Synthesis of New Benzocoumaryl Oxadiazolyls as Strong Blue-Green Fluorescent Brighteners

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ABSTRACT
The benzocoumarin-3-ethylcarboxylate 2 on treatment with hydrazine hydrate at room temperature afforded benzocoumarin-3-carbohydrazide 3. The compound 3 served as key intermediate in the synthesis of the title compounds. Thus, benzocoumarin-1,3,4-oxadiazolyls 6a–e were obtained in two ways, i.e. one by direct cyclization of benzocoumarin-3-carboxylate 3 with substituted benzoic acids in POCl₃ and the other by cyclization of Schiff bases of compounds 5a–e in the presence of bromine/acetic acid. The structures of the novel benzocoumaryl oxadiazolyls 6a–e were confirmed by spectral analysis. The benzocoumarin-1,3,4-oxadiazolyls 6a–e exhibited strong blue and green fluorescent properties. The Stoke’s shifts range from 43 to 165 nm. The absorption and fluorescence maxima of the benzocoumaryl oxadiazolyls showed good bathochromic shifts.

KEYWORDS
Benzocoumarin-3-ethylcarboxylate, benzocoumaryl oxadiazolyls, fluorescent brighteners.

1. Introduction
Coumarin dyes has been of significant interest for the application of dye-sensitized solar cells and many organic devices in the application of light-emitting diodes.¹ The performance of these devices depend mainly on the properties of the structure of coumarin dyes. Hence, many coumarin dyes were designed and found to be successful as photosensitzers in dye sensitized solar cell (DSSC).² Further, Daniel et al. reported the Light-Harvesting Arrays with Ru(II) complexes of 1,10-phenanthroline derivatives of coumarin donors as metal-to-ligand charge transfer (MLCT) acceptors.³ An injection and recombination limitation of coumarin dye-sensitized solar cell upon device performance was reported by Koops et al. 2010.⁴ Wang et al. have reported that NKX-2753 and NKX-2586 (Structures 1 and 2) coumarin dyes as an alternative sensitizers to Ruthenium complexes in DSSCs.⁵ Beside this, in support of our investigation, benz-annulated coumarin derivatives have also found to be useful dyes in organic light-emitting devices and were used as electron-transporting emitters.⁶,⁷ Among these benzocoumarins, benzocoumarin-3-ethylcarboxylate and 3-acyethylbenzocoumarin exhibited high fluorescence intensity. The results apparently show that the fluorescence intensity of the benzocoumarins is influenced by the direction of annulation and by the electronic effects of substituent at position-3. Based on this observation, we have reported fatty acid derivatives of various benzocoumaryl oxadiazolyls as a bright-blue fluorophores¹² (Fig. 1). Hence, in continuation of our work on synthesis and fluorescent studies on benzocoumarins¹² and development of new heterocyclic moieties in our laboratory¹³–¹⁹, we report in this paper the convenient synthesis of benzocoumaryl oxadiazolyls as very strong blue and green fluorescent brighteners.

2. Experimental
All the chemicals used were that of analytical grade. Melting points were determined in open capillary and were uncorrected; purity of the compounds was checked by TLC on silica gel and were purified by using chromatography. ¹H NMR spectra was recorded in a Bruker supercon FT NMR (400 MHz) spectrometer using CDCl₃ and DMSO as the solvents, TMS as an internal standard for reference and the chemical shifts are expressed in δ units. IR spectra were recorded in JASCO FT/IR-300 E spectrometer. Mass spectra were recorded in a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer.

2.1. Synthesis of ethyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (2)
A mixture of 2-hydroxy-1-naphthaldehyde (2.9 mmol, 0.5 g) ¹ and diethyl malonate (2.9 mmol, 0.464 g) was dissolved in absolute ethanol (30 mL) and catalytic amount of piperidine was added. The reaction mixture was refluxed on a water bath for about 30 minutes. The reaction mixture was cooled to room temperature and poured in to 100 g of crushed ice with stirring. The precipitate obtained was filtered, washed with water, dried under vacuum and recrystallized by using ethanol to get pure compound.

2.1.1. Ethyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (2; C₁₉H₁₄O₂)¹²
Yellow crystalline solid; (94 %); m.p.117 °C; IR (KBr): ν = 1748.2 (C=O) cm⁻¹; 1698 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.41 (t, J = 10.7 Hz, 3H, CH₃), 4.39–4.45 (m, 2H, CH₂), 7.41 (d, J = 9.0 Hz, 1H, ArH), 7.53 (t, J = 11.3 Hz, 1H), 7.74 (t, J = 11.7 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 9.35 (s, 1H, CH) ppm; ¹³C NMR (100 MHz, DMSO-d₆): 163.37, 156.47, 155.56, 144.35, 136.47, 130.19, 129.44, 129.42,
2.2. Synthesis of 3-oxo-3\(^H\)-benzo[f]chromene-2-carbohydrazide (3)

A mixture of ethyl 3-oxo-3\(^H\)-benzo[f]chromene-2-carboxylate 2 (3.8 mmol, 1.0 g) and hydrazine hydrate (3.8 mmol, 0.19 g) was dissolved in ethanol and refluxed on a water bath for 2 h. Then the reaction mixture was cooled to room temperature and poured onto 150 g crushed ice with stirring. The separated solid was filtered, washed with water, dried under vacuum and recrystallized with ethanol to get pure yellow compound 3.

