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Substituent effects in stilbene-based merocyanine dyes

Experiments with merocyanine dyes provide a visual reinforcement of the idea that colour in aromatic compounds arises through resonance and extended conjugation.

Students in organic chemistry are taught a number of fundamental principles concerning the factors which govern the properties of organic compounds. Among these principles is the effect of substituents on the properties of aromatic rings, especially the benzene ring. For instance, we teach the students that the reactivity of the benzene molecule towards electrophilic substitution reactions is enhanced by the presence of electron-donating groups (*eg* OR, NR_1R_2) on the ring,[1] and that the degree to which an atom or group of atoms feeds electrons into the aromatic ring determines the level of ring activation. It is well known that the order of decreasing activation power is given by: $O^- > NR_1R_2 > OH > OR$; where R_1 and R_2 = H, alkyl; and R = alkyl.[2] It is also well known that electron-withdrawing groups placed *para* or *ortho* enhance the ability of the above types of groups to feed electrons into the ring.[3]

In related courses concerning the chemistry of dyes and colour, we teach textile chemistry undergraduates that resonance and extended conjugation in an organic compound are essential to the production of colour – no resonance, no colour; and no extended conjugation, no colour. We also emphasise the importance of coplanarity and axis of polarisability to generating colour in organic molecules,[4] and normally do so with the aid of molecular models.

Several years ago Minch and Shah[5] published a paper which described the synthesis and unusual properties of the merocyanine dye 1-methyl-4-[(oxocyclohexadienylidene) ethylidene]-1,4-dihydropyridine (*1*, MOED). The authors noted that the dye possesses a colour in solution which is dependent upon the polarity of the solvent employed (cf Table 1). Colours ranging from yellow in H_2O to blue in pyridine were reported. Several of the high school students in our summer research programme have repeated the synthesis of dye *1*, and more recently we have extended work in the area to include dyes *2–9*.

These new merocyanine dyes provide a chemistry instructor with an additional tool to use as a visual reinforcement of some of the concepts outlined above. It has been demonstrated that solvents influence which resonance structure of MOED predominates in solution.[5] Although a detailed theoretical basis for this observation has been proposed,[6,7] a suitable explanation for undergraduates would be the following: (*i*) polar solvents (*eg* H_2O, MeOH) which stabilise the benzenoidal form (A) of MOED, through intermolecular interactions (see *Fig. 1*), diminish the extent to which the electrons on the O^- group feed

Table 1. The effect of solvents on the colours of merocyanine dyes *2–7*.*

Dye	Colour/ λ_{max} nm (H_2O)	Colour/ λ_{max} nm (MeOH)	Colour/ λ_{max} nm (2-PrOH)	Colour/ λ_{max} nm (Acetone)	Colour/ λ_{max} nm (Pyridine)
1[5]	Yellow/442	Red–orange/509	Violet/545	Blue–violet/577	Blue/603
2	Yellow/440	Orange/468	Orange/472	Orange/464	Orange/488
3	Yellow/396	Yellow/420	Blue–violet/576	Blue/607	Green/616
4	Yellow/358	Yellow/378	Violet/540	Blue/590	Green/724
5	Yellow/416	Yellow–orange/446	Blue/632	Blue/620	Blue/632
6	Yellow/410	Yellow–orange/432	Blue/637	Blue/656	Green/726
7	Yellow/400	Yellow/420	Violet/576	Blue/602	Blue/614

*The dye concentration was 5×10^{-5} M.

Fig. 1. Protic solvent interactions with form B of MOED.

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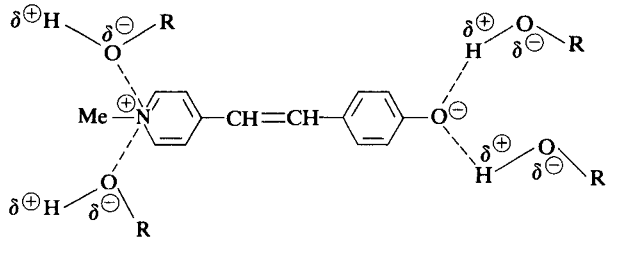


into the conjugated system to produce the much more highly coloured *p*-quinonoidal form (B); and (*ii*) since the less polar aprotic solvents (*eg* acetone, pyridine) are not effective in stabilising the charges in form *A*, form *B* of MOED predominates and blue solutions result (see *Fig. 2*). These results suggest that H-bonding is required to stabilise completely the negative charge on the oxygen atom of *A*.

