predict the electronic and optic properties of the other conjugated polymers and further to design novel materials for organic solar cells.

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