# ORIGINAL PAPER

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# Electronic structure and optical spectroscopy of conducting electrochromic devices

**Abstract** Interest in conductive organic polymers has considerably increased since the discovery in 1977 of the doped molecule polyacetylene. Recently, polymers of dithienopyrrole (DP), dithienothiophene (DT) and thionaphtheneindole (TNI) have been synthesized electrochemically showing for several monomer ratios good electrochromic and conducting characteristics.

The aim of this paper is to investigate theoretically the electrical and optical properties of the above mentioned polymers. Therefore, we have performed a conformational structure study followed by electronic structure calculations. Also we present a spectroscopic study for oligomers built with the monomers of these materials.

In our calculations we utilized the semiempirical method AM1 for the electronic and geometric simulation of the polymers. Optical absorption spectra for neutral and charged systems were calculated using the INDO/S-CI method. All three systems showed similar electronic behavior but significant differences can be seen on the TNI monomer optical spectra. Our results are in good agreement with the experimental ones.

**Keywords** Density of states · Theoretical absorption · Dithienopyrrole · Dithienothiophene · Thionaphtheneindole

## Introduction

Conductive polymeric systems have attracted the increased attention of a vast number of research groups due to their novel physics and chemistry and to their potential technological applications in the areas of biologi-

cal sensors, molecular electronics, surgical plasters containing active ingredients, membranes, etc. [1, 2, 3, 4, 5] High conductivity and stability as well as availability as a film are some of the properties required for the commercial utilization of these materials. One such system, the so called pTNI, [6] has been used as a humidity sensor and was electrochemically synthesized by Casalbore-Miceli et al. [7] In their study the mechanism of charge transport of the polymer for a given amount of water in changeable conditions of humidity and temperature was investigated. From the measurements of *i-t* and *i-V* characterics they found two different regimes. In the first regime the current decreases with time at constant voltage and one can see a reverse current when the voltage is set to zero without disconnecting the electrodes.

The *i-V* characteristic shows non-ohmic behavior. The electric conductivity in this regime, the so called lower temperature regime $T < 50$ °C, is predominantly ionic. For temperatures higher than 50 °C a second regime appears where the current remains constant in time at constant voltage. Also no inverse current is observed for zero voltage. In this second regime, pTNI behaves like an ohmic system showing an electronic mechanism of charge transport. Casalbore-Miceli et al. argued that the first regime is due to the presence of water in the material.

When they investigated the TNI aromatic compound they observed that the overall electrode processes could give rise to different products depending on the reaction medium and the supporting electrolyte. Therefore, they were able to obtain a conducting polymer as a product of thionaphteneindole oxidation when using perchlorate as electrolyte and a neutral polymer when using *p*-toluene-sulfonate as electrolyte.

Other interesting polymeric systems are PDP [8] and PDT. [9] The polymeric composite PDP/PVC is obtained by consecutive potentiodynamic cycles coated by PVC films. [10, 11]

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## Methodology

The molecular geometries of the monomer, dimer and trimer of DP, DT and TNI were fully optimized using semiempirical methods performed through the MOPAC package. [12]

The methods utilized in this package for the calculations of the molecular structure were AM1 (Austin Model 1) [13] and PM3 (Parametric Method 3), [14] where the parameters are those from the original references. [13, 14, 15] For geometry optimization we performed the semiempirical calculations changing the standard convergence criteria adopted on MOPAC to a maximum step size of the 0.05.

The geometry optimization for the different structures started from the planar situation. The results we will show below for the absorption spectra assume the geometry optimization obtained by the AM1 method. This choice gives us the best agreement with the experimental results.

Describing the optical properties, the use of AM1 should be coupled to another method specifically recommended to simulate spectroscopic calculations. For the absorption spectrum determination we used the INDO/S-CI (Intermediate Neglect of Differential Overlap/Spectroscopic – Configuration Interaction), [16, 17, 18, 19, 20, 21, 22] because this method was specifically made to describe the optical UV–visible transitions of organic compounds. We utilized Mataga–Nishimoto gamma parameters in the theoretical spectroscopy calculations. All the calculations included single and double excitations, with an average number of 200 configurations.