2.2.1. 3-Oxo-3\(^H\)-benzo[f]chromene-2-carbohydrazide (3; C\(_{14}\)H\(_{10}\)N\(_2\)O\(_3\))

Yellow crystalline solid; (95 %); m.p. 260 °C; IR (KBr): \(\nu = 3320 \text{ cm}^{-1}, 1708.5 \text{ cm}^{-1}, 1621 \text{ cm}^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 4.77 (s, 2H, NH_2), 7.68 (t, \text{ } J = 7.8 \text{ Hz}, 2H), 7.78–7.82 (m, 1H), 8.11 (d, \text{ } J = 8.0 \text{ Hz}, 1H), 8.33 (d, \text{ } J = 9.0 \text{ Hz}, 1H), 8.63 (d, \text{ } J = 8.4 \text{ Hz}, 1H), 9.43 (s, 1H), 9.69 (s, 1H, NH) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 162.47, 160.89, 154.93, 143.95, 136.07, 130.41, 129.49, 129.26, 129.17, 126.85, 121.97, 116.37, 115.94, 113.22 \text{ ppm}; MS: m/z = 255 (M+1). Anal. Calcd. for C\(_{14}\)H\(_{10}\)N\(_2\)O\(_3\) = C, 66.14; H, 3.96; N 11.02 %. Found: C, 66.03; H, 3.83; N, 10.86 %.

2.3. Synthesis of 4-amino-3-oxo-3,4-dihydrobenzo[f]quinoline-2-carbohydrazide (4)

A mixture of ethyl 3-oxo-3\(^H\)-benzo[f]chromene-2-carboxylate 2 (3.8 mmol, 1.0 g) and hydrazine hydrate (20 mmol, 0.38 g) was dissolved in ethanol and refluxed on a water bath for 2 h. Then the reaction mixture was cooled to room temperature and poured into 150 g crushed ice with stirring. The solid thus separated was filtered and dried and purified by column chromatography (ethyl acetate: methanol) to get compound 4.

2.3.1. 4-Amino-3-oxo-3,4-dihydrobenzo[f]quinoline-2-carbohydrazide (4; C\(_{14}\)H\(_{12}\)N\(_4\)O\(_2\))

White crystalline solid; (97 %) m.p. 183 °C; IR (KBr): \(\nu = 3500 \text{ cm}^{-1}, 3020 \text{ cm}^{-1}, 1765 \text{ cm}^{-1}, 1605 \text{ cm}^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.42 (s, 2H, NNH_2), 5.55 (s, 2H, CONH_2), 7.20 (d, \text{ } J = 8.8 \text{ Hz}, 1H), 7.23 (d, \text{ } J = 10.4 \text{ Hz}, 1H), 7.45–7.52 (m, 1H), 7.74–7.80 (m, 2H), 8.05 (d, \text{ } J = 8.5 \text{ Hz}, 1H) 8.81 (s, 1H), 12.32 (s, 1H, NH) ppm; MS: m/z = 268.1 (M+1).

2.4. Synthesis of N'-benzylidene-3-oxo-3\(^H\)-benzo[f]chromene-2-carbohydrazides (5)

A mixture of 3-oxo-3\(^H\)-benzo[f]chromene-2-carbohydrazide 3 (2.0 mmol, 0.50 g) and benzaldehyde (2.0 mmol, 0.212 g) was dissolved in sufficient quantity of DMF with stirring, then refluxed for 12 h on a water bath. The reaction mixture was cooled and then poured into crushed ice. The solid thus separated was filtered and recrystallised from DMF to obtain pure compound 5a. Similarly the compounds 5b–e were synthesized.

