

## Naphthoquinone Methide-type Near-IR Colour Formers: their Synthesis and Oxidation Properties<sup>1</sup>

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New colourless naphthoquinone methide-type near-IR colour formers **1** have been synthesized, which immediately exhibit intense absorption in the near-IR region upon oxidation by *p*-benzoquinone. The colour development has been investigated using the stopped-flow technique. In the presence of a basic catalyst,  $\text{NEt}_3$ , oxidation of **1** gave the corresponding carbonyl cyanide derivatives **3** as the major products.

Heat- or pressure-sensitive dyes have been widely used for colourless copy papers and special papers for thermal-head printers. These dyes are essentially colourless but have a colour-development function, which has been designated as the 'colour former'. The colourless triphenylmethane lactones<sup>2</sup> and leuco quinones<sup>3</sup> are examples. The lactones develop colour on contact with a Lewis acid such as phenol, and have been used as colour formers. Recently, in connection with high technology developments such as optoelectronics and diode-laser technology<sup>4</sup> there has been considerable interest in near-IR colour formers as heat- and pressure-sensitive dyes. To date, very few types of near-IR colour formers are known.<sup>4</sup> Moreover, their use has been little studied because of the instability of the leucoquinone dyes. However, recently, we have found that several types of quinone dyes having metal complexation properties give rise to stable leuco-dyes which in the presence of metal salts<sup>5</sup> show intense absorption in the near-IR region. In order to develop other types of colour formers, it was important to elucidate the redox process for a suitable near-IR dye. Naphthoquinone methide dyes **2** which have a dicyanomethylene group as a powerful electron acceptor on the quinonoid entity show intense absorption in the near-IR region, making these of potential use as optical storage media.<sup>6</sup> Because of their spectral characteristics we attempted both to synthesize the title compounds **1** and to investigate their colour developing properties. In addition, the reactivity of the leuco-dyes **1** was of interest because of the nature of the malononitrile group. Indeed, the leuco-dyes **1** were found to undergo two types of oxidation: (1) compound **1** in methanol when treated with *p*-benzoquinone as an oxidant underwent two-electron oxidation to give **2** immediately with the development of intense absorption in the near-IR region. (2) In the presence of  $\text{NEt}_3$ , a solution of **1** in tetrahydrofuran (THF) underwent oxygenation of the malononitrile moiety to give the corresponding 1-carbonyl cyanide **3**. In this paper, we report our results in the context of our interest of colour formers.

### Results and Discussion

#### Synthesis and Colour Developing Properties of the Leuco Dyes

**1.**—Reduction of 4-(4-dialkylaminophenylimino)-1,4-dihydro-1-naphthylidenemalononitrile **2** with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  under acidic conditions produced the corresponding leuco dyes **1**, 4-(4-dialkylaminoanilino)-1-naphthylmalononitriles, in 64–74% yield. Interestingly, compounds **1** were stable enough to be isolated and had weak absorption maxima at 350–359 nm in MeOH (Table 1); they were identified on the basis of <sup>1</sup>H NMR, IR and mass spectrometry evidence and their elemental analyses. In particular, the <sup>1</sup>H NMR spectra show chemical

