# Energy Gaps of α,α′-Substituted Oligothiophenes from Semiempirical, Ab Initio, and Density Functional Methods

**Marcos A. De Oliveira,**[†] **Hélio A. Duarte,**[†] **Jean-Michel Pernaut,**[‡] **and Wagner B. De Almeida***[†,§]

*Laboratório de Química Computacional e Modelagem Molecular (LQC-MM) and Laboratório de Novos Materiais, Departamento de Química, ICEx, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG, 31.270-901, Brazil*

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Energy gaps have been estimated for −OMe and $-NO_2$ α,α′-substituted oligothiophenes up to six monomers using semiempirical, Hartree−Fock and density functional methods. Scaled values calculated using noncorrelated methods are in good agreement with the experimental values, and so were nonscaled estimates predicted by density functional methods. Error bars are ca. 0.2 eV for all 11 oligothiophenes studied. The influence of the quality of the basis set on the energy estimates is discussed. The discrepancy observed for the −OMe- and $-NO_2$-substituted sexithiophene result with respect to the experimental value is discussed and has been attributed to a charge transfer in the molecule. The ΔSCF approach has been found to be an alternative way to estimate energy gaps for molecular systems where Koopmans' theorem may not provide good results. Implications for predictions of HOMO−LUMO gaps of $\pi$-conjugated systems are discussed and analyzed in terms of designing new materials with controlled properties.

## 1. Introduction

Molecular organic devices have been intensely studied in the last two decades[1] due to their potential technological importance. Organic polymers like polythiophene, or poly($p$-phenylene)-vinylene, are pointed out to build new generations of electronic and photonic devices.[2] α,α′-Oligothiophenes are particularly good candidates for molecular electronics since they are processable materials and their properties can be easily chemically tailored.[3]

Extensive reviews of $\pi$-conjugated systems, including oligo- and poly(thiophenes), have been published recently and provide comprehensive data concerning synthesis, characterization by a number of physical techniques, and applications.[4]

It is known that control of the band gap ($E_g$) of organic materials is fundamental for building devices and furthermore reducing its value is desired to enhance the intrinsic charge carriers population and also to get a stabilization in both oxidized and reduced doped states. Concerning the last point, thiophene-conjugated systems present generally higher stability than other conjugated systems. We recently investigated a series of α,α′-substituted oligothiophenes in order to get correlation between chemical structure and physical properties.[5] The HOMO and LUMO levels of these $\pi$-electron systems were changed by varying the number of monomer units and by modifying the terminal positions of the chains by electron-releasing (donor) and -withdrawing (acceptor) substituents. Depending on the conjugation length of the oligomers and beyond the direct electronic effect, this was supposed to also influence the rotational disorder, responsible for increasing $E_g$. Finally, the interactions between molecules were also evaluated by studying the oligomer in both solution and condensed state (thin film). Interesting structure−properties correlations have been reported[5] and will be used as experimental data for this theoretical work. The HOMO−LUMO energy gaps of the molecules ($\Delta E$) is generally determined from the low-energy absorption edge of the electronic absorption spectrum or by the crossing point of both the excitation and absorption spectra (in this case, it actually corresponds to $E_{00}$). On the other hand, $\Delta\epsilon$ and $E_g$ can also be measured electrochemically from thermodynamic oxidation ($E_{ox}$) and reduction potentials where $E_g \approx E_{ox} - E_{red}$, neglecting the solvation energy effects.

Extensive analysis of structure and electronic spectra of thiophene oligomers have been performed both at ab initio and semiempirical levels.[6] Correlated calculations including only $\pi$-electrons were performed at spin-coupled level of theory for oligothiophenes from two to six rings, and the spin-coupled orbitals were transferred from relatively large hexamers to the polymer in a such way to predict the electronic structure of the polythiophene.[7] The PPP (Pariser−Parr−Pople) with CI and VEH (valence effective Hamiltonian) approaches[8] were utilized to predict energy gap values for several conducting polymers, among them polythiophene, with the PPP-CI model being able to reproduce spectral transition energies and intensities for oligomers of conjugated systems.[8]

Experimental and theoretical studies have been increasingly reported in the literature, but the relation of the electronic properties of the polymers with their semiconducting properties is not still completely understood at a molecular level.[4] Theoretical calculations could contribute significantly to the understanding of polymeric systems and their electronic and optical properties. However, the computational cost increases rapidly from monomer to oligothiophenes, which prevents

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* Author to whom correspondence should be addressed at: LQC-MM, Depto. Química, UFMG. E-mail: wagner@netuno.qui.ufmg.br. Fax: 55-31-499-5700.

[†] Laboratório de Química Computacional e Modelagem Molecular.

[‡] Laboratório de Novos Materiais.

[§] Visiting Professor, Departamento de Química, ICE, Universidade Federal de Juiz de Fora (UFJF), Campus Universitário, Juiz de Fora, MG, Brazil.

