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An Investigation of the Electronic Spectral Properties of the Merocyanines Derived from Photochromic Spiroindolinonaphth[2,1-*b*][1,4]oxazines

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ABSTRACT

*Spiroindolinonaphth[2,1-*b*][1,4]oxazines are of considerable current interest as photochromic dyes with good colouring power and fatigue resistance. The results of PPP molecular orbital calculations, after refinement by parameter optimisation, were found to provide a reasonable account of the experimental λ_{max} values for the ring-opened merocyanine forms of a range of spirooxazines, although precise interpretation is complicated by the possible presence of a number of geometrical isomers. The electronic structure of the photomerocyanine derived from the parent compound and the nature of the electronic excitation process are discussed in terms of the calculated π-electron charge densities.*

1 INTRODUCTION

Organic photochromic materials have been the subject of intense recent investigation because of their wide variety of potential applications which include ophthalmic and sunglass lenses, optical recording and solar energy storage.[1–4] Spiroindolinonaphth[2,1-*b*][1,4]oxazines (**1**) have emerged as a class of organic photochromes of particular interest. This is due mainly to their ability to impart intense photocoloration in appropriate application media, their good photofatigue resistance and the relative ease of synthesis of the materials. The spirooxazines give colourless or only weakly coloured solutions which, when exposed to UV light, become intensely coloured.

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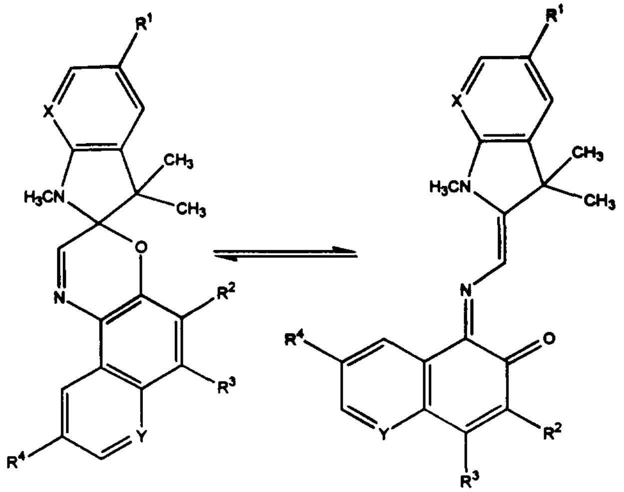
When the light source is removed, the solutions once again become colourless. Absorption of UV light by the spirooxazine (**1**) causes cleavage of the relatively weak spiro carbon–oxygen bond with the formation of a coloured merocyanine structure such as **2** (Scheme 1). Compound **2** reverts to the spirooxazine (**1**) by a thermally induced ring-closure reaction when the light source is removed.[5]



1 2

	R^1	R^2	R^3	R^4	X	Y
a	H	H	H	H	CH	CH
b	H	H	pip	H	CH	CH
c	H	H	ind	H	CH	CH
d	OCH_3	H	H	H	CH	CH
e	H	OCH_3	H	H	CH	CH
f	H	H	OCH_3	H	CH	CH
g	H	H	H	OCH_3	CH	CH
h	OCH_3	H	ind	H	CH	CH
i	H	-CH=CH-CH=CH-		H	CH	CH
j	H	H	H	H	N	CH
k	H	H	H	H	N	N

pip = N-piperidino

ind = N-indolino

Scheme 1

The PPP MO approach has emerged as a useful technique for the prediction of the electronic spectra of organic colorants.[6–8] In this paper, we report the results of an investigation using the PPP MO approach into the electronic spectra of the coloured merocyanine form derived from a series of spirooxazines. The investigation has established a model which provides a reasonable correlation between calculated and experimental spectral data and which has the potential for use in the design of new photochromic materials.

2 RESULTS AND DISCUSSION

Initial PPP MO calculations were carried out on compound **2a**, using a commonly-accepted generalised parameter set.[7] The relevant atom numbering system used in the calculations is illustrated in Fig. 1. A complication in carrying out calculations on photomerocyanines of this type is that, because they are transient species, their molecular geometry is not known with certainty. The molecules are, in principle, capable of existing in eight possible geometrical isomeric forms, illustrated in Scheme 2 as structures A–H for compound **2a**. Table 1 shows the results obtained from calculations carried out on each of the isomers of compound **2a**. For the purposes of the calculations, planar molecular geometry was assumed in each case. This assumption is clearly unrealistic for cisoid isomers E–H because of steric constraints. The approximation is more reasonable, however, for the transoid isomers A–D, although it has been suggested that there may also be some deviation from planarity in those cases.[9] For each of the transoid isomers, single long wavelength absorptions with significant oscillators strengths (0·87–0·94) were predicted, giving

