

## The Effect of Metal Chelate Complexation on the Reactivity and Absorption Spectra of 1,2-Naphthoquinones: New Types of Near-infrared-absorbing Metal Complex Dyes<sup>1</sup>

Katsuhira Yoshida,\* Norio Oga, Tetsunao Koujiri, Miwa Ishiguro, and Yuji Kubo  
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho,  
Kochi 780, Japan

The reaction of sodium 1,2-naphthoquinone-4-sulphonate with various arylamines and 1,1-bis[*p*-(dimethylamino)phenyl]ethylene were efficiently promoted by nickel(II) ion to give 4-aminated, 4-arylated, and 4-vinylated 1,2-naphthoquinones in good yield. The first absorption bands of the products with strongly electron-donating 4-substituents were drastically shifted to longer wavelength together with an increase in the absorption intensity by metal chelate complexation. The resulting metal chelate complexes have an intense absorption band in the near-IR region.

It is generally known that the reactivities and electronic structures of organic ligands are affected by co-ordination to metal ions. Recently we have reported the regioselective 6-amination and 6-arylation of quinoline-5,8-dione promoted by metal chelate complexation.<sup>2</sup> The formation of a metal chelate complex, in which the 1-nitrogen atom and the oxygen atom of the 8-carbonyl group of quinoline-5,8-dione co-ordinate to the metal ion, facilitates a nucleophilic attack of alkyl- and aryl-amines on the 6-carbon to produce the 6-aminated and 6-arylated products selectively. We have also found that the products with strongly electron-donating 6-substituents have a marked metallochromic property:<sup>3</sup> the first absorption bands are drastically shifted to longer wavelengths (in near-IR region) with a concomitant, large increase in the absorption intensity upon metal chelate complexation. Utilizing these metallochromic properties, we synthesized new types of near-IR-absorbing metal complex dyes with quinonoid ligands<sup>4,5</sup> which have potential applications in the fields of diode-laser optical storage, laser printers, and colour filter systems. In this paper, we investigate the effect of metal ions on the desulpho-substitution of sodium 1,2-naphthoquinone-4-sulphonate (1)† with primary arylamines, *N*-alkyl and *N,N*-dialkylanilines, and 1,1-bis[*p*-(dimethylamino)phenyl]ethylene (6), giving the 4-aminated, 4-arylated, and 4-vinylated 1,2-naphthoquinones, respectively, in good yield. The metallochromic properties of the products were also investigated in detail.

### Results and Discussion

*Desulpho-substitution of Compound (1) with Various Arylamines promoted by Nickel(II) Ions.*—As shown in the Scheme various 4-substituted 1,2-naphthoquinones were synthesized by the reaction of sodium 1,2-naphthoquinone-4-sulphonate (1) with various arylamines and 1,1-bis[*p*-(dimethylamino)phenyl]ethylene (6) in acetic acid at 30 °C. With primary arylamines the reaction is already known to give 4-arylamino-1,2-naphthoquinones (2).<sup>6</sup> We found that the reaction is efficiently promoted by nickel(II) ions‡ (Table 1). In the absence of metal salt the reaction of compound (1) with *p*-dimethylaminoaniline gave 4-[(*p*-dimethylamino)anilino]-1,2-naphthoquinone (2a) (51%), along with a small amount of 2-[(*p*-dimethylamino)anilino]-4-[(*p*-dimethylamino)phenylimino]naphthalen-1(4*H*)-one (3a) (3.7%) (run 1). The by-product (3a) was confirmed to be produced from further

