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Semiempirical and *ab initio* investigation of defects in PPV oligomers

J. Del Nero, C. P. de Melo*

Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, Pernambuco, Brazil

Abstract

We report a theoretical study of the excited states and other electronic properties of *para*-phenylenevinylene oligomers and related compounds which present conformational defects. Our results reveal the existence of different electronic delocalization patterns for the lowest singlet and triplet structures of these molecules. A similar behavior is also observed for the corresponding bond lengths

Keywords: Poly(phenylenevinylene), semiempirical methods, ab initio, absorption spectra.

1. Introduction

While conformational defects play an essential role in the transport and nonlinear optical properties of conjugated organic polymers, the absorption properties of these compounds are in large part determined by how different from the ground state are the electronic charge distributions of their low-lying excited states. Hence, it is important to assess how spatially localized excitations affect the charge distribution and the absorption spectrum of polymers. Due to its special luminescent properties, PPV has been extensively investigated [1-3] and has become the paradigm for such studies. For instance, in a theoretical/experimental study of excitons in PPV, D. Beljonne et al. have [1] concluded that the excited states of this polymer are affected by intrachain and interchain polarization effects and estimated the corresponding Davidov splitting to be on the order of 0.1-0.2 eV. Several other contributions in the literature [2,3] are dedicated to the analysis of the nature of the emission process in PPV related systems.

2. Methodology

We consider the two structures depicted in Fig. 1: "PPV.CH_3", a CH_3-capped *p*-phenylenevinylene dimer and the molecule with the same number of carbon atoms but presenting mirror-like symmetry ("PPV-mirror"). For these two 17-carbon atoms molecules, the semiempirical and *ab initio* geometries were fully optimized. The standard 3-21G* basis set was used for all *ab initio* calculations. Semiempirical geometric data used in this work were obtained from fully optimized by AM1 calculations [4]. For the *ab initio* [semiempirical] calculation we have used the Gaussian 94 [5] [MOPAC [6]] package. For obtaining the absorption spectra we have used the ZINDO program [7].

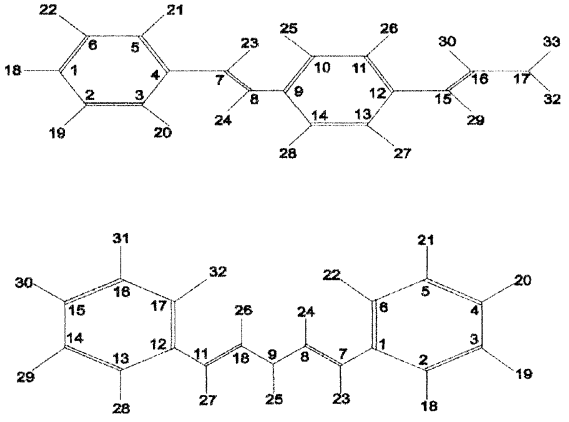

Fig. 1. PPV.CH_3 and PPV-mirror structures.

3. Results and Discussion

For PPV.CH_3, we present in Fig. 2(a) the net differences in the electronic charge distributions and the bond lengths between the ground state (a triplet) and the lowest singlet state. While upon excitation there are no substantial charge or conformational rearrangements for this molecule, as shown in Fig. 2(b) a much larger difference (please note the change in scale) is observed for PPV-mirror. A similar analysis can be made for the difference in bond lengths and

* Corresponding author: celso@df.ufpe.br Fax: 55-81-2710359

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charge distributions resulting from the excitation of these molecules to the first excited triplet state, as shown in Figs. 3(a)[3(b)] for PPV.CH_3 [PPV-mirror]. For the PPV.CH_3 molecule, while the excitation did not bring a remarkable change in the net charge distribution, there is a definite modification in the carbon-carbon distances in the vinylene units, as for example in the region around the 7,8 and 9 carbon atoms. As a general trend, in the PPV.CH_3 excited triplet state the C-C bonds are shorter and the C=C bonds larger than in the ground state, and the aromatic rings assume a more quinoidal character. Once again larger changes are observed for the PPV-mirror system. Comparatively, the trend to a quinoidal behavior is more pronounced in the PPV-mirror and is accompanied by a delocalization pattern over the entire oligomer.