MOED-analogues

These merocyanine dyes can be used to show a number of substituent effects, including differences in the electron-donating ability of the O$^-$, OMe, OH and NMe$_2$ groups. Table 1 outlines the various colours produced by dissolving dyes *2–7* in five different solvents, and *Figs 3* and *4* depict typical visible spectra recorded on the dyes.

It can be seen from Table 1 that the replacement of the O$^-$ group of MOED with an NMe$_2$ group (*2*) results in the loss of red, violet and blue colours from the colour spectrum of this class of dyes, and that solvent interactions contribute little to the λ_{max} of dye *2* (see *Fig. 3*). These results can be attributed to differences in the electron-donating ability of NMe$_2$ *vs* O$^-$, the latter being much more effective. Table 1 and *Fig. 4* show that increasing the electron-rich character of the ring of MOED that contains the O$^-$ group (see *3*) causes a bathochromic shift (a shift in λ_{max} to a region of longer wavelengths), when the resulting dye is dissolved in 2-PrOH, acetone or pyridine. A bright green solution also results when dye *3* is dissolved in γ-picoline.

If the heterocyclic (pyridine) ring of MOED is replaced with the benzohomologue quinoline, the resulting dye (*ie 4*) exhibits a spectrum having a shorter wavelength maximum (a hypsochromic effect) in H$_2$O and MeOH, but a longer wavelength maximum in pyridine. At first glance, one would have predicted a bathochromic shift in the spectrum of *4 vs* MOED in each solvent owing to the increase in stability of form *B* that a benzo group would afford. It is quite possible, though, that in the polar protic solvents, resonance structures such as those in *Fig. 5* form more readily, causing the observed hypsochromic shifts.

Similarly, the addition of a methoxy group to the benzohomologue of MOED, to produce dye *5* results in a shift in the absorption maximum to shorter wavelengths in the more polar solvents (Table 1).

When the O$^-$ group of MOED is moved to the ring carbon that is *ortho* to the vinyl group (*6*), a bathochromic shift (relative to *1*) results when the less polar solvents are employed. This observation suggests that interactions between the dye and the solvents 2-PrOH, acetone and pyridine are further inhibited by the presence of the 1,2-arrangement of the O$^-$ and vinyl groupings. The effect is much less pronounced in the benzohomologue (*7*). In this latter case, it is likely that the second ring of the naphthol moiety is involved in the delocalisation of the charge on the O$^-$ group as a mechanism

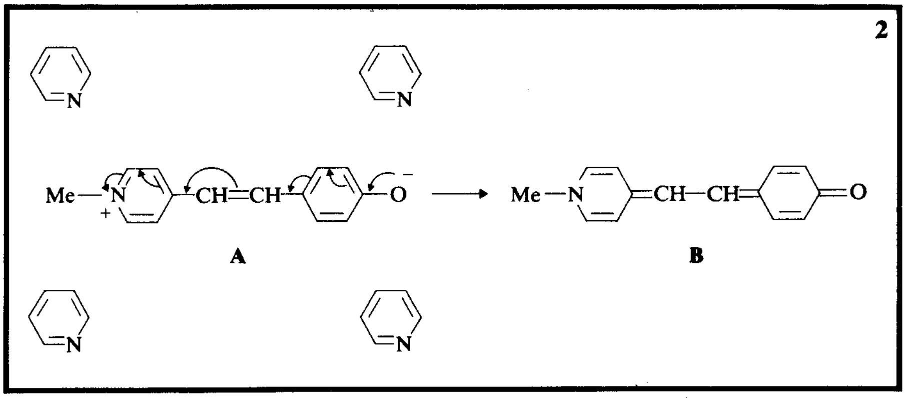


Fig. 2. Formation of form B of MOED in an aprotic solvent.

