

## Naphthoquinone Colouring Matters. Part 1. Synthesis and Electronic Absorption Spectra of 1,4-Naphthoquinone Derivatives with Electron-donating Groups in the Quinonoid Ring

By Kwong-Yung Chu and John Griffiths,\* Department of Colour Chemistry, The University, Leeds LS2 9JT

The syntheses of several yellow to blue 1,4-naphthoquinone derivatives with electron-donating groups (NHMe, NHPH, NMe<sub>2</sub>, and OMe) in the quinonoid ring are described. The visible absorption spectra are discussed in terms of the PPP SCF-MO model. The first  $\pi \rightarrow \pi^*$  transition of the 2-donor derivatives involves electron-density migration from the donor atom to the quinone system. Both electron-donating and -withdrawing groups in the 3-position give rise to bathochromic shifts, and it is concluded that for the former substituents the effect is principally electronic, whereas for electron-withdrawing groups the shifts are caused by steric distortion of the quinonoid ring. Electron-withdrawing groups in the 5- or 8-position of the benzenoid ring also cause bathochromic displacements of the visible band.

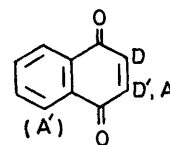
ALTHOUGH quinone derivatives contribute greatly to the commercially important dyestuffs, very few are based on 1,4-naphthoquinone, the majority being 9,10-anthraquinones. Colour generally develops in a quinone if at least one strong electron-donating (+M) group is attached in conjugation with the  $\pi$ -electron system, when the visible  $\pi \rightarrow \pi^*$  band is charge transfer in character.<sup>1</sup> The 1,4-naphthoquinones are particularly interesting in this respect, since there are three different positions for attaching such substituents, whereas in the anthraquinones there are only two. Potentially, therefore, the naphthoquinones should show a greater colour versatility than the anthraquinones, but, apart from a study of hydroxynaphthoquinones,<sup>2</sup> no systematic spectroscopic investigations of the former compounds have been made.

We have examined the synthesis of 1,4-naphthoquinones (1) with one or two electron-donor groups in the quinonoid ring. Modulation of the light absorption characteristics of (1) can be achieved in various ways. Thus, if two donor groups are present, these may be the same or different. Alternatively, electron-withdrawing groups may be attached to the system in the quinonoid or benzenoid rings, or in both. Attention has been directed towards derivatives with amino- and methoxy-donors and chloro- and cyano-acceptors in the quinonoid ring. Electron-withdrawing effects in the benzenoid ring have been studied with the corresponding 5- (or 8-)nitro-derivatives. The visible absorption spectra of

18 compounds have been measured, and have been interpreted with the aid of the PPP SCF-MO procedure.

### RESULTS AND DISCUSSION

*Synthesis of 2-Donor-substituted 1,4-Naphthoquinones.*—Various compounds of general structure (2) were prepared containing one mesomeric electron-donating group in the 2-position of 1,4-naphthoquinone. Donor groups examined included OMe, NHMe, NHPH, and



(1)

D, D' = electron donor  
A, A' = electron acceptor

NMe<sub>2</sub>. Corresponding compounds with 5- (or 8-)nitro-, 3-chloro-, or 3-cyano-groups were also prepared. Amino-groups can be introduced directly into 1,4-naphthoquinone by condensation with amines,<sup>3a</sup> but the reactions tend to be inefficient and isolation of the pure product is often difficult. A superior method involved the reaction of 2-methoxy-1,4-naphthoquinone (2a) with the appropriate amine in boiling ethanol to give (2b—d) in high yields.

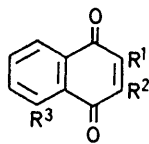
Reaction of 2,3-dichloronaphthoquinone with amines is a useful route to 2-amino-3-chloro-derivatives, and with methanol 2-chloro-3-methoxynaphthoquinone (2g) is formed similarly. The latter compound proved to be

<sup>3</sup> (a) 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, John Wiley, London, 1974, pp. 900—916; (b) p. 53.