2.4.1. N'-Benzylidene-3-oxo-3\(^H\)-benzo[f]chromene-2-carbohydrazide (5a; C\(_{21}\)H\(_{14}\)N\(_2\)O\(_3\))

Yellow crystalline solid; (86 %), m.p. 233–235 °C; IR (KBr): \(\nu = 3429 \text{ cm}^{-1}, 1706 \text{ cm}^{-1}, 1566 \text{ cm}^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.70 (d, \text{ } J = 8.0 \text{ Hz}, 3H), 7.80 (d, \text{ } J = 11.4 \text{ Hz}, 5H), 8.10 (t, \text{ } J = 7.5 \text{ Hz}, 1H), 8.27 (d, \text{ } J = 8.1 \text{ Hz}, 1H), 8.35 (d, \text{ } J = 8.5 \text{ Hz}, 1H), 8.48 (s,
2.5. Synthesis of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3H-benzof[\(c\)]chromene-3-ones (6)

2.5.1. Method I

To the mixture of 3-oxo-3H-benzof[\(c\)]chromene-2-carboxyhydrazide 3 (2.0 mmol, 0.5 g) and benzoic acid (2.0 mmol, 0.27 g) 10 mL of POCl\(_3\) was added and refluxed for about 12–15 h on a water bath. After it was cooled to room temperature, the reaction mixture was poured in to 200 g of crushed ice with stirring and was neutralized by saturated sodium bicarbonate solution. The yellow precipitate thus obtained was filtered washed with water, dried under vacuum and purified through column chromatography by using ethyl acetate and petroleum ether (1:9 v/v) as eluent to obtain analytically pure compound of 6a. Similarly the compounds 6b-e were synthesized.

2.5.2. Method II

To the mixture of N'-benzylidenec-3-oxo-3H-benzof[\(c\)]chromene-2-carboxyhydrazide 5a (3.0 mmol, 1.0 g) and anhydrous sodium acetate (33 mmol, 0.246 g) in 25 mL glacial acetic acid the solution of bromine (0.24, 0.003 mol) in 10 mL glacial acetic acid was added slowly at room temperature with stirring. The stirring was continued for 4 h and the reaction mixture was kept overnight. It was refluxed for further 2 h, cooled to room temperature, and poured onto 250 g crushed ice with stirring. The solid obtained was filtered, washed with water, dried under vacuum and purified through column chromatography by using ethyl acetate and petroleum ether (1:9 v/v) as eluent to obtain analytically pure compound of 6a. Similarly the compounds 6b-e were synthesized. The yields are recorded for POCl\(_3\) cyclization method (route 1, Scheme 2).

2.5.3. 2-[5-Phenyl-1,3,4-oxadiazol-2-yl]-3H-benzof[\(c\)]chromene-3-one (6a; \(C_7H_6Cl\_N_2O_2\))

Yellow crystalline solid: (51 %); m.p. 197–199 °C; IR (KBr): \(\nu = 3060 \text{ cm}^{-1}, 1737 \text{ cm}^{-1}\); \(1^H\) NMR (400 MHz, DMSO-\(d_6\)); \(\delta = 7.7 (d, J = 7.4 \text{ Hz}), 7.65 (d, J = 7.9 \text{ Hz}), 8.13 (d, 1H, J = 8.2 \text{ Hz}), 8.26 (d, 2H, J = 1.6 \text{ Hz}), 8.35 (d, 1H, J = 9.0 \text{ Hz}), 8.87 (d, 1H, J = 7.2 \text{ Hz}), 9.63 (s, 1H) ppm; MS: \(m/z = 341 (M^+ + 1)\).

2.5.4. 2-[5-(2-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-3H-benzof[\(c\)]chromene-3-one (6b; \(C_7H_6Cl\_N_2O_2\))

Yellow crystalline solid: (58 %); m.p. 221–223 °C; IR (KBr): \(\nu = 3050 \text{ cm}^{-1}, 1747 \text{ cm}^{-1}\); \(1^H\) NMR (400 MHz, DMSO-\(d_6\)); \(\delta = 7.2 (d, 1H, J = 8.9 \text{ Hz}), 7.26 (d, 3H, J = 8.8 \text{ Hz}), 8.32 (d, 2H, J = 8.5 \text{ Hz}), 8.36 (d, 2H, J = 9.0 \text{ Hz}), 8.63 (d, 1H, J = 9.4 \text{ Hz}), 8.65 (d, 2H, J = 1.6 \text{ Hz}), 9.61 (s, 1H) ppm; \(13^C\) NMR (300 MHz, CDCl\(_3\)); \(\delta = 172.33, 165.53, 163.23, 156.19, 146.14, 143.93, 143.19, 131.9, 130.47, 130.33, 130.21, 129.71, 129.51, 129.41, 128.56, 128.53, 127.82, 127.26, 124.63, 123.34, 118.82, 118.74. Anal. Calc. for \(C_{14}H_{11}ClN_2O_2\): C, 71.14; H, 3.55; N 8.23 % Found: C, 73.88; H 3.36; N 8.01 %.

