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A comparative study of donor and acceptor groups effect on structural and electronic properties of thienylene-phenylene co-oligomers

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ABSTRACT

In this work, a quantum chemical methods calculations at B3LYP/6-31G(d) study on the structural and electronic properties of thienylene-phenylene co-oligomers substituted by donor and acceptor groups is carried out. Eight co-oligomers based on thiophene and phenylene are studied here. The comparison results of mesomeric donor effect and mesomeric acceptor effect on the structural and electronic properties of thienylene-phenylene co-oligomers are discussed. As the electronic properties of this type of conjugated co-oligomers are governed by their electronic band gap, we shall also present a comparison among HOMO, LUMO and band gap energies of these different materials. We conclude that both acceptor and donor side-chains affect the HOMO and LUMO levels significantly. However, while the acceptor groups stabilize HOMO and LUMO, the donors destabilize them.

Keyword: B3LYP, Electronic properties, HOMO, LUMO, Gap.

INTRODUCTION

Much attention has been focused recently on π -conjugated polymers since they are much applied in various fields [1]. Among the known applications we cite for example photovoltaic cells [2-7], electroluminescent diodes [8-13] and transistors field effect [14-17].

Recently, many researchers have become interested in synthesizing short-chain based on conjugated oligomers [18]. Considerable efforts have been directed towards the study of the optoelectronic properties of these conjugated systems, with the aim to exploit their potential as materials for stable and easy processable devices [19]. These materials offer the unique advantages over polymeric compounds in terms of low cost, light weight, potential use in flexible devices and easy synthesis and purification [20,21]. Therefore, designing and synthesizing molecules with interesting properties play a crucial role in technology [22]. At the same time, it is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials. Recent work in this area has been focused on the theoretical investigations of the electronic structure of conjugated systems in order to establish the relationships between molecular structure and electronic properties [23-26].

In this paper, we describe a theoretical study on comparison of donor and acceptor side groups' effect on structural and electronic properties of the thienylene-phenylene co-oligomers. The quantum chemical at B3LYP/6-

31(d) investigation has been performed to explore the effect of donor and acceptor groups on the structural and electronic properties of a series of different compounds based on thiophene and phenylene.

The theoretical knowledge of the HOMO, LUMO and gap energies of the studied compounds have been calculated and reported. Their properties suggest they are good candidates for optoelectronic applications.

I- Quantum chemical methodology

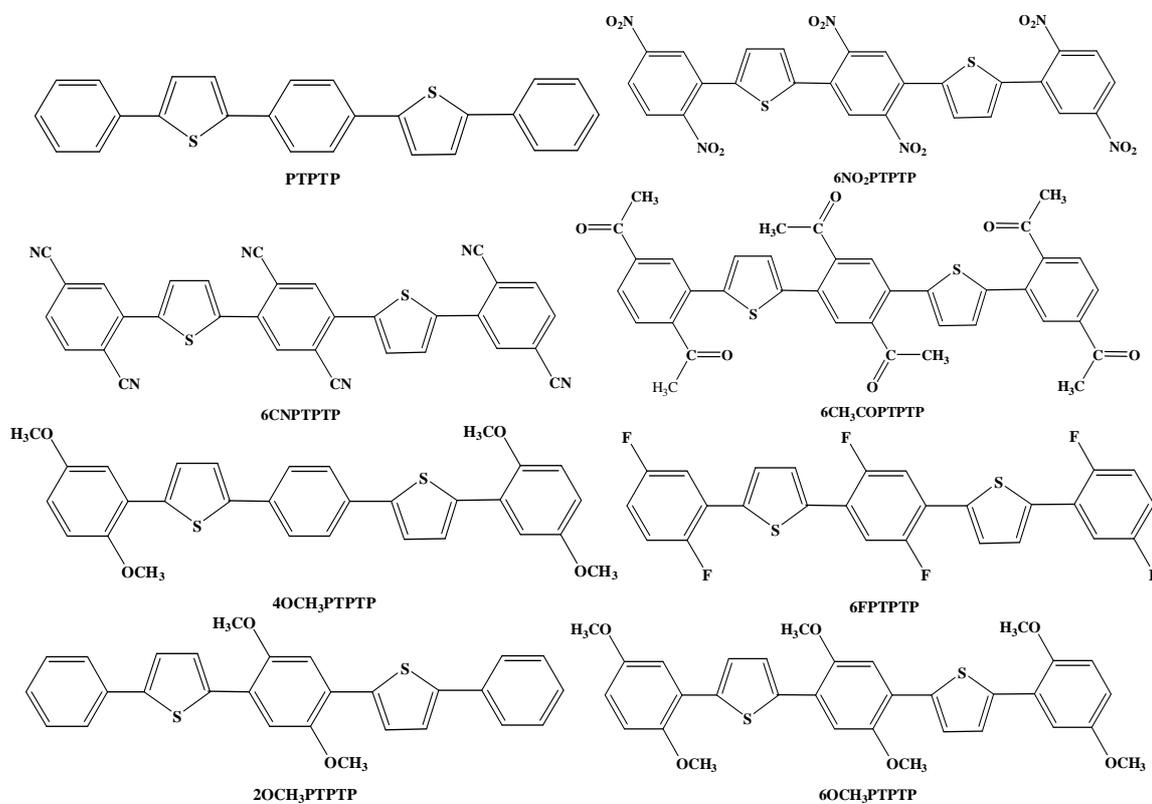
Density function theory (DFT/B3LYP) method of three-parameter compound of Becke [27] was used in all the studied compounds. The 6-31G(d) basis set was used for all calculations [28]. To obtain the most stable structures, we fully optimized the co-oligomers structures under no constraint. The calculations were carried out using the GAUSSIAN 09 program [29]. We have also examined HOMO and LUMO levels; the energy gap is evaluated as calculated by the difference between the HOMO and LUMO energies.