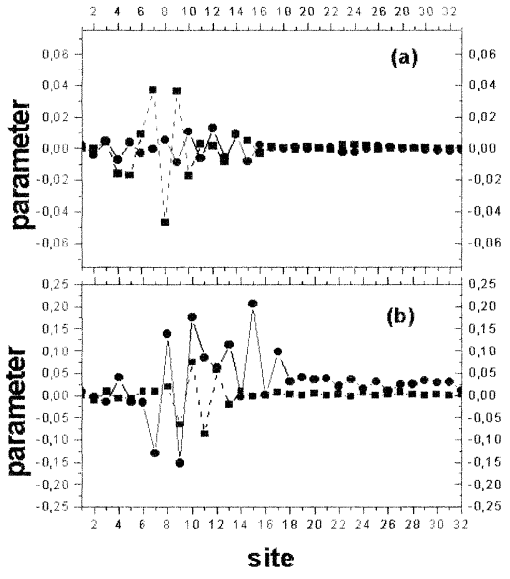

Fig. 2. Net differences in bond length (in Å, continuous line) and in electronic charge distributions (•) between the ground state and first singlet state of (a) PPV.CH_3 and (b) PPV-mirror molecules.

To examine the differences in the optical properties of these two molecules, the INDO/S-CI absorption spectra were calculated for the Hartree-Fock 3-21G* geometry, as shown in Fig. 4. For the PPV.CH_3 molecule, the most important feature is a preeminent peak at ≈ 325 nm (3.8 eV), which has an oscillator strength (o.s.) equal to 1.58 and is basically associated to the $-0.9|H\rightarrow L>$ transition. For this system the most important absorption lines correspond to excitations from the HOMO energy level.

The dashed line in Fig. 4 represents the corresponding absorption spectra for the PPV-mirror molecule. Although only a very small red shift is observed for the principal band, there is a fundamental difference in that two components, $-0.7|H\text{-}1\rightarrow H>$ and $0.6\ |H\rightarrow L>$, with o.s.=1.56 contribute to the transition. Also, at 700nm a very weak absorption is observed which correspond to the same transition as that of the strongest peak (o.s.=0.0033; $0.7\ |H\rightarrow L>$ and $0.5\ |H\text{-}1\rightarrow H>$). In general terms, one can say that, while the PPV.CH_3 absorption spectra is dominated by transitions from the HOMO energy level, for PPV-mirror the most important transitions involve the H-x (x=1,2,...) levels. (Also note that the ground state HOMO energy level is unpaired for the PPV-mirror molecule.)

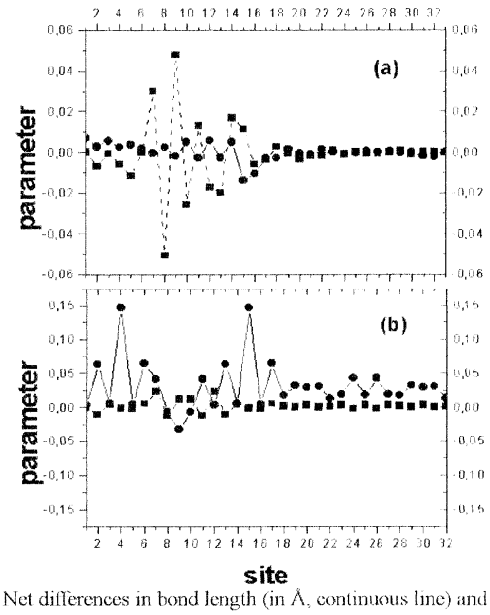

Fig. 3. Net differences in bond length (in Å, continuous line) and in electronic charge distributions (•) between the ground state and first excited triplet state of (a) PPV.CH_3 and (b) PPV-mirror molecules.

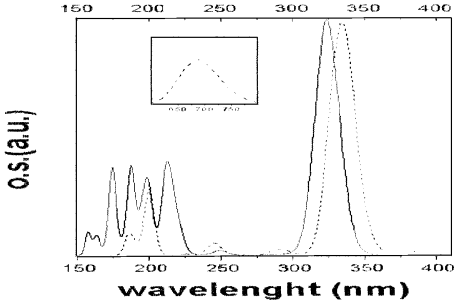

Fig. 4. ZINDO/S-CI theoretical absorption spectra of PPV.CH_3 (continuous line) and PPV-mirror (dashed line) molecules calculated for optimized 3-21G* *ab-initio* geometries.

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