2.5.5. 2-[5-(3-Nitrophenyl)-1,3,4-oxadiazol-2-yl]-3H-benzof[\(c\)]chromene-3-one (6c; \(C_7H_6Cl\_N_2O_2\))

Yellow crystalline solid: (53 %); m.p. 223–225 °C; IR (KBr): \(\nu = 3070 \text{ cm}^{-1}, 1727 \text{ cm}^{-1}\); \(1^H\) NMR (400 MHz, DMSO-\(d_6\)); \(\delta = 7.24 (t, J = 5.1 \text{ Hz}), 7.83 (t, J = 7.4 \text{ Hz}), 7.91 (t, J = 7.9 \text{ Hz}), 8.15 (d, J = 7.8 \text{ Hz}), 8.37 (t, J = 8.9 \text{ Hz}), 8.56 (d, J = 7.4 \text{ Hz}), 8.62 (d, J = 7.5 \text{ Hz}), 8.93 (t, J = 16.2 \text{ Hz}), 9.72 (s, 1H) ppm;
**Scheme 1**

General synthetic procedure for ethyl 3-oxo-3H-benzof][chromene-2-

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<th>Compound</th>
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<td>3</td>
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1.4 ppm due to two protons corresponding to N-NH₂ singlet at δ 9.9 ppm for one proton of NH (D₂O exchangeable) group and another singlet at δ 4.7 ppm for two protons of NH₃ (D₂O exchangeable) group that confirms conversion of benzocoumarin carboxylate to benzocoumarin carbohydrazide 3. Compound 4 exhibited a singlet at δ 1.4 ppm due to two protons corresponding to N-NH₃ (D₂O exchangeable) confirming its assigned structure. The formation of compounds 3 and 4 were also supported by their

**3. Results and Discussion**

The various benzocoumaryl oxadiazoles 6a–e have been synthesized by using benzocoumaryl-3-ethylcarboxylate 3 as key intermediate. The benzocoumarin-3-carbohydrazide 3 was prepared in an excellent yield from benzocoumarin-3-ethylcarboxylate 2 on treatment with hydrazine hydrate in ethanol. The benzocoumarin-3-carboxylate was obtained by Knoevenagel condensation between 2-hydroxy-1-naphthaldehyde and diethylmalonate in presence of catalytic amount of piperidine. While preparing the key intermediate 3, it was interesting to note that, the reaction of compound 2 with hydrazine hydrate with its molar ratio at room temperature furnished only compound 3, whereas the reaction of compound 2 with excess of hydrazine hydrate yielded another interesting new heterocycle, such as 1-amino 3,4-dihydrobenzo/[f]quinoline-3-carbohydrazide 4 (Scheme 1). It was also noticed that the compound 3 was insoluble in ethanol while compound 4 is soluble in ethanol. From the difference in solubility of these two compounds, it can be easily identified physically during their synthesis. So that either compounds could be easily prepared depending upon requirement. Since compound 4 contains active functional groups (-NH₂ and CONHNH₂), it could be synthetically exploited to generate a series of new quinoline derivatives.

The research work in this context is under progress in our laboratory.

The structures of all the newly synthesized compounds were characterized by analytical and spectral studies. ¹H NMR of compound 3 revealed the presence of a singlet at δ 9.9 ppm for one proton of NH (D₂O exchangeable) group and another singlet at δ 4.7 ppm for two protons of NH₃ (D₂O exchangeable) group that confirms conversion of benzocoumarin carboxylate to benzocoumarin carbohydrazide 3. Compound 4 exhibited a singlet at δ 1.4 ppm due to two protons corresponding to N-NH₃ (D₂O exchangeable) confirming its assigned structure. The formation of compounds 3 and 4 were also supported by their

2.6. Recording of UV-visible and Fluorescence Spectral Data

Fluorescence spectra were recorded on a F-7000 FL (SL.

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3.1. UV-visible and Fluorescence Spectral Data Analysis

Coumarin by itself is not fluorescent, it’s derivatives with both electron donating groups at 6 and 7 positions and electron withdrawing group at position 3 develops intense fluorescence as shown in Table 1. The experimental UV-visible spectra of benzocoumarin derivatives 6a–e in chloroform were obtained. The spectra of compounds 6a–e are reproduced in Figs. 2 and 3.
cent intensities are very small when compared to 6b, 6c and 6d. These benzocoumaryl oxadiazolyls show excellent blue fluorescent properties when compared to recently reported coumarin fluorescent labels.20,21

4. Conclusion

In conclusion, a simple, efficient and general method has been developed for the synthesis of benzocoumarin oxadiazolyl compounds 6a–e through a one-pot reaction of aromatic carboxylic acids and benzocoumarin-3-carboxylhydrazide in the presence of POCl₃, at reflux condition. All these compounds are hitherto unknown in literature and are observed to exhibit excellent fluorescence properties.

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