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Dyes and Pigments 42 (1999) 85–93

DYES and PIGMENTS

Studies of fluorescent dyes: part 1. An investigation of the electronic spectral properties of substituted coumarins

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Received 22 September 1998; accepted 21 November 1998

This paper is dedicated to Dr. Geoff Hallas on the occasion of his 65th birthday

Abstract

Coumarin derivatives represent one of the most important chemical classes of organic fluorescent materials. The results of PPP molecular orbital calculations, after refinement by parameter optimisation, were found to provide a good account of the electronic absorption spectra for a series of substituted coumarins. The electronic structures of several of the derivatives and the nature of the electronic excitation process are discussed in terms of the calculated π-electron charge densities. © 1999 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Compounds based on the coumarin ring system give rise to one of the most extensively investigated and commercially significant groups of organic fluorescent materials [1,2]. Coumarin derivatives provide some of the most important commercial fluorescent brightening agents [3,4] and appropriately substituted compounds are also used as fluorescent dyes for use on synthetic fibres and in daylight fluorescent pigments, which impart a vivid brilliance to a range of paint and printing ink applications [5–7]. In addition, fluorescent coumarins may be used in a range of applications which specifically exploit their light emission properties, including non-destructive flaw detection, tunable dye lasers and solar energy collectors.

Coumarins are also of considerable biological and medical interest [8]. Many derivatives, commonly containing hydroxy substituents, are naturally-occurring compounds and a number of these products show marked physiological effects, for example active hypotoxicity, carcinogenicity, anticoagulant action and antibiotic activity. In addition, analytical techniques involving the use of fluorescent coumarin derivatives are of considerable importance in biological and medical research, providing a useful tool in the search for new biologically-active compounds and in the development of new diagnostic methods [1,8].

Coumarins owe their importance as fluorescent brightening agents and dyes to their efficient light emission properties, their reasonable stability and their relative ease of synthesis. The most commonly-encountered fluorescent coumarins either absorb in the UV region and emit blue light (FBAs) or are yellow dyes emitting a green fluorescence. Although several derivatives which both

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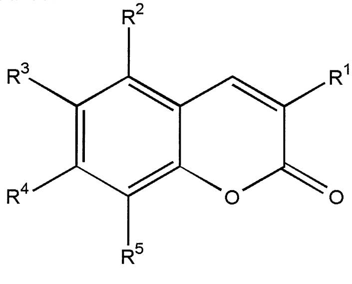
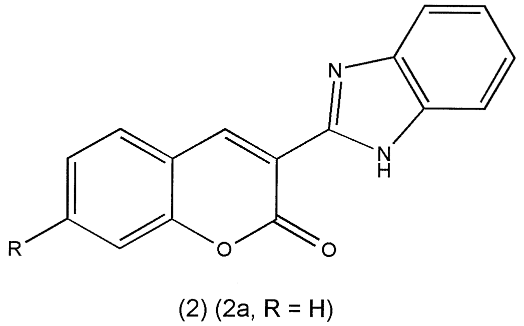
PII: S0143-7208(99)00012-1