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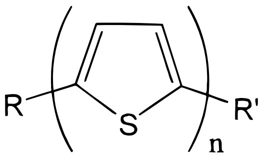


**Figure 1.** Substituted oligothiophenes. R, R′ stand for the substituents: H, OMe, $-NO_2$. *n* is the number of thiophene units: *n* = 2, 3, 4, 5, 6.

treatment of these systems using a high level of theory. The recent introduction of faster computers and new methodologies, able to treat electronic structures with remarkable precision, have provided a motivation for studying such molecular systems.

Semiempirical methods are known to yield satisfactory geometries and can provide a good insight in the electronic structure of large systems. In the present work we have shown that scaled semiempirical energy gaps are in good agreement with reported experimental results. Correlation effects can be very important for the study of electronic structure of molecules and should be taken into account particularly when one is interested in the evaluation of the energy gap. In this sense, density functional theory (DFT), due to its feature of including the electronic correlation in a computationally efficient manner, can be used in larger molecular systems. In its formalism, the ionization potential and electron affinity are well-defined properties[9] that can be calculated. Very recently, Levy et al.[10] developed a DFT version of Koopmans' theorem, showing that the energy gap can be estimated directly from the eigenvalues of the Kohn−Sham equations. However, the accuracy of the predicted properties strongly depends on the approximate exchange/correlation functional used, since the exact one is not known. In this article we have successfully applied Koopmans' theorem to estimate HOMO−LUMO energy gaps of substituted oligothiophenes, using donor (−OMe) and acceptor ($-NO_2$) substituent groups. However, it will be shown that this much-used approach may fail when substitution leads to a charge transfer for the first electronic transition. In the present study we show that, in this situation, the ΔSCF (total energy difference between the ground and excited electronic state) approach is a better choice to estimate energy gaps.

## 2. Computational Procedure

All substituted oligothiophenes studied in this work (see Figure 1) have been fully optimized at AM1[11] and Hartree−Fock (HF) levels of theory. The energy gap has been estimated from Koopmans' theorem, and the values were appropriately scaled to be compared with the available experimental data. Ab initio RHF calculations were performed using the following basis sets: 3-21G,[12−14] 3-21G(S)*,[12−16] 6-31G,[15,16] 6-31G(S)*,[12−16] 6-31G*,[12−16] and 6-31+G*.[12−17] The 3-21G(S)* and 6-31G(S)* notations mean that polarization functions were added only on the sulfur center. The other basis set nomenclature have the usual meaning (* and + mean that polarization and diffuse functions are included, respectively).

Density functional single-point calculations have been performed using the 6-31G* basis set and the HF/6-31G* fully optimized geometries. The exchange/correlation local XC functional with the expression due to Slater[18] for exchange and the VWN[19] for correlation (SVWN), the generalized gradient approximation (GGA) for exchange due to Becke[20] together with the correlation expression due to Lee, Yang, and Parr (BLYP),[21] and the three-parameter hybrid XC functional that includes part of the exact exchange energy (B3LYP) that has been developed from the adiabatic connection by Becke[22] have been used. The calculations were performed using the Gaussian 94[23] and Mopac7[24] programs.

**TABLE 1: Dihedral Angle and Energy Difference for the Syn-gauche and Anti-gauche Bithiophene Conformers**[a]

| method | dihedral angle (S−C−C−S) anti-gauche | syn-gauche | *E*(syn-gauche) − E(anti-gauche) (kJ.mol$^{-1}$) |
|---|---|---|---|
| AM1 | 152 | 36 | 0.84 |
| PM3 | 142 | 30 | −2.18 |
| HF | 147 | 45 | 2.85 |
| MP2 | 141 | 44 | 2.06 |
| B3LYP | 157 | 32 | 2.89 |
| BLYP | 161 | 29 | 2.84 |
| SVWN | 169 | 21 | 3.10 |
| expt[b] | 148 ± 3 | 36 ± 5 | 0.75 |

[a] The 6-31G* basis set was used in all calculations. [b] See ref 31.

The ΔSCF approach in which the energy gap is estimated from the calculated total energy difference between the ground and excited electronic state has been applied using deMon-KS program[25] with the same 6-31G* basis set and the S-VWN XC functional. The excited state is calculated by promoting one electron from the HOMO to the LUMO orbital in an unrestricted SCF calculation.

## 3. Results and Discussion

We have studied oligothiophenes of size varying from two to six monomers, named 2t, 3t, 4t, 5t, and 6t; the α-monosubstituted forms 3to and 3tn mean methoxy (−OMe) and nitro ($-NO_2$ substitutions, respectively, and the 2too, 4too, 6tnn, and 6ton α,α′-disubstituted forms correspond to two methoxy group substitutions (2too and 4too), two nitro substitutions (6tnn), and a methoxy and a nitro substitution (6ton), respectively.

