

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Characterization and optical properties of novel unsymmetrical stilbene-based 1,3,4-oxadiazole derivatives

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ARTICLE INFO

Article history: Received 22 February 2012 Received in revised form 12 March 2012 Accepted 3 April 2012 Available online 23 April 2012

Keywords: Synthesis 1,3,4-Oxadiazole Stilbene Fluorescence

ABSTRACT

A series of novel unsymmetrical stilbene-based 1,3,4-oxadiazole derivatives were efficiently synthesized by a four-pots reaction sequence. All of the title compounds were characterized by MS, ¹H-NMR and elemental analysis. UV–Vis absorption and fluorescence emission spectra of the compounds were investigated in dilute chloroform solution; the compounds exhibit strong blue-green fluorescence ranged from 397 to 499 nm and show potential for application in organic optical materials.

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Introduction

Stilbene derivatives are well known not only for their considerable biological and medical activities, such as anti-microbial and insecticidal effects, vasodilation action, and insect baculovirus synergists [1–5], but also for their interesting features of the stilbene derivatives which are their effects on light and witness applications in main chain liquid crystalline polymers [6–8], optical brighteners [9–11] and PPV-type electroluminescent copolymer [12]. Moreover, stilbene derivatives show distinctive blue fluorescence emission properties to be used in organic electroluminescent (EL) materials [13–15].

1,3,4-Oxadiazoles are a class of heterocycles with a broad spectrum of biological activities, which have attracted significant interest in medicinal and pesticide chemistry [16–20], and the development of materials for organic electroluminescent (EL) devices since these compounds possess high electron-accepting properties and display strong fluorescence with high quantum yield [21–25].

Recently, there is great interest to increase the structural or spatial dimensions of π -conjugated molecules in order to tune and acquire more favorable physical properties [26]. Based on the fact that the 1,3,4-oxadiazole unit has good hole-transporting

* Corresponding author. Tel./fax: +86 20 87110234. E-mail address: daohanghe@yahoo.com.cn (D.-H. He). capability, durability and thermal stability, especially high fluorescent quantum yields, it is envisioned that the introduction of the 1,3,4-oxadiazole unit into the stilbene skeleton can improve their photo-electric properties, durability, and thermal stability [27–28]. In this paper, we report the synthesis of six novel 1,3,4oxadiazole-based stilbene derivatives via the Wittig-Horner reaction with good overall yield. All of the title compounds were characterized on the basis of MS, ¹H-NMR and elemental analysis. The photophysical processes of the title compounds are investigated by UV–Vis absorption and fluorescence emission spectra in chloroform solution. The synthetic route is outlined in Scheme 1 (see the Supplementary material).

Experimental

Chemical and instrument

Melting points were determined using RY-1 melting point apparatus and were uncorrected. ¹H-NMR spectra were recorded in CDCl₃ on a Bruker AVANCE-400 MHz NMR spectrometer using TMS as an internal standard. Mass spectra were obtained with a HPLC/MS LCQDECA spectrometer (APCI). Elemental analyses were performed on a Vario ELIII CHN elemental analyzer. UV–Vis absorption spectra were recorded on a Hitachi UV-3010 spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature. The purity of the compounds was confirmed by TLC on silica gel 'G'-coated glass plates.

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Scheme 1. The synthetic route of the title compounds.

Synthesis

Typical procedure for the synthesis of compounds 1, 2 and 3

Intermediates of compounds **1**, **2** and **3** were prepared by the reported methods [29].

Typical procedure for the synthesis of compounds **4**

To a stirred solution of aromatic aldehydes (1.7 mmol) and the intermediate **3** (0.9 g, 1.7 mmol) in anhydrous N,N-dimethylformamide (15 mL) under nitrogen atmosphere was added dropwise a solution of *t*-BuOK (2 g, 3%) in ethanol. The reaction proceeded at room temperature overnight. Then the resulting mixture was filtered and washed with ethanol. The residue was recrystallized from ethanol/DMSO, giving compounds **4a–g**. Analytical and spectral data were obtained from all compounds (see the Supplementary material).

Results and discussion

The synthesis and characterization

A series of novel unsymmetrical stilbene-based 1,3,4-oxadiazole derivatives were synthesized by a four-pots reaction of the oxidative cyclization, bromination, esterification, and Wittig-Horner reaction. The title compounds were characterized with spectral and analytical methods. 1,3,4-Oxadiazole is the electron-accepting five-membered hetero-aromatic unit containing two imine -C=N- groups, because of the electron-withdrawing ability of the imine -C=N- group. The ¹H-NMR spectra of compounds **4a–h** show that the proton chemical shifts of phenyl ring, naphthalene nucleus and anthracene nucleus ranged from δ 7.31 to δ 8.32 ppm, δ 7.50 to δ 8.23 ppm and δ 7.45 to δ 8.45, respectively. A doublet of CH=CH was obtained between δ 7.15 and δ 8.10 ppm. According to the chemical shifts and coupling constant (16.0–16.6 Hz), it was determined that two protons had different chemical environments because of the effect of substituents belonging to the trans-structure, which could stably exist in

stilbene derivatives. The mass spectra of compounds **4a–f** show the intense molecular ion peaks and the characteristic ion peaks. These molecular ion peaks were consistent with their molecular formula.

