A Theoretical Investigation of α,α'-Dimethyl end-capped Oligothiophenes: Structures, Vibrational Spectra and Conjugational Defects.

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Abstract

Ab initio quantum-chemical methods are used in the study of the effect of ionization on the geometries and vibrational spectra of a series of α,α'-dimethyl end-capped oligothiophenes (from dimer to hexamer). For that purpose we determine the geometric structures, vibrational frequencies, and infrared and Raman intensities of neutral, radical cationic and dicationic oligomers. These theoretical data, when combined with the results of the experimental studies, provide a complete picture of the vibrational structure of the neutral state of doped oligomers.

Keywords: (Ab initio quantum chemical methods and calculations, polythiophene and derivatives)

1. Introduction

Conjugated polymers have attracted considerable attention since the discovery of possible insulator-to-metal transitions following chemical or electrochemical doping. In order to get a deeper insight into the complex properties of the polymers, the study of oligomer analogs has emerged in the past few years as a very useful tool. Polythiophene and its oligomers have attracted much interest due to their good environmental stability in both the neutral and doped states. The large amount of studies dedicated to these compounds has opened the way to major developments in the fabrication of devices [1]. Moreover, the α,α'-dimethyl substitution has recently proved very effective in enhancing chemical stability and crystallinity without damaging the electronic response of the resulting material [2].

In this communication, the geometric and vibrational properties of a series of α,α'-dimethyl end-capped oligothiophenes are theoretically investigated in both neutral and oxidized states; the results are then compared to the experimental data.

2. Methodology

The methyl end-capped oligothiophenes investigated in this work contain from 2 to 6 thiophene units (from the dimer to the hexamer). The geometry optimizations were carried out using wave functions of the Hartree-Fock type: restricted (RHF) for closed-shell systems (the neutral and the dicationic systems), spin unrestricted (UHF) and spin restricted (ROHF) for open-shell systems (the radical cation systems). The basis set used in all calculations was the 6-31G** which is split valence and includes a set of d-polarization functions for heavy atoms and p-polarization functions for the hydrogens. We have initially limited our theoretical investigation to the all-anti planar conformations.

3. Results and Discussion

3.1. Geometric Structures

The 6-31G** optimized geometric structures of the neutral oligomers show that all the inner thiophene rings present almost the same geometry, which slightly differs from that found in the outer units due to the methyl-end substitution. Ab initio calculations are indicative of a degree of bond-length alternation of about 0.07 Å in good correspondence with the experimental data.

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opposite spatial and particle-hole symmetries. Eigenstates with particular quantum numbers are found by explicitly constructing trial states with these quantum numbers in the conjugate gradient algorithm of the DMRG method.

Table 2 lists the vertical excitation energies of the $1^1B_u^+$ and the $2^1A_g^+$ excitons, the lowest triplet exciton, $1^3B_g^+$, and the binding energy (BE) of the singlet exciton with respect to the band gap for various oligomer lengths. (The length of the oligomer refers to the number of phenylene units in the chain.) Although there is no room to present the results in detail here [6], the calculation of our reduced model for stilbene reproduces very well the exact $\nu-\gamma-\nu$ analysis of Soos et al. [7]. In particular, it reproduces the same ordering of states (excluding those resulting from the localized phenylene MOs), and the energy of the $1^1B_u^+$ and the $2^1A_g^+$ excitons is in close agreement (4.38 eV and 4.80 eV, respectively [7]).

We note that the $1^1B_u^+$ exciton approaches 2.7 eV for long chains, with a binding energy of 1.4 eV. There is excellent agreement with the experimental results for oligomers of up to 7 units (where we have taken the middle of the absorption peak as corresponding to the vertical transition). The experimental result for the 0-0 transition of ca. 2.3 eV in oriented stretched thin films is consistent with our prediction of 2.7 eV for the vertical transition for long chains, because first, polarisation effects in thin films will reduce the exciton energy by a few tenths of an eV, and second, there will be a further (small) reduction due to vibronic effects.

Table 2
Calculated vertical transitions in PPV. Also shown are the experimental $1^1B_u^+$ exciton results from (a) stilbene [8], (b) PPV oligomers [9] and (c) fluorescence from stretched, oriented PPV films [10].