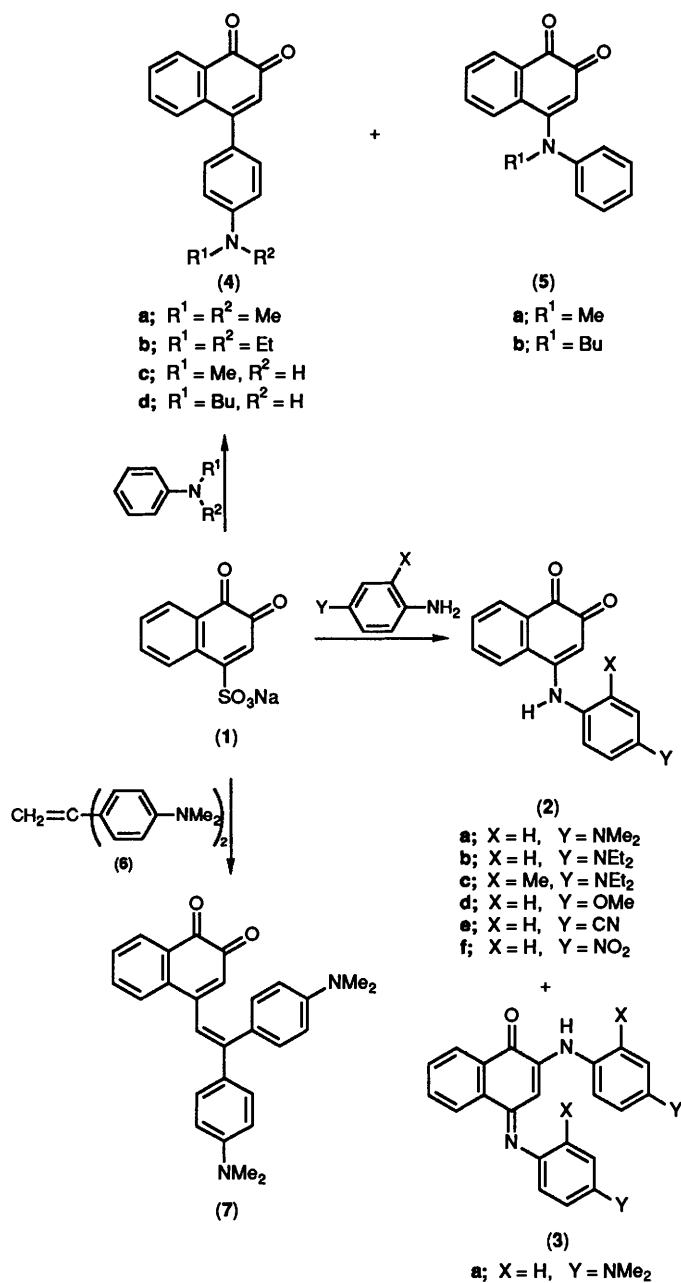
reaction of the first product (2a) with the arylamine; however, in the presence of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, the reaction time was greatly improved and only the 4-aminated product (2a) was obtained, in high yield (93%) (run 2). In the presence of the nickel salt, even with weakly nucleophilic arylamines such as *p*-cyano- and *p*-nitro-anilines, the desulpho-amination proceeded smoothly to give compounds (2e) and (2f) in good yield (runs 6 and 7).

On the other hand, in the reaction of the salt (1) with *N,N*-dialkylanilines the 4-arylated 1,2-naphthoquinones (4) were obtained, and the effect of metal salts was also observed (runs 8–10). As was found in the 4-amination of the salt (1), nickel(II) acetate was more effective than copper(II) and cobalt(II) acetates in the 4-arylation. With *N*-alkylanilines, the reaction gave a mixture of the 4-arylated product (4) and 4-aminated product (5), and the latter product was obtained predominantly (runs 11 and 12). Furthermore, the reaction of compound (1) with 1,1-bis[*p*-(dimethylamino)phenyl]ethylene (6) was also promoted by the addition of nickel(II) acetate and gave the 4-vinylated 1,2-naphthoquinone (7), the structure of which was confirmed by comparison of the spectral and physical data with those described in the literature.<sup>7</sup> In the above reactions, the formation of a metal chelate complex, in which the 1- and 2-carbonyl oxygens of the salt (1) co-ordinate to the metal ion, probably increases the electrophilicity of the 4-carbon atom and facilitates the nucleophilic desulpho-substitution at the 4-position.

*Metallochromic Properties of 1,2-Naphthoquinone Derivatives in 99% Ethanol.*—We found that the products in which strongly electron-donating 4-substituents had been introduced were capable of forming chelate complexes with metal ions (Ni<sup>II</sup>, Cu<sup>II</sup>, and Co<sup>II</sup>), and that upon addition of the metal salt the first absorption band of the free ligand showed a large red shift with an increase in the absorption intensity. The resulting metal chelate complexes have an intense absorption band in the near-IR region. A typical example of the spectral changes for the metal chelate complexation of compounds (2c), (4b), and (7) in 99% ethanol is shown in Figure 1. A set of isosbestic points was observed in all cases, which suggested the presence

† Systematic name: sodium 3,4-dihydro-3,4-dioxonaphthalene-1-sulphonate.

‡ Metal acetates were found to follow the order of activity: Ni<sup>II</sup> > Cu<sup>II</sup> > Co<sup>II</sup>.

