

Synthesis of Merocyanines Analogues Based on the Pyrazolin-5-one System

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The majority of dyes belong to the chromophoric class known as donor-acceptor systems. The essential structural feature of such systems is the presence of one or more electron donating groups conjugated to one or more electron withdrawing groups *via* an unsaturated bridge. The pyrazolin-5-one system is an effective electron acceptor residue, and can also act as a weak electron donor. In our experiments, the various symmetrical and unsymmetrical H-chromophores were synthesized in the indoxyl, imidazo[1,2-a]pyridin-2-one, pyrazolin-5-one, and pyridin-2,6-dione residues, resulting in cross-conjugated donor-acceptor systems. And the visible light absorption was then associated with the migration of electron density from the donor region of the molecule to the acceptor region. Also, it was useful to prepare related non-cross-conjugated donor acceptor chromophores by combining these residues with other electron donor or acceptor moieties. For convenience such chromophores are referred to as *merocyanines*.

Key Words : Merocyanines, H-Chromophore, Pyrazolin-5-one, Bathochromism

Introduction

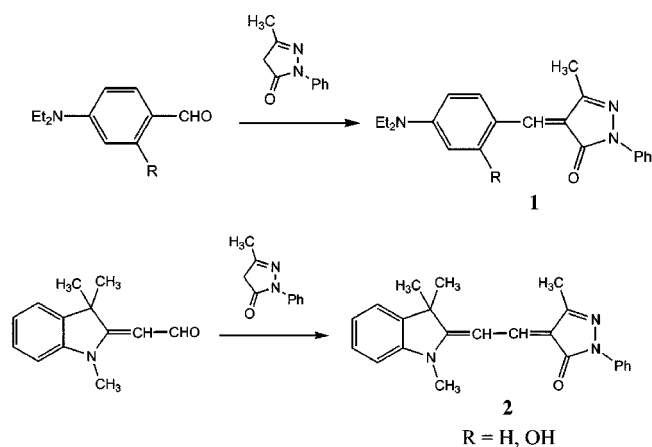
Merocyanines based on the pyrazolin-5-one system.

The pyrazolin-5-one system is an effective electron acceptor residue, and can also act as a weak electron donor.¹ However, all technically useful dyes based on this system (*e.g.* *azamethine photographic dyes, arylazo textile dyes*) utilize the heterocycle as an electron acceptor. In the present study, three representative merocyanine dyes,^{2,3} namely **1a**, **1b** and **2**, were prepared in which the pyrazolinone⁴ residue was also used as an electron acceptor.

As we can be seen in Scheme 1 and these systems were synthesized by condensing 3-methyl-1-phenylpyrazolin-5-one with 4-*N,N*-diethylaminobenzaldehyde, 4-*N,N*-diethyl amino-3-hydroxybenzaldehyde and 1,3,3-trimethyl-2-methyleneindolinealdehyde (Fischer's aldehyde), respectively.⁵

Results and Discussion

Visible absorption spectra for pyrazolin-5-one mero-



Scheme 1. Pyrazolin-5-one Synthesized.

merocyanines. The pyrazolin-5-one system is both electron donating and electron withdrawing, but its electron withdrawing properties are generally the more pronounced. Commercial merocyanine dyes based on this system invariably use it as an acceptor. With the exception of **4b**, which is an H-chromophore⁶ and is included for comparison purposes, the merocyanine dyes in Table 1 all contain pyrazolin-5-one as an acceptor residue. This is also indicated by the strong positive solvatochromism of dyes **1a** and **1b**, which implies relatively weak charge transfer from donor to acceptor in the ground state, with a correspondingly large charge transfer in the excited state. Molar extinction coefficients of the pyrazolin-5-one merocyanines are shown in Table 1.

The symmetrical H-chromophore⁷ **3** (Table 1) "Pyrazole Blue" has been known for more than one hundred years, but there appears to be little documented information about its spectroscopic properties. The H-chromophore **3** was prepared by reacting 3-methyl-1-phenylpyrazolin-5-one as an electron acceptor group or an electron donor. This blue compounds can be synthesized by a direct oxidative dimerisation of 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one (Scheme 2). The visible absorption maxima, measured in toluene and dichloromethane (Table 1), show bathochromic chromophores relatively and that the system has a negligible solvatochromism.⁸

The H-chromophore properties of **3** can be considered to arise from interaction of the resonance forms shown in Figure 1, in which the pyrazolin-5-one ring can act as both an electron donor and an electron acceptor.

