DFT and TD-DFT study on the optical and electronic properties of derivatives of 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene

Fuyu Sun \(^a\), Ruifa Jin \(^b\,*\)

\(^a\) College of Physical and Electronic and Information Engineering, Chifeng University, Chifeng 024000, China
\(^b\) College of Chemistry and Chemical Engineering, Chifeng University, Chifeng 024000, China

Received 31 May 2013; accepted 19 November 2013

Abstract A series of 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene derivatives has been designed to explore their optical, electronic, and charge transport properties for luminescent and charge transport materials. The frontier molecular orbitals (FMOs) analysis have turned out that the vertical electronic transitions of absorption and emission are characterized as intramolecular charge transfer (ICT). Both \(\lambda_{abs}\) and \(\lambda_{fl}\) of the derivatives with 2-thiophene and 2-1H-pyrrole fragments show bathochromic shifts compared with parent compound 2-pyridyl substituted derivative (I), while the corresponding values of the substituted derivatives with 4-pyridyl, 2-pyrazine, and phenyl fragments are similar to those of parent compound I. Our results suggest that the substituted derivatives with 4-pyridyl, 2-pyrazine, phenyl, 2-thiophene, and 2-1H-pyrrole fragments are expected to be promising candidates for luminescent materials for OLEDs. Furthermore, the substituted derivatives with 4-pyridyl, 2-pyrazine, phenyl, and 2-thiophene fragments can be used as promising electron transport materials, while the substituted derivatives with 2-pyrazine and 2-1H-pyrrole fragments can be used as promising hole transport materials. In addition, the substituted derivative with 2-pyrazine fragment may be used as good candidate for ambipolar charge transport material for OLEDs.

© 2013 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

The development of organic light-emitting diodes (OLEDs) has attracted great attention during the past decade because of their potential applications in a new generation of display and lighting technologies (Müllen and Scherf, 2006; Walzer et al., 2007; Grimsdale et al., 2009; Katz et al., 2001). 1,3,4-Oxadiazole derivatives are highly attractive compounds in the research and development of materials for OLEDs devices since these compounds possess high electron-accepting properties and...
exhibit strong fluorescence with high quantum yields (Ono et al., 2008; Hughes and Bryce, 2005; Hegelund et al., 2007). Thus, compounds containing 1,3,4-oxadiazole fragments have been used as electron-transporting layers, hole-blocking layers, and light-emission layers in OLEDs devices (Wang et al., 1999; Antoniadis et al., 1998; Hu et al., 2003). Many strategies have been used to improve the photoluminescent efficiency of OLEDs. The optimization method to improve the performance of OLEDs is that which introduced electron transport moieties into the main luminophor (Feng et al., 2008; Jin et al., 2003). Several 1,3,4-oxadiazole derivatives have been actually used as electron-injection materials to improve the balance of charge carrier and to increase the photon/electron quantum efficiency (Zhang et al., 1994). Charge transport is one of the most important properties in the performance of OLEDs (Tang and VanSlyke, 1987). The location of the electron–hole recombination zone where excitons are created and light is emitted is directly affected by the mobilities of electrons and holes in the materials (Lin et al., 2005). 1,3,4-Oxadiazole derivatives are believed to be excellent charge transport materials (Wang et al., 1999; Antoniadis et al., 1998; Hu et al., 2003). Understanding the relationship between molecular structure and charge transport property of a material is a key point for providing guideline for device design, and a great theoretical research effort is currently being made in this regard (Sitha et al., 2005; Raghunath et al., 2006).

Two novel compounds of symmetrical bis-1,3,4-oxadiazoles were prepared by Chen et al. (2007). It was found that these compounds exhibit strong fluorescence with high quantum yields. Herein we report the investigation of both the optical and electronic properties from the theoretical point of view for this system. To investigate the substituent effects, several 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene derivatives (2–6) with different heterocyclic or phenyl groups, as shown in Scheme 1, have been designed to provide a demonstration for the rational design of new candidates for luminescent and electron transport materials for OLEDs.