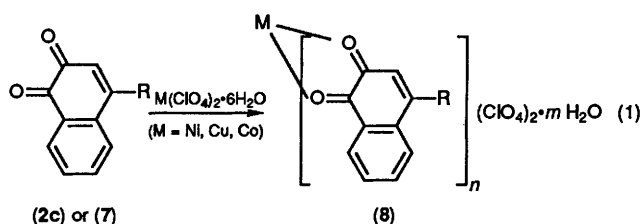


Scheme.

of a simple equilibrium in the solution. In Figure 2, continuous variation plots are illustrated. The absorption maxima employed were those corresponding to new bands which appeared on addition of the metal ions. Figure 2 shows that a maximum appears at  $[\text{ligand}]/([\text{ligand}] + [\text{Metal}])$  0.5 and 0.67, suggesting the formation of 1:1 and 1:2 metal(II)-ligand complexes in the solution, respectively. In Table 2, the spectral data of the free ligands, (2c), (4b), and (7), and their metal complexes in 99% ethanol are summarized. In the cases of ligands (2c) and (7) the maximum and constant absorbance were obtained in the molar ratio range  $[\text{metal ion}]/[(2c)]$  1.2–2.0 and  $[\text{metal ion}]/[(7)]$  2.0–4.0, while for (4b) the constant absorbance was obtained for  $[\text{metal ion}]/[(4b)]$  100–120. These results imply that the complexing ability of ligands (2c) and (7) is far superior to that of (4b). Among the three types of compound, (7) was found to be the most suitable ligand for

the synthesis of near-IR-absorbing dyes, since it has a good ability to form a metal chelate, and a drastic spectral change is induced upon chelate complexation. As the ratio of molecular extinction coefficient ( $R_e$ ) increased 4.2–4.3 times in comparison with that of the free ligand (7), the resulting metal(II)-(7) complexes have an intense absorption band in the near-IR region. The absorption maximum  $[\lambda_{\text{max}}(\text{complex})]$  is controllable by changing the metal ion participating in the chelate complexation.

**Isolation of Metal(II)-(7) Complex Dyes.**—The metal chelate complexes of ligand (7) were prepared by addition of a tetrahydrofuran (THF) solution of  $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$ ) to a THF solution of ligand (7) under argon. A green precipitate was immediately formed. After the mixed solution had been kept overnight in a refrigerator, the green precipitate was filtered off and washed with a small amount of THF. In the IR spectra (KBr) the absorption bands of the two C=O groups of the free ligand (7) appeared at 1694 and 1635  $\text{cm}^{-1}$  and the corresponding bands for the green precipitates of cobalt(II)-(7), nickel(II)-(7), and copper(II)-(7) complexes were all observed at  $\sim 1610$  and  $\sim 1583$   $\text{cm}^{-1}$ . These results suggest that the double-bond character of the C=O groups was decreased by co-ordination of ligand (7) to the metal ions in the solid state. However, as shown in Table 3, the results obtained from the elemental analyses suggest that these precipitates were not pure complexes but were instead a mixture of 1:1 and 1:2 metal(II)-(7) complexes (8). Similar



results were also observed in the case of the metal(II)-(2c) complexes [equation (1)]. The absorption spectra of the isolated complexes also supported the above suggestion: the spectra of complexes in 99% ethanol were essentially in agreement with spectral features at  $[\text{M}^{\text{II}}]/[(2c) \text{ or } (7)]$  0.5–1.0 obtained from the spectral changes upon addition of  $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to 99% ethanol solutions of ligands (2c) and (7) (refer to Figure 1). In spite of the change in mole ratio of metal(II) to (7) during complex preparation, we could not prepare a pure 1:1 or 1:2  $M^{\text{II}}-(7)$  complex. The precipitates obtained always consisted of a mixture of 1:1 and 1:2 metal(II)-(7) complexes in spite of the fact that formation of 1:1 metal complexes was suggested to occur in solution. It was considered that, in solution, the 1:1 and 1:2 metal(II)-(7) complexes were in equilibrium; however, because of lower solubility, the 1:2 metal(II)-(7) complex precipitated from the solution. Similar results were also observed in the preparation of metal(II)-(2c) complexes and metal complexes with other quinonoid ligands.<sup>4b,5b</sup>