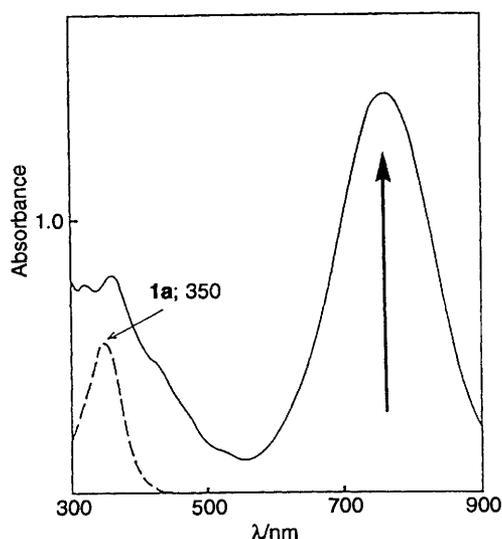
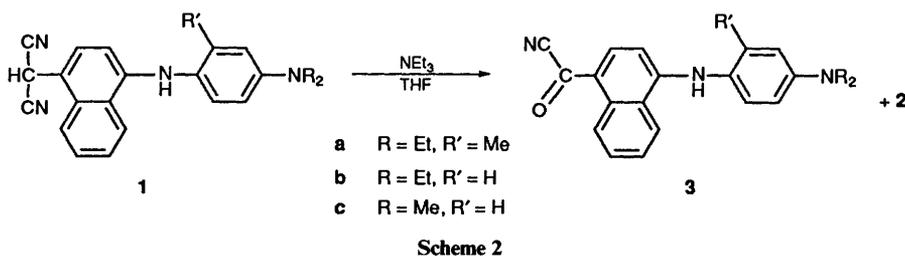
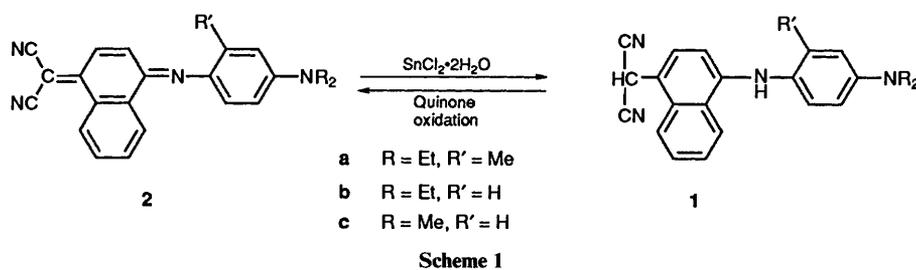
Table 1 Electronic absorption spectra in  $\text{CHCl}_3$

Compd.	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
<b>1a</b>	350 <sup>a</sup>	11 000 <sup>a</sup>
<b>1b</b>	358 <sup>a</sup>	11 000 <sup>a</sup>
<b>1c</b>	359 <sup>a</sup>	11 100 <sup>a</sup>
<b>2a</b> <sup>b</sup>	761	30 800
<b>2b</b> <sup>b</sup>	738	30 800
<b>2c</b> <sup>b</sup>	722	25 500
<b>3a</b>	420	26 000
<b>3b</b>	426	23 000
<b>3c</b>	424	22 900

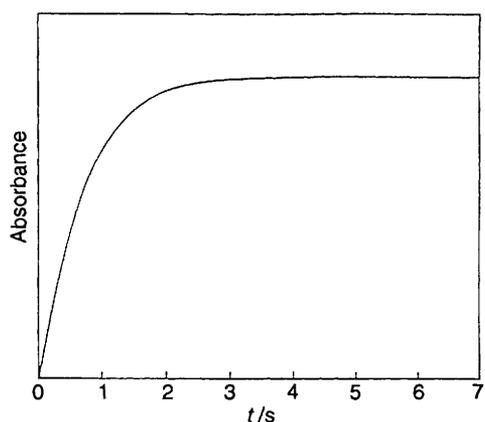
<sup>a</sup> In MeOH. <sup>b</sup> See ref. 6a.

shifts at 5.39–5.42 and 6.045–6.18 ppm [ $(\text{CN})_2\text{CH}$  and  $\text{NH}$ , respectively] indicating that compounds **1** have a leucoquinonoid structure. The oxidation of **1** in the presence of *p*-benzoquinone was also investigated. As shown in Fig. 1, addition of *p*-benzoquinone (10 equiv.) to a methanolic solution of **1a** immediately produced new absorption at ca. 760 nm, the character of which was consistent with the presence of **2a**, formed quantitatively by two-electron oxidation of **1a**.<sup>\*</sup> The very rapid production of an intense absorption band in the near-IR region is noteworthy since such a property is essential for a colour former. The spectral characteristics of the reaction were investigated using the stopped-flow technique. Fig. 2 shows the time dependence of the increase in absorbance at 762 nm observed when a  $1 \times 10^{-4} \text{ mol dm}^{-3}$  solution of **1a** in MeOH was mixed with a  $1 \times 10^{-3} \text{ mol dm}^{-3}$  solution of *p*-benzoquinone in MeOH (1:1 v/v; final concentration of **1a** is  $5 \times 10^{-5} \text{ mol dm}^{-3}$ ). After ca. 2 s, the absorbance at 762 nm was at a maximum. Similar colour development properties were also observed for **1b** and **1c**. The half-value time ( $T_{1/2}$ : time for  $A/A_\infty = 0.5$ ;  $A$  is the absorbance of  $\lambda_{\text{max}}$  of **2**) was used in order to estimate the apparent rate of colour development. In the presence of *p*-benzoquinone (10 equiv.),  $T_{1/2}$  values of 0.43–0.63 s were obtained (see Table 2). These values are closely similar to that of 5-(4-dimethylaminoanilino)quinolin-8-ol in the presence of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (100 equiv.).<sup>5a</sup> These results suggest that the leuco-dyes **1** have potential as near-IR colour formers.