<table>
<thead>
<tr>
<th>Length</th>
<th>$1^1B_u^+$</th>
<th>Exp</th>
<th>$2^1A_g^+$</th>
<th>$1^3B_g^+$</th>
<th>BE</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>4.33</td>
<td>1.55</td>
<td>4.60</td>
<td>2.36</td>
<td>3.12</td>
</tr>
<tr>
<td>3</td>
<td>3.66</td>
<td>3.50</td>
<td>3.63</td>
<td>1.97</td>
<td>2.35</td>
</tr>
<tr>
<td>4</td>
<td>3.32</td>
<td>3.20</td>
<td>3.23</td>
<td>1.80</td>
<td>1.99</td>
</tr>
<tr>
<td>5</td>
<td>3.11</td>
<td>3.05</td>
<td>3.03</td>
<td>1.71</td>
<td>1.80</td>
</tr>
<tr>
<td>6</td>
<td>2.99</td>
<td>2.95</td>
<td>2.92</td>
<td>1.66</td>
<td>1.68</td>
</tr>
<tr>
<td>7</td>
<td>2.71</td>
<td>2.90</td>
<td>2.86</td>
<td>1.63</td>
<td>1.61</td>
</tr>
<tr>
<td>10</td>
<td>2.79</td>
<td>-----</td>
<td>2.79</td>
<td>1.58</td>
<td>1.51</td>
</tr>
<tr>
<td>15</td>
<td>2.73</td>
<td>2.30</td>
<td>2.76</td>
<td>1.56</td>
<td>1.45</td>
</tr>
</tbody>
</table>

The lowest lying triplet is at 1.6 eV, which is consistent with the indirect measurements of the low lying triplet [11]. For long chains the $2^1A_g^+$ exciton lies less than 0.1 eV above the $1^1B_u^+$ exciton, however for shorter oligomers down to the trimer it lies slightly below the $1^1B_u^+$ exciton. This cross-over is probably an artefact of the neglect of longer range Coulomb interactions.

To illustrate this we present in table 3 exact model calculations of the excitation energies for the trimer when the next nearest neighbour Coulomb interactions are included. The changes in the excitation energies are less than 0.05 eV, however the $2^1A_g^+$ lies above the $1^1B_u^+$. Unfortunately, due to computing restrictions we cannot extend this calculation to longer oligomers.

Nonetheless, we expect the $2^1A_g^+$ exciton to lie close to and slightly above the $1^1B_u^+$ for most chain lengths. This result is supported by the location of the $2^1A_g^+$ state by two-photon fluorescence spectroscopy, which indicates that the vertical transition of the $1^1B_u^+$ and $2^1A_g^+$ states are virtually coincidental [12]. There is, however, much broader vibronic structure on the $1^1B_u^+$ peak, resulting in its 0-0 transition being ca. 0.3 eV lower than that for the $2^1A_g^+$ exciton.

Table 3
Calculated vertical transitions including next nearest neighbour Coulomb repulsion.

<table>
<thead>
<tr>
<th>Length</th>
<th>$1^1B_u^+$</th>
<th>$2^1A_g^+$</th>
<th>$1^3B_g^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3.66</td>
<td>3.68</td>
<td>1.98</td>
</tr>
</tbody>
</table>

The binding energy of 1.4 eV for long chains is larger than the reported value of ca. 0.4-1.0 eV for thin films [2]. However, it should be recalled that our result is for a single chain, and neglects polarisation effects. In a molecular crystal it is known that there is a 3 eV reduction in the band excitations compared to the gas phase, whereas there is a modest, ca. 0.3 eV, reduction in the exciton energy. Such a large reduction in the band excitations may also occur for PPV thin films. We intend to address the issue of polarisation effects on the exciton binding energy shortly. In addition to polarisation effects, polaron formation is also expected to reduce the gap for band excitations.

Finally, the consistency of our approach can be examined by considering the energy of the localised $f \rightarrow f'$ transition. This occurs at $\Delta \chi$, i.e. 5.8 eV, in good agreement with the experimental value of 6 eV, and which is independent of our choice of $t$.

References