

## Synthesis and Properties of 6-Substituted Quinoline-5,8-dione Colour Formers

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New 6-substituted quinoline-5,8-dione colour formers which immediately produce intense absorption bands in the visible and near-IR regions on simultaneous metal chelate complexation-oxidation processes have been synthesized. The rapid spectral changes which they undergo have been investigated by using the stopped-flow technique.

Dye precursors which have a colour development function are called 'colour formers'. These compounds are widely used in information recording systems such as heat- or pressure-sensitive papers, dry-silver or free-radical photography and colour copy technology.<sup>1</sup> New colour formers are needed in connection with the progress in optoelectronic technology. Recently, a new class of near-IR colour formers which rapidly produce intense absorption bands in the near-IR region on metal chelate complexation-oxidation processes has been developed.<sup>2</sup> Our interest in developing other types of stabilized leuco-dyes incorporating the same processes has led us to synthesize the title compounds and evaluate their properties as colour formers.

We reported previously that the regioselective 6-amination, 6-arylation and 6-pyrrolylation of quinoline-5,8-dione promoted by metal ions gives the 6-substituted products **1** which are markedly metallochromic:<sup>3</sup> upon metal chelation to give **3**, a large bathochromic shift of the absorption bands with a large increase in molecular extinction coefficients is observed to produce new strong bands in the visible and near-IR regions. Therefore, the leuco-dyes **2** obtained by reduction of the quinones **1** were expected to exhibit intense absorption bands in the visible and near-IR regions immediately on simultaneous metal oxidation and chelation processes (Scheme 1). To confirm this, we chose three typical types of 6-substituted quinoline-5,8-diones **1a–1c** and then reduced them to obtain the leuco-dyes.

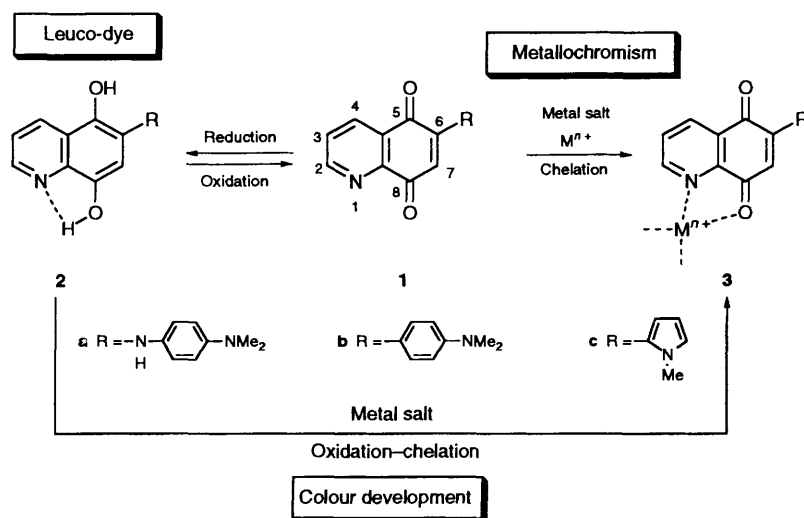
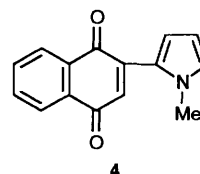
The reduction of **1a–1c** with powdered zinc in acetic acid at room temperature proceeded easily to give the corresponding leuco-dyes **2a–2c**. However, the stability of the leuco-dyes was greatly dependent on the 6-substituents. Compound **2a** was immediately reoxidized back to the starting quinone **1a** on contact with air and could not be isolated. Compound **2b** could