Given the relatively weak electron donor properties of the pyrazolin-5-one system, the bathochromism of **3** is somewhat unexpected, but Pariser-Parr-Pople Molecular Orbital (PPP-MO) calculations^{9,10} predict the shift well. Thus a λ_{\max} value of 606 nm is predicted (with a rather low oscillator strength of 0.42), in comparison with the experimental λ_{\max}

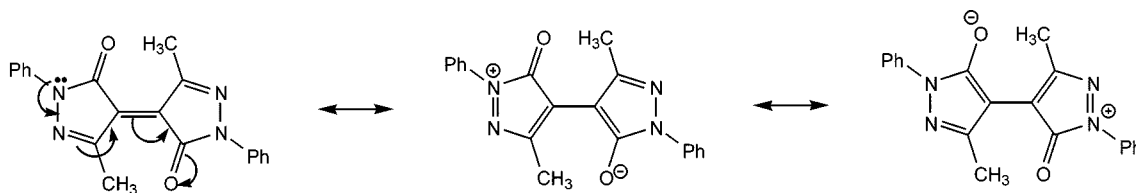
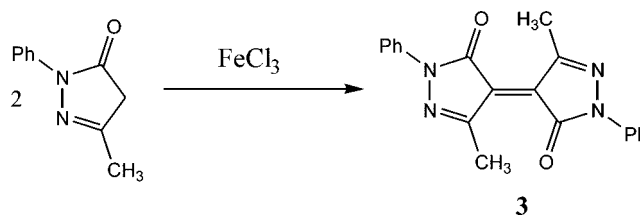
Table 1. Visible Absorption Bands for Pyrazolin-5-one Mero-cyanines

Dye	X	λ_{\max} (tol) ^a /nm	λ_{\max} (DCM) ^b /nm	λ_{\max} (MeOH) ^c /nm	ϵ_{\max} ^d /L mol ⁻¹ cm ⁻¹
1a		—	454	474	22,600 (DCM)
1b		—	442	480	28,700 (DCM)
2		—	470	462	35,300 (DCM)
3		590	589	insoluble	14,000 (DCM)
4a		508	510	504	14,000 (DCM)
4b		509	510	509	15,000 (DCM)

^amaximum of wavelength in toluene. ^bmaximum of wavelength in dichloromethane. ^cmaximum of wavelength in methanol. ^dmaximum of molar extinction coefficient in dichloromethane. DCM: dichloromethane.

value of 590 nm in toluene. Although the electron donor atoms in **3** are amidic and consequently are weak donors, the conjugation pathway between them and the carbonyl groups in the opposite ring (see Scheme 1) is longer than that in the indigo chromophore. Presumably this extra conjugation compensates for the lower electron donating strength. The transition moment of PPP-MO calculations, electron density changes for the visible transition, and the ground and excited state electronic charges for **3** are shown in Figure 2.

The electron density changes for the visible transition

**Figure 1.** Principal Resonance Forms for Chromophore **3**.**Scheme 2.** Dimerization Process of Pyrazolin-5-one.

(Fig. **2b**) show no significant increase in electron density at the carbonyl oxygen but do show that the electron donor pyrazoline N-1 atoms lose electron density in the excited state. This can be understood by examining the ground and excited state charges (Figs. **2c** and **2d** respectively), as the N-1 atoms are not donating as much electron density to the carbonyl groups in the ground state.

Although unsymmetrical H-chromophores can theoretically be made by oxidative dimerisation between two different heterocyclic active methylene compounds, this will lead to mixtures containing the required symmetrical dye and the two corresponding symmetrical species, with consequent problems of isolation and purification in our experiments. Therefore the synthetic route is provided by the reaction of 2-chloroisatin with heterocyclic active methylene compounds as generalized in Scheme 3.

The unsymmetrical H-chromophores (**4a** and **4b**) containing an indoxyl residue are significantly more hypsochromic than **3**, and are red in color. Again, the simple argument that an unsymmetrical H-chromophore will absorb at a wavelength corresponding to an average of the λ_{\max} values of the parent symmetrical structures does not hold, as this would be predicted to be blue in color.

However, Pariser-Parr-Pople Molecular Orbital (PPP-MO) calculations¹¹ predict the color properties of unsymmetrical H-chromophore very well, and a calculated λ_{\max} of 512 nm is obtained for **4b**, which compares well with the experimental value of 509 nm in toluene. A relatively low oscillator strength (0.48) is also predicted, consistent with the observed low extinction coefficient. Like the symmetrical H-chromophore **3**, both **4a** and **4b** show negligible solvatochromism.