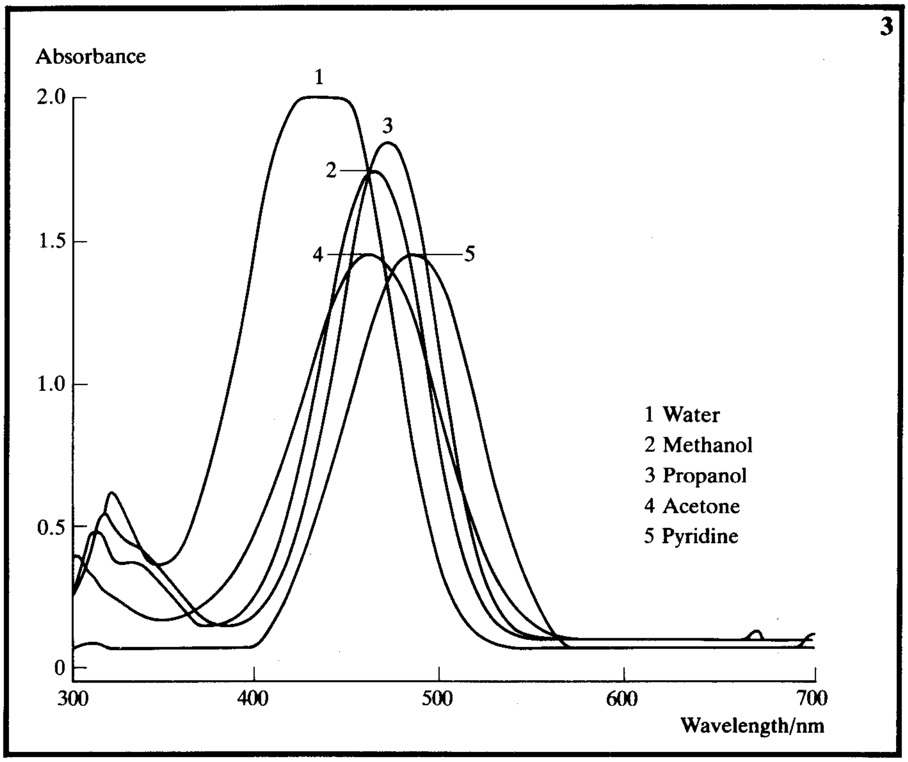
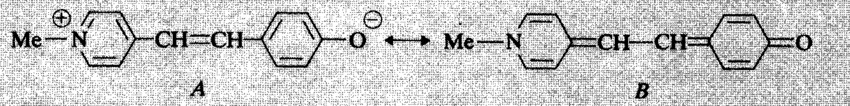
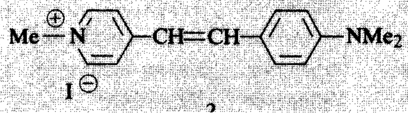


Fig. 3. Singlet oxygen – type reactions.



1 **Structure of MOED**



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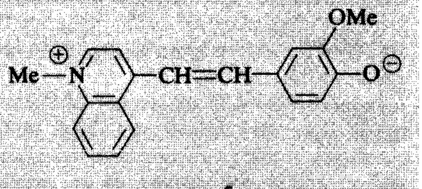

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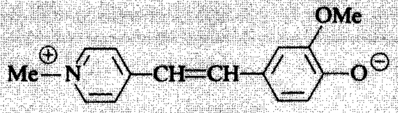

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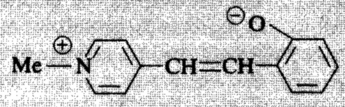

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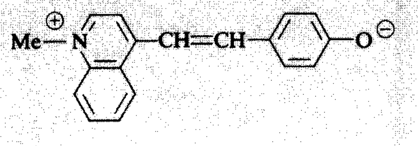

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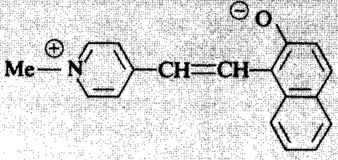

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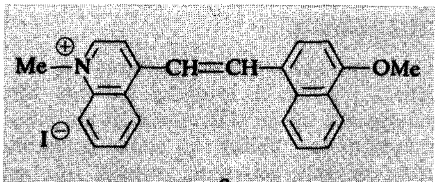

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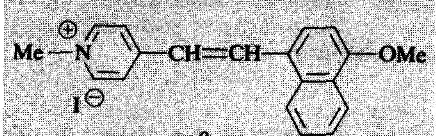

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for stabilising this charge, and this results in a decrease in the concentration of electrons on O⁻ that are available to generate the more highly coloured quinonoid structure. We might also add that it is apparent from plots of λ_{max} *vs* dielectric constant that factors other than solvent polarity contribute to the *magnitude* of the shifts in the absorption maxima of dye *7*, since the wavelength maxima of this dye in the less polar solvents do not correspond to what would be predicted when dye *7* is dissolved in various mixtures of MeOH/H_2O or MeOH/acetone of known dielectric constant.