RESULTS AND DISCUSSION

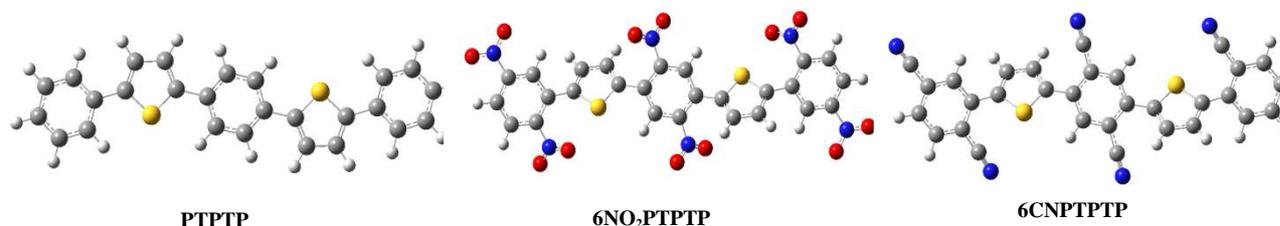
1-Structural parameters

The chemical structures and the name of the studied co-oligomers are presented in fig.1 (a) while their optimized structures are shown in Fig.1 (b).

(a)



(b)



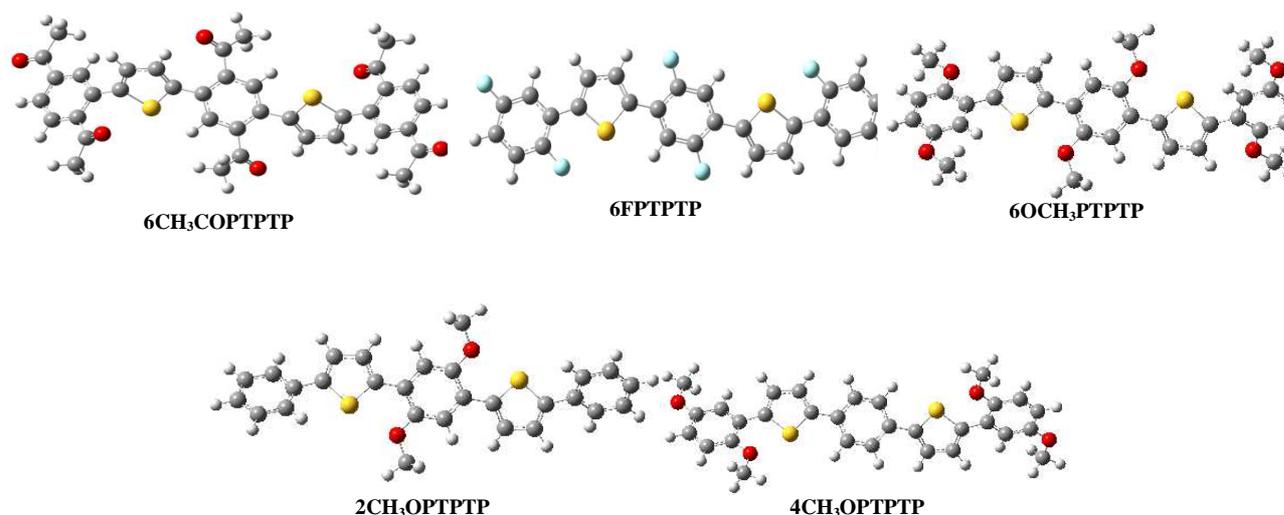


Figure 1:(a)Chemical structures of the studied oligomers (b) the optimized structures obtained by B3LYP/6-31G(d)