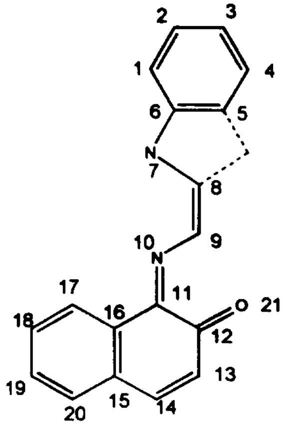
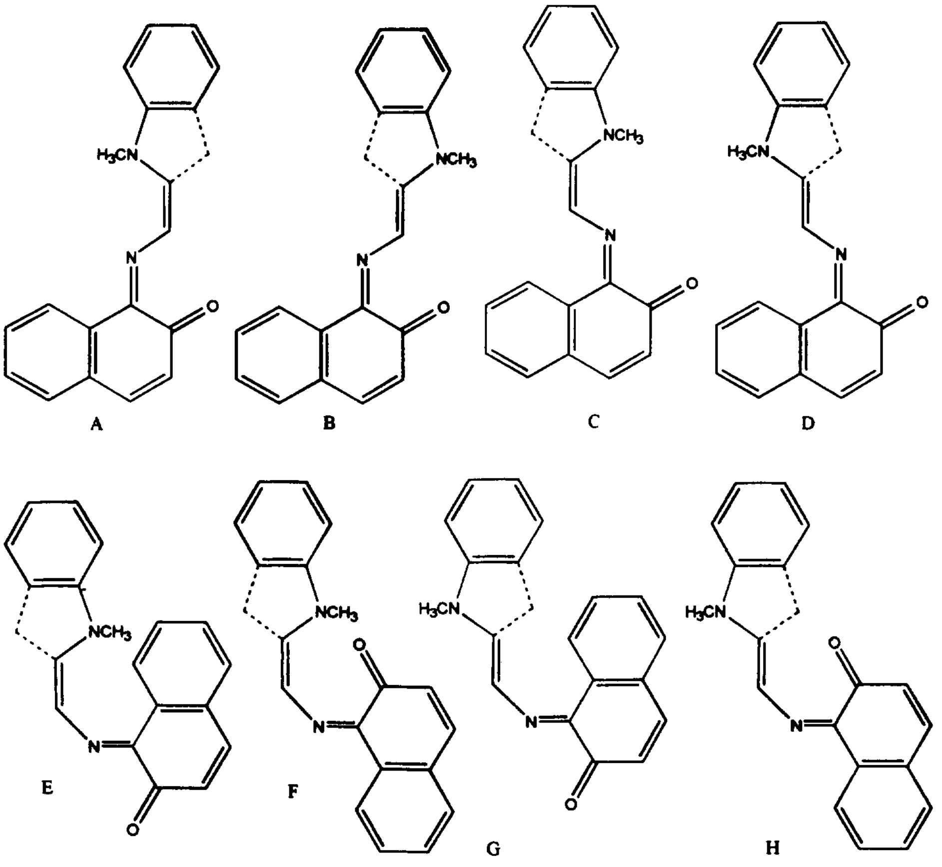


Fig. 1. Relevant atom numbering system for compound **2a**.



Scheme 2

calculated λ_{max} values ranging from 493 to 520 nm. The order of bathochromicities obtained for the isomers (viz. A > B > C > D) is consistent with findings of previous investigations using PPP[10] and INDO/S-CI[9] molecular orbital methods. The cisoid isomers E–H, when constrained to planar molecular geometry, are predicted to be rather more bathochromic (525–613 nm) than the transoid isomers and to give smaller oscillator strength values (0·32–0·44). The question of which particular isomers are formed when **1a** is converted to **2a** has not been fully resolved. However, it is generally accepted that, for obvious steric reasons, the cisoid isomers will be highly unstable and likely to convert rapidly to the more stable transoid isomers. INDO/S-CI MO calculations suggest that the order of stabilities of the transoid isomers is A > B > C > D, with A and B being significantly more stable than C and D.[9] The source of instability in isomers C and D may well be steric congestion involving H_a and H_b, as shown in Fig. 2.