**3.1. Torsional Energy Surface of Bithiophene (2t).** The potential energy surface for the bithiophene (2t) molecule has been found difficult to be described by theoretical methods,[26−28] with rotational barriers being overestimated by DFT and Hartree−Fock methods. Viruela et al.[28] suggested that the MP2 calculated energies using the B3LYP-optimized geometries with the 6-31G* basis set could be a good strategy to describe the torsional potential energy curve of this system, through a six-term fitted Fourier series. They also showed that the energy difference between the two minima on the potential energy surface, i.e., the syn-gauche and anti-gauche conformers, is well described by most of the methods used. However, it is worth noting that other important properties like the energy gap may not be treated using such a strategy.

Table 1 shows the S−C−C−S dihedral angle and the energy difference between syn-gauche and anti-gauche conformations calculated using different methods. The geometry results are in good agreement with the previous theoretical reported results and the available experimental values. The optimized S−C−C−S dihedral angle for the anti-gauche and syn-gauche conformations are 147° and 45°, respectively, at the HF level of theory using the 6-31G* basis set, while Ortí et al.[26] obtained the values of 148° and 44°, respectively (HF/6-31G* value). At the MP2 level of theory, our calculated values of 141° and 44° for the dihedral angle of anti-gauche and syn-gauche conformations can be compared to the Ortí et al.[26] values of 142° and 43°, respectively (MP2/6-31G* value). It can be seen that the torsional angle tends to shift toward the anti and syn planar values 180° and 0°, respectively, when DFT methods are used for geometry optimization. A similar behavior is found for the semiempirical calculations. The SVWN/6-31G* calculations predicted the structures closest to planarity and also the

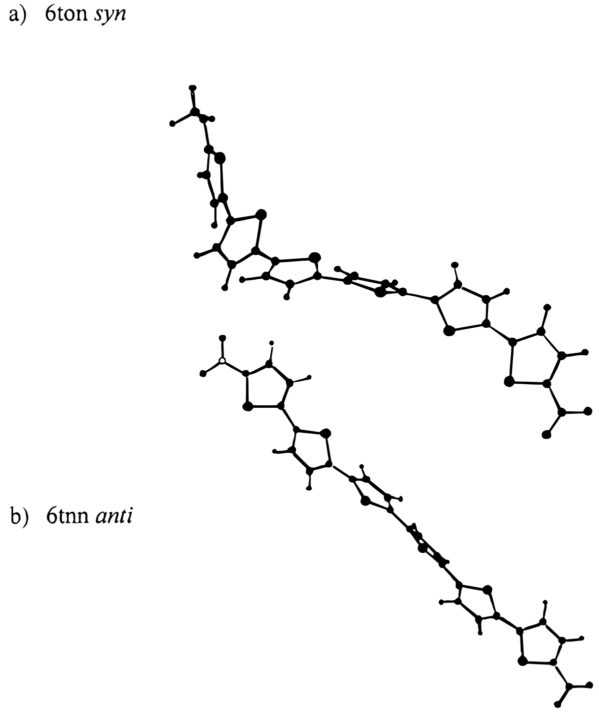


**Figure 2.** 6-31G* optimized 6ton and 6tnn oligothiophenes for (a) syn and (b) anti conformations.

highest deviation with respect to the MP2 energy difference value. Very recently, we have performed high-level ab initio correlated MP4 (fourth-order Mϕller−Plesset perturbation theory) and CCSD (coupled cluster with singles and doubles excitations) calculations for the stationary points located on the PES of the bithiophene molecule,[29] and analyzed in detail the performance of distinct quantum mechanical approaches, and conventional ab initio and DFT methods.

**3.2. Structural Properties of α,α′-Oligothiophenes.** Oligothiophenes present a structure similar to the bithiophene when one compares the consecutive dihedral angles. We found that the corresponding dihedral angle changes about 3° on going from bithiophene to sexthiophene. The substituted oligothiophenes studied in the present work have similar dihedral angle values. The inductive and resonance effects seem unimportant for geometry optimization. In fact, as one can see from Figure 2, the consecutive monomers of an oligothiophene have similar dihedral angles (about 150° for anti and 50° for syn conformers). The syn conformers present a helice-like structure. The bond angles and bond lengths do not suffer appreciable variation with the oligomer size. In fact, the resonance and inductive effects in the geometries are observed only on the chain extremities where the substitution occurs. Substitution by an acceptor or donator electron group produces small changes over bond lengths and angles near to the substitution position. We found that the overall effect of the basis set on the optimized structures is such that without polarization functions planar arrangements are predicted while nonplanar structures are obtained only if polarization functions are added to the sulfur atoms.

Of course, in a practical point of view, the dielectric constant of the surrounding medium should have a determinant role on the stability of each structure as well as the presence of charges in the chains since it is well-known that the carbon backbone changes from a benzenoid character for the neutral oligomer to a quinoid one for the charged species.[30]

**3.3. Energy Gap from Noncorrelated Methods.** It is already known that energy gaps from Koopman's theorem are overestimated since electron correlation is not included in the Hartree−Fock formalism and, furthermore, the electron density relaxation due to the excitation is not taken into account. Even though several disadvantages can be pointed out in getting energy gaps from Koopman's theorem, its simplicity and no additional computational cost make it very attractive and an interesting approach to study larger and complex systems.