### Experimental

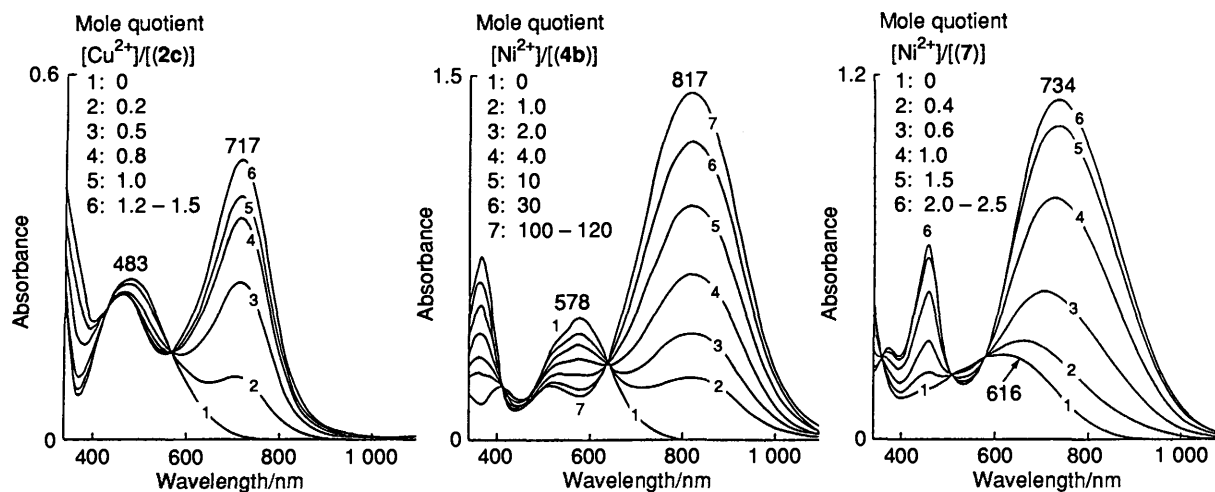
M.p.s were measured on a Sibata melting point apparatus and are uncorrected. Absorption spectra were measured using a JASCO Ubest-30 UV/VIS spectrometer equipped with a temperature controller (JASCO EHC-363). <sup>1</sup>H NMR spectra were taken on a Hitachi Model R-90H spectrometer, with SiMe<sub>4</sub> as internal standard. IR spectra were measured with a

**Table 1.** Effect of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  on the reaction of compound (1) with various anilines in acetic acid.<sup>a</sup>

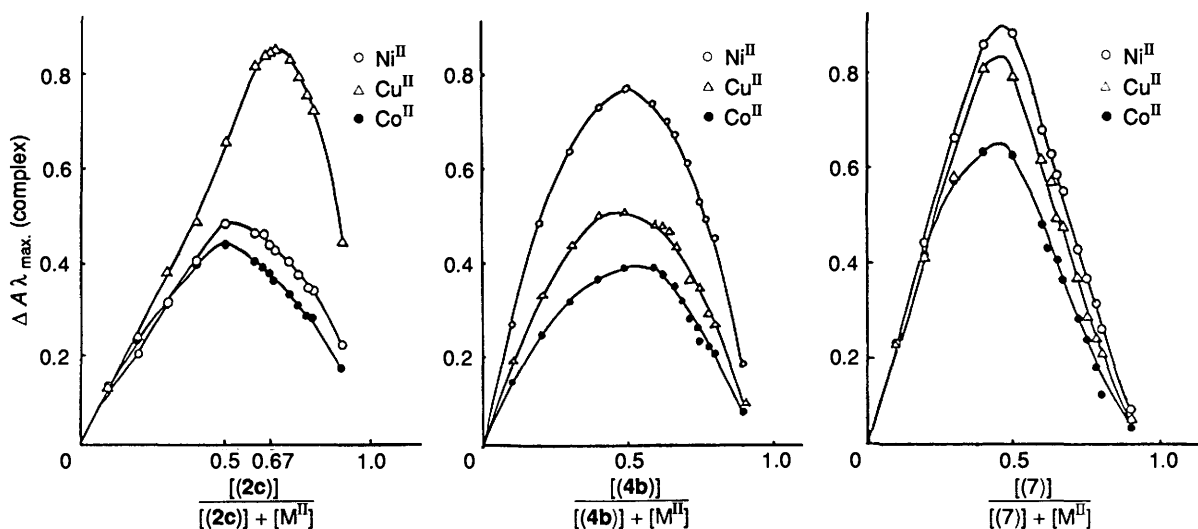
Run	Aniline	Metal salt <sup>b</sup>	Time/h	Product and yield (%) <sup>c</sup>
1	<i>p</i> -Dimethylaminoaniline	N	4.0	(2a) 51 (3a) 3.7
2	<i>p</i> -Dimethylaminoaniline	Y	1.0	(2a) 93 (3a) 0
3	<i>p</i> -Diethylaminoaniline	Y	1.0	(2b) 88 (3b) 0
4	4-Diethylamino-2-methylaniline	Y	1.0	(2c) 95 (3c) 0
5	<i>p</i> -Anisidine	Y	1.0	(2d) 86 (3d) 0
6	<i>p</i> -Cyanoaniline	Y	3.0	(2e) 87 (3e) 0
7	<i>p</i> -Nitroaniline	Y	3.0	(2f) 85 (3f) 0
8	<i>N,N</i> -Dimethylaniline	N	9.0	(4a) 46
9	<i>N,N</i> -Dimethylaniline	Y	2.0	(4a) 77
10	<i>N,N</i> -Diethylaniline	Y	5.0	(4b) 60
11	<i>N</i> -Methylaniline	Y	4.5	(4c) 2.4 (5a) 51
12	<i>N</i> -Butylaniline	Y	4.5	(4d) 6.0 (5b) 42
13	(6)	N	67.0	(7) 51
14	(6)	Y	25.0	(7) 75