In order to extend the investigation, the electronic spectral properties

TABLE 1

Calculated Electronic Spectral Data for Geometrical Isomers A–H of Merocyanine **2a** Using a Generalised Set of Parameters

Isomer	λ_{max} *(calc.) (nm)*	f_{oac} *(calc.)*	λ_{max} *(expt.) (nm)*
A	520	0·87	588
B	515	0·87	
C	506	0·91	
D	493	0·94	
E	525	0·40	
F	613	0·44	
G	601	0·32	
H	583	0·32	

of the merocyanines derived from a series of spiroindolinonaphth[2,1-*b*]-[1,4]oxazines (**1a–1k**) were examined. Compounds **1a–1h** contain electron-releasing substituents in a range of positions, compound **1i** has additional benzannulation and compounds **1j** and **1k** contain heterocyclic nitrogen. These compounds all exhibit characteristic photochromic behaviour when irradiated in solution in toluene with UV light, giving colours which range from reddish-purple through to blue. The merocyanines (**2a–2k**) had sufficiently long lifetimes to allow measurement of their qualitative UV/visible spectra using a diode array spectrophotometer. Electronic spectral data for compounds **2a–2k** are given in Table 2. The wavelength of maximum absorption for the series of compounds varies between 558 and 610 nm. However, in the visible region the spectra are apparently not single absorptions, but show in each case at least one shoulder associated with the main absorption band. Similar observations on the spectra of photomerocyanines of this type have been made previously.[5,9–13]

The λ_{max} values for transoid isomers of the parent compound **2a** calculated using the generalised set of parameters were found to be significantly hypsochromic compared with the experimental value (Table

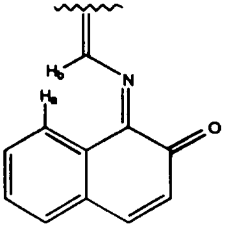


Fig. 2. Steric congestion in isomers C and D of merocyanine.

TABLE 2
Calculated Electronic Spectral Data for Isomers A–D of Merocyanines **2a–2k** Using Optimised Parameters

Compound	λ_{max} *(calc.) (nm)* (f_{oac})				λ_{max} *(expt.) (nm)*
	A	*B*	*C*	*D*	
2a	580 (0·81)	569 (0·82)	559 (0·81)	543 (0·79)	588, 578sh
2b	564 (0·84)	551 (0·84)	541 (0·82)	524 (0·81)	568sh, 562
2c	578 (1·02)	575 (1·01)	559 (1·00)	550 (0·97)	582, 564sh
2d	595 (0·85)	583 (0·85)	576 (0·87)	569 (0·89)	610, 578
2e	580 (0·76)	567 (0·74)	557 (0·82)	550 (0·86)	588sh, 578
2f	568 (0·83)	581 (0·83)	574 (0·82)	536 (0·80)	568sh, 560, 545sh
2g	572 (0·77)	560 (0·77)	550 (0·76)	540 (0·79)	592sh, 570
2h	590 (1·01)	575 (1·01)	571 (1·01)	558 (1·04)	602, 575sh
2i	566 (0·83)	552 (0·86)	544 (0·82)	534 (0·84)	580, 558sh
2j	578 (0·83)	564 (0·82)	553 (0·82)	545 (0·84)	570sh, 558
2k	579 (0·83)	567 (0·81)	552 (0·85)	544 (0·88)	565sh, 558

1). Following a systematic examination of the influence of parameters on the results of the calculations, it was found that much better agreement between the calculated and experimental values could be obtained by adjusting the valence state ionisation potential and electron affinity values for N-10 to 18·0 eV and 4·5 eV respectively. The results of the calculations for each of the transoid isomers A–D of compounds **2a–k** using this new set of parameters are given in Table 2. For each isomer of each compound, a single long wavelength band with a significant oscillator strength was calculated. A reasonable interpretation of this observation is that the complexity of the absorption bands in the spectra may be due to the presence of more than one isomer. In all but one case (compound **2f**), the calculations predicted the order of bathochromicities of the isomers to be A > B > C > D. When examined in this way, the results of the calculations and the spectral data may be considered to correlate reasonably well especially if, as has been suggested,[9] isomers A and B predominate. For example, the method accounts correctly for the hypsochromic shift caused by the presence of the strongly electron-releasing piperidino substituent at C-14 (using the numbering system given in Fig. 1, systematically referred to as the 6'-position). In addition, compounds **2d** and **2h** provide examples of species whose bathochromicities compared with the parent compound **2a** are correctly predicted.

Because of the experimental difficulties involved, molar extinction coefficients for compounds **2a–k** have not been measured in order to test quantitatively the correlation with calculated oscillator strengths. However, it is of interest that for compounds **2c** and **2h**, each of which contains an

TABLE 3
Calculated π-Electron Charge Densities for the Ground State and First Excited State of Merocyanine **2a** (Isomer A). (Numbering System as shown in Figure 1)

Atom	*π-electron charge densities*	
	Ground state	*First excited state*
1, 3	0·99	0·99
2	1·02	0·98
4, 6	1·05	1·00
5	1·00	1·00
7	1·70	1·51
8	1·00	0·99
9	0·97	0·75
10	1·48	1·59
11	0·76	0·82
12	0·86	0·92
13	1·00	1·05
14	0·97	1·03
15	0·99	1·02
16	1·02	1·04
17	0·96	0·96
18	1·00	1·02
19	0·98	1·00
20	1·00	1·01
21	1·20	1·35

indolino group at C-14 (6'-position), significantly higher oscillator strengths are calculated compared with those for the other members of the series. This result is consistent with the patent report that spirooxazines **1c** and **1h** provide enhanced photocoloration intensity.[14]

