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Studies of fluorescent dyes: part 2. An investigation of the synthesis and electronic spectral properties of substituted 3-(2′-benzimidazolyl)coumarins

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Dedicated to our good friend and colleague, Dr. Arnold Peters, with our best wishes for a long and happy retirement

Abstract

A series of 3-(2′-benzimidazolyl) coumarins containing a variety of substituents in the benzene ring of the coumarin system have been synthesised and their spectral properties investigated. The results of PPP molecular orbital calculations, using previously optimised parameters, were found to provide a reasonable account of the electronic absorption spectra for this series of dyes, except for some compounds which are likely to be non-planar as a result of steric congestion. The absorption and emission properties of the dyes are discussed in terms of their electronic structures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coumarin; Fluorescence; Electronic spectra; PPP-MO calculations

1. Introduction

Coumarin derivatives provide some of the most significant organic fluorescent materials [1,2]. They owe their commercial importance to their efficient light emission properties, their reasonable stability and their relative ease of synthesis. Coumarin fluorescent dyes are suitable for use in the coloration of synthetic fibres, in daylight fluorescent pigments and in a range of applications which specifically exploit their light emission properties, including non-destructive flaw detection, tunable dye lasers and solar energy collectors. The most commonly-encountered fluorescent coumarins either absorb in the UV region and emit blue light (FBAs) [3,4] or are yellow dyes emitting a green fluorescence. The yellow coumarin fluorescent dyes typically contain an electron-releasing group (commonly *N*,*N*-diethylamino) in the 7-position and an electron-accepting heterocyclic group in the 3-position. There is some interest in the molecular design and synthesis of new coumarin derivatives which would extend the available range of long-wavelength emitting fluorescent materials. A number of coumarin derivatives which both absorb and emit at longer wavelengths are already known. In these, the shift to longer wavelength has invariably been achieved by strengthening the

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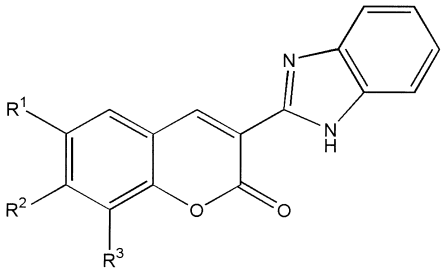
electron-accepting character attached to the pyranone ring [5–7]. To complement these previous approaches, we now report an investigation of the synthesis and electronic spectral properties of some substituted 3-(2′-benzimidazolyl)coumarins aimed at establishing the effect of substituents, both electron-withdrawing and electron-releasing, in the benzene ring of the coumarin system.

The PPP-MO approach is probably the most commonly used method for the prediction of the electronic absorption spectra of organic colorants [8–10]. The method provides information of value in establishing colour and constitution relationships within specific chemical classes of dyes and may thus assist in the design of new coloured molecules and in the selection of synthetic targets. In a previous paper, we reported the results of an investigation into the application of the PPP-MO approach to provide an account of the electronic absorption spectra of a range of simple coumarins, selected to allow systematic examination of substituent effects [11]. The investigation established a model which provided a good correlation between calculated and experimental spectral data and which thus offered practical potential for use in the design of new fluorescent coumarins. In this paper, we report an extension of the application of this model to the range of substituted 3-(2′-benzimidazolyl)coumarins.

2. Results and discussion

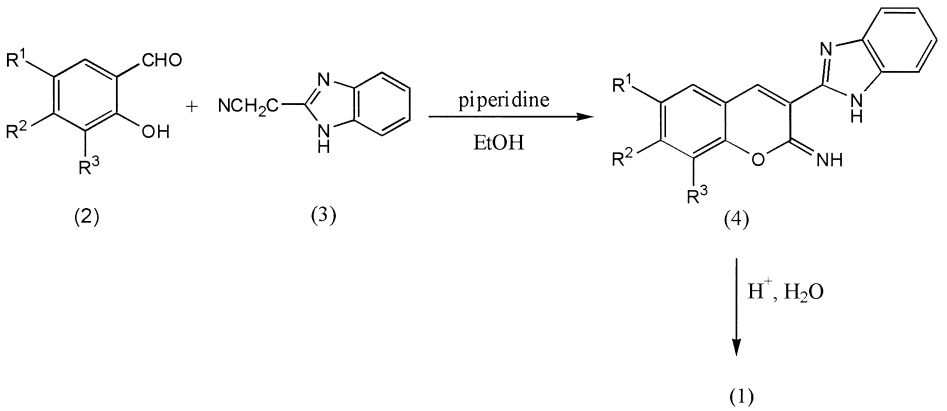
We have previously investigated of a series of coumarins to establish the influence of the electronic character of the substituent and its position of substitution on the UV/visible spectral properties [11]. Benzimidazolyl derivatives **1a** and **1b** were also included in this study since this heterocyclic system is commonly encountered in commercial fluorescent coumarin dyes. The present report extends our investigation to a further range of 3-(2′-benzimidazolyl)coumarins in order to establish the effect of substituents in the benzene ring of the coumarin system. Generally these dyes contain a 7-dialkylamino group as the electron-donor part of the chromophoric system. We were particularly interested in investigating the effect of incorporating additional electron-releasing or electron-withdrawing groups into this ring in the search for coumarin dyes absorbing and emitting at long wavelengths, which to date has focussed on derivatives with increased electron-accepting power attached to the pyranone ring [5–7]. A series of compounds **1a–1k** was selected for investigation on the basis of the pattern of our previous investigation [11] and on the availability of reasonable synthetic routes.