Both the free phenols and the methyl ethers of dyes *2-7* and compounds *8-9* give yellow solutions (λ_{max} 390-440) in each of the five test solvents, as would be expected since hydroxy and alkoxy groups are poorer electron donors than O⁻ or NMe_2.

Most of the new dyes reported here exhibit a hypsochromic shift relative to MOED when dissolved in H_2O and MeOH. The electron delocalisation shown in *Fig. 5* could account for this shift, when *4* and *5* were used. An equally satisfying explanation for the observed hypsochromic shift when dyes *3*, *6* and *7* were used, however, is not readily apparent.

Dye synthesis

The dyes prepared in this study were synthesised by heating an *N*-methylpicolinium halide with a substituted benzaldehyde in ethanol in the presence of piperidine, followed by treatment of the resulting product *12* with warm 0.2M KOH solution (where X □ OH) to ionise the aromatic hydroxyl groups and recrystallise the final products (*1, 3-7*). This sequence is outlined in *Fig. 6*. The reactions were conducted on a 0.1 mol scale, and each dye was readily isolated and purified in two days. It should be added that prolonged heating of the phenols in aqueous KOH resulted in the partial degradation of *6* and *7*. Solutions of these more sensitive dyes were produced at 30°C rather than the usual 70°C.

During the latter stages of this work, we found that γ-picolinium sulphate (prepared

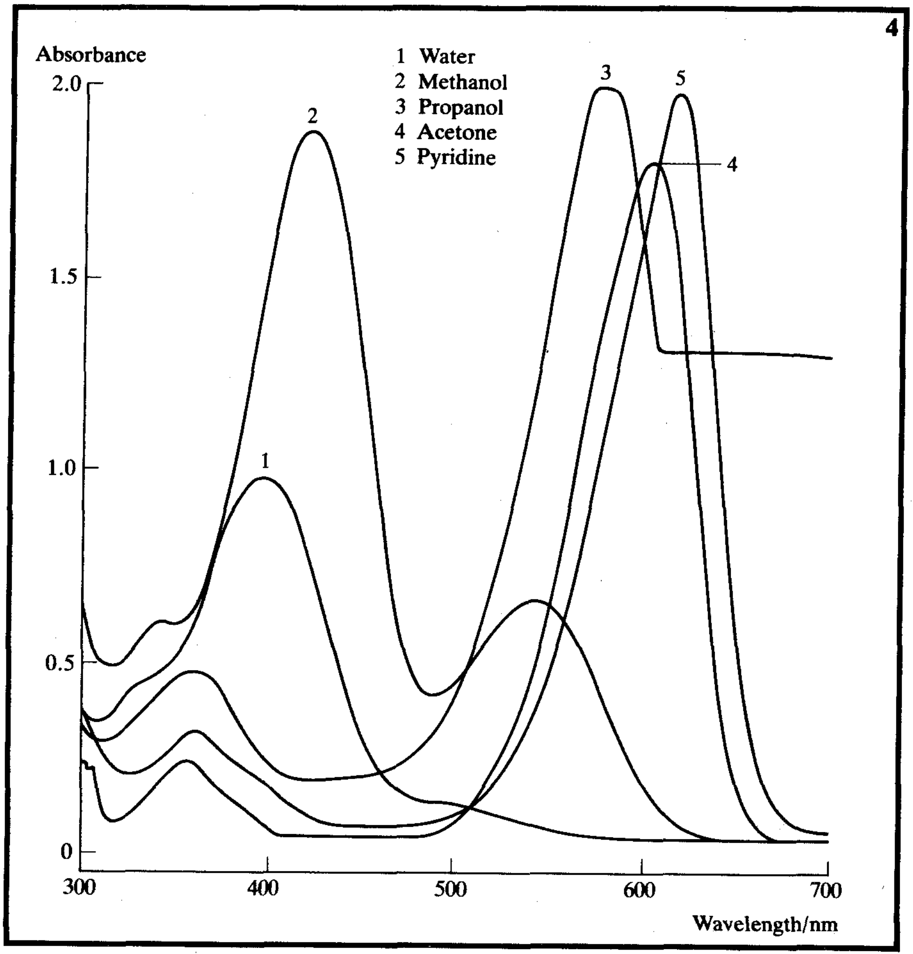

Fig. 4. Absorption spectra of dye *3* in various solvents.