<sup>1</sup> J. Griffiths, 'Colour and Constitution of Organic Molecules,' Academic Press, London, 1976, pp. 173—180.

<sup>2</sup> I. Singh, R. T. Otaga, R. E. Moore, C. W. J. Chang, and P. J. Scheuer, *Tetrahedron*, 1968, **24**, 6053.

reactive towards amines, and interestingly the methoxy-group was replaced in preference to chlorine. Thus derivatives (2e and f) were formed exclusively, even though chloride ion is generally a better leaving group than methoxide. The preferred displacement reaction can be explained in terms of the relative stabilities of the

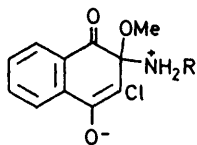


(2)

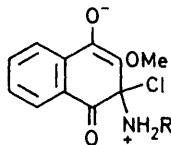
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
a;	OMe	H	H
b;	NHMe	H	H
c;	NHPh	H	H
d;	NMe <sub>2</sub>	H	H
e;	NHMe	Cl	H
f;	NHPh	Cl	H
g;	OMe	Cl	H
h;	NHMe	CN	H
i;	NHPh	CN	H
j;	Cl	NHMe	NO <sub>2</sub>
k;	NHMe	Cl	NO <sub>2</sub>

two alternative nucleophilic addition intermediates (3) and (4). The electron-donating (+M) effect of the methoxy-group will destabilise the anion (4), whereas the chlorine atom will stabilise (3) by electron withdrawal. Consequently, (3) will be formed more rapidly, and methoxide displacement is preferred.

Attempts to introduce a cyano-group into the quinonoid ring of 1,4-naphthoquinone by treating 2-chloro-3-methylaminonaphthoquinone (2e) with cuprous cyanide in boiling dimethylformamide were largely unsuccessful. Only trace amounts of the 2-cyano-3-methylamino-derivative (2h) could be isolated. It was found, however, that 2,3-dicyanonaphthoquinone reacted readily with amines to give the 2-amino-3-cyano-derivative in



(3)



(4)

good yields. Thus (2h) and (2i) were prepared by this procedure. The second cyano-group was inert towards nucleophilic substitution.

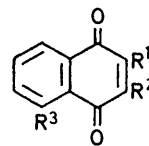
The 3-chloro-2-methylamino-8-(or 5)-nitro-derivatives (2j) and (2k) were prepared by the reaction of 2,3-dichloro-5-nitronaphthoquinone with methylamine. The replacement reactions of the latter quinone with ammonia,<sup>4</sup> and aniline<sup>5</sup> have been studied in some detail, but the reaction with methylamine has not been investigated. Condensation with methylamine was carried out in ethanol, giving a mixture of the two

<sup>4</sup> L. P. Slesarchuk, V. T. Kolesnikov, and B. G. Boldyrev, *J. Org. Chem. U.S.S.R.*, 1973, **9**, 2169.

<sup>5</sup> T. Kasai, R. Kurabayashi, Y. Suzuki, and S. Tsuruoka, *J. Synth. Org. Chem. (Japan)*, 1969, **27**, 162.

isomers (2j) and (2k) in excellent yield. The configuration of each compound was established by reducing the nitro-group to an amino-group, and comparing the products with authentic samples of 2-chloro-3-methylamino-5- and -8-nitro-1,4-naphthoquinone of established structure. Separation of the mixture of (2j) and (2k) by t.l.c. followed by spectrophotometric analysis enabled the product distribution to be determined [(2j) : (2k) = 1 : 0.85].