<sup>a</sup> Reactant (1) (3.84 mmol) was stirred with various anilines (3.84 mmol) and nickel(II) salt (3.84 mmol) in acetic acid (150 ml) at 30 °C.

<sup>b</sup> N = Absence, Y = presence, of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ . <sup>c</sup> Isolated yield after column chromatography.



**Figure 1.** Spectral changes upon addition of  $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to 99% EtOH solutions of ligands (2c), (4b), and (7).  $[(2c)] = [(4b)] = 6.25 \times 10^{-5} \text{ M}$ ,  $[(7)] = 3.12 \times 10^{-5} \text{ M}$ .



**Figure 2** Continuous variation plots for the metal( $\text{M}^{\text{II}}$ )-ligand complexes in 99% EtOH:  $[(2c)] + [\text{M}^{\text{II}}] 1.25 \times 10^{-4} \text{ M}$ ,  $[(4b)] + [\text{M}^{\text{II}}] 2.5 \times 10^{-4} \text{ M}$ ,  $[(7)] + [\text{M}^{\text{II}}] 6.25 \times 10^{-5} \text{ M}$ .

**Table 2.** Spectral data for complex formation between  $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and substrates (**2c**), (**4b**), and (**7**) in 99% ethanol.

Ligand	Complex ( <b>8</b> )					
	Metal ion $M^{2+}$	Mole quotient <sup>a</sup> $[\text{M}^{2+}]/[\text{L}]$	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon_{\text{max}}$ )	Ratio metal:ligand	$\Delta\lambda_{\text{max}}/\text{nm}^b$	$R(\epsilon_{\text{max}})^c$
<b>(2c)</b> 483 (4 290)	$\text{Ni}^{2+}$	1.2–1.5	664 (4 250)	1:1	181	0.99
	$\text{Cu}^{2+}$	1.2–1.5	717 (15 200)	1:2	234	3.54
	$\text{Co}^{2+}$	1.8–2.0	645 (3 950)	1:1	162	0.92
<b>(4b)</b> 578 (8 400)	$\text{Ni}^{2+}$	100–120	817 (24 200)	1:1	239	2.88
	$\text{Cu}^{2+}$	100–120	779 (23 500)	1:1	201	2.80
	$\text{Co}^{2+}$	80–100	803 (18 500)	1:1	225	2.20
<b>(7)</b> 616 (8 700)	$\text{Ni}^{2+}$	2.0–2.5	734 (37 500)	1:1	118	4.31
	$\text{Cu}^{2+}$	2.0–2.5	684 (36 600)	1:1	68	4.21
	$\text{Co}^{2+}$	3.0–4.0	725 (37 000)	1:1	109	4.25

<sup>a</sup> Molar ratio range in which the maximum and constant absorbance were obtained (see Figure 1). <sup>b</sup>  $\Delta\lambda_{\text{max}} = \lambda_{\text{max}}(\text{complex}) - \lambda_{\text{max}}(\text{free ligand})$ .  
<sup>c</sup>  $R(\epsilon_{\text{max}}) = \epsilon_{\text{max}}(\text{complex})/\epsilon_{\text{max}}(\text{free ligand})$ .