Table 1 Cyclic voltammetric reduction potentials for the quinones<sup>a</sup>

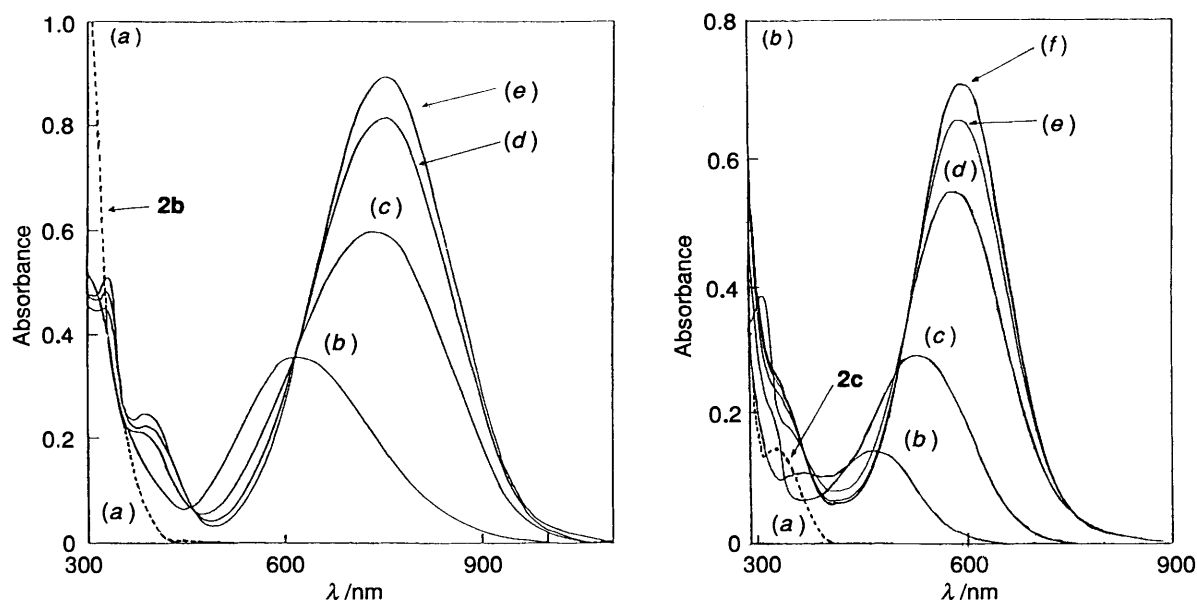
Compound	$E_1/V$	$E_2/V$
<b>1a</b>	-0.726	-1.314
<b>1b</b>	-0.576	-1.264
<b>1c</b>	-0.520	-1.236
<b>4</b>	-0.593	-1.201

<sup>a</sup> In DMF containing 0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub>, compared to SCE.

be isolated but slowly reoxidized to **1b** on continued exposure to air. However, compound **2c** was isolated as a stable compound. To investigate the electrochemical behaviour of these dyes, cyclic voltammetry was performed in 5 × 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the quinones **1a–1c** in dimethylformamide-0.1 mol dm<sup>-3</sup> NEt<sub>4</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> at a glassy carbon electrode. The cyclic voltammograms for the reduction of **1a–1c** all showed two reversible one-electron steps, the midpoints of the anodic and cathodic peaks of which are listed in Table 1. Both the first and second reduction potentials ( $E_1$  and  $E_2$ ) are more positive in the order: **1a** < **1b** < **1c**, which elucidates the order of increasing stability of the corresponding leuco-dyes. The intramolecular hydrogen bond between the 1-nitrogen and 8-hydroxy group must also contribute to the stabilization of leuco-dyes **2**, because the leuco-dye obtained by reduction of



Scheme 1



**Fig. 1** (a) Spectral changes upon addition of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to a 99% EtOH solution of **2b** (---):  $[\mathbf{2b}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Molar ratio  $[\text{Cu}^{\text{II}}]/[\mathbf{2b}]$ : (a) 0; (b) 1.0; (c) 2.0; (d) 3.0; (e) 5.0–6.0. (b) Spectral changes upon addition of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to a 99% EtOH solution of **2c** (---):  $[\mathbf{2c}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Molar ratio  $[\text{Cu}^{\text{II}}]/[\mathbf{2c}]$ : (a) 0; (b) 1.0; (c) 2.0; (d) 3.0; (e) 4.0; (f) 6.0–7.0.