2. Computational methods

All calculations have been performed using the Gaussian 09 package (Frisch et al., 2009). Optimizations have been carried out without symmetry constraints. In our previous study, the B3LYP functional was successfully employed to calculate charge transport parameters for 1,3,4-oxadiazole derivatives (Jin and Zhang, 2011). Recently, the same functional was successfully used to calculate the charge transport parameters for OLEDs’ materials (Irfan and Zhang, 2009; Liu et al., 2008). For these reasons, the geometries of 1–6 in ground states (S0) have been optimized by using the hybrid B3LYP functional with 6–31G(d) basis set. The structures in the first excited single states (S1) for 1–6 have been optimized at the TD-B3LYP level using the 6-31G(d) basis set. The harmonic vibrational frequency calculations using same methods as for the geometry optimizations were used to ascertain the presence of a local minimum. Absorption and fluorescence spectra of 1–6 have been predicted using the TD-PBE0/6-31+G(d,p) method based on the S0 and S1 optimized geometries, respectively. The DMF solvent effect also has been considered using the Polarized Continuum Model (PCM) (Foresman et al., 1992).

The charge transfer rate can be described by Marcus theory (Marcus, 1993 and Marcus, 1964) via the following equation:

$$K = \left( \frac{V^2}{\hbar} \right) \left( \frac{\pi}{\hbar k_B T} \right)^{1/2} \exp\left( -\lambda / 4k_B T \right)$$

(1)

where $T$ is the temperature, $k_B$ is the Boltzmann constant, $\lambda$ represents the reorganization energy due to geometric relaxation accompanying charge transfer, and $V$ is the electronic coupling matrix element (transfer integral) between the two adjacent species dictated largely by orbital overlap. It is clear that two key parameters are the reorganization energy and electronic coupling matrix element, which have a dominant impact on the charge transfer rate, especially the former. In this paper, we focus on their reorganization energies $\lambda$ to investigate their charge transport properties. Generally, the $\lambda$ can be divided into two parts, external reorganization energy ($\lambda_{ext}$) and internal reorganization energy ($\lambda_{int}$). The $\lambda_{ext}$ represents the effect of polarized medium on charge transfer; on the other hand, $\lambda_{int}$ is a measure of structural change between ionic and neutral states (Lemaur et al., 2005; Hutchinson et al., 2005). Our designed molecules are used as charge transport materials for OLEDs in the solid film; the dielectric constant of the medium for the molecules is low. The computed values of the external reorganization energy in pure organic condensed phases are not only small but also are much smaller than their internal counterparts (Cheung and Troisi, 2010; Martinelli et al., 2010). The reorganization energy could be an important factor that governs the mobility of charge carriers (Berlin et al., 2003). Therefore, we only pay attention to the discussion of the $\lambda_{int}$ of the isolated active organic systems due to ignoring any environmental relaxation and changes in this paper. The reorganization energy for electron ($\lambda_e$) and hole ($\lambda_h$) of the molecules have been predicted from the single point energy

![Scheme 1](image-url)
at the B3LYP/6-31G(d,p) level based on the B3LYP/6-31G(d) optimized neutral, cationic, and anionic geometries. Hence, the reorganization energies for $\lambda_a$ and $\lambda_h$ transfer can be defined as (Start, 1997):

$$\lambda_a = (E_{0+}^a - E_{-}^-) + (E_{0}^a - E_0^a)$$

$$\lambda_h = (E_{0+}^h - E_{-}^-) + (E_{0}^h - E_0^h)$$

where $E_{0+}^a$ ($E_{-}^-$) is the energy of the cation (anion) calculated with the optimized structure of the neutral molecule. Similarly, $E_{0+}^h$ ($E_{-}^-)$ is the energy of the cation (anion) calculated with the optimized cation (anion) structure. $E_{0}^a$ ($E_{0}^h)$ is the energy of the neutral molecule calculated at the cationic (anionic) state. Finally, $E_0^a$ is the energy of the neutral molecule at the ground state.