The geometrical data used in this calculation were adapted from AM1. The results obtained for the polaron indicate that the mixtures between $\sigma$ and $\pi$ electrons are quite small. Therefore we treated the polymer as a $\pi$ system with one orbital per site and represented the electronic Hamiltonian for the $2p_z$ carbon and $2p_z$ nitrogen orbitals through a tight-binding model with first neighbor interactions:

$$H = \sum_i \alpha_i |i\rangle\langle i| + \beta_{i,i+1} |i\rangle\langle i+1| + \text{h.c.}$$

where $\alpha_i$ is the ionization energy of the atom at site $I$ and $\beta_{i,i+1}$ is the hopping energy between sites $I$ and $I+1$.

The Hamiltonian matrix elements are obtained from transferred parameters optimized in oligomer calculations using Extended Hückel Theory [23] with Clementi's parametrization, given by:

$$\beta(R) = -A\exp\{-R/b\}$$

where $R$ is the bond length between atoms $i$ and $i+1$, and $A$, $b$ are parameters to be optimized.

The electronic density of states (DOS) is obtained by using the Negative Factor Counting technique [24, 25, 26, 27] proposed by Dean. The eigenvectors associated with the eigenvalues of interest were obtained using the Inverse Interaction Method [14]. We have two cases of

DOS: all adjustable parameters were optimized to reproduce the ground state geometry of DP, DT and TNI and the band gaps associated to $\pi$ bands. [2, 3, 4] The second case is the presence of charge defects; as the exact geometry associated with the dopant–chain complex is not well known, we adopted the distribution obtained by our semiempirical calculation for the study of polymers.

## Results and discussion

The scheme of the chemical conformation in the DP, DT and TNI monomers is shown in Fig. 1.

The results of heat of formation, dipole moment and ionization potential for all oligomers considered in this paper are summarized in Table 1. One can see that for neutral systems the heat of formation (third column) increases with an almost constant ratio per monomer unit.
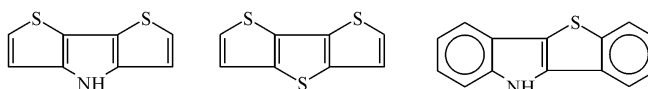


**Fig. 1** Schematic representation of the structures studied in this work: dithienopyrrole (*DP*), dithienothiophene (*DT*) and thionaphtheneindole (*TNI*)

**Table 1** Dipole, heat of formation and ionization potential of DP, DT and TNI oligomers

|  | Dipole (Debye) | $\Delta F$ (kcal) | Ion. Pot. (eV) |
|---|---|---|---|
| Neutral molecule |  |  |  |
| DP 1 | 1.159 | 86.674 | 7.975 |
| DP 2 | 2.319 | 175.696 | 7.722 |
| DP 3 | 3.381 | 264.743 | 7.572 |
| DT 1 | 0.388 | 67.680 | 7.921 |
| DT 2 | 0.612 | 137.739 | 7.975 |
| DT 3 | 0.845 | 207.832 | 7.982 |
| TNI 1 | 1.592 | 92.252 | 7.803 |
| TNI 2 | 3.148 | 191.054 | 7.725 |
| Charge −1 molecule |  |  |  |
| DP 1 | 0.686 | 73.710 | 0.927 |
| DP 2 | 1.633 | 144.040 | 1.965 |
| DP 3 | 2.804 | 225.395 | 2.465 |
| DT 1 | 0.170 | 44.095 | 1.423 |
| DT 2 | 0.740 | 99.224 | 2.250 |
| DT 3 | 2.059 | 164.679 | 2.504 |
| TNI 1 | 1.182 | 71.133 | 1.377 |
| TNI 2 | 1.123 | 158.883 | 1.853 |
| Charge +1 molecule |  |  |  |
| DP 1 | 1.535 | 262.074 | 12.641 |
| DP 2 | 2.661 | 340.409 | 10.820 |
| DP 3 | 4.197 | 426.786 | 10.081 |
| DT 1 | 0.301 | 241.923 | 12.535 |
| DT 2 | 0.368 | 310.912 | 11.190 |
| DT 3 | 0.144 | 379.115 | 10.479 |
| TNI 1 | 1.551 | 259.235 | 12.030 |
| TNI 2 | 15.384 | 357.274 | 11.301 |
| TNI 3 | 18.465 | 462.332 | 10.530 |

**Table 2** Energetic reach for DP, DT and TNI oligomers

| Molecule | $\Delta F_T$ (eV) |
|----------|-------------------|
| DP 1     | −0.5882           |
| DT 1     | −1.0701           |
| TNI 1    | −0.9582           |
| DP 2     | −1.4363           |
| DT 2     | −1.7475           |

These ratios are 1.2, 0.3 and 1.5 Debye/monomer for the DP, DT and TNI systems, respectively. The similarity of the electronic behavior for the three systems is apparent when one compares the ionization potential values (third column). For neutral ground state systems we have values around 7.9 eV. The same situation is seen for the ionization potential of negative ions but the stabilization is around 2.5 eV. These values increase again for positive ions between 10 and 12 eV. In the same table we have included the results for charged systems. It is striking to see that the TNI system with charge −1 exhibits very small changes for the dipole moments even though the two other systems follow the behavior of the neutral systems.

