C. R. Chimie 18 (2015) 1289–1296

Contents lists available at ScienceDirect

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In-depth quantum chemical investigation of electro-optical and charge-transport properties of *trans*-3-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)prop-2-enenitrile

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ARTICLE INFO

Article history:
Received 20 December 2014
Accepted after revision 21 May 2015
Available online 19 September 2015

Keywords:
Semiconductors
Density functional theory
Electro-optical properties
Charge-transport properties

ABSTRACT

The structural, electro-optical and charge-transport properties of compound *trans*-3-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)prop-2-enenitrile (DMNPN) were studied using quantum chemical methods. The neutral, cation and anion molecular geometries were optimized in the ground state using density functional theory (DFT) at the restricted and unrestricted B3LYP/6-31G** level of theory. The excited state geometries were optimized by applying time-dependent DFT at the TD-B3LYP/6-31G** level of theory. The absorption and fluorescence wavelengths were calculated at the TD-CAM-B3LYP/6-31G** and TD-LC-BLYP/6-31G** levels of theory. The distribution pattern of the charge densities on the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are discussed. Intramolecular charge transfer was observed from the dimethoxyphenyl to (nitrophenyl)prop-2-enenitrile moieties. The detailed charge-transport behavior of the DMNPN molecule is investigated based on its ionization potential, electron affinity, hole and electron reorganization energies, hole and electron-transfer integrals, and hole and electron intrinsic mobilities. The total/partial densities of states and structure–property relationship are discussed in detail. The higher computed hole intrinsic mobility than electron intrinsic mobility reveals that DMNPN is an efficient hole-transport material.

1. Introduction

The π-conjugated organic compounds have gained significant attention for use as biological active compounds [1], sensors [2], organic light-emitting diodes (OLEDs) [3,4], organic field-effect transistors (OFET) [5,6], and photovoltaics [7–9]. In the present study, we have selected *trans*-3-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)prop-2-enenitrile (DMNPN) (Fig. 1) with the goal of investigating the structural, electronic (highest occupied molecular orbitals [HOMOs], lowest unoccupied molecular orbitals [LUMOs], and total/partial density of states [TDOS/PDOS]), optical

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http://dx.doi.org/10.1016/j.crci.2015.05.020
1631-0748/

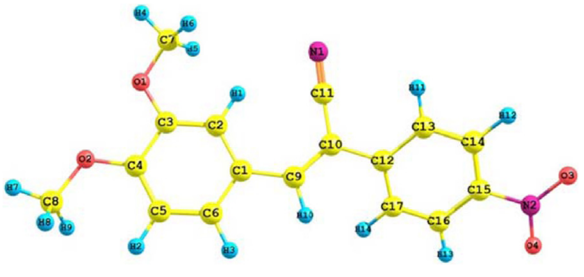

Fig. 1. (Color online.) The optimized labeled structure of *trans*-3-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)prop-2-enenitrile.

(absorption [λ_{abs}] and fluorescence [λ_{fl}] spectra) and charge-transport properties (vertical/adiabatic ionization potentials [IPsv/a], vertical/adiabatic electron affinities [EAsv/a], hole/electron reorganization energies [λ(h)/λ(e)], hole/electron-transfer integrals [V_h/V_e] and hole/electron intrinsic mobilities). Moreover, it is well known that a low hole/electron-injection barrier would lead to efficient charge-transport materials. We have shed light on the hole/electron-injection barrier with respect to gold electrodes, and we have discussed the corresponding injection behavior. To the best of our knowledge, no computational study has previously been performed on DMNPN. This is the first in-depth investigation of DMNPN. The paper is structured as follows: Section 2 presents an outline of 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 presents the frontier molecular orbitals and the electronic, optical and charge-transport properties; and Section 4 presents the major conclusions of the present investigation.