absorb and emit at longer wavelengths are known [9–11], there remains some interest in the molecular design and synthesis of new coumarin derivatives which would extend the available range of long-wavelength emitting fluorescent materials. The PPP MO approach has emerged as a powerful technique for the prediction of the electronic absorption spectra of organic colorants [12–14]. The method provides information of considerable 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. There are a number of previous reports of the application of molecular orbital methods to coumarin derivatives aimed principally at the development of an understanding of the relationships between electronic structure and luminescence properties (particularly for laser applications) [15–19], non-linear optical behaviour [20] or biological activity [21,22]. These previous reports describe the use not only of the PPP-MO method, which incorporates only the π-electrons into the calculations, but also of a variety of all-valence electron methods. There are relatively few publications describing the correlation between calculated and experimental electronic absorption spectral data for coumarins. Nakazumi describes the use of PPP-MO calculations, adopting the variable β approximation, to account for the electronic spectra of some coumarin derivatives, with particular reference to heterocyclic sulphur analogues and the effect of annelation [23]. Other studies have described the correlation between experimental and calculated absorption spectral data for series of hydroxycoumarins, because of particular interest in their biological significance, and have also addressed the effect of ionisation of the hydroxyl function and the relative stabilities of the tautomeric forms [21,22]. A good correlation between experimental absorption maxima and $S_0 - S_1$ transition energies obtained by means of AM1 calculations for a series of coumarin laser dyes has also been reported [19]. In this paper, we report the results of an investigation into the applicability of the PPP-MO approach, using the fixed β approximation, to provide an account of the electronic absorption spectra of a range of coumarins, selected to allow systematic examination of substituent effects in fluorescent coumarin dyes. The investigation has established a model which provides a good correlation between calculated and experimental spectral data and which thus offers practical potential for use in the design of new fluorescent materials. The results of the calculations also provide an insight into the electronic excitation mechanism operating in the series of compounds investigated and into the donor/acceptor character of typical fluorescent coumarin dye molecules.



(1)

Compound	R^1	R^2	R^3	R^4	R^5
1a	H	H	H	H	H
1b	H	H	NO_2	H	H
1c	H	H	H	H	NO_2
1d	H	H	H	OCH_3	H
1e	H	OCH_3	H	OCH_3	H
1f	H	H	OCH_3	OCH_3	H
1g	NH^2	H	H	H	H
1h	H	H	NH_2	H	H
1i	H	H	H	H	NH_2
1j	H	H	H	NEt_2	H



(2) (2a, R = H)
(2b, R = NEt_2)

2. Results and discussion

A series of substituted coumarin derivatives were selected for investigation in accordance with the pattern of previous work carried out in these laboratories on azo pigments [24,25], phthalocyanines [26,27], and photochromic dyes [28,29]. This series, which includes the parent compound **1a**, together with the substituted derivatives **1b–1j**, was selected to allow an investigation of the influence of the electronic character of the substituent and its position of substitution on the UV/visible spectral properties of the compounds. Also included in this initial investigation were the benzimidazolyl derivatives **2a** and **2b** in view of the fact that this type of heterocyclic system is commonly encountered in commercial fluorescent coumarins. The compounds were obtained either from commercial sources or by synthesis using established literature procedures.

The experimental UV/visible spectra of the series of coumarins, illustrated in Fig. 1, were