We observe a large contrast with the results for a positively charged system. The values of the heat formation are summarized on the second column. The differences between the values of heat formation for the negatively charged system and the neutral system, $\Delta F_T$, are gathered in Table 2. It is seen that, in opposition to the DP and DT systems, the results for TNI are independent of the oligomer size.

Calculations of the absorption spectra of the whole series of oligomers have been done by use of the INDO/CI method. In Fig. 2 we present the results for the neutral oligomers. The experimental spectrum obtained by Casalbore-Miceli et al. [3] for TNI under solution of ACN+0.1 TBATos shows a HOMO–LUMO transition corresponding to 333 nm and another large transition at 375 nm. Our calculation methodology gives 333.5 nm and 375.7 nm, respectively for these transitions, in excellent agreement with the experimental data. Beggiatto et al. [6] synthesized the DP system electrochemically. Their measurement of the absorption bands displayed a HOMO–LUMO transition at 500 nm, which is quite close to the 494 nm we get theoretically for the DP dimer. Also the results for the DT absorption show excellent agreement compared with their measurements on a 0.9 μm thick film of PDP/PVC.

In Table 3 the details of the most relevant transitions are shown and, as expected, the HOMO to LUMO gives the largest contribution to the optical absorption spectrum for all the systems. The oscillator strength for $DP_1$ or $DT_1$ [$TNI_1$] is 0.8 [0.9] for the H→L contribution and increases to 1.6 [2.1] and 2.3 [2.7] for dimer and trimer molecules of DP or DT [TNI]. This is an indication of the high planarity of the systems. However the H−2→L+1 transition is possible for all the monomers but H→L+4 only for DP and DT monomers. As the oligomer size increases, the H−1→L+1 transition occurs.
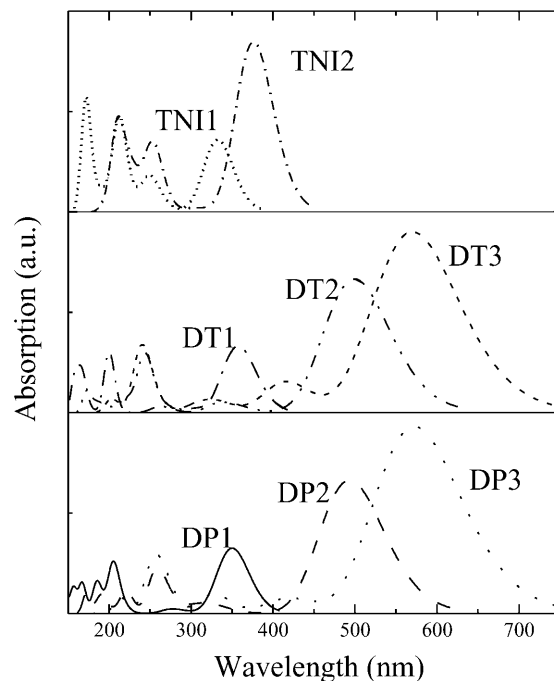


**Fig. 2** Neutral simulated absorption spectra of *DP*, *DT* and *TNI* oligomers as a function of wavelength. These curves were obtained from normalized gaussian functions weighted by the oscillator strengths
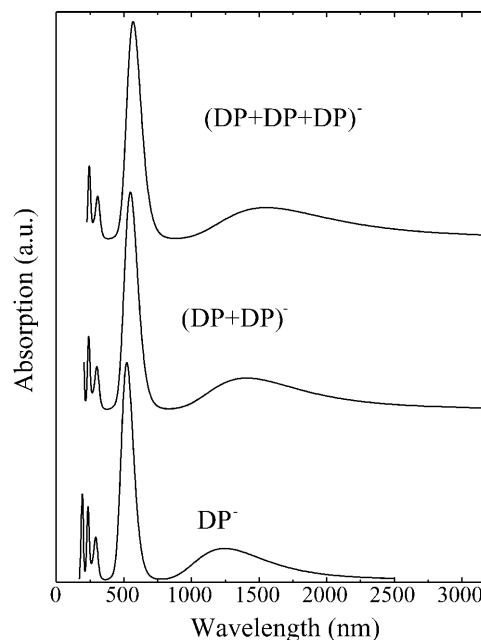