The basis of the synthesis of the 3-(2′-benzimidazolyl)coumarins **1** (Scheme 1) is the base-catalysed condensation of 2-hydroxybenzaldehyde derivatives **2** with 2-cyanomethylbenzimidazole **3** which forms iminolactones **4**. Hydrolysis to the



(1)

Compound	R^1	R^2	R^3
1a	H	H	H
1b	H	NEt_2	H
1c	NO_2	H	H
1d	H	H	NO_2
1e	NO_2	H	NO_2
1f	NH_2	H	H
1g	H	H	NH_2
1h	NO_2	NEt_2	H
1i	H	NEt_2	NO_2
1j	NH_2	NEt_2	H
1k	H	NEt_2	NH_2



	R^1	R^2	R^3
a	H	H	H
b	H	NEt_2	H
c	NO_2	H	H
d	H	H	NO_2
e	NO_2	H	NO_2
h	NO_2	NEt_2	H
i	H	NEt_2	NO_2

Scheme 1.

coumarins is achieved by refluxing in dilute aqueous hydrochloric solution [12]. Routes to the hydroxynitrobenz-aldehydes **2c** and **2d** [13,14] and the dinitro derivative **2e** [15] were readily available. Usefully, both 4-diethylamino-2-hydroxy-5-nitrobenzaldehyde **2h** and 4-diethylamino-2-hydroxy-3-nitrobenzaldehyde **2i** may be prepared from the nitration of the readily available 4-diethylamino-2-hydroxybenzaldehyde **2b** [16]. The syntheses of 3-(2′-benzimidazolyl) coumarins **1a**–**1e**, **1h** and **1i**, as illustrated in Scheme 1, were achieved smoothly and generally in good yield (68–95%). 6-Amino- and 8-amino-3-(2′-benzimidazolyl)coumarins (**1f** and **1g**), were prepared in 68 and 55% yields respectively by reduction of the corresponding nitro compounds (**1c** and **1d**) with iron and hydrochloric acid. 6-Amino-3-(2′-benzimidazolyl)-7-*N*,*N*-diethylamino coumarin **1j** was obtained similarly from nitro compound **1h** although in rather lower yield (18%) and with incomplete conversion of starting material. 8-Amino-3-(2′-benzimidazolyl)-7-*N*,*N*-diethylaminocoumarin **1k** was prepared by reduction of nitro compound **1i** with tin(II) chloride and concentrated hydrochloric acid, although the yield in this case was also rather low (19%). In the ^{1}H-NMR spectra of the series of 3-(2′-benzimidazolyl)coumarins **1a**–**1k**, the chemical shifts and multiplicities of the signals were consistent with the substituent patterns in each case. A characteristic feature of the spectra is the singlet (δ 8.92–9.36 ppm) attributed to the 4-H in the pyranone ring, which is shifted downfield (ca 1 ppm) by the presence of the 3-benzimidazolyl substituent [5,17].

The experimental UV/visible spectra of the series of 3-(2′-benzimidazolyl)coumarins, illustrated in Fig. 1, were obtained using acetonitrile as the common solvent, selected for its ability to provide adequate solubility for all of the compounds of interest and because of its relatively low absorption in the UV region of the spectrum. Table 1 lists the experimental λ_{max} values, together with molar extinction coefficients, for all of the clearly identifiable absorption bands above 210 nm for the series of compounds. Comparison of the spectra of compounds **1a**–**1d**, **1f** and **1g** with those for the corresponding coumarins in which there is no substituent at the 3-position [11] demonstrates that the presence of the 3-benzimidazolyl group causes a bathochromic shift of 30–64 nm and a pronounced increase in intensity of the longest wavelength absorption band, which becomes, in most cases, the dominant band. The unsubstituted derivative **1a** shows three main absorptions at 269, 273 and 363 nm, the longest wavelength band being the most intense. Nitro compounds **1c**–**1e** show similar spectra to that of compound **1a**, the longest wavelength bands experiencing small bathochromic shifts (2, 6 and 16 nm, respectively). The presence of the electron-withdrawing group in the 6- and 8-positions, therefore, does not influence the longest wavelength band significantly, although the shorter wavelength absorption bands increase in intensity. The introduction of the electron-releasing amino group in the 6-position (compound **1f**) causes a 43 nm bathochromic shift and reduction in intensity of the longest wavelength absorption band which appears as a shoulder (406 nm) on a rather more intense absorption at 352 nm. Perhaps surprisingly, the 8-amino derivative **1g** absorbs at a similar position to the unsubstituted compound **1a**, although it shows an increase in molar extinction coefficient. In contrast, the spectrum of compound **1b** demonstrates that the presence of the 7-*N*,*N*-diethylamino group causes a bathochromic shift of 75nm and a twofold increase in the molar extinction coefficient. The presence the additional functional group *ortho* to the 7-*N*,*N*-diethylamino group in compounds **1h**–**1k** (electron withdrawing in **1h** and **1i**, electron-releasing in **1j** and **1k**) causes in each case a hypsochromic shift and decrease in the intensity of the absorption band.