Tables 2 and 3 show the energy gaps calculated from Koopman's theorem using semiempirical and HF approaches for the syn and anti conformers. The anti and syn conformers are true minima on the PES with the anti conformer being at least ca. 20 kJ mol$^{-1}$ more stable than the syn conformer for all 6t oligomers studied. As the syn−anti energy difference is relatively small, as we have already observed for the case of bithiophene, we decided to show both results for comparison and completeness of the work. All structures have been fully optimized using the respective level of theory. Calculated energy gaps have been scaled using the following equation:

$$E^{\mathrm{gap}}_{\mathrm{scaled}} = \frac{E^{\mathrm{gap}} - A}{B} \tag{1}$$

where $A$ and $B$ are scaling parameters.

The scaled energy gaps are in good agreement with the experimental values, with the correlation factor being ca. 0.94 for the scaled values compared to the experimental energy gaps for all noncorrelated methods used. As expected, the energy gaps using Koopman's theorem are about 4 eV ($A$ parameter) larger than the experimental value.

Figure 3 shows the scaled energy gaps compared to the experimental values using different basis sets. An important improvement is observed when a polarization function is added to the sulfur atom basis sets. This is observed even for small basis sets such as 3-21G(S)*. Undoubtedly, this is a requirement that has to be satisfied if one wants to study electronic structure of oligothiophenes. The $-NO_2$-substituted oligothiophenes lead to a decrease of the energy gap observed for either experimental or calculated values. An exception is the 6ton structure, where the decrease of the energy gap predicted theoretically is not accompanied by the experimental value. Adding diffuse functions does not change appreciably the results compared to the 6-31G* basis sets.

Figure 4 shows the HF/6-31G*, AM1, and PM3 semiempirical results. It can be seen that the PM3 profile follows closely the HF/6-31G* one. It is also interesting to observe that semiempirical predicted values are in better agreement with experimental data. However, theoretical methods (except for the AM1 calculation) predict a decrease of the energy gap for the 6ton structure that is not observed in the experimental values.

**3.4. Energy Gaps from Density Functional Methods.** Density functional theory has been used to study systems of increasing complexity due to its relatively low computational cost and also to include in its formalism the electron correlation effects. Ionization potential (IP) and electron affinity (EA) are properties that are well-defined in DFT. Janak's theorem [9] establishes that the HOMO and LUMO energies are respectively the IP and EA (with a minus sign) for a given molecular system. Furthermore, very recently, Levy et al.[10] developed a DFT version of Koopmans' theorem, showing that the energy gap can be estimated directly from the eigenvalues of the Kohn−Sham equations. Consequently, the energy gap can be estimated directly from the HOMO/LUMO energy difference, in a similar way as it is estimated from ab initio calculations using Koopman's theorem. The development of good approximations

**TABLE 2: Scaled Band Gap (eV) Calculations for Optimized Anti α,α-Substituted Oligothiophenes**

| | | | | HF | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | expt[a] | AM1 | PM3 | 3-21G | 3-21G(S)* | 6-31G | 6-31G(S)* | 6-31+G* | 6-31G* |
| *A*[b] | | 4.27 | 4.34 | 3.32 | 3.62 | 3.22 | 3.69 | 4.23 | 4.57 |
| *B*[b] | | 1.07 | 1.09 | 1.86 | 1.91 | 1.86 | 1.86 | 1.69 | 1.64 |
| 2t | 3.68 | 3.64 | 3.59 | 3.66 | 3.60 | 3.69 | 3.58 | 3.62 | 3.62 |
| 2too | 3.37 | 3.52 | 3.62 | 3.56 | 3.49 | 3.54 | 3.50 | 3.47 | 3.53 |
| 3t | 3.11 | 3.05 | 3.06 | 3.06 | 3.08 | 3.04 | 3.08 | 2.99 | 3.07 |
| 3to | 2.99 | 3.00 | 3.01 | 3.01 | 3.03 | 2.99 | 3.04 | 3.04 | 3.01 |
| 3tn | 2.36 | 2.68 | 2.61 | 2.68 | 2.51 | 2.63 | 2.53 | 2.48 | 2.66 |
| 4t | 2.82 | 2.75 | 2.79 | 2.74 | 2.82 | 2.73 | 2.82 | 2.83 | 2.78 |
| 4too | 2.74 | 2.71 | 2.75 | 2.69 | 2.76 | 2.69 | 2.78 | 2.78 | 2.72 |
| 6t | 2.52 | 2.48 | 2.56 | 2.44 | 2.58 | 2.43 | 2.59 | 2.58 | 2.52 |
| 6too | 2.47 | 2.47 | 2.53 | 2.41 | 2.54 | 2.41 | 2.56 | 2.65 | 2.48 |
| 6ton | 2.47 | 2.47 | 2.12 | 2.12 | 2.13 | 2.13 | 2.10 | 2.14 | 2.12 |
| 6tnn | 2.29 | 2.09 | 2.33 | 2.48 | 2.30 | 2.54 | 2.25 | 2.20 | 2.31 |

[a] See ref 5. [b] Scaling parameters according to eq 1.

