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Synthesis, crystal structure and photoluminescent behaviors of 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8]coumarin

Tianzhi Yu [a,*], Yuling Zhao [b], Xiansheng Ding [a], Duowang Fan [a], Long Qian [a], Wenkui Dong [b]

[a] *Key Laboratory of Opto-Electronic Technology and Intelligent Control (Lanzhou Jiaotong University), Ministry of Education, Lanzhou 730070, China*
[b] *School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China*

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Abstract

A novel coumarin derivative containing an electron-transporting moiety (benzotriazole), 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8]coumarin (BMBC), was synthesized and characterized by element analysis, ^{1}H NMR, FT-IR and UV–vis absorption spectra, TG-DTA and single crystal X-ray crystallography. Crystallographic data reveal a dihedral angle of 60.4° between the benzocoumarin and benzotriazole rings, which is attributed to the spatial hindrance of a 4-positioned methyl group. The photoluminescent behaviors of BMBC doped in PMMA were discussed. The compound exhibits a strong blue emission under ultraviolet light excitation. The ground-state geometries, the lowest energy transition and the UV–vis spectrum of BMBC have been studied with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-31G(d) level, showing that the calculation outcomes are in good agreement with experimental data.

Keywords: Synthesis; Crystal structure; Photoluminescence; Coumarin derivative; UV–vis spectrum

1. Introduction

Coumarin and its derivatives occur widely in nature, and have been extensively exploited in biological, chemical and physical fields. Coumarins have outstanding optical properties, including an extended spectral range, high quantum yields, superior photostability and good solubility in common solvents, many natural and synthetic coumarin derivatives are widely used as laser dyes [1,2], nonlinear optical chromophores [3], fluorescent whiteners [4], as well as fluorescent labels and probes for physiological measurement [5–8]. Since Tang et al. [9] first used 3-(2-benzothiazolyl)-7-diehylaminocoumarin (coumarin 6) as a electroluminescent (EL) material successfully, coumarin derivatives have attracted much interest owing to their potential application in organic light-emitting diodes (OLEDs), many efforts have been devoted to explore new EL materials [10–12]. Coumarin derivatives are easily quenching in solid state, so as EL materials they were always doped in polymer host [9,13–15].

Recently, we synthesized a novel coumarin derivative, 3-(1-benzotriazole)-4-methyl-coumarin (BMC), by introducing an electron-accepting benzotriazole in 3-positions of the coumarin ring, which showed ultraviolet emission with a peak at 386 nm [16]. In this communication, we report the results for the synthesis, characterization and photoluminescent (PL) properties of a new coumarin derivative, 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8]coumarin (BMBC). We synthesized it in order to understand the effect of substituting the hydrogen of coumarin skeleton by groups on the photoluminescent properties of coumarin.

2. Experimental

2.1. Materials and methods

2-Acetyl-1-naphthol from Acros Organics and 1H-benzotriazole (BTA) from Aldrich were used without further purification. Chloroacetic acid and Phosphorus oxychloride were analytical grade reagents from Tanjin Fuchen Chemical Reagent Factory. Phosphorus oxychloride was dried and redistilled before using.

* Corresponding author. Tel.: +86 931 4956935; fax: +86 931 4956030.
E-mail address: ytz823@hotmail.com (T. Yu).

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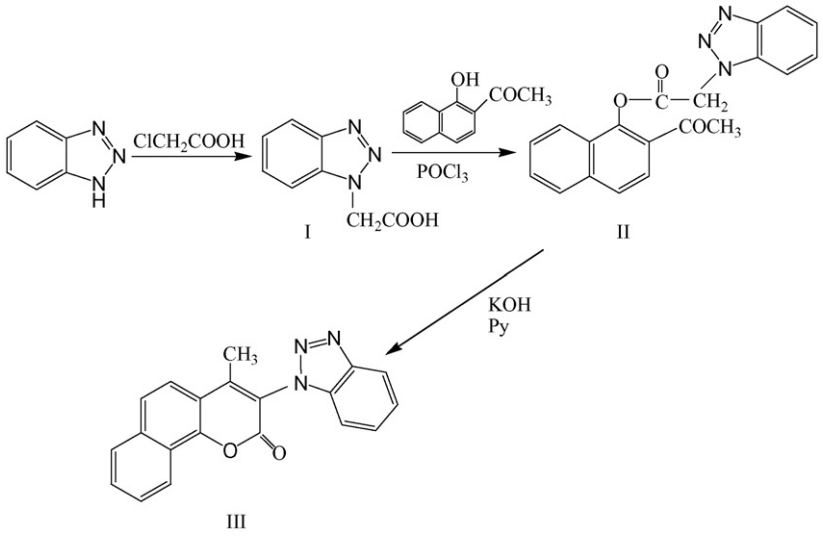