PPP-MO calculations were carried out on this series of coumarins using the parameters optimised for the coumarin series derived from our previous investigation [11]. As required by the approach, planar molecular geometry was assumed in each case. The possibility that rotation about the C3–C2′ bond might lead to deviation from planarity is recognised, although it is anticipated that intramolecular hydrogen-bonding between the hydrogen attached to the heterocyclic nitrogen and the carbonyl oxygen would act to constrain the molecule to planarity. An X-ray single crystal structure determination for compound **1b** has been reported, and demonstrates that, in the crystalline solid state, there is intramolecular hydrogen bonding and the torsion angle between the coumarin and benzimidazolyl ring systems is 9.5° [18]. The assumption of molecular planarity thus represents a reasonable first approximation.

The absorption maxima and oscillator strength values calculated for all of the significant absorption bands above 210 nm for 3-(2′-benzimidazolyl)coumarins **1a**–**1k** are given in Table 1. The calculated spectral data, represented as the vertical lines superimposed on the experimental band spectra, are also shown in Fig. 1. In the case of compounds **1a**–**1g**, the calculated longest wavelength band λ_{max} values show reasonable agreement with the experimental values and the calculated spectral profile correlates reasonably well with the experimental spectra. On the basis of the calculated oscillator strengths, the longest wavelength absorption band of fluorescent coumarin dye **1b** is correctly predicted to be the most intensely absorbing of the series. For compounds **1h** and **1i**, steric congestion as a result of the adjacent *N*,*N*-diethylamino and nitro groups is likely to result in deviation from molecular planarity. The longest wavelength λ_{max} values calculated for these two compounds are bathochromic (40 and 18 nm respectively) of the experimental λ_{max} values for the visible absorption bands. However, the position and shape of the experimental bands for these compounds are reasonably consistent with the composite band which might be expected from the overlap of the two calculated long wavelength absorptions (397 and 454 nm for **1h**, 403 and 440 nm for **1i**), as illustrated in Fig. 1. It is

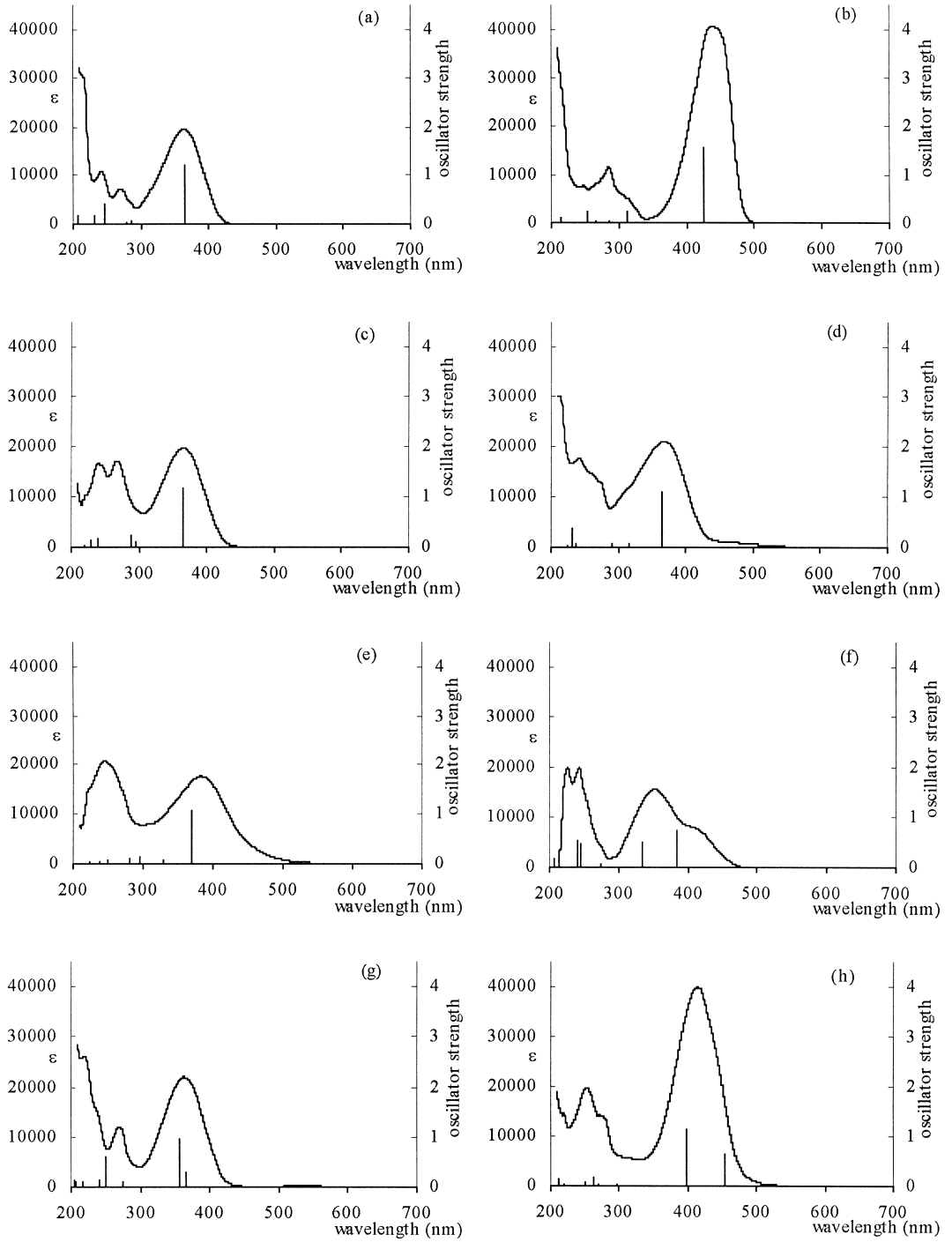


Fig. 1. Correlation between experimental (CH_3CN) and calculated (PPP-MO) electronic spectral data for 3-(2′-benzimidazolyl)coumarins **1a**–**1k**.