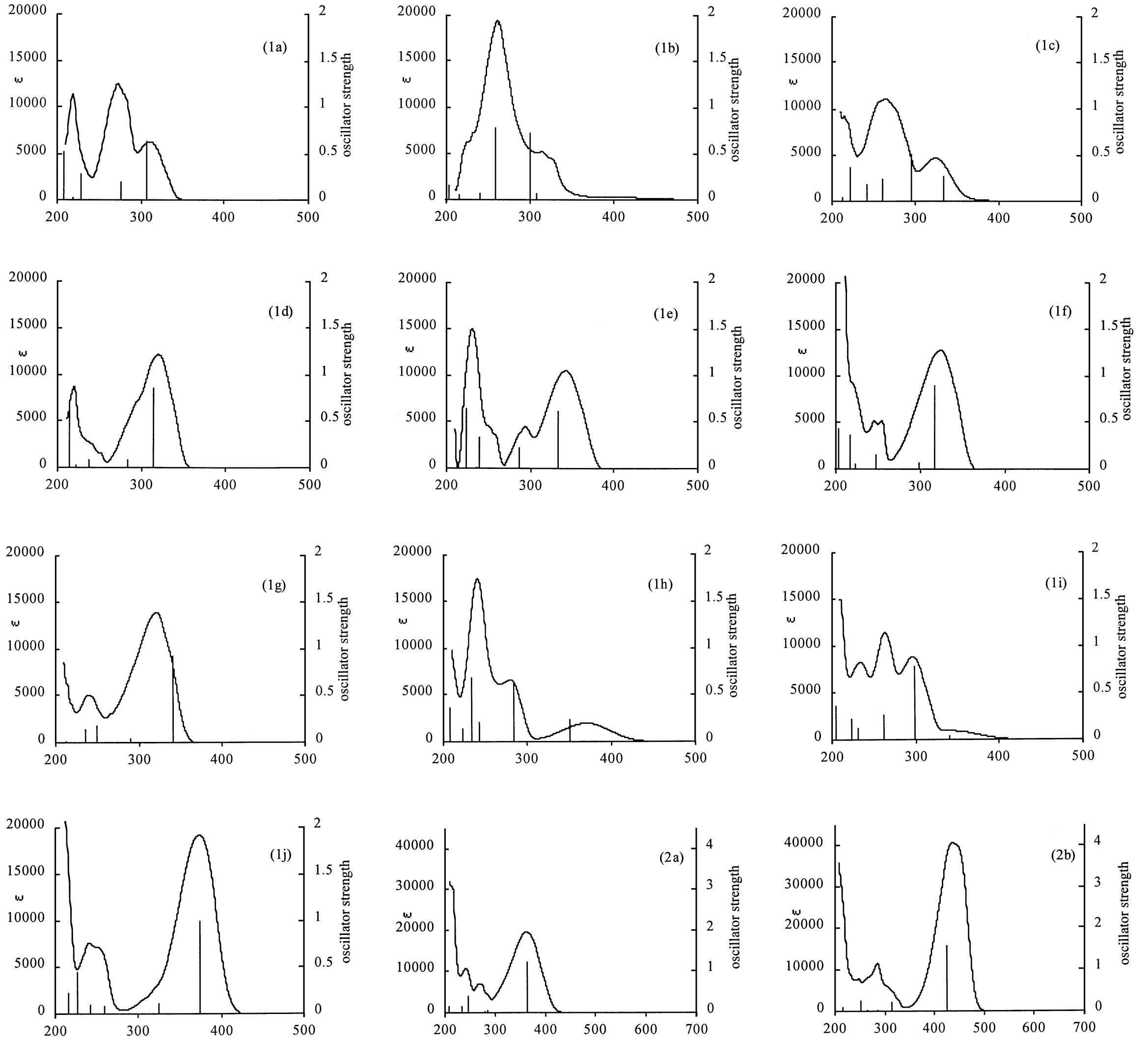


Fig. 1. Correlation between experimental (CH_3CN) and calculated (PPP-MO) UV visible spectra for coumarins **1a**–**1j**, **2a** and **2b**.

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. The spectra generally exhibit two or three main absorption bands, but in some cases are rather more complex showing additional shoulders and inflections. 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. Coumarin **1a** shows two main absorptions at 272 and 311 nm, the lower wavelength band being the more intense. The nitrocoumarins **1b** and **1c** show similar spectra to that of the parent compound in which the longest wavelength band experiences a small (14 nm in each case) bathochromic shift as a result of the presence of the electron-withdrawing nitro group. In the spectra of compounds **1d–1j**, the longest wavelength absorption band experiences a bathochromic shift as a result of the presence of the electron-releasing substituents (methoxy, amino and diethylamino), the magnitude of the shift being dependent on the nature and position of the substituents. In these cases, the relative intensities of the absorption bands show an especially pronounced dependence on the position of the substituent. When the electron-releasing group is in the 3- or 7-position, the longest wavelength band becomes by far the strongest absorption band, whereas, in contrast, when the group is in the 6- or 8-position, the bathochromic shift is accompanied by a reduction in the band intensity. The presence of the benzimidazolyl group (compounds **2a** and **2b**) causes a pronounced bathochromic shift and increase in intensity of the longest wavelength absorption band.