**Table 2** Characteristics of colour development of leuco-dyes in 99% EtOH at 25 °C

Leuco-dye <b>2</b> <sup>a</sup>	Metal salt	Mol ratio <sup>b</sup> [Metal salt]/[ <b>2</b> ]	Complex dye <b>3</b> $\lambda_{\text{max}}/\text{nm}$	$t_{1/2}/\text{s}$ <sup>c</sup>
<b>b</b> <sup>d</sup>	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	8	732	< 0.1
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	4	660	0.36
	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	6	756	0.90
	$\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$	8	774	0.49
<b>c</b> <sup>e</sup>	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	6	578	< 0.1
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	4	500	0.71
	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	7	588	1.70
	$\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$	9	610	0.62

<sup>a</sup>  $[\text{Leuco-dye}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ . <sup>b</sup> Molar ratio in which the maximum absorbance of the metal chelate complex was obtained (see Fig. 1). <sup>c</sup> Time for  $A/A^\infty = 0.5$ :  $A$  is absorbance at  $\lambda_{\text{max}}$  of **3**. <sup>d</sup>  $\lambda_{\text{max}}/\text{nm}$  304 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  21 000) and 251 (18 600). <sup>e</sup>  $\lambda_{\text{max}}/\text{nm}$  335 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  3800), 285 (14 900) and 252 (21 000).

2-(1-methylpyrrol-2-yl)-1,4-naphthoquinone **4** is unstable and easily reoxidized on exposure to air, in spite of the relative positive reduction potentials of **4**.

The spectral changes upon addition of oxidative metal salts to the solutions of the isolated leuco-dyes **2b** and **2c** were examined. As typical examples, Figs. 1(a) and (b) show the spectral changes upon addition of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to 99% EtOH solutions of **2b** and **2c** under anaerobic conditions, respectively. The leuco-dyes showed no absorption bands in the visible region above 400 nm. Addition of an oxidative metal salt to the solutions resulted immediately in the appearance of a new band in the visible and near-IR regions. The absorption spectra produced when ca. 1 mol equiv. of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was added were almost consistent with the presence of **1b** and **1c**, and when more than 5.0 mol equiv. of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was added were almost consistent with the presence of the metal chelate complexes of **1b** and **1c** shown in previous papers.<sup>3b,3c</sup> These results suggest that both oxidation and metal chelation processes proceeded almost simultaneously in the latter cases. Such rapid spectral change characteristics were investigated by using the stopped-flow technique. Fig. 2 shows the time dependence of the increase in absorbance at the longest absorption maxima of metal chelate complexes **3**; the greatest increase appeared when a  $8.0 \times 10^{-5} \text{ mol dm}^{-3}$  solution of **2b** in 99% EtOH was mixed with excess molar ratios of solutions of oxidative metal salts in 99% EtOH under  $\text{N}_2$  (1:1 v/v; final

concentration of **2b** =  $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ). Similar rapid colour development was also observed when a solution of **2c** in 99% EtOH was mixed with solutions of oxidative metal salts in the same manner. The characteristics of colour development upon addition of oxidative metal salts are summarized in Table 2. The half-value period ( $t_{1/2}$ ) was used in order to estimate the apparent rate of colour development. Both the leuco-dyes, **2b** and **2c**, immediately produce new absorption bands in the near-IR region and in the visible region, respectively. The  $\lambda_{\text{max}}$  and  $t_{1/2}$  values are dependent in a complex manner on not only the kind of metal ions but also on the counter anions. The details of the metal chelation-oxidation processes are obscure, however. Leuco-dyes having these colour development characteristics could have potential for use as visible or near-IR colour formers.

## Experimental

**Measurements.**—M.p.s are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Hitachi R-90H spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra were run on a Shimadzu QP-1000 spectrometer and elemental analyses were measured on a Yanaco CHN recorder MT-3. Absorption spectra were measured using a JASCO Ubest-30 spectrophotometer. The stopped-flow data were obtained on a Photal (Otsuka Electronics) stopped-flow spectrophotometer