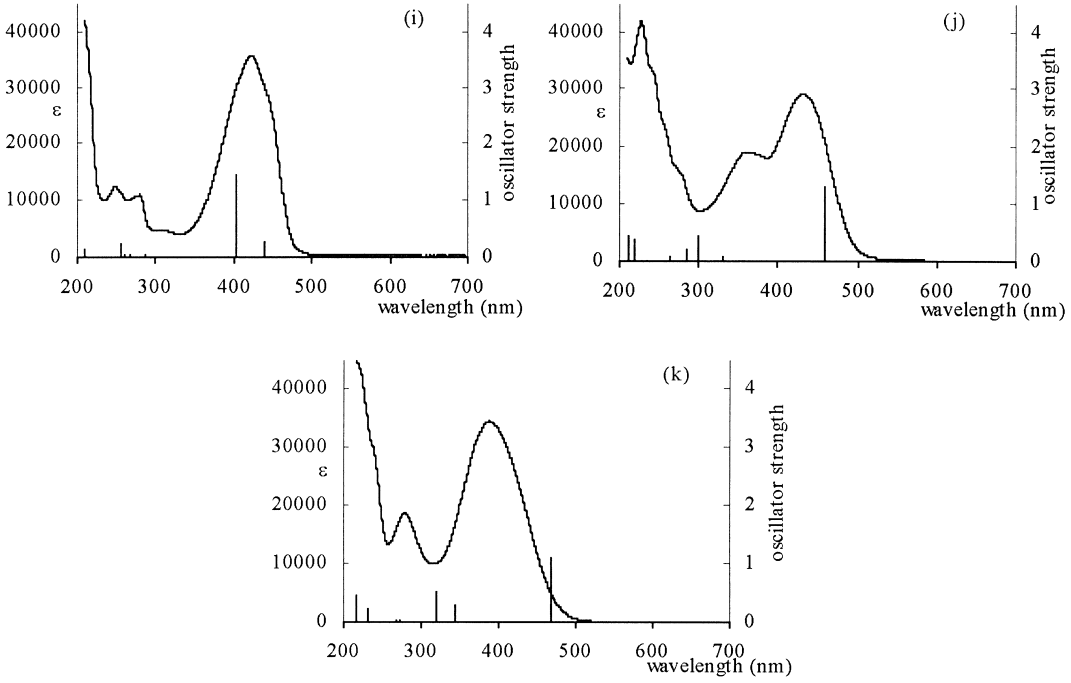


Fig. 1. (*continued*)

Table 1
A comparison between experimental and PPP-MO calculated electronic spectral data for 3-(2′-benzimidazolyl)coumarins **1a**–**1k**

Compound	ν_{max}(expt) (nm) (ε_{max} (10^{-4} mol l^{-1} cm^{-1})	λ_{max} (calc) (nm) (f_{osc})
1a	242 (1.08), 269 (0.71), 273 (0.70), 363 (1.96)	232 (0.17), 247 (0.40), 285 (0.06) 364 (1.23)
1b	249 (0.93), 286 (1.19), 438 (4.05)	252 (0.24), 313 (0.23) 425 (1.56)
1c	240 (1.71), 268 (1.74), 365 (1.95)	239 (0.16), 288 (0.24), 297 (0.11), 364 (1.16)
1d	243 (1.78), 369 (2.36)	231 (0.37), 291 (0.08), 365 (1.11)
1e	247 (2.38), 379 (1.85)	296 (0.12), 369 (1.06)
1f	225 (1.97), 243 (1.97), 352 (1.61), 406 (0.79)	239 (0.52), 245 (0.47), 334 (0.51), 383 (0.74)
1g	269 (1.31), 363 (2.51)	241 (0.15), 250 (0.59), 275 (0.10), 355 (0.96), 365 (0.29)
1h	253 (2.04), 414 (3.92)	262 (0.18), 397 (1.13), 454 (0.64)
1i	249 (1.30), 280 (1.11), 422 (3.66)	256 (0.22), 403 (1.45), 440 (0.26)
1j	228 (4.19), 361 (1.89), 431 (2.90)	210 (0.42), 219 (0.36), 284 (0.20), 299 (0.43), 457 (1.31)
1k	279 (1.89), 389 (3.45)	232 (0.22), 320 (0.53), 344 (0.30), 468 (1.09)

conceivable that, in spite of the steric congestion which is likely to be relieved by bond rotation to a certain extent, there remains significant π-overlap between the electron-releasing diethylamino group and the electron-accepting nitro group, so that the influence on the spectral properties is relatively small.

