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DFT and TD-DFT studies of Alkyl-substituted Oligopyrroles for Optoelectronic devices

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Abstract

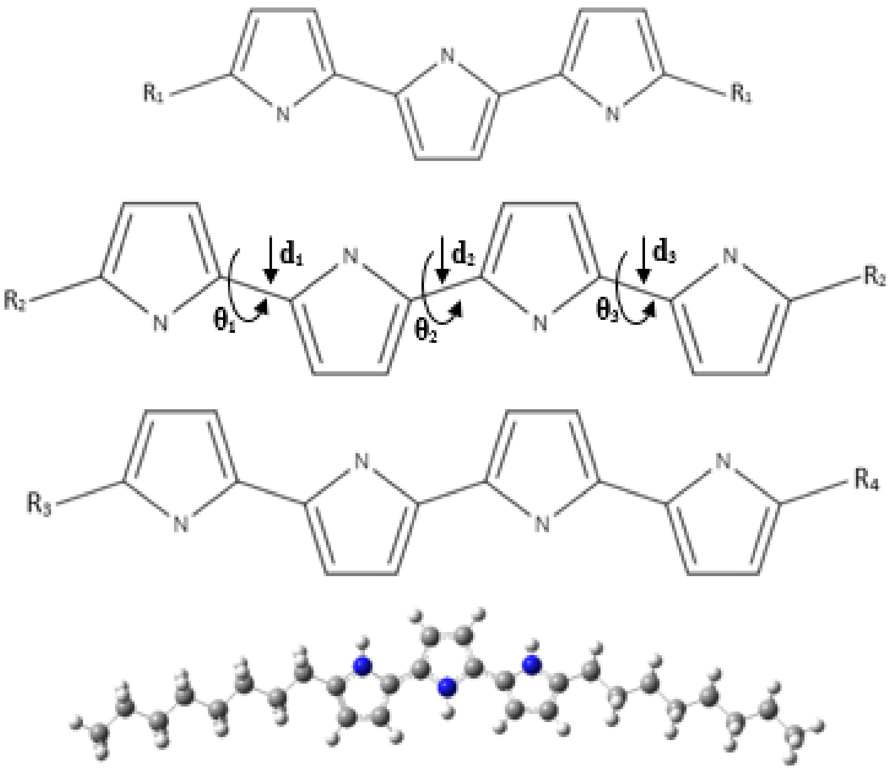
The investigation of 3,3'-dicotylterpyrrole (DOTP), 3,3'-dihexylquaterpyrrole (DH4P) and 3,7-dimethyldienyloctyl-3'dodecylquarterpyrrole (ddoD4P) both in doped and neutral forms was implemented on the basis of density functional theory (DFT) and we have chosen the B3LYP as functional with the 6-31G(d) basis set. Alkyl-substituted Oligopyrrole is unique due to the presence of the alkyl as terminal. The structural and electronic proprieties such as the inter-ring distance, the dihedral angles and band gap respectively were investigated. The change in geometric parameters along with the electronic analysis provides an effective evidence and suggest these compounds to suit optoelectronic applications. Further support to the previous approach, the electronic excited state energies calculation using TD/B3LYP/6-31G(d). As the transition from DOTP to DH4P was set the energy gap decreases, illustrating that how electronic properties can be tuned by the backbone ring or side group. The results become more efficient in the doped form of ddoD4P.

1. Introduction

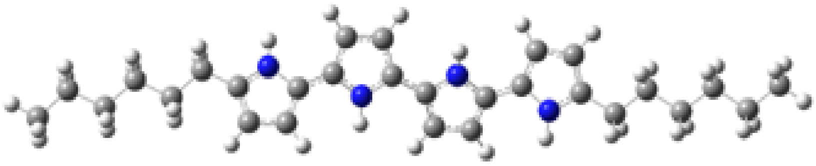
Since the last decade, organic materials seemed to flourish in optoelectronic applications, such as light emitting diode [1], organic solar cells [2] and field effect transistors [3]. Indeed, they have the advantage of possessing optical and electronic properties that can be modulated by molecular and supramolecular engineering [4].These depend on the nature of the monomer units involved as well as the effective lengths of the molecules. Moreover, the theoretical calculations proved their importance in the field of chemistry and conducting organic materials in particularly, ascribable to the various limitations of the experiment. Due to the high level of disorder associated with most of these materials, structural information is not always easy to determine experimentally [5].There may also be several uncertainties in the determination of the electronic properties, linked for example to the effect of the solvent, the presence of impurities etc. [6].Theoretical studies can therefore help to determine the structural and electronic properties of these materials and subsequently contribute to a better understanding of the relationship between structure and properties. Thus we apply the density functional theory (DFT) method [7] of the models derived from these materials to determine the structural, electronic and vibrational proprieties.
In the present work, we examined the alkyl-substituted oligopyrroles. Pyrrole is an organic compound with a planar heterocyclic structure that is found frequently in Natural complexes and bioactive pigments, research has shown that polypyrrole has a high chemical stability and a mechanical resistance to environmental conditions