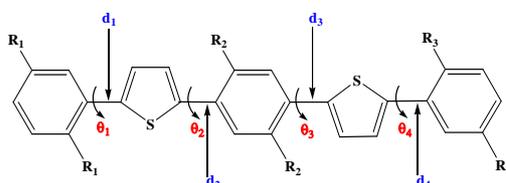


Figure 2:Structure with the dihedral angles θ_i and the inter-ring distances d_i

The co-oligomers with donor substitution are named 6OCH₃PTTP, 2OCH₃PTTP, 4OCH₃PTTP, 6OCH₃PTTP and 6FPTTP those with acceptor substitution are 6CNPTTP, 6CH₃COPTTP and 6NO₂PTTP. The unsubstituted co-oligomer PTTP is used here as a reference[25] to achieve the comparison between the donor and acceptor group's effect on the different properties of these compounds.

The inter-ring bond distances and dihedral angles are summarized in Table 1.

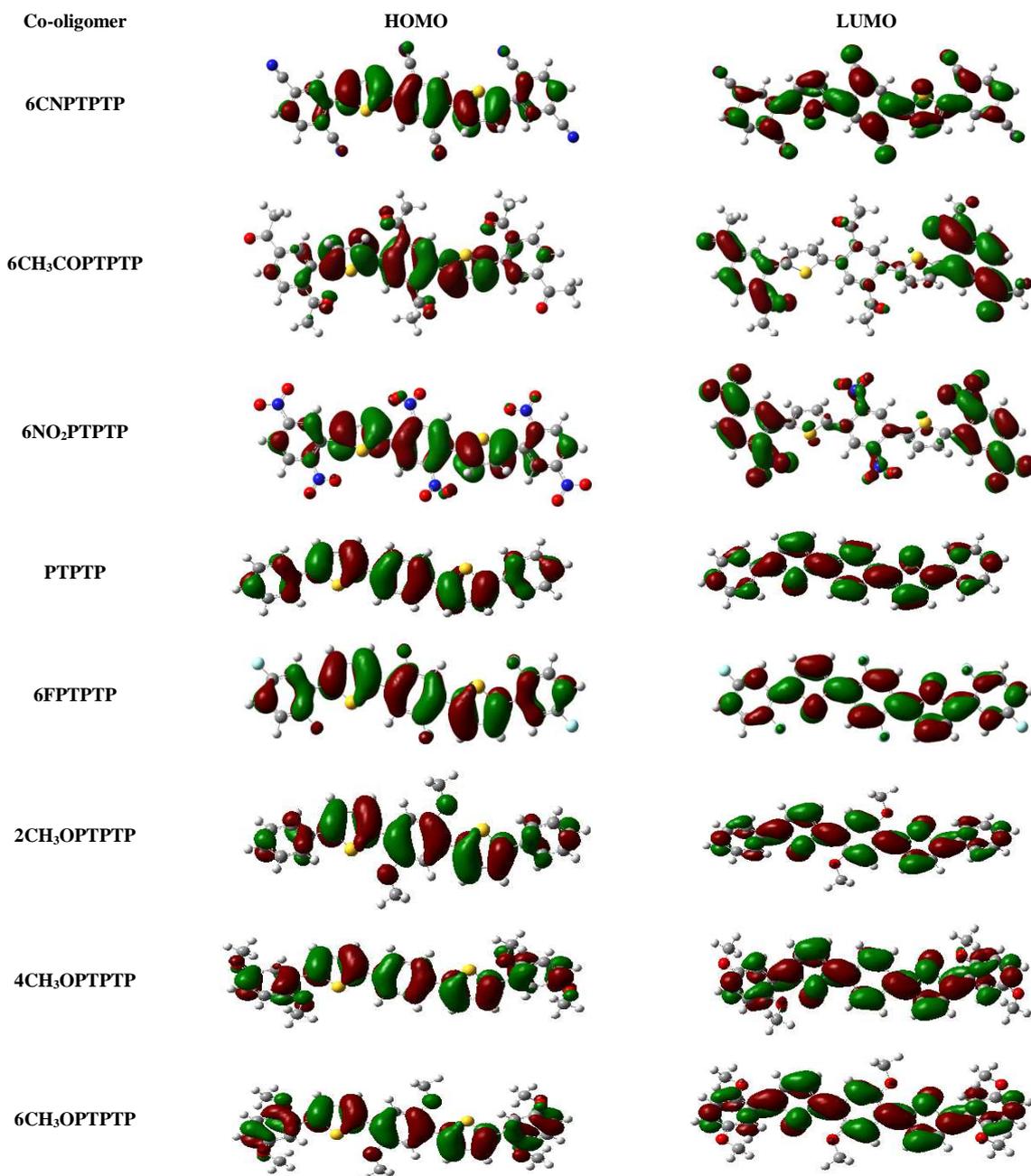
Table 1: Dihedral angles (°) and bond length distances between the consecutive aromatic rings of the studied compounds.

