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STRUCTURE-VISIBLE ABSORPTION RELATIONSHIP IN THE PHOTOCHROMIC SPIRO[INDOLINE-NAPHTHOXAZINE] SERIES.

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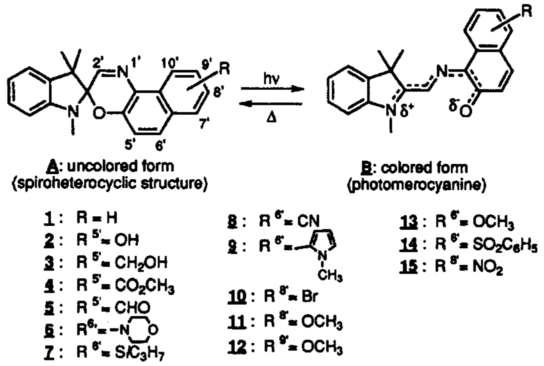
From a set of photochromic spiro[indoline-naphthoxazines] substituted on the oxazine part, a correlation between the electronic charge of the 2′-carbon atom and the absorption wavenumbers of the corresponding coloured forms was found. This relationship is of particular interest to predict the colour developed by this class of photochromic compounds.

INTRODUCTION

Organic photochromic compounds are of particular interest for a wide range of applications related to optical materials, non-linear optics, optical memories etc.[1,2] For this purpose either the reversible colour change or the reversible change in physical properties (polarity, conductivity, etc.) occurring during the photochromic process is used. In the field of materials able to undergo variable optical transmission, spiro[indoline-naphthoxazines] have undergone considerable development[3,4] owing to their good photochromic properties and their high fatigue resistance.[5] It is well established that the uncoloured form **A** absorbs UV radiation to lead, after cleavage of the C—O bond, to the coloured form **B** (Scheme 1). The reverse reaction is thermally induced.

Isomers **B** absorb generally from 18 200 to 16 700 cm^{-1} (about 550 to 600 nm). For the design of photochromic lenses it is necessary to have the best coverage of the visible range and then in commercially available materials spirooxazines need to be associated with other photochromic compounds such as chromenes.[4] However, compounds of both series often show different temperature dependences and different fatigue resistances and it would be preferable to use only one family of photochromic pigments.

For this purpose, we have prepared a series[6,7] of substituted spiro[indoline-naphthoxazines] in order to acquire a better understanding of the relationship between the electronic absorption of the coloured form and the nature and position of substituents which have been selected for their electronic properties. We describe here interesting correlations for spiro[indolinenaphthoxazines] substituted on the naphthalene ring of the oxazine moiety.



Scheme 1. Photochromic equilibrium in the spiro [indoline-naphthoxazine] series

RESULTS AND DISCUSSION

Rickwood *et al.*[8] have recently shown that electron-donating substituents placed in the 6′-position could lead to hypsochromic shifts. We extended the substitution on this particular position, but also on the 5′-, 8′- and 9′-positions. The absorption ν_{max} of the coloured

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species **B** were observed in the spectra obtained in toluene solution after flash photolysis.

Our different attempts to correlate ν_{max} values with Hammett constants characterizing the electronic effect of substituents were unsuccessful.

Surprisingly we found that for compounds monosubstituted at the 6′-, 8′- or 9′-position (**1** and **6–12**), a linear relationship (correlation coefficient 0·97) between the ν_{max} of the coloured form **B** and the $\delta^{13}C$ shift of the 2′-carbon atom of the closed form **A** (Figure 1) is obtained. If substituents at the 5′-position are also taken into account, the correlation coefficient is poor (0·86), but the general trend is maintained. In this case, not only the electronic effect is involved, but also the non-bonded interactions between the 5′-substituent and the oxygen atom in the *ortho* position (especially on the open forms **B**).

Since the ^{13}C shift depends partly on the electronic charge (e_c) of the carbon atom, a similar correlation occurs between the electronic charge of C-2′ of the spiro compound determined by semi-empirical quantum chemistry calculations (the PM3 method[9] was used). The linear correlation obtained was

$$\nu\ (\mathrm{cm}^{-1}) = 65\,470 e_c + 6\,550$$

(correlation coefficient 0·90) for substituents at the 6′-, 8′- and 9′-positions (Figure 2). This is an interesting result, allowing for a reasonable evaluation of the effect of a given substituent on the electronic absorption of the photomerocyanine. For instance, from the calculated electronic charge on C-2′ in **13** (6′-OCH_3), **14** (6′-$SO_2C_6H_5$) and **15** (8′-NO_2), the calculated electronic transitions are $\nu_{max} = 17\,811\ \mathrm{cm}^{-1}$ ($\lambda_{max} = 561$ nm), 15 362 cm^{-1} ($\lambda_{max} = 651$ nm) and 16 154 cm^{-1} ($\lambda_{max} = 619$ nm)m respectively. These values are very close to those measured experimentally, i.e. $\nu_{max} = 18\,050\ \mathrm{cm}^{-1}$ ($\lambda_{max} = 554$ nm), 15 528 cm^{-1} ($\lambda_{max} = 644$ nm) and 16 313 cm^{-1} ($\lambda_{max} = 613$ nm).