[8].In addition, the substitution of the pyrrolic rings can enhance the length of conjugation and enable to increase the solubility of the corresponding polymers, to promote the polymerization, thus to give a positive impact on the electronic states of the polymer and subsequently lead to an increase in conductivity [9,10]. Different alkyl chain R1=C_8H_{17}, R2=C_6H_{13}, R3=$C_{12}H_{25}$ and R4 = $C_{10}H_{17}$are used as a substituent (Fig.1), sidealkyl-chain affect light absorption, and HOMO-LUMO energies and has shown considerable potential for the development of the conjugated polymers performance.

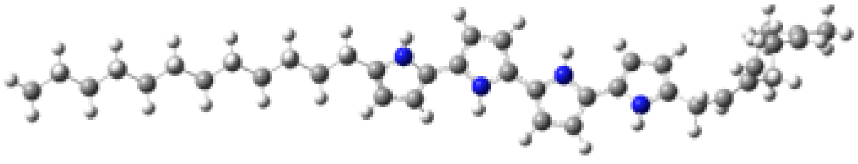
The first section of our work concerned to examine the effect of the elongation of the 3,3'-dioctylterpyrrole (DOTP) and 3,3'- dihexylquaterpyrrole (DH4P) on the geometric, electronic and absorption properties, while the second one revolve around the effects of alkyl chain in 3,3'- dihexylquaterpyrrole (DH4P) and 3-3,7–dimethyldienyloctyl-3'dodecylquaterpyrrole (ddoD4P).



3,3'-dicotylterpyrrole (DOTP)



3,3'-dihexylquaterpyr3,3'-dihexylquaterpyrrole (DH4P)



3,7-dimethyldienyloctyl-3'dodecylquarterpyrrole (ddoD4P)

Figure 1: Structures of the studied compounds and their optimization
R1 = C_8H_{17} R2 = C_6H_{13} R3 = $C_{12}H_{25}$ R4 =$C_{10}H_{17}$

2. Computational approach

The structures of the molecule systems in this paper were investigated at the density functional theory (DFT) methods under B3LYP [Becke 3-Parameter (Exchange), Lee, Yang and Parr] level of theory that known for being the best hybrid functional used for a wide range of organic molecules and have proven to be superior to many functional defined so far [11-12]. All calculations were performed using DFT/B3LYP and 6-31G(d) basis set for neutral forms and unrestricted (UB3LYP) for the doped. We have studied the absorption by the Time Dependent Density Functional Theory TD-DFT which generates the transition energies and oscillator strength. The process was done using the gaussian09 [13], and the results were analyzed by using Gabedit [14] and Gauss view programs [15].

3. Results and Discussion

3.1. *Geometric parameters*

We have performed a total optimization for all structures by the method DFT. Optimization allows to consider the most stable geometries especially that a conjugated molecule appears in several resonant forms, to examine the effect of the monomer length on the geometric parameters such as Inter-ring distances, dihedral angles. Optimized structures of DOTP and DH4P and geometric parameters are given in Fig.1 and Table 1 respectively. Since the length of the distances di (Å) and the dihedral angles θi provide information on the geometry of the carbon skeleton, we determined these two parameters from the optimized structures.

The Inter-ring distances of the DOTP is about d1= 1.44622 Å and d2= 1.44654 Å while in DH4P the distances are d1= 1.44595 Å, d2= 1.44445 Å and d3= 1.4457 Å. For the doped forms the distances are d1=1.41226 and d2=1.41226 in DOTP whereas in DH4P is about d1= 1.42004 Å, d2= 1.4124 Å and d3= 1.42004 Å, these decrease observed in doped form can be due to the quinoid form. A brief look at the values obtained we notice that the distances do not change significantly with the oligomer size, which can inform us about the geometry of the molecule of the parent polymer.