**TABLE 3: Scaled Band Gap (eV) Calculations for Optimized Syn α,α′-Substituted Oligothiophenes**

| | | | | HF | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | expt[a] | AM1 | PM3 | 3-21G | 3-21G(S)* | 6-31G | 6-31G(S)* | 631+G* | 6-31G* |
| A[b] | | 4.60 | 4.62 | 4.06 | 4.20 | 4.30 | 4.14 | 4.19 | 4.90 |
| B[b] | | 1.00 | 0.94 | 1.84 | 1.84 | 1.72 | 1.84 | 1.82 | 1.66 |
| 2t | 3.68 | 3.67 | 3.74 | 3.57 | 3.55 | 3.62 | 3.52 | 3.52 | 3.55 |
| 2too | 3.37 | 3.49 | 3.38 | 3.55 | 3.53 | 3.63 | 3.51 | 3.46 | 3.55 |
| 3t | 3.11 | 3.03 | 3.07 | 3.03 | 3.05 | 3.07 | 3.03 | 3.06 | 3.03 |
| 3to | 2.99 | 2.99 | 2.96 | 3.03 | 3.05 | 2.62 | 3.05 | 3.07 | 3.05 |
| 3tn | 2.36 | 2.69 | 2.78 | 2.52 | 2.48 | 2.47 | 2.41 | 2.42 | 2.55 |
| 4t | 2.82 | 2.78 | 2.78 | 2.81 | 2.86 | 2.87 | 2.88 | 2.89 | 2.86 |
| 4too | 2.74 | 2.7 | 2.67 | 2.79 | 2.84 | 2.87 | 2.85 | 2.86 | 2.84 |
| 6t | 2.52 | 2.51 | 2.49 | 2.58 | 2.65 | 2.65 | 2.66 | 2.66 | 2.65 |
| 6too | 2.47 | 2.48 | 2.45 | 2.57 | 2.54 | 2.64 | 2.65 | 2.58 | 2.14 |
| 6ton | 2.47 | 2.06 | 2.06 | 2.09 | 2.07 | 2.19 | 2.01 | 2.02 | 2.32 |
| 6tnn | 2.29 | 2.34 | 2.34 | 2.27 | 2.26 | 2.22 | 2.20 | 2.21 | 2.32 |

[a] See ref 5. [b] Scaling parameters according to eq 1.

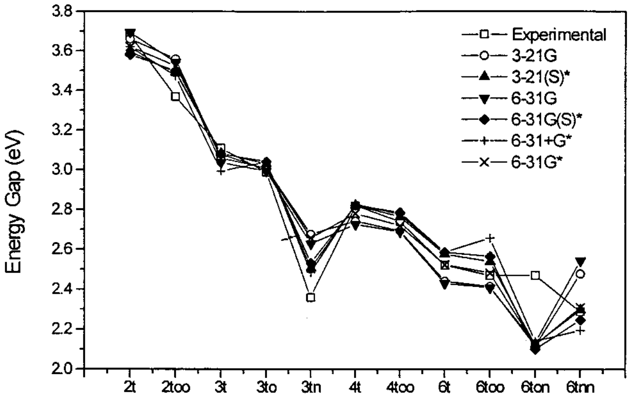


**Figure 3.** Scaled energy gaps (eV) of anti α,α′-oligothiophenes using different basis sets.

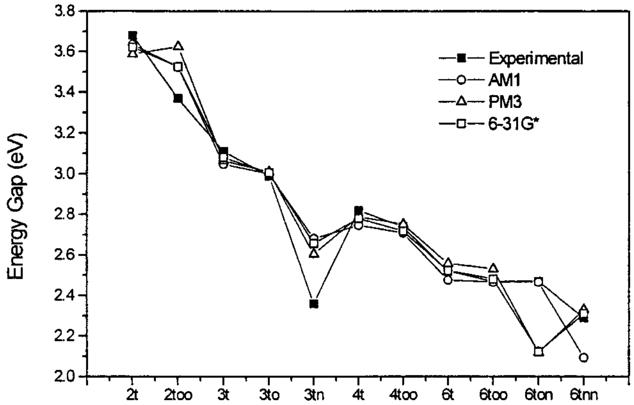


**Figure 4.** Scaled energy gaps (eV) of anti α,α′-oligothiophenes using semiempirical and HF methods.

to the exact exchange/correlation functionals has permitted one to perform accurate calculations on very complex systems.

Tables 4 and 5 show energy gaps estimated from three different exchange/correlation (XC) functionals. The accuracy of the results permitted a direct comparison with the experimental values without scaling. The SVWN XC functional, developed from the homogeneous electron gas theory, predicted energy gaps in good agreement with the experimental values. The error bars are estimated to be ca. 0.25 eV. The 6ton structure is the only one that presents a considerable discrepancy with respect to the experimental energy gap of ca. 0.90 eV. The withdrawing $-NO_2$ group leads to a decrease of the energy gap.