The results of PPP-MO calculations carried out on this series of coumarins are also given in Table 1. The relevant atom numbering system used in the calculations is illustrated in Fig. 2, by way of example, for compound **2a**. For the purposes of the calculations, planar molecular geometry was assumed in every case. Initially, calculations were carried out using a commonly-accepted generalised parameter set [13]. The calculated λ_{max} and oscillator strength values for the longest wavelength absorption band of coumarins **1a–1j**, **2a** and **2b** obtained using this system incorporating

Table 1
A comparison between experimental and PPP-MO calculated electronic spectral data for coumarins **1a–j**, **2a** and **2b**

Experimental data		PPP-MO calculated data	
Compound	λ_{max}/(nm) ($\varepsilon_{max} \times 10^{-4}$/mol litre^{-1} cm^{-1})	λ_{max} (nm)(f_{osc}) for longest wavelength band (generalised parameters)	λ_{max}/(nm)(f_{osc}) (optimised parameters)
1a	272 (1.06), 311 (0.53)	306 (0.64)	276 (0.20), 306 (0.64)
1b	225 (0.63), 232 (0.73), 261 (1.98), 314 (0.52), 325 (0.45)	358 (0.08)	215 (0.06), 239 (0.07), 257 (0.78), 300 (0.73), 307 (0.07)
1c	215 (0.92), 264 (1.14), 325 (0.46)	400 (0.07)	222 (0.36), 242(0.18), 261 (0.23), 295 (0.51), 333 (0.27)
1d	216 (1.17), 320 (1.23)	314 (0.85)	213 (0.62), 221 (0.02), 237 (0.09), 282 (0.09), 314 (0.85)
1e	246 (0.57), 254 (0.58), 325 (1.29)	317 (0.89)	217 (0.36), 247 (0.16), 297 (0.07), 317 (0.89)
1f	229 (1.73), 294 (0.53), 342 (1.08)	332 (0.62)	223 (0.64), 238 (0.33), 286 (0.23), 332 (0.62)
1g	239 (0.63), 322 (1.43)	341 (0.93)	235 (0.14), 249 (0.18), 341 (0.93)
1h	242 (1.74), 281 (0.66), 372 (0.20)	351 (0.23)	223 (0.14), 234 (0.69), 243 (0.20), 284 (0.65), 351 (0.23)
1i	235 (0.82), 264 (1.14), 297 (0.88), 343 (0.17)	341 (0.04)	230 (0.13), 261 (0.27), 299 (0.78), 341 (0.04)
1j	210 (2.2), 241,(0.7), 250 (0.7), 320 (0.3), 374 (1.9)	360 (0.99)	214 (0.22), 226 (0.44), 259 (0.10), 325 (0.10), 374 (0.99)
2a	242 (1.08), 269 (0.71), 273 (0.70), 363 (1.96)	353 (1.26)	232 (0.17), 247(0.40), 285 (0.06), 364 (1.23)
2b	249 (0.93), 286 (1.19), 438 (4.05)	401 (1.52)	214 (0.09), 252 (0.24), 313(0.23), 425 (1.56)

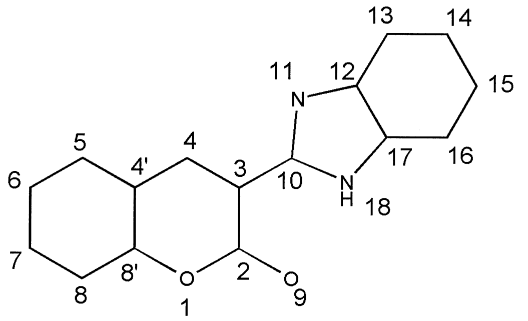


Fig. 2. Relevant atom numbering system for compound **2a**.