**Table 3.** Elemental analyses of the isolated metal complexes.

Complex	C(%)		H(%)		N(%)			
	Ligand	M n m	Reqd.	Found	Reqd.	Found	Reqd.	Found
<b>(2c)</b>	Ni	1 2	41.46	41.2 <sup>aa</sup>	4.40	4.7 <sup>aa</sup>	4.36	4.6 <sup>aa</sup>
	Cu	1 2	40.85	47.9 <sup>aa</sup>	4.36	4.8 <sup>aa</sup>	4.33	5.1 <sup>aa</sup>
		2 0	55.09		5.04		5.84	
	Co	1 2	41.14	48.4 <sup>aa</sup>	4.39	4.7 <sup>aa</sup>	4.36	5.4 <sup>aa</sup>
2 0		55.35		5.07		5.87		
<b>(7)</b>	Ni	1 2	46.96	{ 55.1 <sup>bb</sup>	4.22	{ 4.9 <sup>bb</sup>	3.91	{ 4.5 <sup>bb</sup>
		2 0	61.00	{ 54.8 <sup>bc</sup>	4.75	{ 4.6 <sup>bc</sup>	5.08	{ 4.6 <sup>bc</sup>
	Cu	1 2	46.64	{ 55.8 <sup>bb</sup>	4.19	{ 4.7 <sup>bb</sup>	3.89	{ 4.8 <sup>bb</sup>
		2 0	60.73	{ 56.5 <sup>bd</sup>	4.73	{ 4.5 <sup>bd</sup>	5.05	{ 4.8 <sup>bd</sup>
	Co	1 2	46.95	{ 52.3 <sup>bb</sup>	4.22	{ 4.4 <sup>bb</sup>	3.91	{ 4.8 <sup>bb</sup>
		2 0	60.99	{ 53.5 <sup>bc</sup>	4.75	{ 4.45 <sup>bc</sup>	5.08	{ 4.3 <sup>bc</sup>

\* The complexes were isolated from mixed solutions of different mole quotients of metal(II) to ligand (L); <sup>a</sup>  $[\text{M}^{II}]/[\text{L}]$  0.5; <sup>b</sup>  $[\text{M}^{II}]/[\text{L}]$  1.0; <sup>c</sup>  $[\text{M}^{II}]/[\text{L}]$  2.0; <sup>d</sup>  $[\text{M}^{II}]/[\text{L}]$  4.0.

JASCO FT/IR-5000 spectrophotometer for samples in KBr pellet form. Elemental analyses were obtained using a Yanaco MT-2 or a Perkin-Elmer 240 C C,H,N analyser.

**Materials.**—Sodium 1,2-naphthoquinone-4-sulphonate (**1**), metal acetates, and acetic acid were reagent grade and were used without further purification. Anilines were purified by distillation or recrystallization. Metal perchlorate hexahydrates<sup>8</sup> and 1,1-bis[*p*-(dimethylamino)phenyl]ethylene (**6**)<sup>9</sup> were prepared according to the literature method.

**Reaction of the Salt (1) with Primary Arylamines.**—To a stirred suspension of compound (**1**) (3.84 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3.84 mmol) in acetic acid (100 ml) was added a solution of the amine (3.84 mmol) in acetic acid (50 ml). The reaction mixture was stirred at 30 °C and the reaction was monitored by visible absorption spectroscopy. After the maximum and constant absorbance was obtained, water (100 ml) was added to the reaction solution and the products were extracted with chloroform from the mixture solution. The extraction was repeated several times. After the combined chloroform extracts had been washed successively with aq. sodium carbonate and then with water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated, the crude products were separated by column chromatography (silica gel: Wakogel C-300; chloroform–acetone 5:2 or ethyl acetate–benzene 1:1 as eluant). The yields are summarized in Table 1.

**Reaction of the Salt (1) with *N*-Alkyl- and *N,N*-Dialkyl-anilines.**—To a stirred suspension of compound (**1**) (3.84

mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3.84 mmol) in acetic acid (100 ml) was added a solution of the *N*-alkyl- or *N,N*-dialkyl-aniline (3.84 mmol) in acetic acid (50 ml). The reaction was monitored by visible absorption spectroscopy. After the maximum and constant absorbance was obtained, water (100 ml) was added to the reaction solution and the products were extracted with chloroform. The extraction was repeated several times. After the combined chloroform extracts had been washed successively with aq. sodium carbonate and then with water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated, the crude products were separated by column chromatography (silica gel: Wakogel C-300; chloroform as eluant). The yields are summarized in Table 1.

**Reaction of the Salt (1) with 1,1-Bis[*p*-(dimethylamino)phenyl]ethylene (6).**—To a stirred suspension of the salt (**1**) (1.92 mmol) and  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1.92 mmol) in acetic acid (60 ml) was added a solution of compound (**6**) (1.92 mmol) in acetic acid (15 ml). The mixture was stirred at 30 °C. The reaction was monitored by visible absorption spectroscopy. After the maximum and constant absorbance was obtained, water (70 ml) was added and the products were extracted with chloroform. The subsequent procedures were the same as those in the case of the reaction with *N,N*-dialkylanilines. The yields are shown in Table 1.

