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Synthesis, crystal structures and photoluminescence of 7-(*N*,*N*′-diethylamino)-3-phenylcoumarin derivatives

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ABSTRACT

Two new coumarin derivatives, 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, were synthesized successfully. Their structures were verified by single crystal X-ray crystallography. The UV–vis absorption and fluorescence of the compounds were discussed. The compounds exhibit strong blue emission under ultraviolet light excitation. The molecular structures, the lowest energy transitions and the UV–vis spectra of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin have been studied with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-31G(d) level.

1. Introduction

Coumarin and its derivatives exist widely in plant, and have been broadly studied due to their applications in biological, chemical and physical fields. For example, they have wonderful biological and medical activity [1–3], such as antitumor and anticoagulant effect [4]. Furthermore, this series of compounds has prominent optical properties, such as an extended spectral range, large Stokes shifts, high quantum yields, superior photostability and good solubility in common solvents [5–9]. As a result, the coumarin derivatives are widely used as laser dyes [10,11], ionophores, colorants, non-linear optical chromophores [12], fluorescent probes [13] and fluorescent whiteners [14]. Since Tang et al. [15] first used 3-(2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6) as an electroluminescent (EL) material successfully, coumarin dyes have attracted much interest owing to their potential application in organic light-emitting diodes (OLEDs) [6,16–20].

Although several coumarin derivatives which possess good photoluminescence and electroluminescence properties were investigated in our laboratory [5–9], there remain some interests in the molecular design and synthesis of new coumarin derivatives with high quantum yield of fluorescence and greater stability. The present work is a continuation of our search for high efficient emitting fluorescent materials, two new coumarin derivatives, 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, were synthesized. They contained electron-releasing moieties (i.e., diethylamino) in 7-positions, but the difference between them is that in 3-position of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin is phenol moiety, in the same position of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin is bromophenyl moiety. These moieties could increase the conjugative effect and surely benefit the fluorescence of the compounds. We synthesize them in order to understand the effect of substituents in coumarin skeleton on the photoluminescent properties of coumarin.

2. Experimental

2.1. Materials and methods

4-(*N*,*N*′-Diethylamino)salicylaldehyde from Zhejiang Huadee Dyestuff Chemical Co. Ltd. (China) was recrystallized from ethanol. 4-Hydroxyphenylacetonitrile was purchased from Jinan Haohua Industrial Co. Ltd. (China). 4-Bromophenylacetonitrile was analytical grade reagent from Alfa Aesar China (Tianjin) Co. Ltd. The other solvents were analytical grade reagents.

IR spectra (400–4000 cm^{-1}) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. ^1H NMR spectra were obtained on Unity Varian-500 MHz. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental

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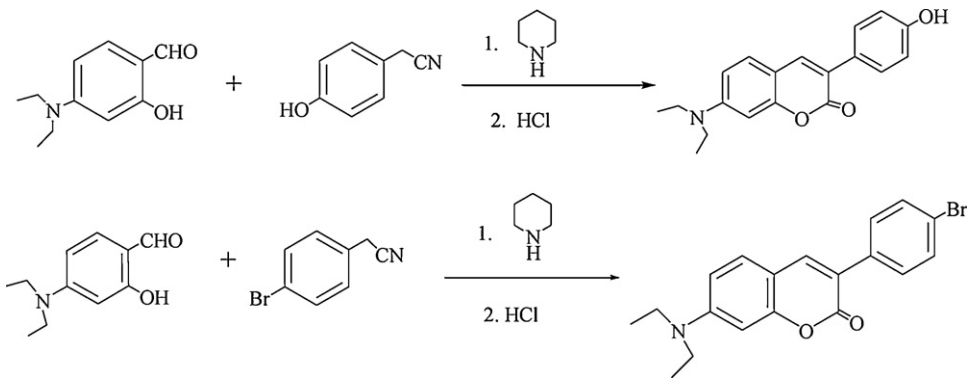

Scheme 1. Synthetic route of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin.

analysis instrument. UV–vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin Elmer LS-55 spectrometer, respectively.

2.2. Synthesis and characterization of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin

The synthetic routes were shown in Scheme 1.