A calculation of the dihedral angles associated respectively with the DOTP and DH4P groups was carried out. The results show that the dihedral angles along the main chain are not modified and stabilized between 156° and 158° for the neutral forms and 179° for the doped, makes the last one better for the electrons delocalization.

Table 1: Inter-ring distances d_i (Å) and dihedral anglesθ_i (deg) of DOTP, DH4P and ddoD4P obtained at B3LYP/6-31G(d). level of theory

Compounds	Form	θ_1	θ_2	θ_3	d_1	d_2	d_3
ddoD4P	neutral	155.88	160.17	156.15	1.446	1.444	1.446
	polaronic	178.14	-176.85	177.55	1.420	1.412	1.419
	bipolaronic	178.50	-179.24	177.24	1.399	1.393	1.400
DH4P	neutral	-157.76	-158.55	156.62	1.445	1.444	1.44
	polaronic	179.99	-179.99	179.99	1.420	1.41	1.420
	bipolaronic	179.32	-179.99	-179.34	1.394	1.387	1.394
DOTP	neutral	157.98	155.61		1.446	1.446	
	polaronic	-179.92	-179.90		1.412	1.412	
	bipolaronic	178.48	-178.49		1.383	1.383	

The investigation of the effect of the substituted alkyl in the DH4P and ddoD4P on the inter-ring distance of the ddoD4P is around 1.39 Å to 1.44 Å for the neutral and doped forms, compared with DH4P. It's clear that the alkyl group has no effect on the inter-cyclic distance. Whereas the effect appears on the dihedral angles, represented in the enhancement of the planarity of the oligomers leading to improve the conductivity, it is more obvious in the doped form.

3.2. *Electronic proprieties*

Theoretically, the energies of highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO can be obtained by the DFT method. The gap between the two levels of HOMO and LUMO is used to estimate the gap energy. At the same time, the ionization potential and Electron affinities is estimated to be the negative of the HOMO and LUMO energies respectively (Koopmans theorem) [16].Table 2 summarizes the values of electronic parameters obtained for the studied compounds, the transition from DOTP to DH4P in the neutral and doped forms decrease the PI and Eg due to the increase in the extent of conjugation. This decrease can be illustrated by increasing the oligomer stability and improving conduction.

Table 2: HOMO (eV), LUMO (eV) and E_{gap} (eV) values of the studied compounds.

Compounds	Form	LUMO (ev)	HOMO (ev)	Eg (ev)	IP(ev)	AE(ev)
ddoD4P	neutral	-0.178	-4.108	3.930	4.108	0.178
	polaronic	-4.013	-7.385	3.372	7.385	4.013
	bipolaronic	-9.193	-9.642	0.448	9.642	9.193
DH4P	neutral	-0.202	-4.095	3.893	4.095	0.202
	polaronic	-4.065	-7.448	3.383	7.448	4.065
	bipolaronic	-9.559	-11.192	1.632	11.192	9.559
DOTP	neutral	0.046	-4.215	4.262	4.215	-0.046
	polaronic	-4.306	-8.046	3.740	8.046	4.306
	bipolaronic	-10.287	-11.333	1.045	11.333	10.287

The table 4 shows that the electronic parameters of ddoD4p and DH4P are not close, so it is noticeable that alkyl group R has an effect on the band gap especially in the doped forms. A change is observed for the HOMO and LUMO energies due to the substituent alkyl character. The Comparison of the alkyl substitutions Suggests that the π bond in R4 group leads to a change of the HOMO and LUMO levels and reduces the energy Gap specially in the doped form (bipolaronic).

3.3. *Absorption parameters*

To refine the study, we used the time dependent density function theory (TD/DFT) to calculate the transition energies and oscillator strength. It is reported in the literature that TD/DFT provides the most credible results compared to other methods [17]. The obtained results showed that it is DH4P has the most important absorption wavelength, with a planar geometry compared with DOTP due to the increase in conjugation, it is obvious in Fig. 2 that the peak wavelength of DH4P tend to be shifted toward the long wavelength region (red-shift). On the other hand, the excitation energy, the wavelength and the oscillator strength of the studied compounds are determined and summarized in Table 2.