**Fig. 3** Charge −1 simulated absorption spectra of DP oligomer as a function of wavelength. These curves were obtained from normalized gaussian functions weighted by the oscillator strengths

We then conclude that the DP and DT systems have a very similar electronic structure while some minor transitions do not appear for TNI oligomers.

In Figs. 3, 4 and 5 we report the absorption spectra corresponding to the charged systems with −1 charge.

**Table 3** Most relevant CI expansion coefficients for fully optimized geometries to DP, DT and TNI. These are the excited states for the first optically active transition. H–$i$→L+$j$ represents HOMO–$i$→LUMO+$j$ orbital excitation

| Molecule | O.S. | CI state |
|---|---|---|
| DP 1 | 0.8153 | 0.993\|H→L⟩ |
|  |  | –0.080\|H-2→L+1⟩ |
|  | 0.5559 | –0.584\|H→L+4⟩ |
|  |  | 0.581\|H–2→L⟩ |
| DP 2 | 1.6640 | 0.969\|H→L⟩ |
|  |  | –0.216\|H–1→L+1⟩ |
|  | 0.5259 | 0.805\|H–3→L⟩ |
|  |  | –0.416\|H–3→L+3⟩ |
| DP 3 | 2.3356 | –0.9197\|H→L⟩ |
|  |  | –0.333\|H–1→L+1⟩ |
|  | 0.2676 | –0.473\|H–2→L+1⟩ |
|  |  | 0.447\|H–4→L+1⟩ |
| DT 1 | 0.8334 | 0.995\|H→L⟩ |
|  |  | –0.070\|H–2→L+1⟩ |
|  | 0.7164 | 0.794\|H→L+4⟩ |
|  |  | –0.450\|H–1→L⟩ |
| DT 2 | 1.6682 | –0.967\|H→L⟩ |
|  |  | –0.232\|H–1→L+1⟩ |
|  | 0.6755 | 0.848\|H–3→L⟩ |
|  |  | 0.318\|H–4→L+1⟩ |
| DT 3 | 2.2573 | 0.923\|H→L⟩ |
|  |  | –0.322\|H–1→L+1⟩ |
|  | 0.4803 | –0.581\|H–5→L⟩ |
|  |  | –0.415\|H–4→L+1⟩ |
| TNI 1 | 0.9251 | 0.432\|H–1→L+3⟩ |
|  |  | –0.427\|H–2→L+1⟩ |
|  | 0.8883 | –0.970\|H→L⟩ |
|  |  | –0.138\|H–1→L⟩ |
| TNI 2 | 2.1234 | 0.915\|H→L⟩ |
|  |  | –0.311\|H–1→L+1⟩ |
|  | 0.7558 | 0.419\|H–5→L⟩ |
|  |  | 0.340\|H–5→L+2⟩ |
| TNI 3 | 2.7132 | –0.921\|H→L⟩ |
|  |  | 0.270\|H–1→L+1⟩ |
|  | 0.6573 | 0.404\|H–4→L⟩ |
|  |  | –0.397\|H–4→L+2⟩ |

The comparison among the charged and neutral systems clearly indicates that, when we remove one electron, the absorption spectra undergo a red shift.

