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On the optical properties of thiophene oligomers: configuration interaction study on their ground (S_0) and first singlet excited (S_1) states

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Abstract

In this paper, oligothiophenes (thiophene)$_n$ ($n=2$–7) were optimized by using Hartree–Fock and restricted configuration interaction/singles (CIS) for their ground states (S_0) and first singlet excited states (S_1) geometries. This was followed by conformational and optical properties investigations using ab initio method in combination with CIS, TD-B3LYP and ZINDO approaches. It is found that bithiophene (BTP) and terthiophene (TTP) are nonplanar in the S_0 states, whereas they almost reach planarity in the S_1 states. The geometry relaxation after excitation contribute much to the Stokes shift observed in their absorption and emission spectra. The global potential energy surface (PES) studies show BTP and TTP have high inter-ring trosional flexibilities, in both the ground-states (S_0) and first excited-states (S_1); the *cis*-conformers should have evident contribution to the absorption and emission spectra of BTP and TTP molecules. These conclusions are also applicable to larger oligomers by a basic study extended to (thiophene)$_n$ ($n=4$–7).

Keywords: Oligothiophenes; Conformation; Excited state; Optical property

1. Introduction

Conjugated organic polymers are gaining increased interest because of their enormous potential in several fields, from light-emitting diodes to thin film transistors and sensing and actuating materials [1,2]. Among the materials of choice, thiophene oligomers have enjoyed much attention in the last few years for their p-type semiconductor properties, great chemical stability, and easy functionalization [3,4]. Though the first light emitting devices employing oligothiophenes have suffered from low photoluminescence efficiency, recently it has been demonstrated functionalized oligothiophenes give rise to new molecules with improved optical properties [5–7]. During the past decade, a vast amount of basic research [8–15] and a growing number of developments [16–19] in the field have been carried out and stressed on their potential for charge transport, nonlinear optics, and light emitting diode (LED) applications. Hence, the characterization of the electronic structure for the ground and excited states, of the conformational properties, and of the spectroscopic and photophysical behavior, are essential to engineer thiophene-based devices.

It is well-known that Quantum chemical calculations provide a lot of useful information that helps chemists to build up good relationship between electronic structures and optical properties of the materials. Recently, several comprehensive and convincing works have been done on the thiophene oligomers or polymers, which give an insight about the electronic properties in such polymers [8–12].

The interest of current work arises from two questions: The first, to the best of our knowledge, only oligomers with *trans* chains were considered in most of the calculations reported, while experimental data from electron diffraction performed for α-α'-bithiophene in the gas phase, showed the existence of *cis* and *trans* forms, with relative

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conformational weights of 44 and 56%, respectively [20]. Do the *cis* conformers have significantly influence on the optical properties (such as UV–vis absorption and emission spectra, etc.) of oligothiophenes, or they are neglectable? Recently, the electronic structures of poly (furan-thiophene-furan) oligomers, which are almost structurally the same as oligothiophene, were theoretically analyzed by R.L. Doretto and B. Laks [21], and they conclude that models based on oligomers with *trans* chains are not enough to explain the experimental spectra for doped polyfuran and polythiophene. So it is worth carrying out a conformational analysis to predict the equilibrium torsion angles and energy barriers, so as to get the relationship between the conformational and optical properties and provide a better answer to this question. The second, though vast of theoretical investigations have been conducted for the electronic ground state of oligothiophenes, comparably few calculations have been published for the excited states, and even few include changes in molecular structure upon excitation, i.e. optimization of excited-state geometries. But in fact, excited-state optimized geometries are important for the investigation of emission properties because structure relaxation after photo-excitation cannot reproduced by ground-state optimizations. Optimized ground-state geometries can act as the bases for the predication of absorption energies, but the optimization of the S_1 states is essential for the computation of emission energies, which are largely concerned for conjugated polymers in LED applications. To better understand the optical properties of thiophene oligomers, quantum chemistry calculation methods at relative high level are required to characterize their excited state potential energy surface.

Hence, in this paper, we analyze the global potential energy surfaces (PES) of both the ground state (S_0) and the first excited state (S_1) using the configuration interaction/singles (CIS) approach [22], in combination with Zerner's Intermediate Neglect of Diatomic Differential Overlap Hamiltonian (ZINDO) [23] and Time-Dependent Density Functional (TD-DFT) [24] methods, aim to contribute to the better understanding of the electronic and optical characteristics of oligothiophenes.

2. Method of calculation

Fully geometry optimization and conformational analysis were carried out on the conformers of bithiophene (BTP) and terthiophene (TTP) molecules. The S_0 geometries of the thiophene oligomers were optimized with the Hartree–Fock method at the 6-31G(d,p) level combining frequency analysis to confirm to be minima (NIMAG = 0) or transition states (NIMAG = 1) on the potential energy surface. The conformational analysis of all the oligomers was done by changing the torsional angle θ by stepsize = 5° for bithiophene (BTP) and θ and $\phi = 10°$ for terthiophene. During the potential energy surface scanning, tight convergence was used to provide sufficient accuracy.

In fact, many methods could be chosen during the ground-state geometry optimizing, such as the popular Density functional Theory (DFT), the Perturbation Theory (MP_n), etc. which can provide more accurate results than Hartree–Fock approach, due to the contribution of electron correlation energy, but their shortages in doing excited-state optimization make us turn to Hartree–Fock method. For the consistency of methodology, the restricted CIS/6-31G(d,p) approach was used to determine the excited state structures. The geometries of the S_1 states in CIS calculations have been fully optimized for all conformers and their stability were also determined by vibrational analysis. Same technique was used to obtain the potential energy surface for S_1 state.

To provide more convincing optical spectroscopic properties, the vertical transition energies from $S_0 \rightarrow S_1$ based on ground state conformers, corresponding to the experimental absorption peak, were also calculated by using ZINDO and Time-Dependent B3LYP/6-31G(d,p) approaches, in combination with the CIS method. The vertical transition energies from $S_1 \rightarrow S_0$, which denote the peak of fluorescence, were also done by using the same methods mentioned-above. In addition, the normalized absorption and fluorescence spectra were simulated by using the SWizard program, revision 4.12 [25], using the Gaussian model. The half-bandwidths, $\Delta_{1/2}$, were taken to be equal to 3000 cm^{-1}.

3. Results and discussions

3.1. Ground-state (S_0) geometries of BTP and TTP

Recently, the conformational analyses have been performed for thiophenes-base oligomers [26,27], but to our surprise, in most of calculations only the *trans*-conformers were stressed and the *cis*-conformers were almost totally ignored. Thus, two out-of-plane torsional conformers of BTP and six conformers of TTP, optimized at RHF/6-31G(d,p) level, were shown in Fig. 1, and their selected bond lengths and dihedral angles between inter-unit were listed in Table 1.

The stable conformers of BTP and TTP show good consistency in their inter-ring distances and dihedral angles, and the geometric variation is no more than 0.002 Å and 1.2°, respectively. The distances between two connected thiophenes, with average value 1.465 Å, represent typical single C–C bond characters; while the inter-ring dihedral angles, with average value 43.88° (*cis*) and 148.61° (*trans*), show evident angular distortions between connecting thiophene-planes, which further obstruct the formation of delocalized Π orbital among building blocks in thiophene oligomer at S_0 state. Among these conformers, the global minima of BTP and TTP, are *trans*-BTP (C_2 symmetry)