Novel Merocyanine Dyes are converted into the Spiropyran Form by Irradiation with Visible Light

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New photochromic spiropyrans existing in a stable coloured form are prepared from merocyanine dyes by irradiation with visible light.

Organic photochromic compounds have attracted much attention from the point of view of colour change and their potential application in erasable optical recording media.

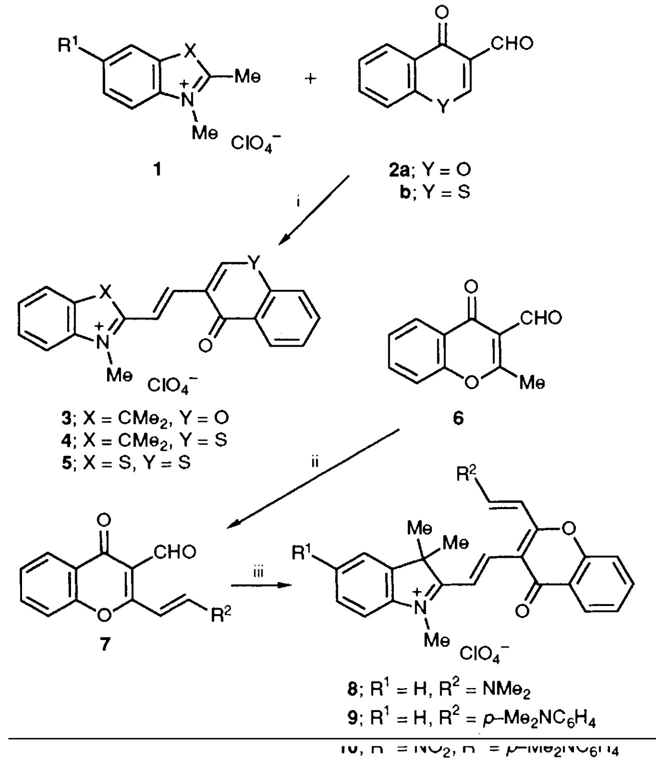
Though indolinospiropyran,[1] diarylethene,[2] and fulgides[3,4] have been extensively investigated as photochromic compounds, there are few examples[5] in which photochromic compounds can be made from the stable coloured form of a photochromic system by further modification. Such an approach offers the means to vary the colour of the photochromic molecule within wide limits. In spiropyran compounds, the coloured form is generally unstable but it is stabilized by chelation to divalent metals.[6] In the present work, we report the first photochromic spiropyrans in which the coloured form is very stable.

Merocyanine dyes, **3**–**5**,† were prepared by the condensation of indolinium or benzothiazolinium salts with 3-formyl-4*H*-1-benzopyran-4-one **2a** or 3-formyl-4*H*-1-benzothiopyran-4-one **2b** in yields of 32–75%. These dyes are regarded as analogous to the ring-opened form (merocyanine form) of the spiropyran, which is produced by the photoirradiation of indolinospiropyran.

Introduction of a conjugated donor group into the 2-position of the benzopyran ring bathochromically shifts the absorption maximum of the merocyanine dye. 2-Aminovinyl-3-formylchromone **7** was prepared from **6** and dimethylformamide dimethyl acetal or *p*-(dimethylamino)benzaldehyde. These aldehydes reacted with **1** to give merocyanine dyes, **8**–**10**,† with the conjugated chain at the 2-position of the benzopyran ring, in yields of 58–96%.

The main features of the absorption spectra of dyes **3**–**5** and **8**–**10** are summarized in Table 1. The extension of the π-conjugated chain of the benzopyrano-merocyine dyes results in a shift to longer wavelength of the absorption maxima, consequently, they change from yellow to green. The introduction of the nitro group also produces a significant bathochromic shift.

Fig. 1 shows the absorption spectral change of a solution of **4** in $CHCl_2CHCl_2$ after irradiation with visible light (>390 nm) for 1 min. A yellow solution of **4** changed to a colourless solution on irradiation with visible light [line (*a*)]; then the original colour was reversibly recovered within 125 min at 20 °C.