\* The naphthoquinone methide dye **2** was identified as follows. A methanolic solution of **1** (0.4 mmol) and *p*-benzoquinone (4 mmol) was stirred for 5 min at room temperature after which it was diluted with water and evaporated. Recrystallization of the residue from EtOH gave compound **2** as evidenced by comparison of its <sup>1</sup>H NMR spectrum with that of an authentic sample.



**Fig. 1** Spectral changes upon addition of *p*-benzoquinone to a MeOH solution of **1a** (---): [*p*-benzoquinone]/[**1a**] = 10, [**1a**] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup>



**Fig. 2** Formation of **2a** in MeOH at 25 °C: the plot of the absorbance at 762 nm vs. time: [*p*-benzoquinone]/[**1a**] = 10, [**1a**] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup>

*Oxygenation of the Leuco-dyes 1.*—Although, as mentioned above, the leuco-dyes **1** were stable enough to be isolated, the presence of the malononitrilo substituent on the naphthalene ring gave the opportunity for an alternative reaction to occur.

**Table 2** Half-value period for colour development in MeOH at 25 °C<sup>a</sup>

Leuco-dye <sup>b</sup>	Near-IR dye (λ <sub>max</sub> /nm)	T <sub>1/2</sub> /s <sup>c</sup>
<b>1a</b>	<b>2a</b> 762	0.55
<b>1b</b>	<b>2b</b> 735	0.63
<b>1c</b>	<b>2c</b> 718	0.43

<sup>a</sup> In the presence of *p*-benzoquinone ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>; 10 equiv.).  
<sup>b</sup> [Leuco-dye] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup>. <sup>c</sup> Time for A/A<sub>∞</sub>; A is absorbance of **2** at λ<sub>max</sub>.

Thus, a THF solution of **1a** containing NEt<sub>3</sub> (2 equiv.) when stirred at room temperature for 10 h gave the novel oxidation product **3a**, 4-(4-diethylamino-2-methylanilino)naphthalene-1-carbonyl cyanide (41%), together with **2a** (11%) (Table 3, entry 2). These products were separated by column chromatography. The structure assignment of **3a** was established on the basis of analytical results (see Experimental section). Interestingly, the malononitrile group of **1a** had been converted into a carbonyl cyanide as indicated by the appearance of a signal for carbonyl carbon at 164.7 ppm in the <sup>13</sup>C NMR spectra. Not only did the oxidation fail to occur in the absence of NEt<sub>3</sub>, but an increase in the amount of NEt<sub>3</sub> reduced the reaction time whilst slightly increasing the yield of **3a** (Table 3, entry 3). It seems likely that the malononitrile is deprotonated by NEt<sub>3</sub> to give the carbanion form and that this is followed by the addition of oxygen at the malononitrile site. Similar reactions occurred with **1b** and **1c** to give **3b** (38%) and **3c** (48%), respectively (Table 3, entry 4 and 5). As shown in Table 1, compounds **3** in CHCl<sub>3</sub> absorb visible light at 420–426 nm; in comparison with compounds **2**, they also show a large hypsochromic shift at 298–341 nm. This results from lack of a quinonoid structure. Thus compounds **2** and **3** obtained have quite different electronic absorption properties.

### Conclusion

The reduction of naphthoquinone methide dyes **2** with SnCl<sub>2</sub>·2H<sub>2</sub>O gave the corresponding leuco-dyes **1** in reasonable yield, compounds which were stable enough to be isolated. It is noteworthy that oxidation of **1** affords two types of compound, **2** and **3**, the yields of which depend upon the reaction conditions. Use of *p*-benzoquinone as an oxidant produced the quinone **2** immediately with rapid increase in the intense absorption in the near-IR region; these properties suggest that compounds **1** have potential as near-IR colour formers.

