

Effect of the Length of Alkyl Side Chains in the Electronic Structure of Conjugated Polymers

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Computational modeling studies of conjugated polymers have been shown to present many challenges. One such challenge is to find ways to reduce the computational cost for these studies without compromising the quality of the results. An approach longly used in the literature for this purpose is replacing long alkyl side chains (with six or more carbons) with a methyl group. This work reports on a theoretical study conducted with the conjugated polymer poly(3-hexylthiophene), which contains a hexyl side chain attached to the monomer, to verify the influence of the size of the alkyl side chain on its electronic structure. The results indicated that, for polymers containing long alkyl side chains, replacement with a propyl group offered full saturation of all properties under review, showing it to be a good approach.

Keywords: *computer modeling, conjugated polymers, electronic structure calculation, poly(3-hexylthiophene), P3HT, exciton binding energy*

1. Introduction

Nowadays, there is great interest in the use of organic materials in electronic devices^{1,2}. Of these, the class of conjugated polymers has been the subject of intense study, mainly because of their potential for employment in the active layers of organic solar cells¹⁻⁷. These materials have several advantages compared to their inorganic counterparts, for example, low cost of raw materials and easy processing. However, because of deficiencies in their intrinsic properties, they continue to be the subject of many theoretical and experimental studies aimed at discovering improvements that will make them more attractive and useful for technological applications^{1,2}.

Molecular modeling of conjugated polymers has been a challenge for the scientific community for several reasons, for example, the fact that they are large molecules and thus easily deformable and the presence of side chains². Several theoretical studies of these materials have been conducted based on quantum or classical mechanics⁸⁻¹³, but the number of variables that must be taken into account in any model carries a high computational cost⁸. Thus, it is necessary to find ways to reduce this cost to simulate these materials without compromising the quality of results.

One approach to reducing the computational costs in studies of conjugated polymers is the use of oligomers^{14,15}, in which the properties of the polymers are theoretically estimated by extrapolating data obtained for the oligomers. This approach has been shown to yield very efficient results, compared with experimental ones¹⁴⁻¹⁶. However, the computational cost is not significantly reduced, because

many of the polymers currently employed have monomeric units with long and complex side chains, which hinders the conformational search for them⁸.

In conjunction with the oligomers approach, a simplification has been developed for polymers that have long alkyl side chains (having six or more carbons). These side chains are replaced by a methyl group^{17,18}, so that the conformational search becomes easier. However, it is known from literature that the size of the alkyl side chains can influence the structural conformation and electronic properties of polymers^{8,19}. This suggests that replacing a long alkyl side chain with a methyl group can be a risky approach, which could compromise the results obtained for theoretical studies of conjugated polymers.

We therefore conducted a theoretical study with the aim of determining the influence of the length of the alkyl side chain on the electronic structure of conjugated polymers. We also tried to discover whether there might be a characteristic length of the side chains at which the electronic properties would remain unchanged; this might be suitable for use as a modeling approach. We chose to study poly(3-hexylthiophene) (P3HT), a polymer widely used in organic devices (Figure 1)^{8-10,20-24}. This polymer has a hexyl side chain in each monomer unit. The results indicated that the size of the side chains adopted influenced the electronic structure of P3HT, up to propyl size.

2. Calculation Procedures

To conduct this study, we adopted the oligomers approach, employing P3HT oligomers ranging from two

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to six monomeric units. To verify the effect of the size of the alkyl side chain, we studied the oligomers with ramifications ranging from methyl to hexyl, the actual size of the ramifications of P3HT.

To obtain the oligomers for our study, we employed an optimized geometrical structure by a semiempirical method and electronic structure data from density functional theory (DFT) calculations²⁵. This approach has been applied with satisfactory results in studies of conjugated polymers^{8,9,16}, and is feasible owing to the size of the systems studied here, as well as the number of conformers analyzed. The exclusive use of *ab-initio* methods would result in considerable computational cost. We adopted fully coplanar polymeric structures, as expected in the solid state^{1,10,14,16}, and the alkyl branches were initially predisposed in an antiperiplanar conformation, as we had predicted in previous studies to be the most likely^{8,9}.