There is poor agreement between calculated and experimental data for compounds **1j** and **1k**. Since coumarin dyes are generally regarded as belonging to the donor–acceptor chromophoric type, the presence of the additional amino group in compounds **1j** and **1k** might have been expected to cause bathochromic shifts of the absorption bands

compared with compound **1b**, as a result of enhancing the electron releasing power in the donor part of the chromophoric system. The PPP-MO calculations for these compounds are in agreement with this expectation, predicting bathochromic shifts of 19 and 30 nm, respectively. In fact, the reverse is true. The compounds experience hypsochromic shifts of the absorption band, compared with compound **1b**, of 7 and 49 nm respectively. The PPP-MO calculations thus overestimate the bathochromicity of the long wavelength band of compounds **1j** and **1k** by 26 and 78 nm, respectively. The explanation for this may well be the steric congestion between the *ortho* amino groups, which is relieved by bond rotation. The consequence is that electron-release into π-system by either or both of the amino nitrogen lone pairs is reduced to an extent which is sufficiently significant to cause a hypsochromic shift. An alternative, or contributing, explanation is the possibility of intramolecular hydrogen-bonding between the amino group and the adjacent diethylamino group in these molecules for which no allowance was made in the calculations, although the geometrical arrangement of these groups would not appear to favour strong intramolecular hydrogen bonding. In the case of compound **1k**, the pronounced overestimation of the bathochromic shift (78 nm) may be explained by the possibility of intramolecular hydrogen-bonding between the amino group and the heterocyclic oxygen atom.

In the series of 3-(2′-benzimidazolyl)coumarins described in this paper, only compound **1b** was fluorescent, based on visual observation in daylight. It is apparent, especially since amino compounds **1f** and **1g** are non-fluorescent, that through conjugation from the 7-diethylamino group to the 3-benzimidazolyl group is essential for fluorescence. Introduction of an additional substituent at the 6- or 8-position (compounds **1h**–**1k**) causes loss of fluorescence. This may be due to a combination of factors, for example vibrational deactivation of the excited state due to the presence of the additional substituent, and the reduction in molecular planarity and its consequent effect on the through conjugation. It is not surprising that compounds **1h** and **1i** are non-fluorescent since it is commonly observed that the nitro group quenches fluorescence by increasing singlet excited state lifetimes and enhancing the possibility of intersystem crossing to the triplet state.

Table 2 shows that there is a good correlation between the carbonyl stretching frequencies obtained from the FTIR spectra of the series of compound under investigation and the π-electron bond orders for the carbonyl group. The decrease in the carbonyl stretching frequencies as a result of the presence of electron-releasing groups is consistent with the decrease in calculated π-electron bond orders, while the opposite effect is obtained with electron-withdrawing substituents. The significantly lower carbonyl stretching frequency in the infrared spectrum of compound **1j**, compared with compound **1b**, demonstrates that the 6-amino group has an electron-releasing effect which is transmitted through to the carbonyl group. This is not necessarily inconsistent with the reasoning proposed for the observed hypsochromic shift of the visible absorption band in the electronic spectrum of compound **1j**. The former observation reflects the electron distribution in the ground state. The latter result reflects the change in electron distribution when the molecule is raised from its ground state to its first electronic excited state. Our previously reported analysis of calculated π-electron charge densities illustrate that the donor/acceptor behaviour in these dyes is complex and that charge transfer from the donor group to the carbonyl

Table 2
Correlation between FTIR carbonyl absorption frequencies and calculated π-electron bond orders for coumarins **1a**–**1k**

Compound	C=O absorption frequency (cm^{-1})	C=O group π-electron bond order
1a	1709	0.856
1b	1693	0.844
1c	1742	0.860
1d	1735	0.862
1e	1742	0.866
1f	1693	0.851
1g	1695	0.851
1h	1701	0.851
1i	1702	0.851
1j	1680	0.838
1k	1695	0.841

oxygen plays a relatively minor part in the electronic excitation process [11]. We envisage exploring the origin of some of these effects in further detail with the aid of more sophisticated molecular modelling calculations.

3. Conclusions

The PPP-MO method, using a previously-optimised parameter set, provides a reasonable correlation between calculated and experimental data for a series of substituted 3-(2′-benzimidazolyl) coumarins. The presence of an electron-releasing group in the 7-position is important in these dyes to ensure intense aborption and emission properties. Introduction of an additional amino group in either the 6- or 8-position leads to a hypsochromic shift of the absorption band and loss of fluorescence. The hypsochromic shift may be due to steric congestion between the two electron releasing groups which causes non-planarity of the molecule, combined with the possibility of intramolecular hydrogen bonding.

4. Experimental

4.1. Instrumental methods

Infrared spectra were recorded as KBr discs with a Nicolet Protege 460 Fourier Transform spectrophotometer. Melting points were peak temperatures determined using a Mettler (DSC12E) Differential Scanning Calorimeter. UV/visible spectra were measured on a Perkin-Elmer Lamda 2 spectrophotometer for solutions in acetonitrile. Fast atom bombardment (FAB) mass spectra were performed using a VG (Vacuum Generators) MS9 double-focusing, forward geometry mass spectrometer, with an argon FAB gun and 3-nitrobenzyl alcohol (NOBA) as the liquid matrix. ^{1}H NMR spectra were recorded on two different spectrometer models, Bruker AC 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz) with sample changer, Bruker DPX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) at room temperature for solutions in hexa-deuteriodimethyl sulfoxide.

