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ORIGINAL ARTICLE

The electro-optical and charge transport study of imidazolidin derivative: Quantum chemical investigations

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Abstract Imidazolidin derivatives gained significant attention in our daily life from better biological activity to the semiconducting materials. The present investigation deals with the in depth study of (Z)-2-sulfanylidene-5-(thiophen-2-ylmethylidene)imidazolidin-4-one (STMI) with respect to their structural, electronic, optical and charge transport properties as semiconducting material. The ground and first excited state geometries were optimized by applying density functional theory (DFT) and time dependent DFT, respectively. The light has been shed on the frontier molecular orbitals (FMOs) and observed comprehensible intramolecular charge transfer (ICT) from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs). The absorption, emission, ionization potentials (IP), electron affinities (EA), total and partial densities of states and structure-property relationship have been discussed. Finally, hole as well

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as electron reorganization energies, transfer integrals and intrinsic mobilities have been calculated then charge transport behavior of STMI was discussed, intensively.

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1. Introduction

The imidazolidin have distinctive properties which make them suitable for biological active compounds [1] and sensors [2]. These are also potential candidates for application in semiconducting devices [3–5], nitrogen-atom transfer agent [6] and optical absorption of fluorescent protein [7]. Moreover, thiophene based materials are auspicious because of the semiconducting nature, non-linear optical behavior [8] and efficient electron transport properties [9–11]. Previously, thiophene based heterocyclic compounds showed improved properties [12].

In the present study, we have selected (Z)-2-Sulfanylidene-5-(thiophen-2-ylmethylidene)imidazolidin-4-one (STMI) [13] with the aim to investigate the structural, electronic (highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), total/partial density of states (TDOS/PDOS)), optical (absorption (λ_{abs}) and fluorescence (λ_{fl}) spectra) and charge transport properties (ionization potentials (IPs), electron affinities (EAs), hole/electron reorganization energies ($\lambda_{\text{h}}/\lambda_{\text{e}}$), hole/electron transfer integrals ($V_{\text{h}}/V_{\text{e}}$)), hole and electron intrinsic mobilities. To the best of our knowledge no computational study has been carried out previously on the above selected system. This is the first time that we are going to conduct an in depth study of this STMI. The paper is structured as follows: Section 2 presents an outline of the density functional theory (DFT) and time dependent density functional theory (TDDFT), including the rationale for choosing the hybrid functional and the basis set; Section 3 explains the frontier molecular orbitals, electro-optical and charge transport properties; in Section 4 the major conclusions of the present investigation have been drawn.

2. Computational details

In previous studies it has been shown that the B3LYP functional is the best one among the standard DFT functionals for small organic molecules [14]. Previously the absorption spectra of hydrazone, azobenzene, anthraquinone, phenylamine and indigo have been calculated by B3LYP functional with an average deviation close to 0.20 eV [15]. Recently, different properties of materials have been computed by using B3LYP functional which were in good agreement with their experimental reported data. Moreover, the geometries, electro-optical and charge transport properties [16,17] have been studied at B3LYP/6-31G** and TD-B3LYP/6-31G** level of theories and found a reliable approach. The thiophene based materials have been studied and it was showed that B3LYP/6-31G** level of theory is optimal to reproduce the experimental evidences [18].

In the present study, ground state neutral, cation and anion geometries have been optimized by using restricted and unrestricted B3LYP/6-31G** level of theory. The excited state

geometry has been optimized at TDDFT [19] using TD-B3LYP/6-31G** level of theory. The absorption and emission spectra have been computed by TDDFT which has been proved an efficient approach [20].

The charge transfer rate can be described by Marcus theory via the following equation: [21]

$$W = V_2/h(\pi/\lambda k_B T)^{1/2} \exp(-\lambda k_B T) \quad (1)$$

here transfer integrals (V) and λ are two important parameters. The λ can be divided into inner λ and outer λ ; inner λ means the molecular geometry modifications when an electron is added or removed from a molecule while outer λ is modifications in the surrounding medium due to polarization effects. Here, we focus on inner λ which is further divided into two parts: $\lambda_{\text{rel}}^{(1)}$ and $\lambda_{\text{rel}}^{(2)}$, where $\lambda_{\text{rel}}^{(1)}$ corresponds to the geometry relaxation energy of one molecule from neutral to charged state, and $\lambda_{\text{rel}}^{(2)}$ corresponds to the geometry relaxation energy from charged to neutral state [22].

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} \quad (2)$$

In the evaluation of λ , the two terms were computed directly from the adiabatic potential energy surfaces [23].

$$\begin{aligned} \lambda &= \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} \\ &= [E^{(1)}(Y^+) - E^{(0)}(Y^+)] + [E^{(1)}(Y) - E^{(0)}(Y)] \end{aligned} \quad (3)$$

Here, $E^{(0)}(Y)$, $E^{(0)}(Y^+)$ are the ground-state energies of the neutral and charged states, $E^{(1)}(Y)$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(Y^+)$ is the energy of the charged state at the geometry of the optimized neutral molecule. It should be noted that the polarization effects from the surrounding molecules, as well as the charge reorientation, have been neglected to minimize the complications involved in the theoretical calculations [24]. Moreover, the IPa, IPv, EAa, EAv, λ (h) and λ (e) have been computed at B3LYP/6-31G** level of theory. All these calculations have been performed by using Gaussian09 package [25].

To calculate the transfer integrals, inter-molecular nearest-neighboring hopping pathways have been generated using the single-crystal structures. There are two widely employed approaches to obtain transfer integrals; one is Koopmans' theorem based method [26] and the other one is direct evaluation method for the frontier molecular orbitals (FMOs) [27,28]. By Koopmans' theorem the transfer integrals are computed as half of HOMO or LUMO levels splitting for electrons/holes. Bredas et al. [29] have extensively investigated the transport parameters by frontier orbital splitting on many conjugated systems and found it suitable. Similarly Valeev et al. [30] also cautioned recently that due to the crystal environment the site-energy correction should be taken into account when the dimer is not co-facially stacked. We have also used the direct approach [27,28] to investigate the transfer integrals in this study by using our homemade code [31]. The hole/electron transfer integrals in this approach can be expressed as:

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