All studied structures were optimized by the Hartree-Fock semiempirical Parametric Method 6 (PM6)²⁶ implemented in the computational package MOPAC2012²⁷. We chose PM6 because of its satisfactory performance in studies with polythiophene derivatives^{8,9,16,28,29}. The geometry optimization process was considered completed when the gradient norm drops below 0.01 kcal.mol⁻¹/Å. After geometrical optimizations, we obtained the electronic structure data of oligomers through DFT calculations with the hybrid functional B3LYP³⁰ on GAMESS software³¹. The basis functions set chosen was 6-31G(1d)³². The self consistent field electronic structure was considered converged when the energy of two cycles changes by less than 10⁻⁵ Hartree. The DFT/B3LYP/6-31G(1d) methodology has been widely employed in studies of conjugated polymers, where it has been shown to yield good results^{14,16,28}. We analyzed the data for the lowest unoccupied and highest occupied molecular orbitals energy (LUMO and HOMO, respectively) and the energy gap between LUMO and HOMO (E_g). All calculations were performed in vacuum.

As well as evaluating data on the electronic structure of the oligomers in side chains with variable sizes, we also evaluated the exciton binding energy (E_b), one of the parameters that govern charge generation in materials used in organic electronics³³. E_b can be estimated as the difference between E_g and the vertical transition energy from the ground state to first dipole-allowed excited state (E_{vert}), i.e., $E_b = E_g - E_{vert}$ ^{34,35}. Such data can be obtained by calculation of electronic structure. In order to observe the influence of the alkyl side chain size in E_b , we calculated this property only for the largest structures studied, with six monomer units. We performed the calculations for E_{vert} by two methods:

the semiempirical method ZINDO/S^{36,37}, coupled with the Configuration Interaction with Single Excitations (CIS) method^{38,39}, using computational package ORCA⁴⁰, and the Time-Dependent Density Functional Theory (TD-DFT)⁴¹, with the same functional and basis set described above, used in computational package GAMESS. We calculated ten transitions (roots) for each oligomer under consideration, including only transitions between singlet states.

For the extrapolation of the HOMO, LUMO, and E_g values, various fitting methods are reported in the literature. The most popular are Kuhn^{14,18}, Meier^{8,9,42}, linear³⁴, and polynomial^{12,15}. However, it should be noted that, in studies conducted with oligomers with up to eight monomer units, the use of linear or polynomial fitting in relation to the inverse quantity of monomeric units (1/n) produced reasonable results^{15,34}. Thus, for our extrapolations, we adopted linear fits.

3. Results and Discussion

We present the extrapolated results obtained for the electronic structure of P3HT with side chains ranging from methyl to hexyl in Table 1. The experimental results for HOMO, LUMO, and E_g values of P3HT are respectively -4.6 eV, -2.7 eV, and 1.9 eV⁴³. Thus, we also present in Table 1 the deviations obtained in the calculations for such properties. Figure 2 presents graphs of the extrapolations made.

It is already known from the literature on polymer modeling studies that the use of the DFT with B3LYP functional shows the best results for electronic properties. Using this methodology, the values for HOMO and E_g exhibit deviations up to 10% compared to the experimental values, regardless of the fitting method employed for the extrapolations^{15,44}. For the LUMO, deviations of up to 1 eV can be observed; as these orbitals are not occupied (first virtual orbital), the lack of electrons and the self-consistent field solution for the system's wave function are the main reasons suggested for discrepancies between the calculated and experimental values⁴⁴. Therefore, the deviations found

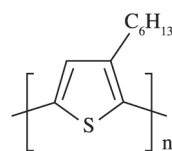


Figure 1. Structural formula of P3HT.

Table 1. Extrapolated values obtained for electronic structure data of P3HT with different side chains.