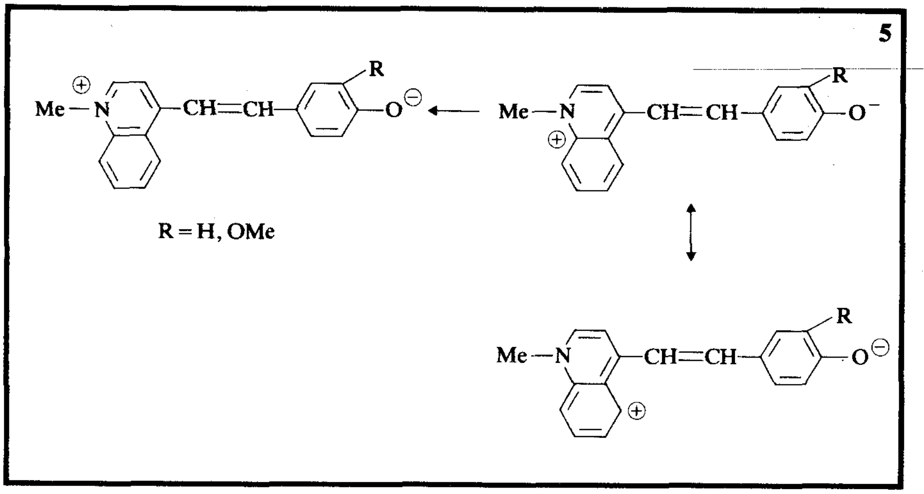

Fig. 5. Delocalisation of the cationic charge of dyes *4* and *5* in protic solvents.

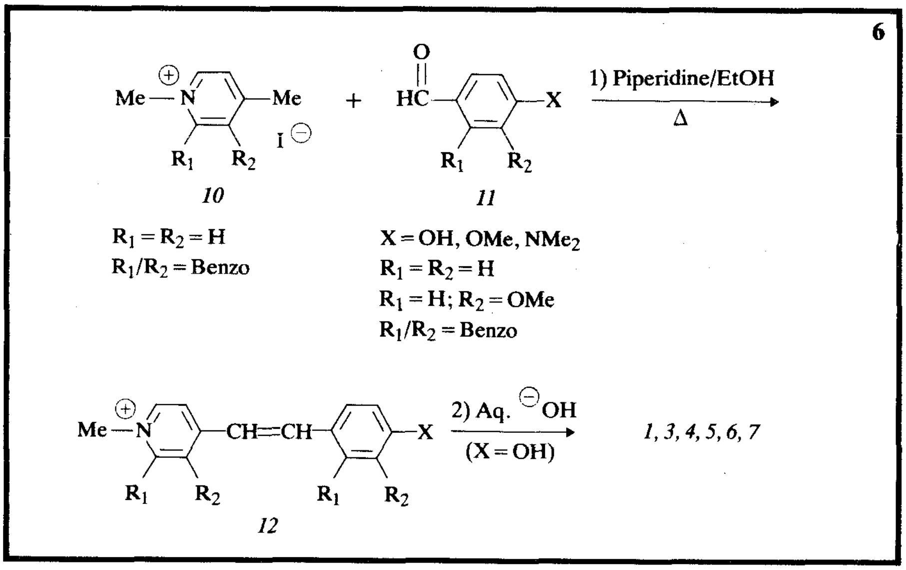

Fig. 6. Preparation of MOED-type stilbene dyes.

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by mixing dimethylsulphate (DMS) with a 5 per cent solution of γ-picoline at 5°C) could be readily substituted for the corresponding methiodide in the preparation of these merocyanine dyes. In this way, two moles of the *N*-methyl picolinium derivative of γ-picoline could be obtained for each mole of alkylating agent used.

Summary

The merocyanine dyes reported in this article provide a teaching aid for the description of: (*i*) differences in the electron-donating ability of some common aromatic ring activating groups; (*ii*) the importance of H-bonding stabilising in dipolar organic molecules; and (*iii*) differences in the polarity of some commonly used laboratory solvents.

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