generalised parameters for the all substituents and heterocyclic atoms are given in the centre column in Table 1. The carbonyl group oxygen atom (O–9) was considered as non-hydrogen bonded and the carbon atoms of the pyranone ring were considered as aromatic as this was found to give rather better agreement between the calculated λ_{max} value (306 nm) and the experimental value (311 nm) for the longest wavelength band in the spectrum of the parent compound **1a** than when alkene-type parameters were used (292 nm). The set of results provided some encouragement in that the trends in the calculated positions and intensities of the absorption bands were generally as expected, providing reasonable qualitative agreement with experimental values. Nevertheless, in order to devise a model with improved quantitative predictive capability, it was decided to carry out some systematic parameter optimisation where this was judged to be of value in providing a more accurate calculation, particularly of the position of the longest wavelength band. The longest wavelength band of nitrocoumarins **1b** and **1c** were correctly calculated using the generalised parameter set to be bathochromic of the experimental values, although the bathochromicity was considerably overestimated (by 23–75 nm). It was found that an improved result was obtained by reducing the valence state ionisation potential for the nitrogen atom of the nitro group from 24.8 to 22.3 eV and the electron affinity for the same atom correspondingly from 12.5 to 10.0 eV. It was also found to be appropriate to amend the valence state ionisation potential for the nitrogen atom of the diethylamino group (compound **1j**) from 17.5 to 16.7 eV and the electron affinity for this group from 7.5 to 6.7 eV. Some attention was also paid to the parameters for the heterocyclic nitrogen atoms of the benzimidazolyl derivative **2a**, because of the particular commercial significance of compounds of this type, because of our interest in extending the calculations to a much wider range of related compounds and because anomalous results have been reported previously using generalised heterocyclic parameters [30]. The results of the calculations were observed to be relatively insensitive to the parameters for the π-equivalent heterocyclic nitrogen atom (N-11) which were therefore left unchanged, but it was found that adjustment of the valence state ionisation potential for the π-excessive nitrogen atom (N-18) from 21.0 to 26.0 eV and of the corresponding electron affinity value from 10 to 15.0 eV gave improved agreement.

The absorption maxima and oscillator strength values for all of the significant absorption bands above 200 nm for coumarins **1a–1i**, **2a** and **2b** calculated using the optimised parameter set are given in the final column of Table 1. In most cases, the calculated longest wavelength λ_{max} values, which are arguably of most interest to the dye chemist, show good agreement with the experimental values and there is a reasonable qualitative correlation between experimental molar extinction coefficients and the calculated oscillator strengths. Further, a comparison between the experimental and calculated spectral data (represented as the vertical lines superimposed on the experimental band spectra), as illustrated in Fig. 1 for each compound, demonstrates that the calculations are capable of providing a good account of the complete spectral profile for the series of compounds. The method accounts reasonably well for the λ_{max} values of the two main absorption bands in the spectrum of coumarin **1a**. However, the calculated oscillator strength values account rather less well for the relative intensites of the two peaks in the case of the parent compound, probably because the paramerisation was focussed on the calculation of λ_{max} values. A somewhat improved account of the spectral profile of the nitrocoumarins **1b** and **1c** is obtained and the method can be seen to provide a reasonably good prediction of the relative positions and intensities of the absorption bands in the spectra of compounds **1d–1j** each of which contains electron-releasing substituents. For example, the order of bathochromicities is accurately accounted for. In the spectra of compounds **1d**, **1e**, **1f**, and **1j**, each of which contains an electron-releasing group in the 7-position, the longest wavelength absorption is correctly predicted to be the dominant peak in the spectrum. The three isomeric aminocoumarins **1g**, **1h** and **1i** show significantly different spectral characteristics and these are predicted well by the PPP-MO calculations. 3-Aminocoumarin **1g** shows an intense absorption at 321 nm and a smaller band at 239 nm. The PPP-MO predicts the spectral profile reasonably well, although the bathochromicity of the long wavelength absorption is overestimated by 19 nm. This result may be due to intramolecular hydrogen-bonding between the amino group and the adjacent carbonyl group for which no allowance was made in the calculations. The spectra of 6-aminocoumarin **1h** and 8-aminocoumarin **1i** show bathochromically-shifted but weak long wavelength absorptions in the visible region and more intense absorptions in the UV region. The PPP-MO calculations provide a remarkably accurate account of the spectra for these two compounds. Using the optimised parameter set, the fluorescent coumarin dye **2b** was successfully calculated to be the most bathochromic of the series (λ_{max} 425 nm, which is within 13 nm of the experimental value) and also was predicted to be the most intensely absorbing of the series. An extension of the correlation between the results of PPP-MO calculations and experimental spectral data to a much wider series of heterocyclic coumarins of this type will be reported in a future publication.