To predict the stability of 1–6 from a viewpoint of molecular orbital theory, the absolute hardness, $\eta$, of 1–6 was calculated using operational definitions (Cornard and Lapouge, 2006) given by equations below:

$$\eta = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right) = \frac{1}{2} \left( \frac{\partial E}{\partial N^2} \right) = \frac{IP - EA}{2}$$

where $\mu$ is the chemical potential and $N$ is the total electron number. The values for adiabatic ionization potential (IP) and adiabatic electron affinity (EA) of the molecules were calculated as described in the equations below:

$$IP = E(M^+) - E(M^0)$$

$$EA = E(M^0) - E(M^-)$$

where $E(M^0)$, $E(M^+)$, and $E(M^-)$ are the total energies of the neutral, cationic, and anionic forms of the molecules at the B3LYP/6-31G(d) level, respectively.

### 3. Results and discussion

#### 3.1. Electronic transition

The origin of the geometric difference introduced by excitation can be explained, at least in qualitative terms, by analyzing the change in the bonding character of the orbital involved in the electronic transition for each pair of bonded atoms (Forés et al., 1999). It is useful to examine the frontier molecular orbitals (FMOs) of the compounds under investigation. The qualitative molecular orbital representations of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for 1–6 in $S_0$ are shown in Fig. 1. When the HOMO $\rightarrow$ LUMO transition involves the loss of the bonding character of a bond (or the gain of antibonding character), the bond concerned is lengthened and vice versa. As shown in Fig. 1, both the HOMOs and LUMOs have $\pi$ symmetry. The $S_0 \rightarrow S_1$ excitation process can be mainly assigned to HOMO $\rightarrow$ LUMO transition, which corresponds to a $\pi \rightarrow \pi^*$ excited singlet state. One can see that the HOMOs and LUMOs are delocalized on the whole conjugated molecules for investigated compounds as shown in Fig. 1. It indicates that the spatial overlap between the HOMO and LUMO is strong, which may result in stronger optical absorption corresponding to the transition from HOMO to LUMO. Furthermore, the distribution patterns of HOMOs and LUMOs also provide a remarkable signature for the charge-transfer character of the vertical $S_0 \rightarrow S_1$ transition. It is well known that the photophysical properties of intramolecular charge transfer are highly dependent on the electron donor/acceptor strength [34]. Analysis of the FMOs for 1–6 indicates that the excitation of the electron from the HOMO to the LUMO leads the electronic density to flow mainly from the side groups to the two 1,3,4-oxadiazole and benzene rings.

#### 3.2. Spectral simulation

TD-PBE0/6-31 + G(d,p) has been used on the basis of the optimized geometry to obtain the nature and the energy of the electronic transitions of 1–6. Table 1 presents the absorption wavelengths ($\lambda_{abs}$), the oscillator strength ($f$), the main assignment, and excitation energies ($E$) of 1–6. As shown in Table 1, the predicted $\lambda_{abs}$ values of 1 both in gas phase and in DMF are in excellent agreement with experimental results (Chen et al., 2007), with the maximum deviation being 25 and 28 nm (2392 and 2656 cm$^{-1}$), respectively. As mentioned above, the transitions correspond to the excitation from the HOMO to LUMO. Inspection of Table 1 reveals clearly that the $\lambda_{abs}$ values of 2–4 are similar to that of 1, the deviations are 2, 6, and 4 nm (178, 522, and 350 cm$^{-1}$), respectively. The $\lambda_{abs}$ values of 5 and 6 have slight bathochromic shifts compared with that of 1, the deviations being 22 and 32 nm (1829 and 2588 cm$^{-1}$), respectively. It suggests that the 4-pyryil, phenyl, and 2-pyrazine substitutions do not significantly affect the absorption spectra, while the 2-thiophene and 2-H-pyrrole substitutions show bathochromic shifts compared with that of 1. Moreover, we find in Table 1 that the $f$ values of 2–6 are similar to that of 1 except the $f$ value of 6 which is
An electronic excitation results in some electron density redistribution that affects the molecules. Changes in the bond lengths in the excited states with respect to their ground state geometries can be ascribed to the changes in bonding character. Comparing the geometry of 1 in S0 with that in S1 state (for atoms labeling, see Scheme 1), the bond lengths of C2−C4, C5−C6, C1−C7, C4−C12, N2−N6, and N13−N14 are shortened, while the corresponding bond lengths of C1−C2, C3−C6, C4−C5, C7−N6, C10−N6, C12−N13, and C15−N14 are stretched. Furthermore, the dihedral angles between 2-pyridyl and 1,3,4-oxadiazole rings and between benzene and 1,3,4-oxadiazole rings in both S0 and S1 are almost 0 or ±180°. It suggests stronger coupling among the 2-pyridyl, 1,3,4-oxidiazole, and benzene rings in 1. Similar phenomena are found for 2-6. It indicates stronger coupling among the side groups, 1,3,4-oxadiazole, and benzene rings. As a consequence, the electron can move more fluently from the electron-donating side groups to the two 1,3,4-oxadiazole and benzene rings. Therefore, the intramolecular charge transfer transition for 1-6 in S1 becomes much easier than those in S0, resulting in the bathochromic shift in their fluorescence spectra compared with their absorption spectra.