The π DOS is shown in Figs. 6, 7 and 8 for DP, DT and TNI polymers utilizing the Hückel methodology described above for (a) neutral and (b) –1 charged systems. Figures. 6a and 7a exhibit a Peierls gap of 2.07 [2.19] eV for DP [DT] polymers. For the TNI polymer in Fig. 8a we have a Peierls gap of 1.92 eV. The arrows indicate the HOMO level and we obtain metallic behavior for the charged polymers (Figs. 6b, 7b and 8b) because the HOMO state has a red shift. For the charged system the HOMO level is delocalized, giving a good indication again of metallic behavior. The TNI has five valence bands corresponding to π orbitals between –10 eV and 2 eV; otherwise the conduction bands are not well defined. We have superposition of the bands. The DOS of TNI under the effect of defects has the same behavior in the bands but the HOMO level goes down (please note the red shift of the arrow between Fig. 8a and b). This
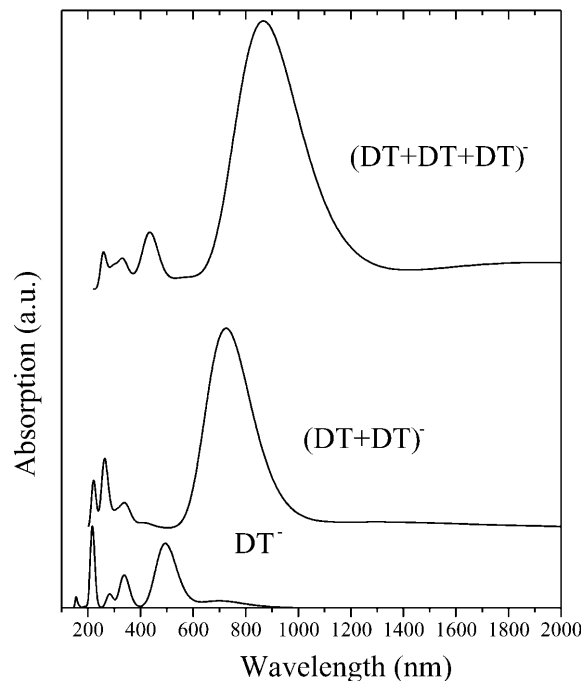


**Fig. 4** Charge –1 simulated absorption spectra of DT oligomer as a function of wavelength. These curves were obtained from normalized gaussian functions weighted by the oscillator strengths
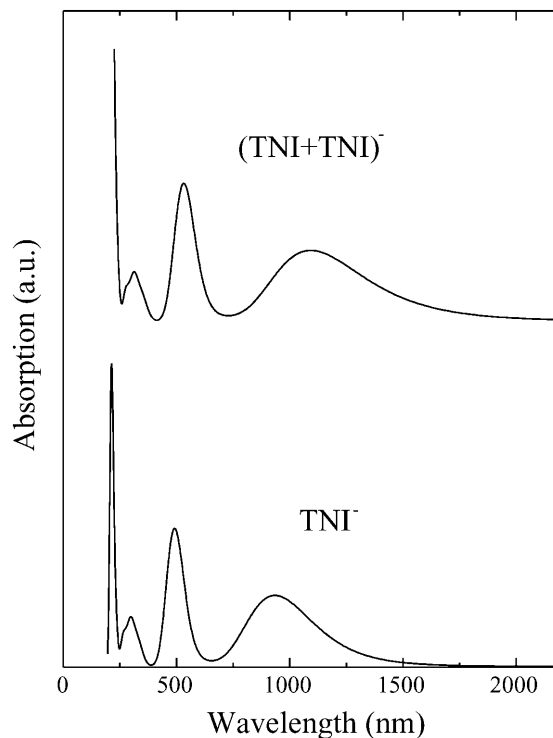


**Fig. 5** Charge –1 simulated absorption spectra of TNI oligomer as a function of wavelength. These curves were obtained from normalized gaussian functions weighted by the oscillator strengths
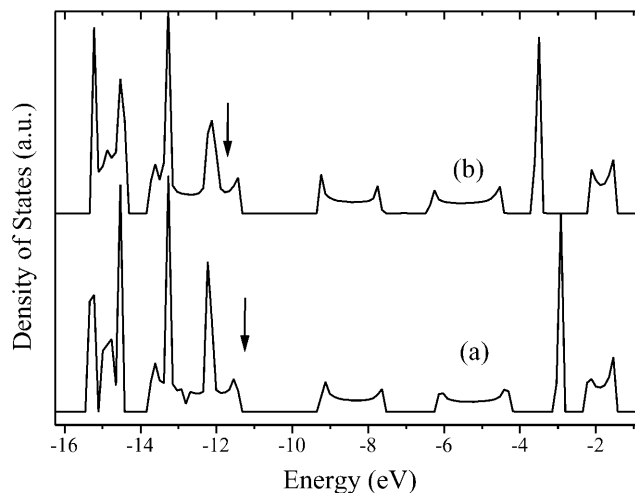
**Fig. 6** Density of states for DP polymer in the (**a**) neutral and (**b**) −1 charged system. The *arrows* indicate the position of the Fermi level
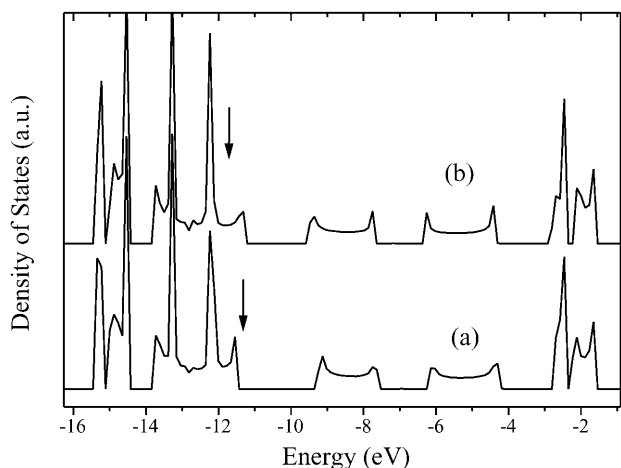