Experimental Section

General Methods. All the chemicals and solvents used during the reactions were purchased from Aldrich (U.S.A. Chemical Co.), Acros (U.K. Chemical Co), and Junsei (Japan Chemical Co). Before being used, some of them were purified using normal procedures. All reactions were

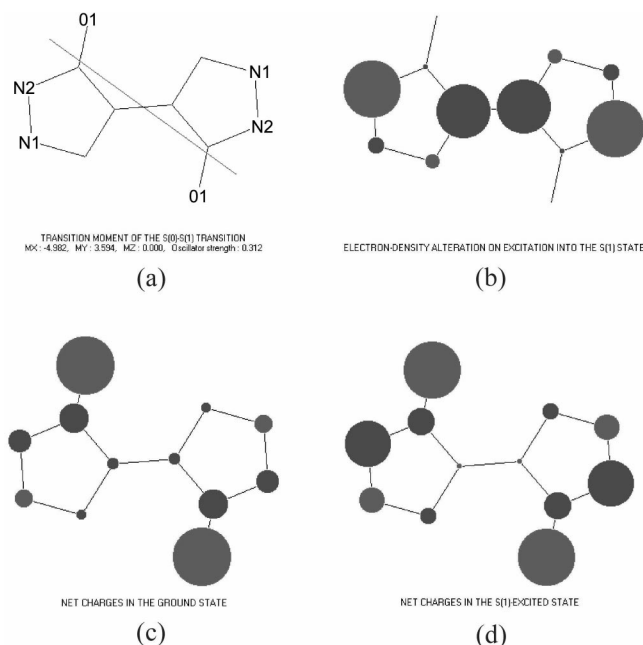
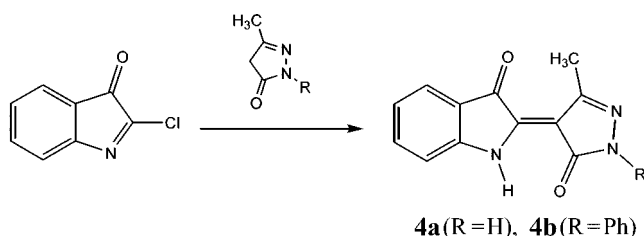


Figure 2. Calculated Molecular Orbital (MO) Data for Chromophore **3**; (a) transition moment; (b) p-electron density changes for the visible transition (red = increase, blue = decrease); (c) and (d) electronic charges in ground state and first excited state, respectively (red = negative, blue = positive)



Scheme 3. Reaction of 2-Chloroisatin with Heterocyclic Methylene.

monitored by thin layer chromatography (TLC). Ultraviolet and visible spectra were determined on a Perkin-Elmer Lambda 15 Spectrophotometer. Melting points were measured on an electrothermal melting point apparatus. Elemental microanalysis and mass spectrometric analyses were performed by the EPSRC National Mass Spectrometry Service, using either fast atom bombardment sampling in a *m*-nitrobenzyl alcohol matrix, electron impact ionization, chemical ionization or electrospray. Nuclear magnetic resonance spectra (^1H NMR) were performed on Bruker 300 spectra at 300.13 MHz in deuteriochloroform and chemical shifts were referenced to tetramethylsilane as an internal standard (δ (^1H) = 0.00).

Merocyanine 1a: 4-Diethylaminobenzaldehyde (0.53 g, 3 mmol) and 3-methyl-1-phenyl-2-pyrazolin-5-one (0.522 g, 3 mmol) were dissolved in ethanol (10 mL). The reaction mixture was refluxed 3 h, cooled to room temperature and then evaporated to give a red solid. The solid was recrystallized from ethanol, giving 4-(4-diethylamino-benzylidene)-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one **1a** (0.9 g, 90%). mp. 159-161 $^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}$: C,

75.65; H, 6.95; N, 12.60. Found: C, 75.55; H, 6.85; N, 12.85. ^1H NMR (300 MHz, CDCl_3) δ 1.24 (t, J = 7.1 Hz, 6H), 2.33 (s, 3H), 3.48 (q, J = 7.0 Hz, 4H), 6.72 (d, J = 8.9 Hz, 2H), 7.15 (s, H), 7.25 (t, J = 7.4 Hz, H), 7.4 (t, J = 7.6 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 8.57 (d, J = 8.9 Hz, 2H).

Merocyanine 1b: 4-Diethylaminosalicylaldehyde (0.58 g, 3 mmol) and 1-phenyl-3-methyl-2-pyrazolin-5-one (0.522 g, 3 mmol) were dissolved in ethanol (10 mL) and the solution refluxed 3 h. Following the isolation procedure described for **1a**, 4-(4-diethylamino-benzylidene)-1-phenyl-3-methyl-2-pyrazolin-5-one **1b** was obtained as a red solid (0.52 g, 50%). mp. 172-174 $^{\circ}\text{C}$. Mass Spectrum (FAB): Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_2$: $[\text{M} + \text{H}]^+ = 350$. Found $[\text{M} + \text{H}]^+ = 350$. Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_2$: C, 72.18; H, 6.63; N, 12.03. Found: C, 72.20; H, 6.20; N, 12.25. ^1H NMR (300 MHz, CDCl_3) δ 1.17 (t, J = 7.1 Hz, 6H), 2.27 (s, 3H), 3.38 (q, J = 7.0 Hz, 4H), 6.26 (d, J = 8.9 Hz, 2H), 7.11 (s, H), 7.24 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 8.1 Hz, 2H), 7.90 (d, J = 7.9 Hz, 2H).