4.2. PPP molecular orbital calculations

A standard PPP-MO procedure was used within the fixed approximation [9]. A previously reported set of parameters was used [11]. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship [19] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly-excited configurations obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals.

4.3. Synthesis

2-Cyanomethylbenzimidazole (**3**) was prepared by the condensation of *o*-phenylenediamine with ethyl cyanoacetate [20]. 2-Hydroxybenzaldehyde (**2a**) and 4-*N*,*N*-diethylamino-2-hydroxybenz-aldehyde (**2b**) were commercial samples. A mixture of 2-hydroxy-5-nitrobenzaldehyde **2c** and 2-hydroxy-3-nitrobenzaldehyde **2d** was obtained by nitration of 2-hydroxybenzaldehyde **2a**. The isomers were separated by fractional crystallisation of the sodium salts, neutralisation of their aqueous solution and recrystallisation [13,14]. 3,5-dinitro-2-hydroxybenzaldehyde **2e** was prepared by further nitration of the mixture of mononitro compounds **2c** and **2d** [15]. 4-(*N*,*N*-diethylamino)-2-hydroxy-5-nitrobenzaldehyde **1h** and 4-(*N*,*N*-diethylamino)-2-hydroxy-3-nitrobenzaldehyde **1i** were obtained by nitration of 4-diethylamino-2-hydroxybenzaldehyde **1b** followed by separation by extraction and fractional crystallisation from hexane [16].

4.3.1. *3-(2′-Benzimidazolyl)-7-*N,N-*diethylamino-coumarin* **1b** *[12]*

2-Cyanomethylbenzimidazole **3** (1.57 g, 0.01 mol) and 2-hydroxy-4-*N*,*N*-diethylaminobenzaldehyde **2b** (1.93 g, 0.01 mol) were added to ethanol (30 cm^{3}). Piperidine (0.1 cm^{3}) was then added and the mixture stirred at room temperature for 24 h. The yellow precipitate which gradually separated out of the solution was collected and heated under reflux in 2% aqueous hydrochloric acid solution (150 cm^{3}) for 6 h. The mixture was cooled and excess sodium acetate added. The precipitate of

compound **1b** (2.45 g, 73%) was then filtered, washed with water, dried and recrystallised from ethanol as orange prisms; m.p. = 233°C (lit [12] = 232–234°C); δ_H (400 MHz, DMSO) 9.24 (1 H, s, 4-H) 7.56 (1 H, d, $J_{5,6}$ = 9.1 Hz, 5-H) 6.90 (1 H, dd, $J_{6,5}$ = 9.1 Hz, $J_{6,8}$ = 2.3 Hz, 6-H) 6.71 (1 H, d, $J_{8,6}$ = 2.2 Hz, 8-H) 7.76–7.81 (2 H, m, 4′,7′-H) 7.45–7.50 (2 H, m, 5′, 6′-H) 3.55 (4 H, t, N($\underline{CH_2}CH_3)_2$) 1.15 (6 H, q, N($CH_2\underline{CH_3})_2$); *m/z* (FAB) requires M(333) Found: 334(MH^+ 100%) 318(6) 304(5) 55(2) 43(3) 29(11) 27(11); ν_{max} (KBr) cm^{-1} 3338(NH), 2935(alkyl CH), 1693(C=O), 1620, 1592, 1530, 1275, 1253, 782, 766.

4.3.2. The following compounds were obtained using the above protocol

3-(2′-Benzimidazolyl)coumarin **1a** from 2-hydroxybenzaldehyde **2a**, but with a final reflux time of 2 h, as lemon-yellow crystals (92%) from ethanol; m.p. = 247.5°C; δ_H (200 MHz, DMSO) 9.15 (1 H, s, 4-H) 8.02 (1 H, dd, $J_{5,6}$ = 1.4 Hz, $J_{5,7}$ = 8.7 Hz, 5-H) 7.66–7.70 (3 H, m, 6,7,8-H) 7.40–7.55 (2 H, m, 4′,7′-H) 7.15–7.28 (2 H, m, 5′,6′-H); *m/z* (FAB) requires M(262) Found: 263(MH^+ 100%) 235(17) 217(5) 202(7) 194(7) 168(11) 158(7) 135(7) 132(11) 119(11) 94(8) 93(10) 69(24) 65(11) 51(14) 37(17); ν_{max} (KBr) cm^{-1} 3324(NH), 1709(C=O), 1607, 1409, 1316, 1121, 765, 738.

3-(2′-Benzimidazolyl)-6-nitrocoumarin **1c** from 2-hydroxy-5-nitrobenzaldehyde **2c**, as yellow crystals (88%) from dimethylformamide; m.p. = 333.5°C; δ_H (400 MHz, DMSO) 9.28 (1 H, s, 4-H) 8.98 (1 H, d, $J_{5,7}$ = 2.7 Hz, 5-H) 8.48 (1 H, dd, $J_{7,8}$ = 9.1 Hz, $J_{7,5}$ = 2.8 Hz, 7-H) 7.73 (1 H, d, $J_{8,7}$ = 9.1 Hz, 8-H) 7.69–7.71 (2 H, m, 4′,7′-H) 7.25–7.27 (2 H, m, 5′,6′-H); *m/z* (FAB) requires M(307) Found: 308(MH^+ 29%) 290(14) 272(8) 255(8) 242(24) 176(78) 77(78) 55(34) 39(100) 29(24) 23(52); ν_{max}(KBr) cm^{-1} 3256(NH), 1742(C=O), 1610, 1575, 1480, 1454, 1092, 947, 897.