*Synthesis of 2,3-Bis-donor-substituted 1,4-Naphthoquinones.*—The 1,4-naphthoquinones (5) with two electron-donating (+M) groups (NHMe, NHPh, and OMe) in the quinonoid ring were prepared. An obvious route to compounds of this type would involve replacement of chlorine in the 2-amino-3-chloronaphthoquinones with amines or methoxide ion, but the deactivating effect of the amino-group renders these compounds very resistant to nucleophilic substitution. Although 2-chloro-3-methylaminonaphthoquinone (2e) reacted with sodium methoxide in boiling toluene, the yields of the 2-methoxy-3-methylamino-compound were very low. Reaction of (2e) with amines could not be detected under equally vigorous conditions. Acylation,<sup>6</sup>



(5)

a;	NHMe	NHMe	H
b;	NHMe	NHPh	H
c;	NHMe	OMe	H
d;	NHPh	OMe	H
e;	OMe	OMe	H
f;	OMe	OMe	NO <sub>2</sub>
g;	(OMe, NHMe)		NO <sub>2</sub>

or *N*-nitrosation,<sup>7</sup> of the amino-group of the 2-amino-3-chloro-compounds renders the chlorine atom more labile, and thus a second amino-group can be introduced without difficulty. It was found in the case of (2e) that *N*-nitrosation gave better yields of the derivatives (5a) and (5b), as subsequent denitrosation could be effected readily, whereas hydrolysis of the *N*-acetyl compounds gave complex mixtures.

The 2-amino-3-methoxy-derivatives (5c) and (5d) could be prepared similarly by reaction of the 2-chloro-3-*N*-nitrosamino-1,4-naphthoquinones with boiling methanol, but the yields were low. Denitrosation occurred during the reaction. A better route to these compounds proved to be the direct nucleophilic substitution of 2,3-dimethoxynaphthoquinone (5e) with the appropriate amine. With methylamine, the reaction proceeded smoothly in ethanol to give (5c) in 92% yield, whereas with aniline the reaction was very inefficient. In glacial acetic acid, however, aniline gave (5d) in 85% yield.

2,3-Dimethoxy-5-nitronaphthoquinone (5f) was prepared by heating 2,3-dichloro-5-nitronaphthoquinone

<sup>6</sup> K. Fries and P. Ochwat, *Ber.*, 1923, **56**, 1291.

<sup>7</sup> K. Fries and K. Billig, *Ber.*, 1925, **58**, 1128.

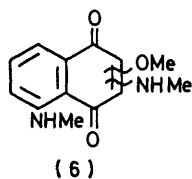
with sodium methoxide in methanol. This intermediate was reactive towards amines, but with methylamine a mixture of three products was produced. One of the components had the molecular formula  $C_{13}H_{14}N_2O_3$  (mass spectrum) and the i.r. spectrum showed amino-absorption but no nitro-peaks. In addition, the

character of the longest wavelength band was indicated by its intensity ( $\epsilon > 10^3$ ) and its displacement to longer wavelengths in polar solvents. In view of the sensitivity of this band towards the electron-donating strength of the donor atom, it is reasonable to assume that the transition involves electron-density transfer from the

Visible absorption spectral data for the 2-donor and 2,3-bis-donor 1,4-naphthoquinones

Compound	Substituents			$\lambda_{\max.}(C_6H_{12})/nm$	$\lambda_{\max.}(EtOH)/nm$	$\epsilon_{\max.}(C_6H_{12})/l mol^{-1} cm^{-2}$
	2	3	5			
(2a)	OMe	H	H	328	333	3 400
(2b)	NHMe	H	H	423	452	2 800
(2c)	NHPh	H	H	451	472	4 800
(2d)	NMe <sub>2</sub>	H	H	444	471	3 400
(2e)	NHMe	Cl	H	454	477	1 100
(2f)	NHPh	Cl	H	468	482	4 200
(2g)	OMe	Cl	H	334	338	3 100
(2h)	NHMe	CN	H	431	432	3 000
(2i)	NHPh	CN	H	440	440	4 000
(2j)	Cl	NHMe	NO <sub>2</sub>	481	490	3 200
(2k)	NHMe	Cl	NO <sub>2</sub>	482	490	3 600
(5a)	NHMe	NHMe	H	525	544	2 200
(5b)	NHMe	NHPh	H	549	552	2 700
(5c)	NHMe	OMe	H	484	492	2 800
(5d)	NHPh	OMe	H	495	500	3 200
(5e)	OMe	OMe	H	329	335	2 900
(5f)	OMe	OMe	NO <sub>2</sub>	327	386	2 600
(5g)	(OMe, NHMe)		NO <sub>2</sub>	498	526	2 900