**Fig. 7** Density of states for DT polymer in the (**a**) neutral and (**b**) −1 charged system. The *arrows* indicate the position of the Fermi level
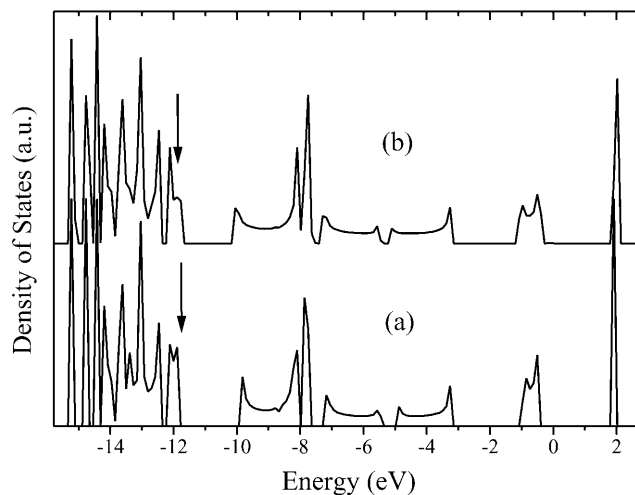


**Fig. 8** Density of states for TNI polymer in the (**a**) neutral and (**b**) −1 charged system. The *arrows* indicate the position of the Fermi level
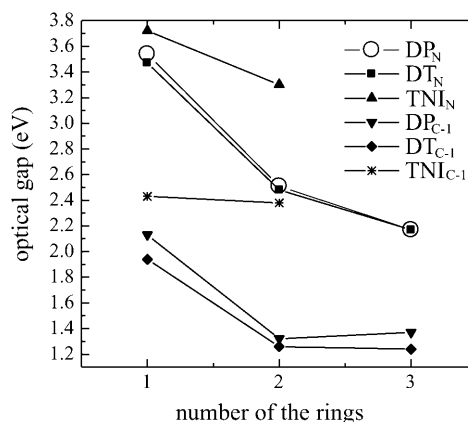


**Fig. 9** First optically active transition energies (eV) of DP, DT and TNI as a function of the numbers of oligomers

specific behavior is the same for the DP and DT density of states (Figs. 6 and 7).

In Fig. 9 we display the energy gap for the neutral and −1 charged systems by semiempirical methodology. Obviously the energy gap decreases as the chain length increases; however, we point out a very large red shift. The 2.55 eV energy gap obtained by Beggiato et al. for PDP/PVC is in excellent agreement with the 2.51 eV obtained in our calculation for the DP2 system. For DT the energy gap decreased from 3.47 eV to 2.21 eV for a trimer in a neutral system.

## Conclusions

In this work we have used semiempirical methods for geometry optimization coupled to spectroscopic methods for the study of the electronic structure of three conducting polymers. Our results suggest the conformational stability for all polymers studied.

This conclusion is corroborated by the high planarity of the whole system as well as the behavior of the heat of formation as a function of oligomer size.

Our calculations also suggest that there are no major changes in the basic geometry of the systems when doped, but the band gap can alter significantly. The results indicate a very fast saturation of the band gap with increasing length of the oligomer corroborated by polymer calculations.

The absorption spectra obtained for DP and DT emphasize the similarity between the electronic properties of both polymers. However the most relevant CI expansion coefficients for fully optimized polymers indicate a different optical behavior for the TNI system.

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