The GGA (gradient generalized approximation) BLYP XC correlation functional is an improvement, since part of the inhomogeneous nature, *f* the electron density, is taken into account from the electron density gradient. The DFT geometries and energies have been greatly improved with the development of the GGA XC functionals.[21,22] However, as can be seen from Tables 4 and 5, the predicted energy gaps have the same behavior as observed for the local SVWN XC functional. Another important improvement of the XC functional is the B3LYP functional that has included part of the exact exchange energy from the adiabatic connection method.[32] Properties of organic molecules are well predicted by such hybrid method; however, the predicted energy gaps are significantly overestimated. The absolute error bars are ca. 1.0 eV., but the overall behavior follows the same tendency as the other XC functionals, as one can see in Figure 5. From Figures 4 and 5 it can be

**TABLE 4: Energy Gap (eV) Calculations for Anti α,α′-Substituted Oligothiophenes; and Deviations Relative to the Experimental Values (in Parentheses)**

| | expt[a] | B3LYP | BLYP | SVWN |
|---|---|---|---|---|
| 2t | 3.68 | 4.80 (1.12) | 3.40 (−0.28) | 3.43 (−0.25) |
| 2too | 3.37 | 4.50 (1.13) | 3.11 (−0.26) | 3.11 (−0.26) |
| 3t | 3.11 | 4.16 (1.05) | 2.86 (−0.25) | 2.88 (−0.23) |
| 3to | 2.99 | 4.01 (1.02) | 2.71 (−0.28) | 2.71 (−0.28) |
| 3tn | 2.36 | 3.48 (1.12) | 2.23 (−0.13) | 2.23 (−0.13) |
| 4t | 2.82 | 3.83 (1.01) | 2.59 (−0.23) | 2.61 (−0.21) |
| 4too | 2.74 | 3.69 (0.95) | 2.44 (−0.30) | 2.45 (−0.29) |
| 6t | 2.52 | 3.53 (1.01) | 2.33 (−0.19) | 2.35 (−0.17) |
| 6too | 2.47 | 3.01 (0.54) | 2.23 (−0.24) | 2.24 (−0.23) |
| 6ton | 2.47 | 2.92 (0.45) | 1.54 (−**0.93**) | 1.52 (−**0.95**) |
| 6tnn | 2.29 | 3.30 (1.01) | 1.95 (−0.34) | 1.96 (−0.33) |

[a] See ref 5.

**TABLE 5: Energy Gap (eV) Calculations to Syn α,α′-Substituted Oligothiophenes and Deviations Relative to the Experimental Values (in Parentheses)**

| | expt[a] | B3LYP | BLYP | SVWN |
|---|---|---|---|---|
| 2t | 3.68 | 5.00 (1.32) | 3.58 (−0.10) | 3.60 (−0.08) |
| 2too | 3.37 | 4.80 (1.43) | 3.36 (−0.01) | 3.36 (−0.01) |
| 3t | 3.11 | 4.39 (1.28) | 2.86 (−0.25) | 3.08 (−0.03) |
| 3to | 2.99 | 4.30 (1.31) | 2.94 (−0.05) | 2.95 (−0.04) |
| 3tn | 2.36 | 3.60 (1.24) | 2.32 (−0.04) | 2.32 (−0.04) |
| 4t | 2.82 | 4.17 (1.35) | 2.87 (0.05) | 2.89 (−0.07) |
| 4too | 2.74 | 4.06 (1.32) | 2.74 (0.0 | 2.74 (0.0) |
| 6t | 2.52 | 3.93 (1.41) | 2.66 (0.14) | 2.68 (0.16) |
| 6too | 2.47 | 3.84 (1.37) | 2.56 (0.09 | 2.59 (0.12) |
| 6ton | 2.47 | 3.11 (0.64) | 1.65 (−**0.82**) | 1.63 (−**0.84**) |
| 6tnn | 2.29 | 3.54 (1.25) | 2.10 (−0.19) | 2.11 (−0.18) |

[a] See ref 5.

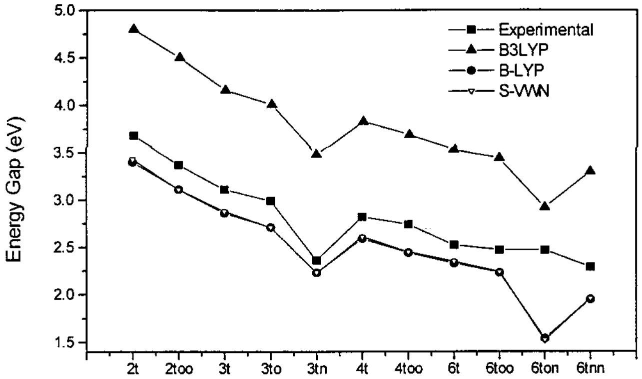


**Figure 5.** Energy gaps (eV) of anti α,α′-oligothiophenes using different DFT methods.

pointed out that either BLYP or SVWN functional is adequate for calculating energy gap for α,α′-substituted oligothiophenes. By examining the experimental and theoretical energy gap difference values quoted in parentheses (Tables 4 and 5), it is observed that they provide an indication that the syn form should be the preferred one in the experimental study carried out for measuring energy gaps.[5] This is an important result since the source of experimental structural information for oligothiophenes is predominantly for the compounds in the solid state, where it is well-known that planar or near-planar spatial arrangements are observed.