normally single quinone carbonyl band was split into two, indicating the presence of a 5- (or 8-)amino-group hydrogen bonded to one of the carbonyl groups. The evidence thus suggests that the product is a mixture of the isomeric structures (6). The second methylamino-group is presumably introduced by displacement of the



nitro-group, reactions of this type being well known in anthraquinone chemistry.<sup>8</sup> The two remaining components had almost identical  $R_F$  values on t.l.c., and could not be separated. The mixture had a sharp melting point, and i.r. and elemental analysis indicated the expected 2-methoxy-3-methylamino-5- and -8-nitronaphthoquinone structures (5g). The two isomers are presumably present in approximately equal amounts.

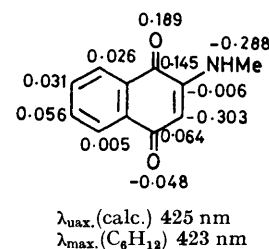
Attempts to prepare 2,3-bis(methylamino)-5-nitronaphthoquinone by reaction of acetylated or *N*-nitrosated (5g) with methylamine proved unsuccessful, since deacetylation led to decomposition, and denitrosation using reducing conditions resulted in reduction of the nitro-group.

**Visible Absorption Spectra.**—The visible spectra of the 2-donor- and 2,3-bis-donor-substituted 1,4-naphthoquinones are summarised in the Table. Wavelength maxima were measured in cyclohexane and ethanol, and absorption intensities in the former solvent. The  $\pi \rightarrow \pi^*$

donor group to the quinone system, as in the similarly substituted benzoquinones<sup>9</sup> and anthraquinones.<sup>1</sup>

The nature of the transition was examined by the PPP SCF-MO procedure. For these calculations, the molecular geometry of the compounds studied was taken as an average of the bond lengths and angles of variously substituted 1,4-naphthoquinones.<sup>3b</sup> The molecular parameters have been described elsewhere.<sup>10</sup> Using 2-methylamino-1,4-naphthoquinone as an example, the  $\pi$ -electron density changes accompanying the first electronic transition were evaluated, and are summarised in the Figure.

It can be seen from the Figure that the transition clearly involves the transfer of negative charge from the



$\pi$ -Electron density changes for the first electronic transition of 2-methylamino-1,4-naphthoquinone, calculated by the PPP method

amino-group to the carbonyl groups, and interestingly it is the C(1) carbonyl that shows the greatest increase in electron density (0.334). Resonance theory would predict that the carbonyl group directly conjugated with the amino-group (*i.e.* the C<sub>4</sub> carbonyl) would be the dominant electron acceptor, and yet the electron-

<sup>8</sup> See, for example, R. E. Schmidt, *Ber.*, 1904, **37**, 72; G. D. Wood and A. T. Peters, *J. Chem. Soc.*, 1962, 3373.

<sup>9</sup> M. Klessinger, *Theor. Chim. Acta*, 1966, **5**, 251.

<sup>10</sup> J. Griffiths and M. Lockwood, *J.C.S. Perkin I*, 1976, 48.

density increase (0.016) is very small. Similar conclusions were reached by Klessinger for the visible transition of the aminobenzoquinones.<sup>9</sup>

The predicted electron-density changes at other positions are informative, and, for example, the increase in electron density at positions 5 and 8 suggests that attachment of an electron-withdrawing group at these sites would give a bathochromic shift of the visible band. This is confirmed by comparison of 2-chloro-3-methylamino-1,4-naphthoquinone [ $\lambda_{\text{max}}$ . (C<sub>6</sub>H<sub>12</sub>) 454 nm] with the 2-chloro-3-methylamino-5- and -8-nitro-1,4-naphthoquinones (2j) and (2k) ( $\lambda_{\text{max}}$ . 481 and 482 nm respectively).