The results of the PPP MO calculations provide an insight into the π-electronic charge distribution in the merocyanine form of the spirooxazines, both in their ground states and in the first excited states. A valence-bond (resonance) representation of the structure of compound **2a** (isomer A) is given in Fig. 3. There has been some conjecture in the literature concerning the relative contributions of the neutral ‘quinonoid’ form I and zwitterionic or charge-separated forms, particularly II, to the overall structure of these species.[9] Calculated π-electron charge densities for the ground state and first excited state of isomer A of the parent compound (**2a**) are given in Table 3. The ground state charge densities are generally consistent with the valence bond approach illustrated in Fig. 3. For example, they show reduced charge density on N-7 and a corresponding increased charge density on the carbonyl oxygen (O-21) consistent with an important

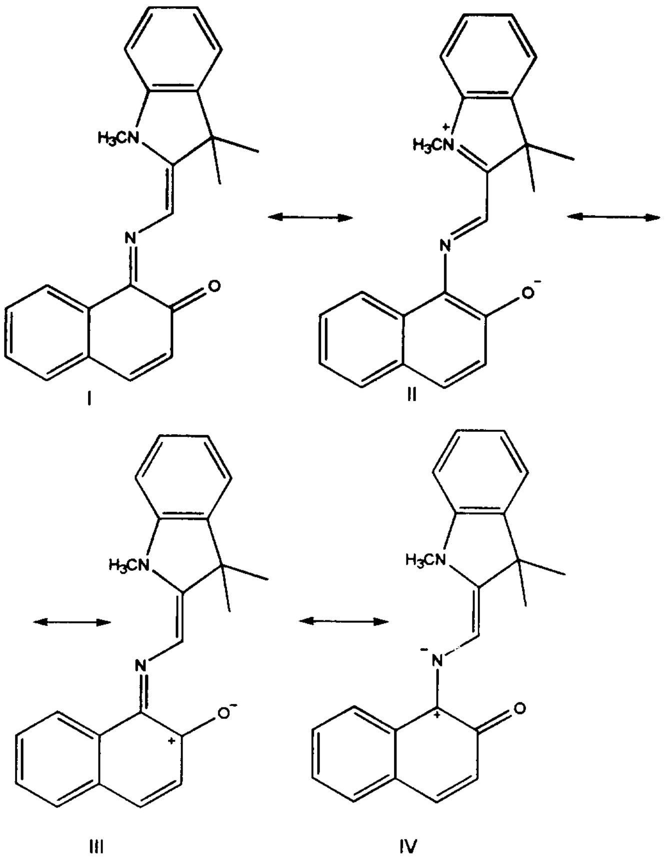


Fig. 3. Resonance forms of merocyanine **2a**.

contribution from structure II. The relatively high charge density on N-10 and reduced charge density on C-12 and C-11 suggest considerable polarisation of the C—O and C—N bonds as illustrated by resonance forms III and IV respectively. The first excited state charge densities suggest substantial further charge transfer from N-7 and to N-9 and O-21. The significant reduction in charge density on C-9 on excitation, however, does not appear to be in agreement with any obvious valence bond interpretation.

3 CONCLUSIONS

A method for the prediction of the electronic absorption spectra of the merocyanine forms of spiroindolinonaphth[2,1-*b*][1,4]oxazines using the PPP MO approach has been devised which provides a reasonable correlation with experimental data for a series of substituted derivatives. The method has the potential to be applied, for example, to investigate the possibility of extending the available shade range of colours available from spirooxazines, and as an aid to the design of new related molecules with photochromic properties. Strict application of the method is complicated by a degree of uncertainty with regard to the isomer distribution of the photomerocyanine structures.

4 EXPERIMENTAL

4.1 UV-visible spectra

We are grateful to Pilkington plc, Pilkington Technology Centre, Lathom, Ormskirk, Lancashire, UK, for supplying us with the spectra of the photomerocyanines of spirooxazines **1a–1k** which were prepared by literature methods.[5,14,15] UV/Visible spectra of the ring-opened species **2a–2k** were obtained by irradiation of solutions of spirooxazines at 365 nm using a flash gun. The spectra of the coloured solutions were recorded immediately using a Hewlett Packard 8452A diode array spectrophotometer.

4.2 PPP molecular orbital calculations

A standard PPP MO procedure was used within the fixed β approximation.[6] A generalised set of parameters was used and modifications carried out as described in Section 2. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship[16] 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.

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