Side Chain Type	HOMO (eV)	HOMO Deviation (%)	LUMO (eV)	LUMO Deviation (%)	E_g (eV)	E_g Deviation (%)
Methyl	-4.21	8.47	-2.23	17.41	1.97	3.68
Ethyl	-4.27	7.17	-2.27	15.92	2.00	5.26
Propyl	-4.24	8.04	-2.24	17.04	1.99	4.73
Butyl	-4.24	8.04	-2.24	17.04	1.99	4.73
Pentyl	-4.24	7.82	-2.24	17.04	1.99	4.73
Hexyl	-4.24	7.82	-2.24	17.04	1.99	4.73

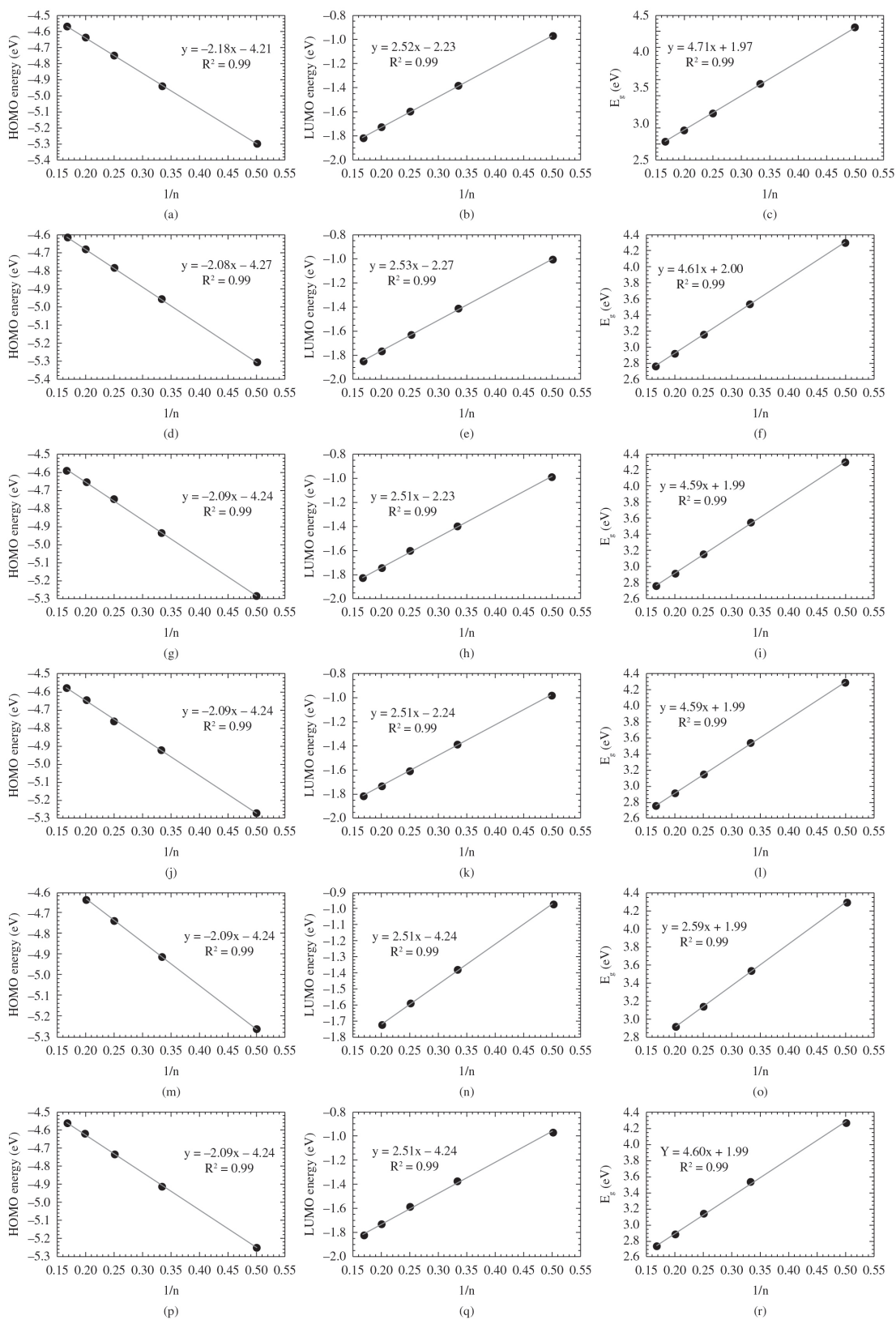


Figure 2. Extrapolation graphs for electronic properties of studied cases: (a) HOMO, (b) LUMO and (c) E_g energies for methyl side chains, (d) HOMO, (e) LUMO and (f) E_g energies for ethyl side chains, (g) HOMO, (h) LUMO and (i) E_g energies for propyl side chains, (j) HOMO, (k) LUMO and (l) E_g energies for butyl side chains, (m) HOMO, (n) LUMO and (o) E_g energies for pentyl side chains, and (p) HOMO, (q) LUMO and (r) E_g energies for hexyl side chains.

