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Merocyanine and Photomerocyanine Dyes

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We give a review of results from work on merocyanines (MC) and photomerocyanines (PMC) reporting the most stable isomeric forms from X-ray structural and NMR spectral analysis. We also give new X-ray data, ^{1}H-^{1}H NOESY, ^{1}H and ^{13}C-NMR results for MC's.

Keywords: Merocyanine; deuterium isotope shift; NMR; XRD

INTRODUCTION.

Photomerocyanines (PMC) are transient, so it is often difficult to carry out detailed NMR or crystallographic studies. Low conversion and solubility are common problems for many of these dyes. Even ^{1}H-NMR can prove problematic and ^{13}C-NMR is rarely reported. Spiro-oxazine and chromene PMC's have been studied at low temperature, or

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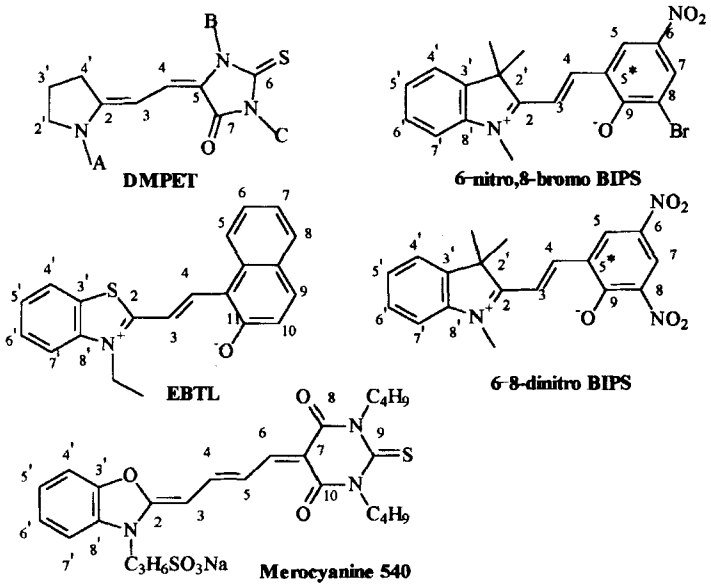
results.[1,2,3,4] We studied the PMC's and MC's in **Scheme 1** presenting a summary here. Detailed experimental and theoretical discussion has been previously published.[5,6,7]



SCHEME 1.

RESULTS AND DISCUSSION

The first notable result was that the spiro-pyran merocyanine's (SP-MC) 3C proton isotopically exchanges with deuterium from D_2O in organic solvents such as DMSO acetone or chloroform, in the way of a kinetically slow D_2O shake.[5] This exchange is also observed for EBTL, but both DMPET and merocyanine 540 needed deuteroacids to start

similar exchange processes. All D-exchanges are consistent with electron donation/charge delocalisation from a conjugated nitrogen or a conjugated oxygen. For example merocyanine 540 exclusively deuterates at C3 and C5 of the methine bridge, but not at C4 and C6. For SP PMC's and EBTL this exchange indicates that the C3 site is δ- whereas the C4 site is δ+.

Electrospray ionisation (ESI)-MS experiments[5] showed that C3 deuterated and protonated forms of SP-PMC's and EBTL had the expected mass difference of one Dalton when detection was carried out in +ve ion mode but had identical mass in -ve ion mode. The ion detected in -ve ion mode must therefore be deprotonated or dedeuterated at C3. ESI is a soft technique for transporting solution phase ions to the gas phase, however it is still nominally an ionisation technique and gas phase proton abstraction may occur. C3 deprotonation is not proven in unperturbed solution chemistry.

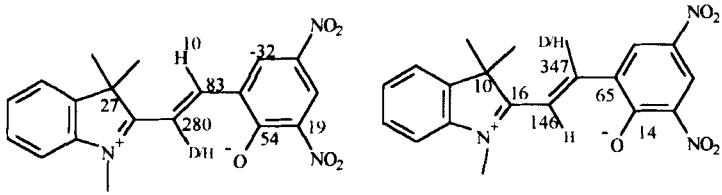
6,8-dinitro BIPS PMC crystallised in part as red rods that were suitable for X-ray analysis. These were found to be made of the TTT isomer.[5]

^{1}H-^{1}H-NOESY shows that the significant 6,8-dinitro BIPS PMC isomers in the solvents acetone, chloroform and DMSO are TTC and TTT, with TTC dominant. Line broadening in 6,8-dinitro BIPS ^{1}H-NMR spectra indicate an intermediate isomerisation rate on the 400 MHz ^{1}H-NMR timescale between the TTT and TTC isomers.[5]