2. Computational details

Previously, it has been proven that DFT and TDDFT are reliable approaches to optimize and elucidate electro-optical and charge-transport properties and that they offer an accurate way to reproduce experimental data [10–17]. It has been shown in previous studies that B3LYP is a suitable and consistent functional to calculate the properties of interest for both small and large π-conjugated organic compounds [18–20]. In particular, it has reproduced the experimental data for compounds such as azo dyes [21,22], triphenylamine dyes [23], chemosensors [24], phthalocyanines [25], chromene derivatives [26] and oxadiazoles [27]. Preat et al. optimized the geometries at the B3LYP/6-31G** level of theory to investigate charge injection and found that this level of theory is adequate [28]. Huong et al. studied the electronic and charge-transport properties of naphtho[2,3-b]thiophene derivatives at the B3LYP/6-31G** and PBE0/6-31G** levels of theory and concluded that B3LYP/6-31G** is a decent method to replicate the experimental data [29]. Recently, experimental data on the electronic and charge-transport properties of dianthra[2,3-b:20,30-f]thieno[3,2-b]thiophene was reproduced using the B3LYP/6-31G** level of theory [30]. Additionally, geometric, electro-optical and charge-transport properties have been studied at the B3LYP/6-31G** level of theory, and it was proven that this level of theory is a reliable approach [31]. Scalmani and co-workers calculated the absorption and emission wavelengths by TDDFT [32].

In the present study, ground-state geometries have been optimized at the DFT/B3LYP/6-31G** level of theory. The excited state geometries have been optimized at TDDFT using the TD-B3LYP/6-31G** level of theory. The absorption and emission spectra have been computed by TDDFT, which has been proven an efficient approach. The absorption spectra were calculated by the TD-CAM-BLYP/6-31G** and TD-LC-BLYP/6-31G** levels of theory at the optimized geometry at the B3LYP/6-31G** level, and the fluorescence wavelengths were computed at the same levels of theory, as were the absorption spectra at the optimized geometry at the TD-B3LYP/6-31G** level.

The intrinsic mobility (μ) can be calculated by the Einstein equation as:

$$\mu = eD/K_BT, \tag{1}$$

where μ, D, e, T and K_B are the carrier mobility, charge-diffusion constant, electronic charge, temperature and Boltzmann constant, respectively.

The charge transfer rate can be described by Marcus theory via the following equation [33]:

$$W = V^2/h(\pi/\lambda k_BT)^{1/2}\exp(-\lambda/4k_BT), \tag{2}$$

where the electronic coupling constant/transfer integral (V) and reorganization energy (λ) are the main parameters that determine the self-exchange electron-transfer rates and, subsequently, the charge mobility. For efficient charge transport, higher V and lower λ values are necessary.

The λ term can be divided into an inner λ (the molecular geometry relaxation when an electron is added or removed from a molecule) and outer λ (the alterations in the surrounding medium due to polarization effects). We calculated the inner λ, which reveals the geometric variations in the molecules. The λ term can be divided into two parts: $\lambda_{rel}^{(1)}$ and $\lambda_{rel}^{(2)}$, where $\lambda_{rel}^{(1)}$ and $\lambda_{rel}^{(2)}$ correspond to the geometry relaxation energy of a molecule from neutral to a charged state, and from charged to a neutral state, respectively [5].

$$\lambda = \lambda_{rel}^{(1)} + \lambda_{rel}^{(2)} \tag{3}$$

These terms were calculated from the adiabatic potential energy surfaces [34]:

$$\begin{aligned}\lambda &= \lambda_{rel}^{(1)} + \lambda_{rel}^{(2)} \\ &= \left[E^{(1)}\left(\mathrm{N}^{+/-}\right) - E^{(0)}\left(\mathrm{N}^{+/-}\right)\right] + \left[E^{(1)}(\mathrm{N}) - E^{(0)}(\mathrm{N})\right],\end{aligned} \tag{4}$$

where $E^{(0)}(\mathrm{N})$ and $E^{(0)}(\mathrm{N}^{+/-})$ are the ground-state energies of the neutral and charged states, $E^{(1)}(\mathrm{N})$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(\mathrm{N}^{+/-})$ is the energy of the charged state at the geometry of the optimized neutral molecule. All calculations were performed using the Gaussian09 package [35].

In 2006, Valeev et al. concluded that the site-energy correction should be taken into account [36]. This can be achieved using single-crystal V values that have been computed by a direct approach [37–42] by our homemade code [43–46]. The hole as well as electron-transfer