It is worth reminding that Salzner et al.[33] in their study of the low band gap polymers using density functional theory hybrid functionals concluded that DFT hybrid methods provide energy gaps in good agreement with vertical excitation energies from UV-absorption spectra. In our point of view, assuming that there is no significant difference between the ground and excited state geometries, HOMO−LUMO energy gaps from DFT might be compared with the energy of the 0,0 transitions ($E_0^0$) usually taken as the crossing point of both the excitation and absorption spectra. The UV-absorption spectra overestimate the HOMO−LUMO gap, in part due to the vibrational structure associated to the electronic spectra, which has not been eliminated. Probably this fact lead to a fortuitous good agreement with the B3LYP results because this functional also overestimates the HOMO−LUMO energy gap as explained above. It is opportune to mention that, contrary to the hybrid XC functionals and conventional ab initio Hartree−Fock approach, most of the GGA and local XC functionals underestimate the HOMO−LUMO energy gap, as we have also observed in the present work. It should be said that the HOMO−LUMO gap is simply an energy level difference between two orbitals, and, in principle, it should be corrected by exchange and correlation effects to be compared with experimental data. In this context, the BLYP and SVWN functionals are shown to perform very well.

All methods that have been used in the present work predicted a lowering of the energy gap of the 6ton structure. We previously observed[5] a bathochromic shift of the energy gap of the nitro-substituted terthiophenes and we suggested that an intramolecular charge transfer takes place in the excited states of these molecules based on this solvatochromic effect. Interestingly, the substituent effects decrease from 3t to 6t and no charge transfer is directly observed for 6ton from optical data.

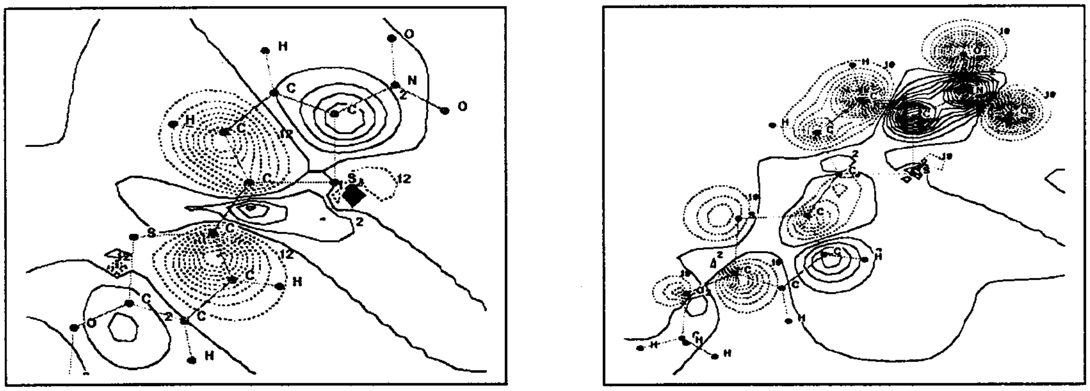
Two questions then arise from the analysis of our results:

1. For the withdrawing groups, Koopmans' theorem is not able to adequately describe the energy gap. If a charge transfer is actually occurring, one could say that electron density relaxation of the excited state is important and, consequently, the vertical excitation approach is not an adequate method.

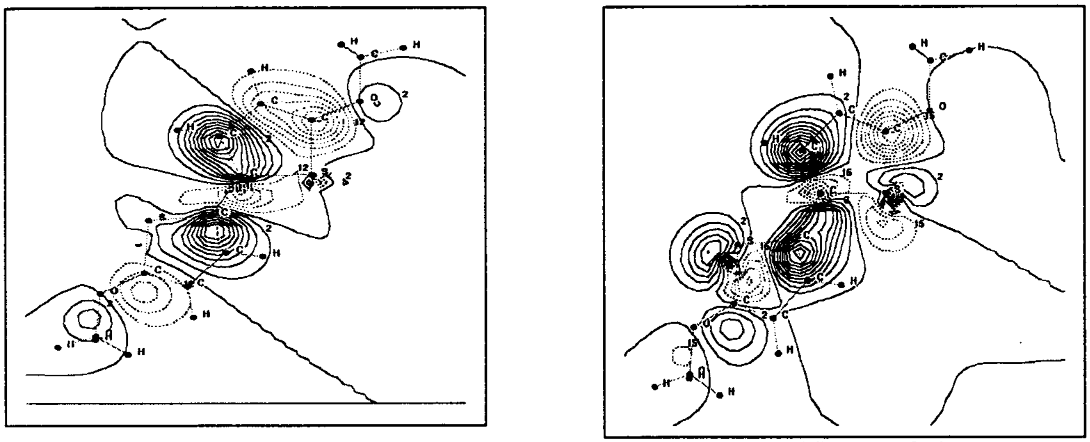
2. If the charge transfer is actually occurring in the excited state, could it be the explanation for the discrepancy between experimental and calculated values for the nitro-substituted oligomers? One could calculate small oligomers (2ton, for example) and verify if the same behavior is observed and then how this happens.