For 6-nitro,8-bromo BIPS PMC below 183 K the C5 resonance resolved into two resonances for the TTC and TTT isomers. From line

shape analysis we estimated the activation energy of the isomerisation to be 43.6 kJ.mole^{-1} and from resonance integrals a ΔG of 4.6 kJ.mole^{-1} was calculated.[6]

Using HETCOR/COLOC the ^{13}C spectrum of 6,8-dinitro BIPS PMC was assigned.[7] Notably the C4 and C3 resonances respectively at 151.7 ppm and 110.8 ppm reflect polarisation of the C3-C4 bond and the C9 resonance at 182.4 ppm is clearly for a partial carbonyl bond with the oxygen at C9 taking a δ-.



^{13}C D-isotope shift mapping[7] in DMSO upon deuterating at C3 and C4 is shown above (numbers in ppb). Compared with C4 deuteration the long range, position and magnitude of the isotope shift upon C3-deuteration indicate the isotopic effect transfers via a C3-H---O-C9 interaction that is either steric or electrostatic, probably the latter as tiny changes in torsion angles are expected upon deuteration relative to the C3 protonated form, whereas the C3-H/D bond and the C9-O bonds are obviously rather polar. The 6-nitro,8-bromo BIPS ^{13}C spectrum was not fully assigned due to overlapping equilibrated closed form peaks. Where resonances were clear similar C3 D-isotope shifts were observed. For example; *C9* (*54* ppb), *C4* (*83* ppb), C2' (23 ppb).

^{1}H-^{1}H-NOESY showed the DMPET MC isomer in DMSO was exclusively TTC. TTC was also found by X-ray diffraction (**figure 1**).

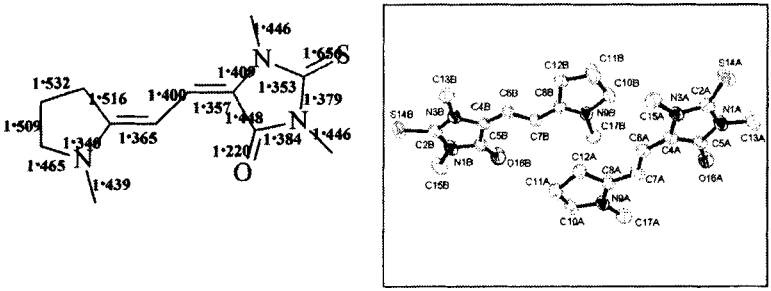


FIGURE 1. X-ray analysis of DMPET crystalised from DMSO.

^{13}C and ^{1}H-NMR spectra of DMPET in DMSO are listed below .

(**H4**: 6.7), (**H3**: 6.3), (**H2'**:3.55), (**N-CH$_3^B$**:3.45), (**N-CH$_3^C$**: 3.15), (**H4'**: 2.92), (**N-CH$_3^A$**: 2.90), (**H3'**: 1.95).
(**C6**: 167.7), (**C2**: 164.2), (**C7**: 160.7), (**C4**: 126.3), (**C5**: 114.7), (**C3**: 88.0), (**C2'**: 55.5), (**N-CH$_3^A$**: 33.1), (**N-CH$_3^B$**: 30.0), (**C4'**: 29.9), (**N-CH$_3^C$**: 27.4) (**C3'**: 20.1). (All numbers in ppm)

These ^{13}C-NMR results show that the C3-C4 bond is polarised with C3 being δ- and C4 δ+. Bond lengths indicate the electron delocalisation of N-CH$_3^A$ is not directly to the oxygen at C7, but via a conjugated path including N-CH$_3^B$, N-CH$_3^C$ and the C=S. The fact that only H3 is replaced with deuterium upon deuteroacidification indicates the direction of electron donation is N-CH$_3^A$ to N-CH$_3^B$.

protons on the molecule. Heating resulted in the coalescence of most of the peaks, however even at 453 K not all peaks were sharp. Room temperature EXSY indicated four conformations cis and trans about the two end methine bridge bonds, but the spectrum was very complex.

CONCLUSION.

PMC's and MC's have charge alternation on the methine bridge. D-isotope shifts in SP-PMC indicate an interaction between C3-H--O-C9. Predominant SP-PMC isomers were TTC and TTT. D-exchange indicates the direction of electron donation and occurs as a kinetically slow D_2O shake for the zwitterionic MC's and PMC's.

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