**Table 3** Oxidation of **1** in the presence of NEt<sub>3</sub> in THF<sup>a</sup>

Entry	Substrate	NEt <sub>3</sub> (mol) <sup>b</sup>	Reaction (T/h) <sup>c</sup>	Products (yield/%) <sup>d</sup>	
1	<b>1a</b>	0	24	<i>e</i>	<i>e</i>
2	<b>1a</b>	2	10	<b>3a</b> (41)	<b>2a</b> (11)
3	<b>1a</b>	10	3	<b>3a</b> (43)	<b>2a</b> (8)
4	<b>1b</b>	2	10	<b>3b</b> (38)	<b>2b</b> (11)
5	<b>1c</b>	2	10.5	<b>3c</b> (48)	<b>2c</b> (15)

<sup>a</sup> Reaction was carried out under room temperature. <sup>b</sup> Molar ratio: [NEt<sub>3</sub>]/[**1**]. <sup>c</sup> Time for **1** to be consumed. <sup>d</sup> Isolated yield after purification. <sup>e</sup> Substrate **1a** was recovered.

### Experimental

M.p.s were measured on a Mitamura micro-melting point apparatus and are uncorrected. Absorption spectra were measured using Hitachi 220A and JASCO Ubest-30 spectrophotometers. IR spectra were obtained using FT/IR-5000 spectrometer. NMR spectra were taken on a Hitachi R-90H spectrometer. Mass spectra were run on a Hitachi M-80A spectrometer and elemental analyses were obtained using a Perkin-Elmer 240C C, H, N, analyser. The stopped-flow data were obtained on a photol (Otsuka Electronics) stopped-flow spectrophotometer Model RA-401 by mixing equal volumes of MeOH solutions of the leuco-dyes and *p*-benzoquinone.

**Materials.**—The naphthoquinone methide dyes **2**, 4-(4-dialkylaminophenylimino)-1,4-dihydronaphthylidenemalononitriles, were prepared by an improved literature procedure.<sup>6a</sup>

**General Procedure for Obtaining the Leuco-dyes 1.**—To an acetic acid solution (50 cm<sup>3</sup>) of **2** (2.7–2.9 mmol) at room temperature under an argon atmosphere was added an HCl solution of SnCl<sub>2</sub>·2H<sub>2</sub>O (5.4–5.8 mmol). The mixture was stirred at room temperature for 20 min after which it was poured into water (200 cm<sup>3</sup>) and neutralized with saturated aqueous Na<sub>2</sub>CO<sub>3</sub>. The yellowish precipitate was collected, and recrystallized from THF–hexane (**1a**, 64% yield; **1b**, 67% yield; **1c**, 74% yield).

**4-(4-Diethylamino-2-methylanilino)-1-naphthylmalononitrile 1a.** This had m.p. 172–174 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.20 (6 H, t), 2.18 (3 H, s), 3.38 (4 H, q), 5.39 (1 H, s), 6.045 (1 H, br d), 6.43 (1 H, d, *J* 8.13), 6.52–6.63 (2 H, m), 7.00–7.10 (1 H, m), 7.44 (1 H, d, *J* 8.35), 7.51–7.78 (2 H, m), 7.83–7.935 (1 H, m) and 8.035–8.14 (1 H, m); ν(KBr)/cm<sup>-1</sup> 2212 and 3390 (Found: C, 77.7; H, 6.6; N, 14.8%; M<sup>+</sup>, 368. C<sub>24</sub>H<sub>24</sub>N<sub>4</sub> requires C, 78.2; H, 6.6; N, 15.2%; M, 368).

**4-(4-Diethylaminoanilino)-1-naphthylmalononitrile 1b.** This had m.p. 142–145 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.19 (6 H, t), 3.37 (4 H, q), 5.40 (1 H, s), 6.16 (1 H, br d), 6.73 (2 H, d, *J* 9.0), 6.85 (1 H, d, *J* 8.1), 7.10 (2 H, d, *J* 9.0), 7.47 (1 H, d, *J* 8.1), 7.50–7.78 (2 H, m), 7.82–7.93 (1 H, m) and 8.02–8.13 (1 H, m); ν(KBr)/cm<sup>-1</sup> 2104 and 3426 (Found: C, 77.8; H, 6.3; N, 15.5%; M<sup>+</sup>, 354. C<sub>23</sub>H<sub>22</sub>N<sub>4</sub> requires C, 77.9; H, 6.3; N, 15.8%; M, 354).