In order to address these two questions, we have calculated the energy gap using the ΔSCF approach, i.e., calculating the ground and the excited electronic state separately using the ground electronic state optimized geometry and taking the difference of the total energy as an estimate of the energy gap. We have used the deMon-KS program[25] to perform these calculations. The results are shown in Table 6. It is observed that the ΔSCF method corrects the discrepancies observed for 6ton. When the excited state is calculated by the ΔSCF method, the virtual orbital is relaxed in such a way that the energy gap is in good agreement with the experimental value. We observed that the discrepancies are related to the withdrawing group $-NO_2$. This substitution leads to a charge transfer. Figure 6 shows the HOMO and LUMO densities. The HOMO is localized along the thiophene rings and the LUMO is predominantly localized on the $-NO_2$ group for the 2ton species, showing that a charge transfer occurs when the molecule is excited. With respect to 2too, one does not observe the same behavior; HOMO and LUMO are localized along the thiophene rings. Our results show that when charge transfers play a significant role Koopman's theorem should be used with care and may not be adequate to evaluate energy gaps.

Finally, a word should be said about the nonobservance of charge transfer for the 6ton α,α′-disubstituted form in our experimental study reported previously.[5] The charge transfer was experimentally recognized for the 3tn species indirectly



(a) HOMO 2ton (b)LUMO 2ton



(c) HOMO 2too (d)LUMO 2too

**Figure 6.** HF/6-31G* contour maps of the HOMO and LUMO orbitals of the 2ton (a, b) and 2too (c, d) substituted bithiophenes.

**TABLE 6: Energy Gaps of Substituted Bithiophene and Sexithiophene Using the Koopmans' Theorem and ΔSCF Method (SVWN/6-31G*//HF/6-31G* Calculations)**

| | energy gap (eV) | | |
|---|---|---|---|
| oligothiophene | expt[a] | Koopmans' theorem | ΔSCF |
| 2t | 3.68 | 3.43 | 3.44 |
| 2too | 3.37 | 3.11 | 3.13 |
| 2tnn | | 2.67 | 2.77 |
| 3t | 3.11 | 2.88 | 2.89 |
| 3tn | 2.36 | 2.23 | 2.55 |
| 3ton | | 1.89 | 2.40 |
| 4t | 2.82 | 2.61 | 2.62 |
| 4tn | | 1.98 | 2.37 |
| 5t | | 2.42 | 2.43 |
| 5tn | | 1.81 | 2.25 |
| 6t | 2.52 | 2.35 | 2.36 |
| 6too | 2.47 | 2.24 | 2.27 |
| 6tnn | 2.29 | 1.96 | 2.16 |
| 6ton | 2.47 | 1.52 | 2.13 |

[a] See ref 5.

through a solvatochromic effect, where a bathochromic shift of the energy gap of the nitro-substituted terthiophene was observed. The absence of solvatochromism is associated with the nonexistence of charge transfer in the molecular system under study. On the basis of our theoretical results, we suggest that other effects, such as the solvent effect, might be obscuring the experimental observation of charge transfer in the 6ton species.

This theoretical study confirmed our experimental results[5] where it was shown that the use of electroactive substituents could greatly modulate and improve the electronic properties of short oligomers. Furthermore, the energy gap predicted for the hexamer is, as expected, close to the experimental energy gap of the polymer due to rotational disorder and other defects that occur in the polymer. This turns the oligomer approach attractive for electronic materials.[34]

## 4. Conclusions

Energy gaps of different substituted oligothiophenes up to six monomers have been estimated by semiempirical, Hartree–Fock, and density functional methods. Scaled values obtained from the noncorrelated methods are in good agreement with experiment with exception of the 6ton where a charge transfer is predicted theoretically. For a direct comparison to the experimental values, density functional methods provide good estimates. The error bars are ca. 0.2 eV with respect to the experimental energy gaps. We have shown that the 6ton structure has not been well described because the charge transfer is not adequately treated in Koopmans' theorem. The ΔSCF method, in which the ground and excited electronic state is treated separately and the difference of the total energy is taken as an estimate of the energy gap, turns out to be a good approach to treat substituted oligothiophene systems.

Using simple theoretical methodologies, we showed that is possible to predict reasonably the electronic properties of short conjugated systems and we are convinced that the systematic use of those theoretical tools should contribute to orientate the synthesis efforts and help understand the structure–properties relation of these conjugated materials. Work is now in progress to develop a new methodology to study charged oligomers and to simulate the solid-state packing effects of the crystallized molecules.

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