Table 2. Values obtained for E_g , E_{vert} , and E_b for six monomeric units of P3HT and different side chains.

Side Chain Type	TD-DFT			ZINDO/CIS	
	E_g (eV)	E_{vert} (eV)	E_b (eV)	E_{vert} (eV)	E_b (eV)
Methyl	2.75	2.49	0.26	2.22	0.53
Ethyl	2.77	2.48	0.29	2.26	0.51
Propyl	2.76	2.47	0.29	2.26	0.50
Butyl	2.76	2.47	0.29	2.26	0.50
Pentyl	2.75	2.47	0.28	2.26	0.49
Hexyl	2.75	2.47	0.28	2.26	0.49

in this study agree with those estimated for the calculation tools adopted here.

As can be seen from Table 1, the values obtained for polymers with different side chains have slightly different values. Among the factors that can influence these properties, withdrawing or donating electrons from/to the main chain by a substituent is one of the most important^{14,19}. These effects can move the position of HOMO and LUMO levels, depending on the amount of charge in the main chain¹⁹. The alkyl groups can donate electrons by both induction and resonance⁴⁵, thus causing changes in the electronic levels of the polymer. The intensity of this effect can be accounted for by the Hammett constants. Methyl and ethyl groups have slightly different values compared to the other alkyl groups studied here⁴⁶. This suggests that no changes in electronic properties would be observed, owing to charge donation for groups larger than ethyl.

Structures with groups larger than ethyl have an approximately constant value for HOMO and LUMO; however, the values found for structures with the ethyl group were the closest to the experimental value. The structure with the methyl group shows the closest value for E_g , which explains why substitutions of long alkyl side chains with methyl groups show good results, as reported in the literature^{17,18}. With groups larger than methyl, the value of E_g is essentially unchanged. Thus, the values obtained for structures with the ethyl group have the smallest deviations for HOMO and LUMO, but for groups larger than ethyl we did not notice significant changes. The results suggest that alkyl groups with more than two carbons promote a charge distribution in the polymer backbone, so that electronic levels do not show significant variations. Such differences may be due to interactions between the neighboring side chains that can modify the charge distribution in the polymer, suggesting that for groups larger than ethyl these interactions would be stabilized.

Table 2 shows the results obtained for E_b for oligomers with six monomer units of P3HT and side chains ranging from methyl to hexyl. We present the values calculated by ZINDO/CIS and TD-DFT. According to experimental reports, the value of E_b for P3HT in the solid state can range from 0.2 to 0.7 eV⁴⁷⁻⁵¹ and decrease with increasing polymer chain length⁵². The results obtained for oligomers with six monomer units yield values that are within the range of

values found experimentally. We note that the value of E_b remained constant, independent of the type of side chain adopted, approximately 0.3 eV and 0.5 eV for TD-DFT and ZINDO/CIS calculations, respectively. So, the size of the alkyl side chain does not interfere significantly in E_b .

4. Conclusions

In theoretical studies of polymers, several structural approximations have been proposed, such as the oligomers approach and replacing long alkyl side chains with methyl groups. We conducted a study with the conjugated polymer P3HT to verify the influence of the length of the alkyl side chain on the electronic properties of the polymer.

The methodology adopted for the oligomer modeling proved to be reliable, since we found deviations for the HOMO, LUMO, and E_g consistent with previous studies in the literature.

Variations in the electronic properties were observed according to the size of the alkyl side chain adopted in the theoretical calculations. We have verified that, with groups larger than ethyl, the results obtained for the HOMO, LUMO, and E_g were constant, showing a saturation of such properties. Because of the similar values obtained for all the cases studied, the substitution of long ramifications by methyl groups may be plausible, but these do not take into account interactions between neighboring side chains. We did not notice significant changes for E_b values of the structures with different side chain sizes.

Thus, we conclude that it is possible to reduce the computational cost without compromising the quality of the results in studies with polymers containing long alkyl side chains. The use of methyl groups is a good approximation, but the smaller group that presents the best reproduction of the energies of the frontier electronic levels is the propyl group.

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