**4-(4-Dimethylaminoanilino)-1-naphthylmalononitrile 1c.** This had m.p. 192–194 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 2.975 (6 H, s), 5.42 (1 H, s), 6.18 (1 H, br d), 6.79 (2 H, d, *J* 9.0), 6.86 (1 H, d, *J* 8.1), 7.13 (2 H, d, *J* 9.0), 7.49 (1 H, d, *J* 8.1), 7.50–7.80 (2 H, m), 7.83–7.95 (1 H, m) and 8.04–8.15 (1 H, m); ν(KBr)/cm<sup>-1</sup> 2220 and 3432 (Found: C, 76.8; H, 5.5; N, 16.7%; M<sup>+</sup>, 326. C<sub>21</sub>H<sub>18</sub>N<sub>4</sub> requires C, 77.3; H, 5.6; N, 17.2%; M, 326).

**General Procedure for the Oxygenation of Compound 1.**—To a THF solution (30 cm<sup>3</sup>) of the compound **1** (1 mmol) at room temperature was added 2 or 10 equiv. of NEt<sub>3</sub>. The mixture was stirred at room temperature until TLC indicated the absence of starting material. The reaction mixture was then poured into water and extracted with CHCl<sub>3</sub>. The CHCl<sub>3</sub> layer was washed with water, evaporated and purified by column chromatography on silica gel (Wakogel C-300) with CHCl<sub>3</sub> as eluent to give the oxygenated product **3** together with **2** (see Table 3).

**4-(4-Diethylamino-2-methylanilino)naphthalene-1-carbonyl cyanide 3a.** This had m.p. 189–190 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.215 (6 H, t), 2.18 (3 H, s), 3.40 (4 H, q), 6.51 (1 H, d, *J* 8.8), 6.55–6.64 (2 H, m), 6.99–7.14 (2 H, m), 7.59–7.77 (2 H, m), 7.96–8.07 (1 H, m), 8.295 (1 H, d, *J* 8.8) and 9.36–9.47 (1 H, m); δ<sub>C</sub>(CDCl<sub>3</sub>) 12.7, 18.4, 44.4, 105.05, 110.4, 113.6, 114.6, 117.9, 120.2, 121.8, 123.9, 126.5, 126.9, 128.5, 130.5, 133.1, 136.2, 142.3, 147.4, 152.2 and 164.7; ν(KBr)/cm<sup>-1</sup> 1609, 2214 and 3338 (Found: C, 77.2; H, 6.6; N, 11.7%; M<sup>+</sup>, 357. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O requires C, 77.3; H, 6.5; N, 11.8%; M, 357).

**4-(4-Diethylaminoanilino)naphthalene-1-carbonyl cyanide 3b.** These had m.p. 194–195 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.215 (6 H, t), 3.41 (4 H, q), 6.74 (2 H, d, *J* 9.1), 6.84 (1 H, d, *J* 8.8), 7.11 (1 H, br d), 7.16 (2 H, d, *J* 9.1), 7.57–7.81 (2 H, m), 7.93–8.04 (1 H, m), 8.29 (1 H, d, *J* 8.8) and 9.39–9.44 (1 H, m); ν(KBr)/cm<sup>-1</sup> 1614, 2214 and 3334 (Found: C, 77.0; H, 6.25; N, 12.2%; M<sup>+</sup>, 343. C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O requires C, 76.9; H, 6.2; N, 12.2%; M, 343).

**4-(4-Dimethylaminoanilino)naphthalene-1-carbonyl cyanide 3c.** This had m.p. 182–183 °C; δ<sub>H</sub>(CDCl<sub>3</sub>) 3.02 (6 H, s), 6.80 (2 H, d, *J* 8.9), 6.83 (1 H, d, *J* 8.8), 7.13 (1 H, br d), 7.18 (2 H, d, *J* 8.9), 7.60–7.83 (2 H, m), 7.94–8.04 (1 H, m), 8.31 (1 H, d, *J* 8.8) and 9.35–9.47 (1 H, m); ν(KBr)/cm<sup>-1</sup> 1614, 2214 and 3364 (Found: C, 77.4; H, 5.75; N, 12.4%; M<sup>+</sup>, 315. C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O requires C, 76.2; H, 5.4; N, 13.3%; M, 315).

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