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Synthesis, crystal structure and photoluminescence of 3-(1-benzotriazole)-4-methyl-coumarin

Tianzhi Yu *, Yuling Zhao, Duowang Fan

Key Laboratory of Opto-Electronic Technology and Intelligent Control (Lanzhou jiaotong University),
Ministry of Education, Lanzhou 730070, China

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Abstract

A novel coumarin derivative containing an electron-transporting moiety (benzotriazole), 3-(1-benzotriazole)-4-methyl-coumarin (BMC), was synthesized from starting substances, i.e. benzotriazole and 2-hydroxyacetophenone. The compound structure was verified by FT-IR, ^{1}H NMR, element analysis and single crystal X-ray crystallography. Crystallographic data reveal a dihedral angle of 108° between the coumarin and benzotriazole rings, which is attributed to the spatial hindrance of a 4-positioned methyl group. The fluorescence and UV–vis absorption of BMC were discussed. The compound exhibits a strong UV emission peak at 385 nm under 360 nm excitation. The molecular structure of BMC was optimized using density functional theory (DFT) at B3LYP/6-31G(d) level, showing that the optimized geometric parameters are in good agreement with experimental data. In addition, the HOMO and LUMO levels of BMC were deduced.

Keywords: Benzotriazole; Coumarin derivative; Crystal structure; Photoluminescence

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1. Introduction

Coumarin and its derivatives have been extensively studied due to their commercial applications in several fields. They possess excellent biological activity, such as anticancer and anticoagulant activity [1]. Moreover, this series of compounds has outstanding optical properties, including an extended spectral range, high quantum yields, superior photostability and good solubility in common solvents. So these compounds are widely used as laser dyes [2–3], nonlinear optical chromophores [4], fluorescent whiteners [5], as well as fluorescent labels and probes for physiological measurement [6–9]. Another feature of the coumarin derivatives is that photophysical and spectroscopic properties can be readily modified by the introduction of substituents in the coumarin ring, giving themselves more flexibility to fit well in various applications [10–13]. For example, electron-releasing substituents in 3- or 7- positions not only bring bathochromic shifts of the absorption edge towards long wavelength side, but also enhance band intensity (in absorption and fluorescence). Since 3-(2-benzothiazolyl)-7-diehylaminocoumarin (coumarin 6) is widely used as an emissive dopant in organic light–emitting diodes (OLEDs) based on polymers [14–16] and small molecules [17–18], coumarin derivatives have attracted much attention due to their potential application for OLEDs [19–20].

In this study, we report on the synthesis and photophysical properties of a novel coumarin derivative, 3-(1-benzotriazole)-4-methyl-coumarin (BMC), containing an electron-accepting moiety (benzotriazole). Benzotriazole moiety is chosen as a substituent for the following reasons. First, UV emission of the coumarins was less studied in spite of their well-known fluorescence in visible range; second, the electron-accepting benzotriazole moiety surely benefits the electron-transporting properties of the compounds [21].

2. Experimental

2.1. Materials and methods

2-Hydroxyacetophenone 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

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

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Chemical Reagent Factory. Phosphorus oxychloride was dried and redistilled before using.

IR spectra (400–4000 cm^{-1}) were measured on a Nicolet Magna FT-IR spectrophotometer. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. 1H NMR spectra were obtained on Unity Varian-500MHz. UV–vis absorption and fluorescence spectra were recorded on a Hitachi UV-3010PC spectrometer and on a Hitachi MPF-4 spectrometer, respectively. Melting points were observed by the capillary tube method.

2.2. *(1-Benzotriazolyl) acetic acid (**1**)*

13.1 g (0.11 mol) of 1H-benzotriazole and 9.45 g (0.1 mol) of chloroacetic acid were dissolved in dry toluene (100 ml), and then the solution was heated to 130 °C and refluxed for 18 h with magnetic stirring. After cooling the solution to room temperature, it was poured into a concentrated aqueous solution of $NaHCO_3$. The water phase was separated and extracted with dichloromethane three times. The aqueous solution was adjusted to a pH of 4 by adding 2N HCl and allowed to sit overnight. After this, the precipitate was filtered and washed successively with distilled water and methanol. The product was dried under reduced pressure and purified with re-crystallization from methanol to yield 10.6 g (60%) of white crystalline solid; m.p. 213–215 °C (Ref.[22]: 214–216 °C).