Scheme 1 *Reagents and conditions*: i, EtOH, reflux; ii, Me_2N-$CH(OMe)_2$ or Me_2N-PhCHO, piperidine, dry benzene, reflux; iii, $1(R^1 = H$ or NO_2, $X = CMe_2)$, EtOH, reflux

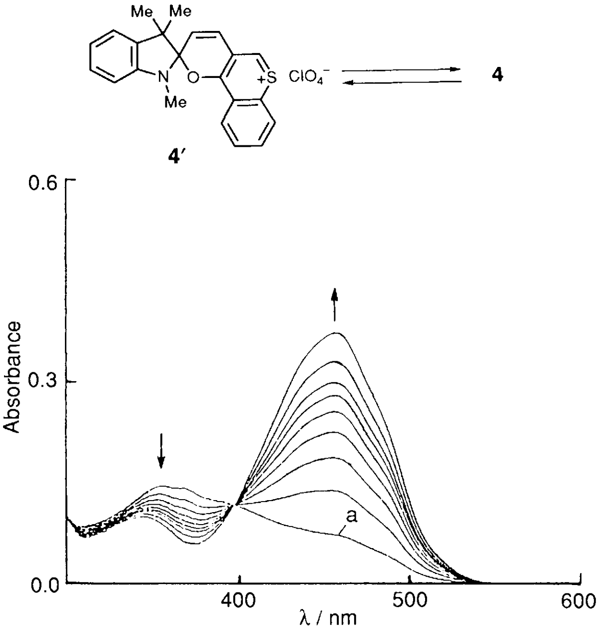


Fig. 1 Absorption spectral changes of **4′** in $CHCl_2CHCl_2$ (initial [**4**] 1×10^{-4} mol dm^{-3}) produced by irradiation with visible light at 10 min intervals (last two intervals: 20 and 45 min, respectively) at 20 °C

Table 1 Absorption spectra in $CHCl_2CHCl_2$

Dye	λ_{max}/nm	log (ε/dm^3 mol^{-1} cm^{-1})
3	403	4.48
4	456	4.54
5	435	4.58
8	556	4.84
9	651	4.63
10	725	4.67

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† All new merocyanine dyes described here were identified from their ^1H NMR spectra, and gave satisfactory elemental analyses.

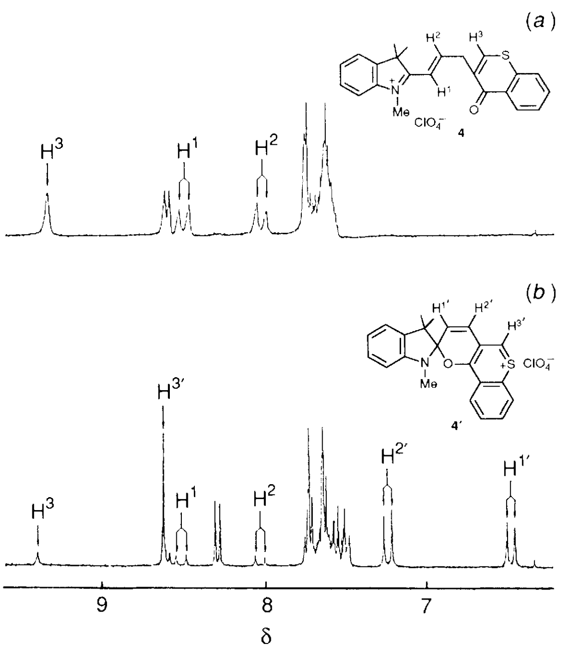

Fig. 2 ^1H NMR spectra of **4** and **4'** in $CDCl_2CDCl_2$ (*a*) before and (*b*) after irradiation with visible light, respectively

The colourless species formed by photoirradiation was assigned to the spiropyran derivative **4'**, a ring-closure form, by comparison of the ^1H NMR spectra of **4** before and after photoirradiation, as shown in Fig. 2. After irradiation, the resonance peaks assigned to alkenic protons H^1, H^2 and H^3 in the merocyanine dye **4** diminished; new resonance peaks were then observed at δ 6.47, 7.24 and 8.63, these were assigned to the resonances for $H^{1'}$, $H^{2'}$ and $H^{3'}$ of the ring-closed form, respectively, as shown in Fig. 2(*b*). The peak of the *N*-methyl protons in the spiropyran form also shifted upfield (δ 3.0). These peaks are consistent with the typical spectral data of spiropyrans. The conversion of **4** into **4'** by photoirradiation was 80% from the ratio of the integrated intensity.

Conversions for the decolouration of dyes **3** and **5** were 85% and 43%, respectively, and similar spiropyran species were confirmed by use of ^1H NMR spectroscopy. Merocyanine dyes, **8–10**, having an extended π-conjugated chain produced no colourless spiropyran derivatives under similar conditions on irradiation with visible light, but decolouration of these dyes in a polyester film was observed.

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