7.2 g (37.6 mmol) of 4-(*N*,*N*′-diethylamino)salicylaldehyde and 5.0 g (37.6 mmol) of 4-hydroxyphenylacetonitrile were dissolved in 30 mL of ethanol at room temperature and treated with piperidine (0.5 mL). The reaction mixture was held for 24 h at 80 °C, treated with HCl (50 mL, 7%) and boiled for 8–10 h to hydrolyze the iminocoumarin. After the reaction was finished, the acidic solution was neutralised with aqueous ammonia until the pH was 7. Some of solvent was removed by rotary evaporation and the resulting mixture was poured into 100 mL water and extracted with dichlormethane (3× 60 mL). The organic phase was washed with water (2× 50 mL) and dried over anhydrous $MgSO_4$. After filtering, the filtrate was evaporated to dryness under reduced pressure. The crude was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:5, v/v) as the eluent to give 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (6.16 g, 53.4%). m.p. 187–189 °C. IR (KBr pellet, cm^{-1}): 3298 (ν_{O-H}, phenol), 1714 ($\nu_{C=O}$, lactone), 1618 ($\nu_{C=C}$), 1519, 1520, 1355, 1235. ^1H NMR (Actone-D6, δ, ppm): 8.415 (s, 1H, 4-H), 7.839 (s, 1H, –OH), 7.604 (d, J = 7.2 Hz, 2H, Aryl-H), 7.460 (d, J = 8.8 Hz, 1H, Aryl-H), 6.868 (d, J = 7.2 Hz, 2H, Aryl-H), 6.734 (d, J = 8.8 Hz, 1H, Aryl-H), 6.525 (s, 1H, Aryl-H), 3.525 (m, 4H, N-CH_2), 1.219 (t, J = 6.8 Hz, 6H, CH_3). Anal. Calc. for $C_{19}H_{19}NO_3$ (%): C, 73.77; H, 6.19; N, 4.53. Found: C, 74.20; H, 6.30; N, 4.23.

5.0 g (25.9 mmol) of 4-(*N*,*N*′-diethylamino)salicylaldehyde, 5.2 g (26.5 mmol) of 4-bromophenylacetonitrile were placed into a round bottom flask (100 mL) and dissolved in 50 mL of ethanol. 2 mL of piperidine was added into the mixed reaction, and then the mixture was refluxed with stirring for 48 h. After the reaction was complete, 10 mL of aqueous solution of HCl was added into reaction, and then the mixture was refluxed with stirring for 24 h. The resulting solution was evaporated to dryness under reduced pressure. The precipitate was recrystallized from ethyl acetate, and 6.01 g of brown crystal was 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin obtained (yield 63%). m.p.: 159–160 °C. IR (KBr pellet, cm^{-1}): 3421(ν_{N-H}), 1716 ($\nu_{C=O}$), 1128 (ν_{C-O-C}), 719 (ν_{C-Br}). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.472–7.678 (m, 4H, phenyl-H), 7.261–7.315 (t, 1H, coumarin skeleton), 6.514–6.610 (m, 3H, coumarin skeleton), 3.364–3.450 (m, 4H, CH_2), 1.167–1.236 (m, 6H, CH_3). Anal. Calc. for $C_{19}H_{18}NO_2Br$ (%): C, 61.30; H, 4.87; N, 3.76. Found: C, 61.83; H, 4.60; N, 3.43.

2.3. Crystallography

Suitable single crystal of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were obtained by evaporation of ethyl acetate solution, respectively. The diffraction data were collected with a Bruker Smart Apex CCD area detector using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 20 °C. The structures were solved by using the program SHELXL and Fourier difference techniques, and refined by full-matrix least-squares method on F^2. All hydrogen atoms were added theoretically. The crystal and experimental data of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin are shown in Table 1. The selected bond lengths and bond angles of the compounds are listed in Tables 2 and 3, respectively.

2.4. Quantum chemical calculations

The structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were optimized by semi-empirical density functional theory (DFT) using a B3LYP/6-31G(d) basis set. The structural energies of the compounds were calculated at B3LYP/6-31G(d) levels. The structure optimizations and energy calculations were performed with the GAUSSIAN 98 program.

3. Results and discussion

3.1. X-ray crystal structures

The structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were measured by X-ray crystallography. Their crystal structures and packing diagrams are given in Figs. 1–4 , respectively. The crystal data and experimental details are shown in Table 1. The selected bond lengths and bond angles of the compounds are listed in Table 2.

The crystal of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin belongs to the triclinic space group *P*-1. As shown in Fig. 1, there is an asymmetric unit consisted of two molecules in crystal structure of the compound due to the different space configuration of hydroxy groups in 4′-position of benzene ring, these two molecules are space conformers. In every molecule, the phenol ring is not coplanar with the coumarin ring and the dihedral angle is 38.13°. As shown in Fig. 2, the distance of the coumarin rings between two adjacent molecules along *a*-axis in crystal lattice is about 3.8 Å, which means weak intermolecular π–π stacking interaction between 7-(*N*,*N*′-diethylamino)-3-(4-