Table 2 : Absorption data obtained by TD-DFT methods for the studied compounds atoptimized geometries.

Compounds	λ_{max} (nm)	O,S	Excitation energy (eV)
ddoD4P	347.15	1.59	3.57
DH4P	349.22	1.49	3.55
DOTP	314.25	1.20	3.94

In order to study the impact of substitution on the absorption of the compounds ddoD4P and DH4P, the wavelength of maximum absorption (λ_{max}) and the oscillator strength (O.S) are shown in Table 2. These values were calculated from the optimized geometries using the Time Dependent DFT method. Absorption is represented by a vertically excited transition in an ascending sense from the ground state of the optimized structure to the excited one ($S0 \rightarrow S1$) so that the electron jumps from the low energy orbital to the higher energy orbital. The maximal absorption shows a bathochromic shift when passing from ddoD4P to DH4P which also can be notice respectively 347.15 nm and 349.22 nm with higher probability of absorption for ddoD4P [19]. This clearly indicated the significant influence of the alkyl groups that lead to enhance the conjugation on the studied structures.

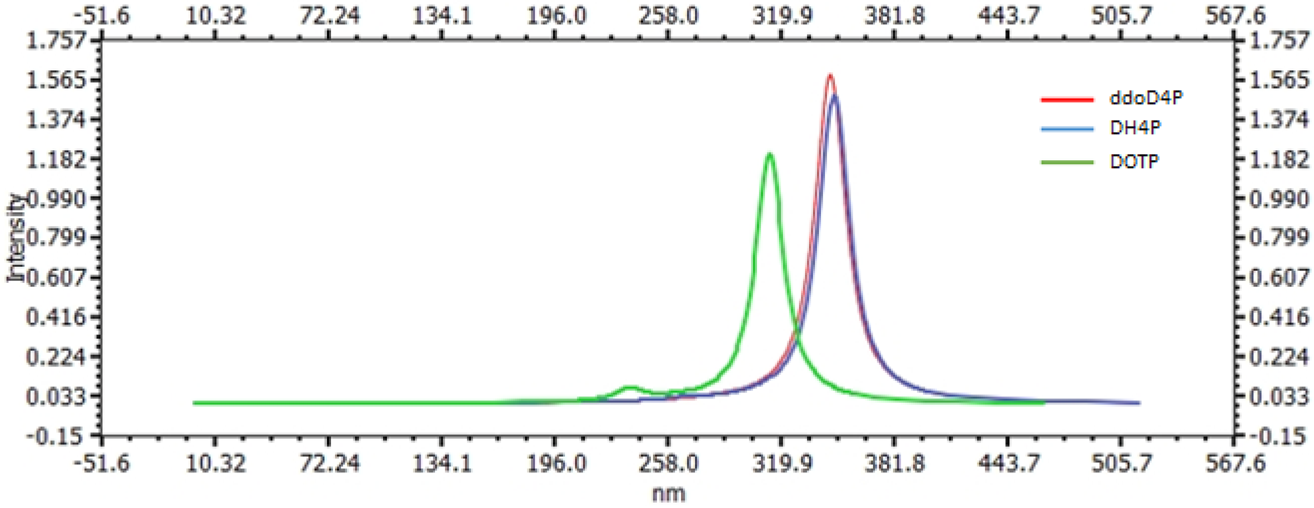


Figure 2: Simulated UV-visible absorption spectra of studied compounds at theTD-DFT/CAM-B3LYP/6-31G (d) level

Conclusion

In this paper we carried out a study on Alkyl-substituted Oligopyrrole (DOTP), (DH4P) and (ddoD4P) integrating theoretical approaches, it can be seen that the optoelectronic properties are improved for large or doped oligometric chains. The calculations carried out by the DFT method with the 6-31G(d) basis set. The comparison of the results obtained for the various compounds makes it possible to discover the effect of the transition from the DOTP to DH4P as well as of the doping on the structure and on the properties. The quinoid contribution appears strongly in the doped structures, and the increase in size is accompanied by a decrease in gap and a high stability. Investigation of substituted alkyl groups at sites 3 of the pyrrole cycle suggests that R3 = $C_{12}H_{25}$ and R4 substitution leads to the HOMO and LUMO stabilization and reduces gap energy. The absorption was also influenced by substitution, then a red shift is observed from ddoD4P to DH4P.

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