3-(2′-Benzimidazolyl)-8-nitrocoumarin **1d** from 2-hydroxy-3-nitrobenzaldehyde **2d**, as yellow flakes (81%) from 1,2,4-trichlorobenzene; m.p. = 394°C; δ_H (400 MHz, DMSO) 9.26 (1 H, s, 4-H) 8.32–8.36 (2 H, m, $J_{5,7}$ = 1.5 Hz, 5, 7-H) 7.61 (1 H, t, $J_{6,5}$ = 7.9 Hz, 6-H) 7.66–7.70 (2 H, m, 4′,7′,-H) 7.22–7.27 (2 H, m, 5′,6′-H); *m/z* (FAB) requires M(307) Found: 307(2) 242(38) 176(99) 149(38) 77(30) 39(78) 29(100) 23(59); ν_{max}(KBr) cm^{-1} 3361(NH), 1735(C=O), 1610, 1531, 1412, 1344, 1267, 934, 777. Found C, 62.3; H, 2.8; N 13.5%; $C_{16}H_9N_3O_4$ requires C, 62.5; H, 3.0, N, 13.7%.

3-(2′-Benzimidazolyl)-6,8-dinitrocoumarin **1e** from 3,5-dinitro-2-hydroxybenzaldehyde (**2e**), as yellow flakes (68%) from dimethylformamide; m.p. > 390°C; δ_H (400 MHz, DMSO) 9.36 (1 H, s, 4-H) 9.03 (1 H, d, $J_{5,7}$ = 2.7 Hz, 5-H) 9.28 (1 H, d, $J_{7,5}$ = 2.7 Hz, 7-H) 7.69–7.72 (2 H, m, 4′,7′-H) 7.24–7.30 (2 H, m, 5′,6′-H); *m/z* (FAB) requires M(352) Found: 176(52) 149(44) 131(9) 111(5) 89(29) 69(42) 57(95) 41(100) 39(84) 27(61) 23(40); ν_{max}(KBr) cm^{-1} 3406(NH), 1742(C=O), 1541, 1340, 1261, 1119, 1040, 773, 763, 622, 548. Found C, 54.3; H, 2.1; N 15.8%; $C_{16}H_9N_3O_4$ requires C, 54.6; H, 2.3, N, 15.9%.

3-(2′-Benzimidazolyl)-7-*N*,*N*-diethylamino-6-nitrocoumarin **1h** from 4-*N*,*N*-diethylamino-2-hydroxy-5-nitrobenzaldehyde **2h**, as orange crystals (94%) from ethanol/*N*-methyl-2-pyrrolidone; m.p. > 390°C; δ_H (400 MHz, DMSO) 9.05 (1 H, s, 4-H) 8.40 (1 H, s, 5-H) 7.20 (1 H, s, 8-H) 7.67–7.71 (2 H, m, 4′,7′-H) 7.27–7.32 (2 H, m, 5′,6′-H) 3.55 (4 H, t, N($\underline{CH_2}CH_3)_2$) 1.15(6 H, q, N($CH_2\underline{CH_3})_2$); *m/z* (FAB) requires M(378) Found: 379(MH^+ 100%) 378(25) 363(6) 176(14) 89(7) 77(11) 75(11) 53(15) 51(15) 39(32) 27(10); ν_{max}(KBr) cm^{-1} 3368(NH), 1700(C=O), 1560, 1321, 1263, 1079, 780, 756, 546.

3-(2′-Benzimidazolyl)-7-*N*,*N*-diethylamino-8-nitrocoumarin **1i** from 4-*N*,*N*-diethylamino-2-hydroxy-3-nitrobenzaldehyde **2i**, as orange crystals (1.19 g, 95%) from ethanol/*N*-methyl-2-pyrrolidone; m.p. > 390°C; δ_H (400 MHz, DMSO) 9.05 (1 H, s, 4-H) 7.94 (1 H, d, $J_{5,6}$ = 9.2 Hz, 5-H) 7.63 (2 H, m , 7′-, 4′-H) 7.17–7.23 (3 H, m, 5′-, 6′- and 6-H) 3.55 (4 H, t, N($\underline{CH_2}CH_3)_2$) 1.15 (6 H, q, N($CH_2\underline{CH_3})_2$); *m/z* (FAB) requires M(378) Found: 379(MH^+ 82%) 378(41) 304(21) 242(18) 176(37) 149(16) 89(36) 77(37) 39(100) 31(42) 29(64) 27(57); ν_{max}(KBr) cm^{-1} 3377(NH), 1701(C=O), 1618, 1597, 1534, 1358, 1282, 1252, 1064, 773, 668.