2.3. *(2-Acetyl) phenol 2-(1-benzotriazolyl) acetate (**2**)*

To a stirred solution of 10 g (0.073 mol) of 2-hydroxyacetophenone and 13.99 g (0.079 mol) of (1-benzotriazolyl) Acetic acid (1) in 100 ml of dry pyridine cooled at 5–10 °C, 6 ml of phosphorus oxychloride was added stepwise. The mixture was stired for 10 h at room temperature. After the reaction was complete, the mixture was allowed to sit overnight. Then the mixture was poured into an aqueous solution of HCl containing fragment ice with vigorous stirring, and a 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, 17.35 g (80%) of primrose fine crystals were obtained. m.p. 136–138 °C (Lit. [23]: 137–138 °C).

2.4. *3-(1-Benzotriazole)-4-methyl-coumarin (**3**)*

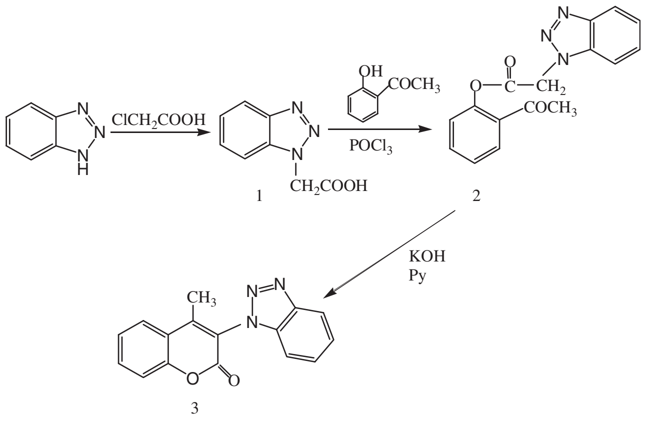
6 g (0.02 mol) of (2-acetyl) phenol 2-(1-benzotriazolyl) acetate was dissolved in 50 ml of dry pyridine, then 1.4 g (0.025 mol) of potassium hydroxide was added stepwise and the reaction mixture was stirred vigorously for 5 h at room temperature. The mixture turned brown during the reaction, and the solution became ropy. After completing, the mixture was poured into the aqueous solution of HCl containing fragment ice with vigorous stirring and a yellow precipitate was formed. Then the crude product was filtered and washed with distilled water and purified with recrystallization from ethanol to yield 4.61 g (81.9%) of yellow crystalline solid. m.p. 172–174 °C. Anal. Calc. for $C_{16}H_{11}N_3O_2$ (%): C, 69.31; H, 4.00; N, 15.15. Found: C, 69.16; H, 3.94; N, 15.04. IR (KBr pellet, cm^{-1}): 1718 ($\nu_{C=O}$). 1H NMR (500 MHz, $CDCl_3$, δ, ppm): 2.32m (s, 3H, CH_3), 7.25–8.21 (m, 8H, Ar-H). The compound is soluble in common organic solvents such as chloroform, acetone and tetrahydrofuran.

Table 1
Crystal data and structure refinement for BMC

Empirical formula	$C_{16}H_{11}N_3O_2$
Formula weight	277.28
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	$a=18.303$ (3) Å, $\alpha=90^{\circ}$ $b=5.4256$ (8) Å, $\beta=90^{\circ}$ $c=13.4928$ (19) Å, $\gamma=90^{\circ}$
Volume (Å^3), Z	1339.9 (3), 4
Density (calculated) (g/cm^3)	1.375
Absorption coefficient (mm^{-1})	0.094
F (000)	576
Crystal size (mm)	0.31 × 0.11 × 0.08
θ range for data collected (°)	2.23 to 26.04
Limiting indices	$-20\leq h\leq 22$, $-6\leq k\leq 6$, $-13\leq l\leq 16$
Reflections collected	7024
Independent reflections	2295 ($R_{\mathrm{int}}=0.0372$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9922 and 0.9716
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2295/1/191
Goodness-of-fit on F^2	1.024
Final R indices [$I>2\sigma(I)$]	$R_1=0.0494$, $wR_2=0.1120$
R indices (all data)	$R_1=0.0700$, $wR_2=0.1238$
Largest diff. Peak and hole (e Å^{-3})	0.147 and −0.125

2.5. *Crystallography*

A suitable single crystal of BMC was obtained from methanol solution. The diffraction data were collected with a Bruker Smart Apex CCD area detector using a graphite monochromated Mo Kα radiation ($\lambda=0.71073$ 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.



Scheme 1. Synthetic route to the titled compound **3**.