The PPP MO method was also used to calculate the π-electronic charge distribution in the series of coumarins, both in their ground states and in the first excited states, thus providing an insight into the mechanism of the electronic excitation processes. Calculated π-electron charge densities for the ground state and excited states for coumarins **1a**, **1g**, **1h**, **1i**, **1j**, **2a** and **2b** are given in Table 2. The ground state -electron charge densities for the parent compound **1a** are generally consistent with a traditional valence-bond (resonance) representation of the molecule. For example, there is a reduction in the charge density on the heterocyclic oxygen atom (O-1) and a corresponding increased charge density on the carbonyl oxygen (O-9), while each of the carbon atoms is polarised as expected from the electron-releasing character of O-1 and electron-accepting character of O-9. In the first excited state of coumarin **1a**, there is significant electron transfer from the carbonyl oxygen atom (O-9) into the ring system with C-2, C-4 and C-5 experiencing the most pronounced increases in charge density. This observation is consistent with recently-reported results of calculations carried out on the parent molecule using the PPP-CI approach [22]. In the second excited state of coumarin **1a**, rather more in agreement with a traditional valence bond interpretation, there is, in general, a transfer of electron density from the benzene ring (with the exception of C-7 which shows a small increase in charge density) towards the pyranone ring, with the carbonyl oxygen (O-9) showing a significant increase in charge density. The π-electron charge densities for coumarins **1g–1j** (Table 2) permit an investigation of the donor-acceptor behaviour associated with the presence of the electron-donating amino groups. In the ground state of each of these derivatives, the amino nitrogen atom shows reduced electron density as a result of its electron-releasing character. Perhaps surprisingly, it is the carbon atoms of the ring system which show an increase in π-electron charge density, whereas the carbonyl oxygen (O-9) has a charge density which is similar to that in the parent compound **1a**. However, a similar interpretation of the electronic charge distribution has been suggested previously from the results of AM1 calculations on some aminocoumarin laser dyes [19]. For each aminocoumarin, the carbon atoms which experience an increase in charge density in their ground states are generally as expected from a valence-bond interpretation of the electron-releasing effect of the amino group. In the case of 3-aminocoumarin **1g**, the electron transfer on excitation to the first excited state takes place essentially within the pyranone ring, from the amino group and C-4 towards C-2, C-3 and O-9, while the benzene ring remains relatively