		$\theta_1 = \theta_4$ (°)	$\theta_2 = \theta_3$ (°)	$d_1 = d_4$ (Å)	$d_2 = d_3$ (Å)
Acceptor groups substitution	6NO ₂ PTTP	37.990	41.820	1.476	1.468
	6CH ₃ COPTTP	54.350	47.980	1.475	1.470
	6CNPTTP	35.050	34.100	1.469	1.465
Unsubstitutedco-oligomer	PTTP	26.500	23.500	1.466	1.463
Donor groups substitution	2OCH ₃ PTTP	25.900	19.300	1.467	1.464
	4OCH ₃ PTTP	22.500	24.700	1.468	1.464
	6CH ₃ O PTTP	26.800	19.600	1.468	1.464
	6FPTTP	06.510	15.900	1.465	1.461

These results reveal that the effect of different side groups on the dihedral angles and the interring distances between the different aromatic units is clear. As can be seen, the inter-ring distances (fig. 2 and table 1) are slightly larger in the acceptor co-oligomers in comparison with the donor ones. We note also that the dihedral angles in the co-oligomers with acceptor groups are higher than those in the other co-oligomers (Table 1). For the co-oligomers with donor groups, the angles are smaller compared with the acceptor groups. The unsubstituted co-oligomers have dihedral angles intermediate between those of the other two types.

The donor groups attached to the PTTP co-oligomer push the electron cloud towards the main chain (cf. Fig. 3). The acceptor groups, in contrast, pull the electron cloud from the main chain. Therefore, the donor groups favour the planarity of the cycles[25], while the acceptor groups cause a distortion in the main chain. This distortion is reflected in the inter-cyclic distances and dihedral angles; they increase in the acceptor groups case in comparison with the co-oligomers with donor ones.

Figure 3: Contour plots of the frontier orbitals HOMO and LUMO for the studied co-oligomers



2-Electronic properties

To investigate the influence of the effect of side groups on the electronic properties of the studied compounds, we present in Table 2 the B3LYP/6-31G(d)-calculated HOMO, LUMO, and band gap energies. The gap was evaluated theoretically as the difference between the LUMO and HOMO levels. In experimental viewpoint the HOMO and LUMO energies can be obtained from an empirical formula proposed by Brédas *et al.*[30] based on the onset of the oxidation and reduction peak measured by cyclic voltammetry.

$$\text{HOMO} = E_{\text{onset(ox)}} + 4.8 - E(\text{Foc})$$

$$\text{LUMO} = E_{\text{onset(red)}} + 4.8 - E(\text{Foc})$$

However, it is to be noted that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in thin films compared to isolated molecules as considered in the present calculations.

Table 2: Optimized HOMO, LUMO and Gap energies (eV) of the co-oligomers

		E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
Acceptor groups substitution	6NO ₂ PTPTP	-6.584	-3.489	3.095
	6CH ₃ COPTPTP	-5.660	-2.557	3.103
	6CNPTPTP	-6.465	-3.138	3.327
Unsubstituted co-oligomer	PTPTP	-5.160	-1.690	3.470
Donor groups substitution	2OCH ₃ PTPTP	-4.840	-1.570	3.270
	4OCH ₃ PTPTP	-4.790	-1.460	3.330
	6CH ₃ OPTPTP	-4.600	-1.440	3.160
	6FPTPTP	-5.404	-2.170	3.234

It can be seen that 6NO₂PTPTP has the smallest band gap E_g . Then E_g increases in the following order: 6CH₃COPTPTP, 6OCH₃PTPTP, 6FPTPTP, 6CNPTPTP and finally the unsubstituted PTPTP. E_g decreases in the co-oligomers with acceptor or donor groups compared with the unsubstituted one.