3.3. Charge transport property and stability

The calculated reorganization energies for hole and electron are listed in Table 3. It is well-known that the lower the reorganization energy values, the higher the charge transfer rate (Ran et al., 2009; Zou et al., 2008). The reorganization energies calculated for hole λh of 3 and 6 are smaller than that of N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl)-4,4′-diamine (TPD) which is a typical hole transport material λh = 0.290 eV (Gruhn et al., 2002). This implies that the hole transfer rates of 3 and 6 might be higher than that of TPD. Thus, 3 and 6 could be hole transport materials from the stand point of the smaller reorganization energy. The λe values of 2-5 are smaller than that of tris(8-hydroxyquinolino)aluminum(III) (Alq3), which is a typical electron transport material λe = 0.276 eV (Marcus, 1964). This indicates that their electron transfer rates might be higher than that of Alq3. The λe values of 2-5 are smaller than those of their λh values, suggesting that the carrier mobility of the hole is larger than that of the electron. Hence, 2-5 can be used as promising electron transport materials in the OLEDs from the stand point of the smaller reorganization energy. In addition, the difference between the λh and λe values for 3 is 0.035 eV, implying that 3 has better equilibrium properties for hole- and electron-transport. Therefore, 3 may be used as good candidate for ambipolar charge transport material.

![Table 1](https://example.com/table1.png)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Main assignment</th>
<th>E (eV)</th>
<th>λabs (nm)</th>
<th>f</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H → L (0.66)</td>
<td>3.63</td>
<td>336 (339)</td>
<td>1.43</td>
<td>311</td>
</tr>
<tr>
<td>2</td>
<td>H → L (0.66)</td>
<td>3.71</td>
<td>334 (338)</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H → L (0.66)</td>
<td>3.63</td>
<td>342 (346)</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H → L (0.66)</td>
<td>3.64</td>
<td>340 (345)</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H → L (0.66)</td>
<td>3.46</td>
<td>358 (365)</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>H → L (0.67)</td>
<td>3.37</td>
<td>368 (384)</td>
<td>1.22</td>
<td></td>
</tr>
</tbody>
</table>

* Data in parenthesis were obtained considering PCM solvent effects.

* Experimental data for 1 in DMF solvent from Chen et al. (2007).

![Table 2](https://example.com/table2.png)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Main assignment</th>
<th>E (eV)</th>
<th>λabs (nm)</th>
<th>f</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H → L (0.70)</td>
<td>3.14</td>
<td>395 (402)</td>
<td>1.60</td>
<td>367</td>
</tr>
<tr>
<td>2</td>
<td>H → L (0.70)</td>
<td>3.17</td>
<td>391 (400)</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H → L (0.70)</td>
<td>3.13</td>
<td>396 (405)</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H → L (0.70)</td>
<td>3.12</td>
<td>398 (408)</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H → L (0.70)</td>
<td>2.98</td>
<td>416 (428)</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>H → L (0.70)</td>
<td>2.99</td>
<td>415 (435)</td>
<td>1.42</td>
<td></td>
</tr>
</tbody>
</table>

* Data in parenthesis were obtained considering PCM solvent effects.