Table 2
Calculated π-electron charge densities for some coumarin derivatives

	1a			**1g**		**1h**		**1i**		**1j**		**2a**		**2b**	
Atom	G. St.[a]	1st Exc. St.[b]	2nd Exc. St.	G. St.	1st Exc. St.	G. St.	1st Exc. St.	G. St.	1st Exc. St.	G. St.	1st Exc. St.	G. St.	1st Exc. St.	G. St.	1st Exc. St.
O-1	1.86	1.86	1.85	1.86	1.88	1.87	1.86	1.87	1.88	1.87	1.89	1.87	1.88	1.87	1.88
C-2	0.85	0.91	0.92	0.85	0.99	0.85	0.92	0.85	0.93	0.85	0.94	0.85	0.87	0.85	0.87
C-3	1.01	1.01	1.19	0.99	1.04	1.01	1.16	1.02	1.21	1.06	1.11	1.04	1.08	1.09	1.08
C-4	0.96	1.06	1.17	1.13	1.01	0.96	1.18	0.95	1.19	0.95	1.20	0.90	1.07	0.89	1.18
C-4′	1.03	0.98	1.07	1.01	1.01	1.02	1.02	1.02	1.05	1.11	0.97	1.03	1.02	1.11	0.98
C-5	0.98	1.06	0.82	1.01	1.04	1.08	1.13	1.04	0.91	0.98	1.10	0.98	1.04	0.96	1.05
C-6	1.01	0.98	0.82	1.01	1.00	0.98	0.90	1.00	0.98	1.13	1.02	1.01	1.00	1.13	1.03
C-7	0.99	1.01	1.08	1.02	1.02	1.07	1.03	1.08	1.01	1.01	1.07	0.97	1.02	1.01	1.06
C-8	1.02	1.06	0.77	1.03	1.07	1.01	1.04	0.99	0.91	1.18	1.06	1.02	1.04	1.17	1.06
C-8′	0.98	0.94	0.88	1.01	0.95	1.01	0.87	1.05	1.01	0.96	0.99	0.97	0.99	0.95	1.00
O-9	1.31	1.14	1.42	1.32	1.38	1.32	1.33	1.32	1.44	1.33	1.38	1.32	1.28	1.29	1.32
C-10												0.80	0.82	0.79	0.87
N-11												1.37	1.35	1.39	1.41
C-12												0.97	0.86	0.96	0.96
C-13												1.01	0.96	1.01	0.95
C-14												1.01	1.00	1.02	1.02
C-15												1.01	0.90	1.02	1.02
C-16												1.03	1.02	1.03	1.04
C-17												1.01	0.94	1.01	1.00
N-18												1.85	1.86	1.85	1.86
NR_2				1.76	1.60	1.81	1.56	1.80	1.47	1.58	1.27			1.56	1.30

[a] Ground state.
[b] Excited state.

unaffected. In the case of compounds **1h**, **1i** and **1j**, in which the electron-donating substituent is attached to the benzene ring, there is significant charge transfer in the first excited states from the amino group and the benzene ring carbon atoms to the pyranone ring carbon atoms and the carbonyl oxygen (O-9). This mechanism in which the benzene ring acts as the donor and the pyranone ring as the acceptor presents a somewhat similar situation to the second excited state in the parent compound **1a**. In the unsubstituted benzimidazolyl derivative **2a**, the ground state π-electron charge densities within the coumarin ring system are similar to those in the parent compound **1a**. The π-equivalent heterocyclic nitrogen (N-11) shows increased electron density, while the π-excessive nitrogen (N-18) shows reduced charge density, features which are consistent with a traditional valence-bond interpretation. On excitation of this molecule which, like coumarin **1a**, contains no electron-donating substituent, there is a general transfer of charge away from the benzimidazolyl ring system into both rings of the coumarin system, and, as in the case with the first excited state of coumarin **1a**, the carbonyl oxygen (O-9) experiences a reduction in charge density. Compound **2b** is structurally typical of the range of commercial fluorescent coumarin dyes and has been suggested to be of a typical donor/acceptor chromogenic type [1,11]. The π-electron charge densities for this compound confirm that this is the case, but illustrate that the donor/acceptor behaviour is rather complex. In the ground state, the π-electron charge densities are as expected from a valence bond description, in which the diethylamino group is a strong electron donor. On excitation, a pronounced further electron-release from the amino group is experienced. Electron transfer to the carbonyl oxygen (O-9) and to the π-equivalent heterocyclic nitrogen (N-11) is observed, but the increases in charge density are relatively small. The largest increase in charge density in the first excited state is experienced at C-4 in the pyranone ring. Significant changes in π-electron charge density are observed on most of the other coumarin ring carbons, in general involving an inversion of charge density compared with the ground state. The benzene ring of the benzimidazolyl system is relatively unaffected by the excitation process, except for C-13 which experiences a small decrease in charge density. It is worth noting that the π-electron charge densities on the two π-excessive heterocyclic atoms, oxygen (O-1) for the entire series of coumarin derivatives and nitrogen (N-18) in benzimidazolyl derivatives **2a** and **2b**, are effectively constant throughout illustrating that these atoms are substantially unaffected by the presence of substituents and that they are not involved significantly in the electronic excitation process.