Optical properties

Table 1 shows the UV-Vis absorption and fluorescence emission spectra in dilute chloroform solution. The UV-Vis absorption spectra and fluorescence spectra of the compounds are shown in Fig. 1 and Fig. 2 (in 10^{-5} mol L⁻¹ chloroform solution). The absorption spectra of compounds **4a-h** show maximum absorption (λ_{max}) at 309– 343 nm. The maximum absorption peaks (λ_{abs}), which can be attributed to the charge-transfer type $\pi - \pi *$ electronic transitions, situate in 311-342 nm in solution. The charge-transfer absorption band of the compounds strongly depends on the conjugation length of molecular structure. Compared with the fluorescence characteristic emission wavelengths of the title compounds, the maximum fluorescence emission wavelength of compounds 4e and 4h had a greater shift toward higher wavelengths than the other compounds owing to increasing the conjugation length of the molecule, which would make the electron-pair in the highest occupied molecular orbit possess a lower energy; the electron-pair could be excited easily to transit into a higher orbit. Compounds 4a, 4b, 4c and 4f had the different maximum emission wavelength peaks, indicating that the halogen substituents have a great effect on their electronic energy levels. The fluorescence quantum yields $\Phi_x = (A_s \times F_x \times n_x^2 \times n_y^2)$ $(\Phi_s)/(A_x \times F_s \times n_s^2)$ where A is the absorbance at the excitation wavelength. F the area under the fluorescence curve and n the refraction index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol (Φ = 0.89) was taken as the standard [30]. It can be seen that compounds **4d** and **4g** had a greater fluorescence quantum yield, which can be explained by the conjugative effect. The molecular structure containing naphthalene nucleus can increase the conjugation length and rigid structure of the molecule. As can be seen in Table 1,

Absorption and fluorescence characteristics of the title compounds in dilute chloroform solution at room temperature (concentration: 1×10^{-5} mol L⁻¹).

Compound	λ_{\max} (nm)	$\times 10E^{-4}\varepsilon_{max}(L \text{ mol}^{-1} \text{ cm}^{-1})$	λ_{ex} (nm)	$\lambda_{\rm em} ({\rm nm})$	Stokes shifts (nm)	$\Phi_{\rm x}{}^{ m a}$
4a	343	6.40	344	397	53	0.82
4b	333	5.74	346	398	54	0.78
4c	333	4.53	348	402	54	0.67
4d	342	3.21	358	436	78	0.74
4e	314	3.15	317	498	181	0.23
4f	342	5.53	350	403	53	0.69
4g	342	3.09	364	438	74	0.73
4h	309	3.68	322	499	177	0.21

^a Fluorescence quantum yield.



Fig. 1. The UV–Vis absorption spectra of target compounds $(1\times 10^{-5}\mbox{ mol }L^{-1}$ in chloroform).



Fig. 2. The fluorescence emission spectra of target compounds (1 \times 10 $^{-5}$ mol L^{-1} in chloroform).

compounds **4e** and **4h** had a smaller fluorescence quantum yield, which maybe attributed to the difference in the steric hindrance imposed by the 1,3,4-oxadiazole, anthracene skeleton, π -bridges, linkages and dihedral angles between two units that seem to affect the planarity of the molecules. The influence of solution on the fluorescence intensities of the compounds **4a** and **4b** was investigated. Fig. 3 showed fluorescence emission spectra of the two compounds in chloroform, THF and DMF (concentration: 1×10^{-5} mol L⁻¹). We



Fig. 3. The fluorescence emission spectra of the compounds **4a** and **4b** in chloroform, THF and DMF at room temperature (concentration: 1.0×10^{-5} mol L⁻¹).



Fig. 4. Fluorescence spectra of **4a** and **4b** at different concentration of THF; $1,1.0 \times 10^{-4}$ mol L⁻¹; $2, 1.0 \times 10^{-5}$ mol L⁻¹; $3, 1.0 \times 10^{-6}$ mol L⁻¹.

could see that the emission wavelengths and fluorescence intensity of the two compounds were different in three solutions at the same concentration. All these indicated that the solution molecules had strong coordination effect and the environment played an important role in determining the fluorescence intensity of the compounds. The influence of concentration on fluorescence intensity of the two compounds was also studied (Fig. 4). It can be seen that the emission intensity of fluorescence was greatly decreased with gradual increasing in concentration of 4a and 4b in THF.

Conclusion

A series of novel unsymmetrical stilbene-based 1,3,4-oxadiazole derivatives were synthesized, characterized by spectral studies and their fluorescence spectra were recorded in order to study the changes in the photophysical properties with structural modifications. The results showed that the compounds exhibited strong blue fluorescence emission. It can be concluded that the absorption and fluorescence characteristic of the new target compounds show a significant dependence on their molecular structure. The influence of solution on the fluorescence intensities of the compounds indicated that the solutions and the environment played an important role in determining the fluorescence intensity of the compounds.

Acknowledgements

The authors thank the Fundamental Research Funds for the Central Universities (No. 2012ZM0035) and Guangdong Provincial Natural Science Foundation of China (No. 04300531) for the financial assistance.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.04.013.

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