4.3.3. 6-Amino-3-(2′-benzimidazolyl)coumarin **1f**

3-(2′-Benzimidazolyl)-6-nitrocoumarin **1c** (0.6 g, 0.002 mol) was suspended in hot water (15 cm^3) acidified with concentrated hydrochloric acid (0.3

cm^3) followed by the slow addition of iron filings (0.56 g, 0.01 mol). The mixture was refluxed for 6 h, cooled, made alkaline by the addition of sodium hydrogen carbonate, and filtered. The precipitate was Soxhlet extracted with acetone to give 6-amino-3-(2′-benzimidazolyl)coumarin **1f** (0.28 g, 51.7%), as yellow needles from toluene/*N*-methyl-2-pyrrolidone; m.p. = 317°C; δ_H (400 MHz, DMSO) 8.92 (1 H, s, 4-H) 7.63–7.68 (2 H, m, 5- or 7-, 8-H) 7.17–7.25(3 H, m, 5- or 7-, 7′-, 4′-H) 6.87–6.95 (2 H, m, 5′,6′-H) 5.40 (2 H, s, NH_2); *m*/*z* (FAB) requires M(277) Found: 278(MH^+ 100%) 277(92) 259(11) 243(12) 205(9) 191(9) 180(21) 176(59) 132(15) 78(15) 69(31) 55(55) 39(43) 30(40) 29(26); ν_{max}(KBr) cm^{-1} 3450, 3308(NH), 3183, 1692(C=O), 1633, 1570, 1316, 1120, 743.

4.3.4. The following compounds were obtained in a similar manner

8-Amino-3-(2′-benzimidazolyl)coumarin **1g** from 3-(2′-benzimidazolyl)-8-nitrocoumarin **1d**, as yellow crystals (55.4%) from toluene/*N*-methyl-2-pyrrolidone; m.p. = 296.7°C; δ_H (400 MHz, DMSO) 9.01 (1 H, s, 4-H) 7.63–7.70 (2 H, m, 5,6-H) 7.00–7.02 (1 H, m, 7-H) 5.20 (2 H, s, NH_2) 7.18–7.23 (2 H, m, 4′,7′-H) 7.11–7.14 (2 H, m, 5′,6′-H); *m*/*z*(FAB) requires M(277) Found: 278(MH^+ 100%) 277(44) 205(8) 180(13) 176(11) 149(59) 89(9) 77(12) 69(5) 57(33) 41(26) 39(23) 29(18); ν_{max}(KBr) cm^{-1} 3393(NH), 3171, 1694(C=O), 1602, 1579, 1319, 1123, 778, 734.

6-Amino-3-(2′-benzimidazolyl)-7-*N*,*N*-diethylaminocoumarin **1j** from 3-(2′-benzimidazolyl)-7-*N*,*N*-diethylamino-6-nitrocoumarin **1h** by reduction at 60°C for 6 h and purification of the acetone extract by flash chromatography on silica using ethyl acetate, as a yellow solid (18%); m.p. = 223°C; δ_H (200 MHz, DMSO) 8.90 (1 H, s, 4-H) 4.97 (2 H, br s, NH_2) 7.61–7.68 (2 H, m, 4′,7′-H) 7.08–7.24 (2 H, m, 5-, 8-, 5′,6′-H) 3.09 (4 H, t, $N(\underline{CH_2}CH_3)_2$) 1.05 (6 H, q, $N(CH_2\underline{CH_3})_2$); *m*/*z*(FAB) requires M(348) Found: 349(MH^+ 34%) 348(20) 305(6) 207(6) 175(7) 165(10) 128(11) 109(26) 83(42) 69(83) 55(96) 41(100) 29(49); ν_{max}(KBr) cm^{-1} 3393, 3323(NH), 2966(alkyl CH), 1680(C=O), 1599, 1556, 1504, 1398, 1283, 1249, 1198.

*4.3.5. 8-Amino-3-(2′-benzimidazolyl)-7-*N,N*-diethylaminocoumarin* **1k**

Tin (II) chloride (1.2 g, 0.002 mol) was added to a vigorously stirred suspension of 3-(2′-benzimidazolyl)-7-*N*,*N*-diethylamino-8-nitrocoumarin **1i** (0.756 g, 0.002 mol) in concentrated hydrochloric acid (15 cm^3) at room temperature. After the addition, the mixture was warmed to 70°C for 6 h. The reaction mixture was then cooled, made alkaline with ammonia, and filtered. The residue was washed with water and dried to yield a dark yellow solid. Column chromatography on silica using diethyl ether as eluent was used to give 8-amino-3-(2′-benzimidazolyl)-7-*N*,*N*-diethylaminocoumarin 1k (0.12 g, 19%) as yellow crystals; m.p. = 198.9°C; δ_H (200 MHz, DMSO) 9.01 (1 H, s, 4-H) 5.00 (2 H, br s, NH_2) 7.61–7.71 (2 H, m, 4′,7′-H) 7.08–7.26 (3 H, m, 5′-, 6-, 5- and 6-H) 3.06 (4 H, t, $N(\underline{CH_2}CH_3)_2$) 1.02 (6 H, q, $N(CH_2\underline{CH_3})_2$); *m*/*z* (FAB) requires M(348) Found: 349(MH^+ 12%) 348(10) 319(6) 123(10) 109(13) 69(62) 55(100) 43(76) 41(87) 29(49) 27(39) 15(7); ν_{max}(KBr) cm^{-1} 3442, 3384(NH), 2959, 2924, 2853 (alkyl CH, 3 bands), 1695(C=O), 1621, 1597, 1310, 1243, 1117.

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