**Preparation of Metal(II)–(2c) Complex Dyes.**—To a solution of the free ligand (**2c**) (0.29 mmol) in benzene (50 ml) under argon was added a solution of the metal perchlorate hexahydrate (0.145 mmol) in THF (2 ml). After the mixture had been stirred for 2 h the precipitated metal(II)–(2c) complex

formed was filtered off, washed with a small amount of benzene, and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Results of the elemental analyses are given in Table 3.

**Preparation of Metal(II)-(7) Complex Dyes.**—To a solution of the free ligand (7) (0.24 mmol) in THF (30 ml) under argon was added a solution of the metal perchlorate hexahydrate (0.24, 0.48, or 0.96 mmol) in THF (10 ml). After the mixture had been kept overnight in a refrigerator, the precipitated green metal(II)-(7) complex formed was filtered off, washed with a small amount of THF, and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Results of the elemental analyses are given in Table 3.

**Characterization and Identification of Products.**—The following compounds were prepared:

4-[*p*-(Dimethylamino)anilino]-1,2-naphthoquinone (**2a**), m.p. 239–241 °C (from EtOH) (lit.,<sup>10</sup> 239–241 °C); λ<sub>max</sub>(EtOH) 517 nm (ε 5900) (Found: C, 73.8; H, 5.4; N, 9.4. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>; C, 73.96; H, 5.52; N, 9.58%).

4-[*p*-(Diethylamino)anilino]-1,2-naphthoquinone (**2b**), m.p. 240–241 °C (from EtOH); λ<sub>max</sub>(EtOH) 530 nm (6 290) (Found: C, 74.8; H, 6.4; N, 8.6. C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires C, 74.98; H, 6.29; N, 8.74%).

4-[4-(Diethylamino)-2-methylamino]-1,2-naphthoquinone (**2c**), m.p. 236–237 °C (from EtOH); λ<sub>max</sub>(EtOH) 483 nm (4 290) (Found: C, 75.3; H, 6.7; N, 8.2. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> requires C, 75.42; H, 6.63; N, 8.38%).

4-(*p*-Anisidino)-1,2-naphthoquinone (**2d**), m.p. 239–240 °C (from MeOH) (lit.,<sup>10</sup> 238–240 °C); λ<sub>max</sub>(benzene) 479 nm (6 000) (Found: C, 73.2; H, 4.9; N, 5.1. Calc. for C<sub>17</sub>H<sub>13</sub>NO<sub>3</sub>; C, 73.11; H, 4.70; N, 5.02%).

4-(*p*-Cyanoanilino)-1,2-naphthoquinone (**2e**), m.p. 283–284 °C (from MeOH) (lit.,<sup>11</sup> 285 °C); λ<sub>max</sub>(benzene) 433 nm (4 030) (Found: C, 74.3; H, 3.7; N, 10.1. Calc. for C<sub>17</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>; C, 74.45; H, 3.67; N, 10.02%).

4-(*p*-Nitroanilino)-1,2-naphthoquinone (**2f**), m.p. 238–240 °C (from benzene–MeOH); λ<sub>max</sub>(EtOH) 420 nm (4 950) (Found: C, 65.1; H, 3.4; N, 9.7. C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub> requires C, 65.30; H, 3.42; N, 9.52%).

2-[*p*-(Dimethylamino)anilino]-4-[*p*-(dimethylamino)phenyl-imino]naphthalen-1(4H)-one (**3a**), m.p. 223–225 °C (from EtOH); λ<sub>max</sub>(benzene) 587 nm (11 300); δ<sub>H</sub>(CDCl<sub>3</sub>) 2.91 (6 H, s), 2.96 (6 H, s), 6.5–7.2 (10 H, m), 7.45–7.8 (2 H, m), 8.1–8.3 (1 H, m), and 8.5–8.7 (1 H, m) (Found: C, 75.9; H, 6.3; N, 13.2. C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O requires C, 76.07; H, 6.38; N, 13.65%).

4-[*p*-(Dimethylamino)phenyl]-1,2-naphthoquinone (**4a**), m.p. 178–179 °C (from benzene); λ<sub>max</sub>(EtOH) 566 (6 460) and 523 sh nm (6 000); δ<sub>H</sub>(CDCl<sub>3</sub>) 3.06 (6 H, s), 6.40 (1 H, s), 6.77 (2 H, d, *J* 8.8 Hz), 7.37 (2 H, d, *J* 8.8 Hz), 7.3–7.6 (3 H, m), and 8.05–8.25 (1 H, m) (Found: C, 77.9; H, 5.15; N, 5.15. C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 77.96; H, 5.45; N, 5.05%).