Table 3 shows the carbonyl stretching frequencies obtained from the FTIR spectra of the series of compounds under investigation, together with the π-electron bond orders for the carbonyl group in the molecular ground states calculated by the PPP-MO method. For coumarins **1a**–**1j**, the two sets of data are reasonably consistent. The increase in the carbonyl stretching frequency as a result of the presence of the electron-withdrawing nitro substituent in compounds **1b** and **1c** (compared with the parent compound **1a**) is consistent with the increase in calculated π-electron bond order, while the opposite effect is observed with coumarins **1d**–**1j**, each of which contains electron-releasing substituents. Benzimidazolyl derivatives **2a** and **2b** give carbonyl stretching frequencies which are rather lower than might have been expected solely on the basis of a comparison of their calculated π-electron bond orders with those for coumarins **1a**–**1j**. The additional lowering of the bond stretching frequency is almost certainly due to intramolecular hydrogen-bonding involving the C=O group and the heterocyclic N–H.

Table 3
Correlation between FTIR carbonyl absorption frequencies and calculated π-electron bond orders for coumarins **1a**–**1j**, **2a** and **2b**

Compound	C=O absorption frequency (cm^{-1})	C=O group π-electron bond order (PPP calc.)
1a	1728	0.852
1b	1736	0.856
1c	1736	0.858
1d	1706	0.848
1e	1712	0.845
1f	1709	0.845
1g	1708	0.851
1h	1707	0.847
1i	1704	0.846
1j	1703	0.838
2a	1709	0.856
2b	1693	0.844

3. Conclusions

A parameter set has been developed which enables the prediction of the electronic absorption spectra of a series of coumarins using the PPP-MO method. A reasonable correlation between calculated and experimental data is obtained for a series of substituted derivatives using the modified parameters. The method has the potential to be applied, for example, to investigate the possibility of extending the available shade range of colours available from coumarin dyes and as an aid to the design of new related molecules with fluorescent properties.

4. Experimental

4.1. Instrumental methods

Infrared spectra were recorded as KBr discs with a Nicolet Protege 460 Fourier Transform spectrometer. UV/visible spectra were recorded on a Perkin–Elmer Lamda 2 spectrophotometer for solutions in acetonitrile.

4.2. PPP molecular orbital calculations

A standard PPP-MO procedure was used within the fixed β approximation [13]. A generalised set of parameters was used and modifications carried out as described in the results and discussion section. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship [31] 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 of the coumarins

Coumarin (**1a**), 7-methoxycoumarin (**1d**), 5,7-dimethoxycoumarin (**1e**) and 6,7-dimethoxycoumarin (**1f**) were commercial samples obtained from the Aldrich Chemical Company, The Old Brickyard, New Road, Gillingham, Dorset SP8 4XT, UK. 6-Nitrocoumarin (**1b**) and 8-nitrocoumarin (**1c**) were prepared by treating a mixture of 3- and 5-nitrosalicylaldehydes with acetic anhydride and sodium acetate, followed by chromatographic separation of the isomeric nitrocoumarins [32]. 6-Aminocoumarin (**1h**) and 8-aminocoumarin (**1i**) were prepared by reduction of the mixture of nitrocoumarins with iron and acetic acid, followed by chromatographic separation of the isomeric aminocoumarins [32]. 3-Aminocoumarin (**1g**) was prepared by the reaction of salicylaldehyde, glycine and acetic anhydride to form 3-acetylaminocoumarin, followed by acid hydrolysis [32]. 7-*N,N*-diethylaminocoumarin (**1j**) was prepared by the reaction of 3-diethylaminophenol with malic acid and concentrated sulphuric acid [33]. 3-(2′-benzimidazolyl)coumarin (**2a**) was synthesised from the reaction of 2-cyanomethylbenzimidazole with 2-hydroxybenzaldehyde [34]. 3-(2′-benzimidazolyl)-7-*N,N*-diethylaminocoumarin (**2b**) was synthesised from the reaction of 2-cyanomethylbenzimidazole with 4-*N,N*-diethylamino-2-hydroxybenzaldehyde [34].

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