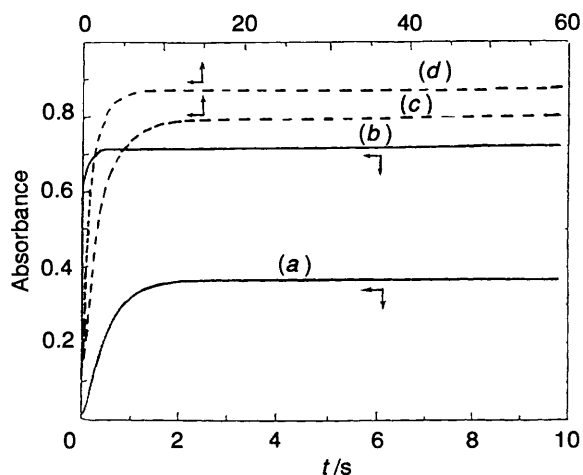


Fig. 2 Time dependence of the increase in absorbance at  $\lambda_{\max}$  of the new band which appeared on mixing 99% EtOH solutions of **2b** and oxidative metal salts at 25 °C;  $[\mathbf{2b}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Molar ratio [Metal salt]/ $[\mathbf{2b}]$  ( $\lambda_{\max}$  of new band): (a)  $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]/[\mathbf{2b}] = 4.0$  (660 nm); (b)  $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]/[\mathbf{2b}] = 8.0$  (732 nm); (c)  $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]/[\mathbf{2b}] = 6.0$  (756 nm); (d)  $[\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}]/[\mathbf{2b}] = 8.0$  (774 nm).

(Model RA-401). Cyclic voltammetry was performed by means of a Yanaco Cyclic Polarograph (P-900). The measurements were carried out under an inert atmosphere at room temperature. All the potentials were referred to a saturated calomel electrode (SCE).

**Materials.**—6-Substituted quinoline-5,8-diones **1a–1c** were synthesized by the methods described previously.<sup>3</sup> Metal salts were reagent grade and were used without further purification.

**Procedure for the Synthesis of Leuco-dyes 2.**—To the quinones **1** (1 mmol) in acetic acid (15 cm<sup>3</sup>) was added zinc powder (4 mmol) at room temperature. After being stirred for 5 min, the mixture was filtered and the residue was washed with CHCl<sub>3</sub>. To the combined filtrates was added water (10 cm<sup>3</sup>), and the products were extracted from the resulting mixture with CHCl<sub>3</sub>. The combined CHCl<sub>3</sub> extracts were concentrated under

reduced pressure. The residue was chromatographed on a silica gel column using diethyl ether as eluent under N<sub>2</sub> to give leuco-dyes **2b** (91%) and **2c** (97%). The products were recrystallized from diethyl ether.

**6-[4-(Dimethylamino)phenyl]-5,8-dihydroxyquinoline 2b.**

M.p. 167–169 °C;  $\delta_{\text{H}}(\text{CDCl}_3; J/\text{Hz})$  3.02 (6 H, s), 6.86 (2 H, d,  $J$  8.8), 7.08 (1 H, s), 7.40 (2 H, d,  $J$  8.8), 7.44 (1 H, dd,  $J$  4.2, 8.4), 8.55 (1 H, dd,  $J$  1.5, 8.4) and 8.74 (1 H, dd,  $J$  1.5, 4.2) (Found: C, 72.5; H, 5.7; N, 10.2. C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires C, 72.85; H, 5.75; N, 9.99%).

**5,8-Dihydroxy-6-(1-methylpyrrol-2-yl)quinoline 2c.** M.p. 145–147 °C;  $\delta_{\text{H}}(\text{CDCl}_3; J/\text{Hz})$  3.56 (3 H, s), 6.31 (2 H, m), 6.84 (1 H, dd), 7.01 (1 H, s), 7.45 (1 H, dd,  $J$  4.2, 8.4), 8.56 (1 H, dd,  $J$  1.5, 8.4) and 8.79 (1 H, dd,  $J$  1.5, 4.2);  $m/z$  240 (M<sup>+</sup>) (Found: C, 70.0; H, 5.2; N, 11.4. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 69.99; H, 5.03; N, 11.66%).

### Acknowledgements

The authors thank Assistant Professor Y. Kubo of Saitama University for valuable discussions. The authors also thank the Hodogaya Chemical Co., for mass spectral and elemental analyses.

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Paper 4/03877K

Received 27th June 1994

Accepted 15th July 1994