* Experimental data for 1 in DMF solvent from Chen et al. (2007).

![Table 3](https://example.com/table3.png)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λh (eV)</th>
<th>λe (eV)</th>
<th>η (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.304</td>
<td>0.281</td>
<td>3.082</td>
</tr>
<tr>
<td>2</td>
<td>0.307</td>
<td>0.270</td>
<td>3.109</td>
</tr>
<tr>
<td>3</td>
<td>0.275</td>
<td>0.240</td>
<td>3.062</td>
</tr>
<tr>
<td>4</td>
<td>0.298</td>
<td>0.260</td>
<td>3.057</td>
</tr>
<tr>
<td>5</td>
<td>0.308</td>
<td>0.233</td>
<td>2.949</td>
</tr>
<tr>
<td>6</td>
<td>0.269</td>
<td>0.299</td>
<td>2.941</td>
</tr>
</tbody>
</table>
As the stability is a useful criterion to evaluate the nature of devices for charge transport and luminescent materials, the $\eta$ values of investigated molecules were calculated and shown in Table 3. The $\eta$ is the resistance of the chemical potential to change in the number of electrons. Inspection of Table 3 reveals clearly that the $\eta$ values of 2-6 are similar to that of 1, indicating that the stabilities of 2-6 are equal to that of 1. Furthermore, the electrostatic surface potentials (Irfan and Zhang, 2009) of investigated molecules were calculated as shown in Fig. 2. As shown in Fig. 2, the partial negative charges are on the 1,3,4-oxadiazole ring while the partial positive charges are on the phenyl and two side fragments for 1-6. The profiles of electron densities of 2-6 are similar to that of 1, implying that the substitution effect does not significantly affect the stability of the substituted derivatives. These results show qualitative agreement with the results based on the absolute hardness.

4. Conclusion

Our computational results predicted the electronic and optical properties for a number of newly designed 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene derivatives. On the basis of the equilibrium geometries, the effect of the substitution on the absorption and emission spectra is evaluated for the substituted derivatives, confirming a new set of candidates for emitting materials. The FMO analysis has turned out that the vertical electronic transitions of absorption and emission of 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene derivatives are characterized as intramolecular charge transfer. The study of substituent effect by introducing different heterocyclic or phenyl groups revealed that the substitution effect does not significantly affect the stability of the substituted derivatives. Both $\lambda_{abs}$ and $\lambda_{em}$ of the derivatives with 2-thiophene and 2-1H-pyrrole fragments show bathochromic shifts compared with parent compound 2-pyridyl substituted derivative (1), while the corresponding values of the substituted derivatives with 4-pyridyl, 2-pyrazine, and phenyl fragments are similar to that of parent compound 1. Our results suggest that the substituted derivatives with 4-pyridyl, 2-pyrazine, phenyl, 2-thiophene, and 2-1H-pyrrole fragments are expected to be promising candidates for luminescent materials for OLEDs. Furthermore, the substituted derivatives with 4-pyridyl, 2-pyrazine, phenyl, and 2-thiophene fragments can be used as promising electron transport materials, while the substituted derivatives with 2-pyrazine and 2-1H-pyrrole fragments can be used as promising hole transport materials. In addition, the substituted derivative with 2-pyrazine fragment may be used as good candidate for ambipolar charge transport material for OLEDs.

Acknowledgments

Financial support from the Natural Science Foundation of Inner Mongolia Autonomous Region (2011ZD02) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2013.11.037.

References


Please cite this article in press as: Sun, F., Jin, R. DFT and TD-DFT study on the optical and electronic properties of derivatives of 1,4-bis(2-substituted-1,3,4-oxadiazole)benzene. Arabian Journal of Chemistry (2013), http://dx.doi.org/10.1016/j.arabjc.2013.11.037