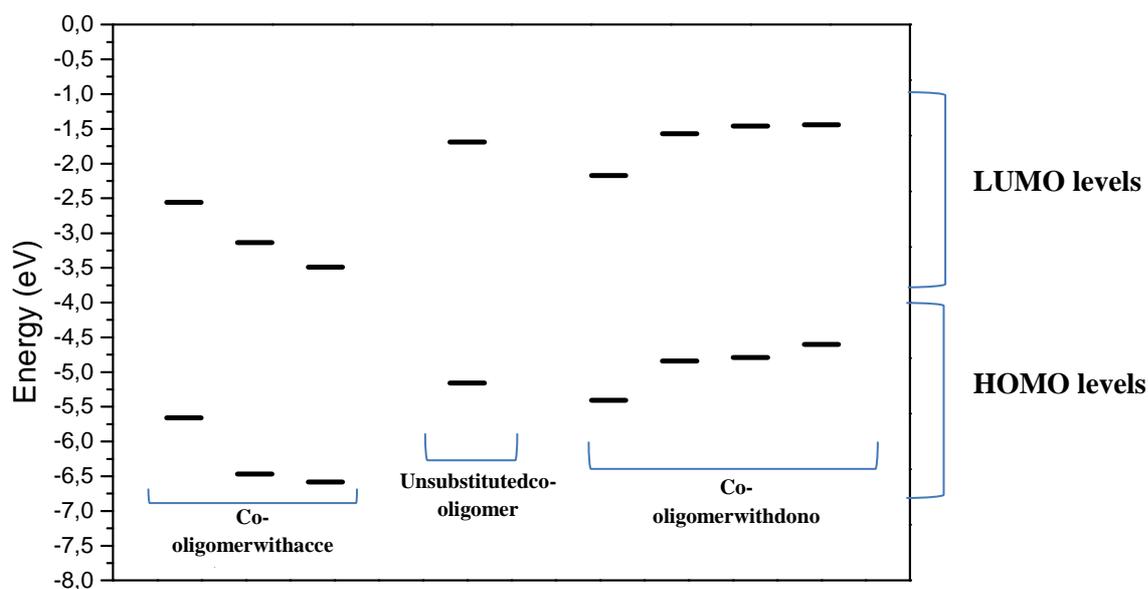


Figure 4: HOMO and LUMO positions for all co-oligomers.

The positions of HOMO and LUMO levels are resummarized according to Fig. 4. It is seen that both acceptor and donor side-chains affect the HOMO and LUMO levels significantly. However, while the acceptor groups stabilize HOMO and LUMO, the donors destabilize them (fig. 4).

The band gap energies found for the co-oligomers 6CNPTPTP, 6NO₂PTPTP, 6FPTPTP, 6CH₃COPTPTP, 6OCH₃PTPTP, 4OCH₃PTPTP, 2OCH₃PTPTP and 4OCH₃PTPTP are all less than the value found for the unsubstituted co-oligomer. This is due to the side chain group's effect.

E_g decreases with the increase of mesomeric effect in the acceptor groups (-M) in the NO₂, CH₃CO and CN groups. This explains also the difference between the value of E_g in the co-oligomers with donor groups and that in the unsubstituted one.

It was found that E_g in the co-oligomers with acceptor groups is comparable to that in the oligomers with donor groups. This is probably because the mesomeric effects $-M$ and $+M$ have approximately a same absolute value, namely, $|-M_{\text{acceptor}}| \approx |+M_{\text{donor}}|$.

CONCLUSION

In this work, we have studied the structural and electronic properties of some co-oligomers based on thiophene and phenylene. Three types of co-oligomers have been studied: unsubstituted, substituted with acceptor groups, and substituted with donor groups. It has been found that the acceptor groups decrease the gap. The same tendency has also been observed for the donor groups. However, the acceptor groups stabilize the HOMO and LUMO levels in contrast with the donors. The studied co-oligomers show the promising electronic properties make them the good candidates for electronic applications.

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