Merocyanine 2: 1,3,3-trimethyl-2-methyleneindoline-aldehyde (Fischer's aldehyde) (0.60 g, 3 mmol) and 1-phenyl-3-methyl-2-pyrazolin-5-one (0.52 g, 3 mmol) were dissolved in ethanol (10 mL). The reaction mixture was refluxed 3 h and then evaporated to give red solid. The solid was recrystallized from ethanol, giving **2** (0.55 g, 51%). mp. 169-171 $^{\circ}\text{C}$. Mass Spectrum (FAB): Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}$, $[\text{M} + \text{H}]^+ = 358$. Found $[\text{M} + \text{H}]^+ = 358$. Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}$: C, 77.28; H, 6.49; N, 11.76. Found: C, 75.65; H, 6.20; N, 12.45. ^1H NMR (300 MHz, CDCl_3) δ 1.70 (s, 6H), 2.30 (s, 3H), 3.48 (s, 3H), 6.95 (d, J = 7.8 Hz, H), 7.30 (d, J = 7.0 Hz, H), 7.39 (m, 5H), 7.90 (d, J = 8.3 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H).

3,3'-Dimethyl-1,1'-diphenyl-1H,1'H-[4,4']bipyrazolylidene-5,5'-dione 3: 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one (254 mg, 1 mmol) was dissolved in ethanol (3 mL). Ferric chloride (160 mg, 1 mmol) was slowly added with vigorous stirring at room temperature and the solution was kept at room temperature 12 h. A small amount of hydrochloric acid was added to neutralise the solution and the solid was filtered off. The solid was recrystallized from ethanol to give 5,5'-dimethyl-2,2'-diphenyl-2H,2'H-(4,4')-bipyrazolidine-3,3'-dione as a dark blue solid **3** (0.07 g, 42%). mp. 240-244 $^{\circ}\text{C}$. Mass Spectrum (FAB): Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2$, $[\text{M} + \text{H}]^+ = 345$. Found $[\text{M} + \text{H}]^+ = 345$.

Unsymmetrical H-chromophore 4a: 2-Chloroisatin¹² (1.67 g, 10 mmol) and 3-methyl-5-pyrazolone (0.98 g, 10 mmol) were dissolved in dry tetrahydrofuran (20 mL). The reaction mixture was refluxed 6 h, at which point t.l.c. showed no 2-chloroisatin remaining. The reaction mixture was evaporated to give a red solid. The solid was recrystallized from ethanol and dried in an oven 50 $^{\circ}\text{C}$, giving **4a** (1.18 g, 52%). mp. 178-181 $^{\circ}\text{C}$. Mass Spectrum (FAB): Calcd. for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$, $[\text{M} + \text{H}]^+ = 228$. Found $[\text{M} + \text{H}]^+ = 228$. Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.21; H, 4.15; N, 18.77. ^1H NMR (300 MHz, MeOH-*d*) δ 1.28 (s, 3H), 6.91-7.25 (m, 4H), 7.53 (d, J = 6.9 Hz, H), 7.54 (d, J = 7.5 Hz, H).

Unsymmetrical H-chromophore 4b: 2-Chloroisatin (1.7

g, 10 mmol) and 1-phenyl-3-methyl-5-pyrazolone (1.74 g, 10 mmol) were dissolved in dry tetrahydrofuran (20 mL) and refluxed 6 h. The same experimental procedure as described for **4a** was followed, giving **4b** as a red solid (1.46 g, 48%). mp. 215-217 °C. Mass Spectrum (FAB): Calcd for $C_{18}H_{13}N_3O_2$, $[M + H]^+ = 304$. Found $[M + H]^+ = 304$. Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.55; H, 4.25; N, 13.60. 1H NMR (300 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.04 (d, $J = 7.78$ Hz, H), 7.13 (t, $J = 7.6$ Hz, H), 7.20 (t, $J = 7.8$ Hz, H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.57 (t, $J = 7.7$ Hz, H), 7.71 (d, $J = 7.7$ Hz, H), 7.97 (d, $J = 8.15$ Hz, 2H), 11.35 (s, H).

Conclusions

The H-Chromophores or the merocyanines based on the pyrazolin-5-one system were synthesized to examining their color properties with various solvents. They also showed a bathochromic shift on protonation. This effect was even more pronounced in the symmetrical or unsymmetrical H-chromophores containing pyrazoline-5-one and indoxyl terminal groups. We extended this study by examining new

merocyanine systems containing the same terminal groups used for the H-chromophores combined with various electron acceptor residues.

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