Scheme 1. Synthetic route of 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8]coumarin.

IR spectra (400–4000 cm^{-1}) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. ^{1}H NMR spectra were obtained on Unity Varian-500 MHz. UV–vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and on a Perkin-Elmer LS-55 spectrometer, respectively. The thermogravimetry (TG) and differential thermal analysis (DTA) were recorded on a Shimadzu DT-40 thermal analysis instrument. Melting points were measured by using a X-4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

2.2. Synthesis and characterization of 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8] coumarin (BMBC)

The synthetic route was shown in Scheme 1.

2.2.1. (1-Benzotriazolyl) acetic acid (I)

It was synthesized from ^{1}H-benzotriazole and chloroacetic acid according to the method reported earlier [16].

2.2.2. (2-Acetyl) naphthol (1-benzotriazolyl) acetate (II)

Ten gram (0.0537 mol) of 2-acetyl-1-naphthol and 10.24 g (0.0578 mol) of (1-benzotriazolyl) acetic acid (I) were dissolved in 100 ml of dry pyridine. Then 6 ml of phosphorus oxychloride was added stepwise with magnetic stirring under 5–10 °C, and the mixture was stirred for 10 h at room temperature. After the reaction was complete, the mixture was poured into an aqueous solution of HCl containing fragment ice with vigorous stirring, and white precipitate was produced. The precipitate was filtered, and washed successively with diluted aqueous solution of $NaHCO_3$ (10%) and distilled water, respectively. After ethanol recrystallization, filtration and drying in vacuum, 13.71 g (74.0%) of white flocculent crystals was obtained. mp 166–168 °C. Anal. Calc. for $C_{20}H_{15}N_3O_3$ (%): C, 69.56; H, 4.38; N, 12.17. Found: C, 69.43; H, 4.61; N, 12.25. IR (KBr pellet, cm^{-1}): 1766 (ester C=O), 1676 (ketone C=O), 2991, 2953, 1466, 1357, 1185.

2.2.3. 3-(1H-benzotriazol-1-yl)-4-methyl-benzo[7,8]coumarin (III)

Into a one-neck, 100 ml round-bottomed flask were placed 6.9 g (0.02 mol) of (2-acetyl) naphthol (1-benzotriazolyl) acetate and 50 ml of dry pyridine, then 1.4 g (0.025 mol) of potassium hydroxide was added stepwise and the reaction mixture was stirred vigorously for 5 h at room temperature. After completing, the mixture was poured into the aqueous solution of HCl containing fragment ice with vigorous stirring, and primrose yellow precipitate was formed. Then the crude product was filtered and washed with distilled water, and purified with recrystallization from ethanol to yield 5.13 g (78.44%) of primrose yellow crystalline solid. mp 262–264 °C. Anal. Calc. for $C_{20}H_{13}N_3O_2$ (%): C, 73.38; H, 4.00; N, 12.84. Found: C, 73.05; H, 4.13; N, 12.37. IR (KBr pellet, cm^{-1}): 1727 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 2.407 m (s, 3H, CH_3), 7.256–8.646 (m, 10H, Ar–H).

2.3. Crystallography

Suitable single crystal of BMBC was obtained by evaporation of acetone solution. 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 structure was 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 are shown in Table 1.

2.4. Quantum chemical calculations

The structure of BMBC was optimized by semiempirical density functional theory (DFT) using a B3LYP/6-31G(d)