4-[*p*-(Diethylamino)phenyl]-1,2-naphthoquinone (**4b**), m.p. 123–125 °C (from benzene); λ<sub>max</sub>(EtOH) 578 (8 400) and 525 sh nm (7 120); δ<sub>H</sub>(CDCl<sub>3</sub>) 1.24 (6 H, t), 3.45 (4 H, q), 6.42 (1 H, s), 6.43 (2 H, d, *J* 9.0 Hz), 7.67 (2 H, d, *J* 9.0 Hz), 7.3–7.6 (3 H, m), and 8.05–8.25 (1 H, m) (Found: C, 78.3; H, 6.1; N, 4.7. C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> requires C, 78.66; H, 6.27; N, 4.59%).

4-[*p*-(Methylamino)phenyl]-1,2-naphthoquinone (**4c**), m.p. 162–164 °C (from benzene); λ<sub>max</sub>(EtOH) 567 (5 650) and 528 sh nm (5 420); δ<sub>H</sub>(CDCl<sub>3</sub>) 2.92 (3 H, s), 4.19 (1 H, s), 6.40 (1 H, s), 6.68 (2 H, d, *J* 8.6 Hz), 7.33 (2 H, d, *J* 8.6 Hz), 7.4–7.65 (3 H, m), and 8.03–8.25 (1 H, m) (Found: C, 77.7; H, 5.0; N, 5.2. C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 77.55; H, 4.98; N, 5.32%).

4-[*p*-(Butylamino)phenyl]-1,2-naphthoquinone (**4d**), m.p. 167–

168 °C (from benzene); λ<sub>max</sub>(EtOH) 571 (6 860) and 532 sh nm (6 100); δ<sub>H</sub>(CDCl<sub>3</sub>) 0.99 (3 H, t), 1.15–1.9 (4 H, m), 3.20 (2 H, t), 4.0 (1 H, br), 6.41 (1 H, s), 6.67 (2 H, d, *J* 8.8 Hz), 7.31 (2 H, d, *J* 8.8 Hz), 7.4–7.65 (3 H, m), and 8.05–8.25 (1 H, m) (Found: C, 78.5; H, 6.5; N, 4.7. C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> requires C, 78.66; H, 6.27; N, 4.59%).

4-(*N*-Methylanilino)-1,2-naphthoquinone (**5a**), m.p. 174–175 °C (from EtOH) (lit.,<sup>12</sup> 173–174 °C); λ<sub>max</sub>(benzene) 453 nm (5 750); δ<sub>H</sub>(CDCl<sub>3</sub>) 3.50 (3 H, s), 6.28 (1 H, s), 6.9–7.5 (8 H, m), and 8.0–8.15 (1 H, m) (Found: C, 77.6; H, 4.8; N, 5.25. Calc. for C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub>; C, 77.55; H, 4.98; N, 5.32%).

4-(*N*-Butylanilino)-1,2-naphthoquinone (**5b**), m.p. 100–102 °C (from benzene); λ<sub>max</sub>(benzene) 463 nm (5 610); δ<sub>H</sub>(CDCl<sub>3</sub>) 0.94 (3 H, t), 1.2–1.95 (4 H, m), 3.90 (2 H, t), 6.31 (1 H, s), 6.9–7.5 (8 H, m), and 7.95–8.13 (1 H, m) (Found: C, 78.9; H, 6.3; N, 4.6. C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> requires C, 78.66; H, 6.27; N, 4.59%).

4-{2,2-Bis[*p*-(dimethylamino)phenyl]ethenyl}-1,2-naphthoquinone (**7**), m.p. 197–199 °C (from MeOH–acetone) (lit.,<sup>7</sup> 199–201 °C); λ<sub>max</sub>(EtOH) 616 nm (8 700); δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO] 2.94 (6 H, s), 3.02 (6 H, s), 6.03 (1 H, s), 6.80 (1 H, s), 6.65 (2 H, d, *J* 9.0 Hz), 6.75 (2 H, d, *J* 9.0 Hz), 7.07 (2 H, d, *J* 9.0 Hz), 7.31 (2 H, d, *J* 9.0 Hz), and 7.5–8.1 (4 H, m) (Found: C, 79.4; H, 6.1; N, 6.6. Calc. for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>; C, 79.60; H, 6.20; N, 7.63%).

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