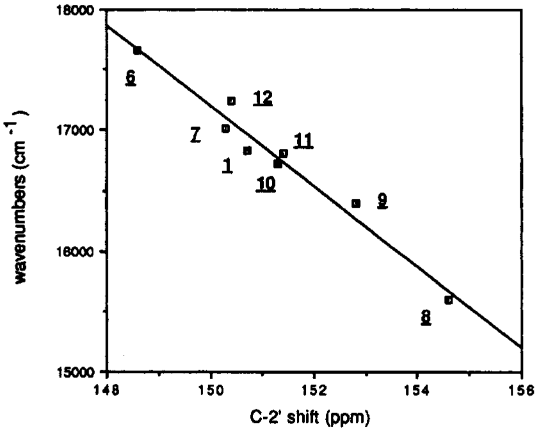

Figure 1. Correlation ($r = 0{\cdot}97$) between the $\delta^{13}C$ shift (ppm) of the C-2′ of the closed forms A and ν_{max} (cm^{-1}) of absorption of the open forms B (toluene as solvent) for spiro[indoline-naphthoxazines] substituted at the 6′-, 8′- or 9′-position

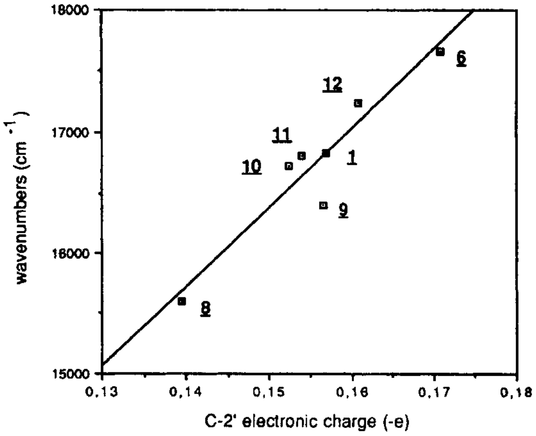

Figure 2. Correlation ($r = 0{\cdot}90$) between the electronic charge ($-e$) of C-2′ of the closed forms A and ν_{max} (cm^{-1}) of absorption (toluene as solvent) of the open forms B for spiro[indoline-naphthoxazines] substituted at the 6′-, 8′- or 9′-position

At this stage of the work, one cannot explain the reason for the occurrence of a relationship between a characteristic of the ground state of a closed form (electronic charge of C-2′) and a characteristic of an excited state of an open form **B** (electronic transition). If the electronic transitions were related to the variation of the electronic distribution on the naphthoxazine part, one could expect the same kind of relationship with the electronic charge of C-2′ of the **B** form. We have verified the lack of such a correlation by different semi-empirical calculations. Nevertheless, it is necessary to point out the weak reliability of semi-empirical calculations to describe electronic properties of photomerocyanines of spirooxazines.[10,11] Work is in progress to extend the discovered correlation to new substituents and also to bi-substituted compounds which are able to undergo large wavelength shifts.

EXPERIMENTAL

The substituted spiro[indoline-naphthoxazines] were synthesized recently in our laboratory.[6,7]

The ^{13}C chemical shifts were measured in $CDCl_3$ as solvent on a Bruker BM250 spectrometer.

The coloured isomers **B** were obtained by flash photolysis (xenon lamp, 250 W) of toluene solutions (about $10^{-4}\ \mathrm{mol}^{-1}$) of the spirooxazine compounds **A**. The visible spectra were immediately recorded on a diode-array spectrophotometer (Beckman DU 7000) to measure the λ_{max} of absorption of the **B** forms.

The electronic charges of the C-2′ were calculated using the semi-empirical PM3 program.[9] The geometries of the molecules were optimized by the same method.

For each compound, we give here successively the values of $\delta^{13}C$ of C-2′ (ppm vs TMS, $CDCl_3$ as solvent) of isomer A, the calculated electronic charge ($-e$) of C-2′ and ν_{max} (cm^{-1}) and λ_{max} (nm) of the open form **B**: **1**, 150·7, 0·1570, 16 835, 594; **2**, 151·4, 0·1463, 16 949, 590; **3**, 150·5, 0·1549, 16 556, 604; **4**, 151·1, 0·1501, 16 286, 614; **5**, 151·8, 0·1545, 15 847, 631; **6**, 148·6, 0·1707, 17 667, 566; **7**, 150·3, 0·1439, 17 007, 588; **8**, 154·6, 0·1395, 15 601, 641; **9**, 152·8, 0·1565, 16 363, 610; **10**, 151·3, 0·1524, 16 722, 598; **11**, 151·4, 0·1539, 16 807, 595; **12**, 150·4, 0·1608, 17 241, 580; **13**, 147·3, 0·1720, 18 050, 554; **14**, 154·6, 0·1346, 15 528, 644; **15**, 152·0, 0·1467, 16 313, 613.

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