The large electron-density decrease at position 3 of (2b) (Figure) suggests that an electron donating group at that position should give a pronounced bathochromic shift. This is amply confirmed by the 2,3-bis-donor systems (5). For example, 2,3-bismethylamino-1,4-naphthoquinone absorbs at 525 nm in cyclohexane, and is violet, whereas 2-methylamino-1,4-naphthoquinone is orange, and absorbs at 423 nm in the same solvent. The extent of the shift depends on the electron-donating strength of the second donor group, e.g. the methoxy-methylamino-derivative (5c) is red and absorbs at 484 nm in cyclohexane. The spectra of the nitro-derivatives (5f) and (5g) indicate that, as in the 2-donor system, electron-withdrawing groups in the 5- and 8-positions of a 2,3-bis-donor system also produce bathochromic shifts.

As a second electron-donor group in the quinonoid ring causes a bathochromic shift, conversely an electron-withdrawing group at position 3 should produce a hypsochromic shift. However, it is clear from the Table that the reverse is true, and both 3-chloro- and 3-cyano-2-methylamino-1,4-naphthoquinone absorb at longer wavelengths than the 2-methylamino-derivative. This anomalous behaviour may be attributed to steric crowding in the 2,3-disubstituted compounds. Rotation about the C(2)-N bond, which would give a hypsochromic shift, would do little to relieve strain between the flanking carbonyl, 3-substituent, and the amino-group, whereas distortion of the 2,3 double-bond would be more favourable. X-Ray crystallographic studies on 3-substituted-2-amino-1,4-naphthoquinones have shown this to be the case.<sup>11</sup> The molecular orbital calculations show a high  $\pi$ -bond order for the 2,3-bond in the ground state, and a large decrease in  $\pi$ -bond order in the first excited state. Thus twisting about this bond will produce a bathochromic shift and a decrease in intensity. It is noteworthy that the chloro-compound (2e) has less than half the intensity of the parent methylamino-compound (2b). The smaller bathochromic shift observed for the cyano-compound (2h) presumably reflects the smaller steric requirement of the cyano-group.<sup>12</sup>

<sup>11</sup> J. Gaultier and C. Hauw, *Acta Cryst.*, 1966, **20**, 620; 1966, **21**, 694.

<sup>12</sup> W. A. Sheppard, in 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience, London, 1970, p. 209.

<sup>13</sup> L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491.

The 2-donor- and 2,3-bis-donor-substituted 1,4-naphthoquinones evidently can provide almost the full spectral range of colours. The 2-donor systems are yellow to orange, the 2-amino-3-methoxy-derivatives red, and the 2,3-bis-amino-derivatives violet to blue. More subtle bathochromic modifications are possible by introducing electron-withdrawing groups into the benzenoid ring. The intensities of the compounds studied ( $\epsilon$  ca. 3 000) were, however, all low compared with related anthraquinone dyes ( $\epsilon$  ca. 8 000).

In general, the light fastness properties of these dyes were poor, but it was notable that the anilino-derivatives always showed better photochemical stability than their methylamino- and dimethylamino-counterparts. Only the derivatives (2c) and (2i) approached commercial acceptability in this respect (on polyester substrates).

#### EXPERIMENTAL

*Reactions of 2-Methoxy-1,4-naphthoquinone (2a) with Amines.*—A solution of (2a) (1 mequiv.) and the amine (3 mequiv.) in ethanol (10 ml) was heated under reflux for 30 min. The solution was concentrated and cooled, and the deposited crystals filtered off. The following compounds were prepared (% yield, m.p., °C): 2-methylamino-1,4-naphthoquinone, 86, 232–234 (lit.,<sup>13</sup> 234 °C); 2-anilino-1,4-naphthoquinone, 59, 188–190 (lit.,<sup>14</sup> 190–191 °C); 2-dimethylamino-1,4-naphthoquinone, 80, 108–109 (lit.,<sup>13</sup> 120 °C).

*Reaction of 2-Chloro-3-methoxy-1,4-naphthoquinone with Methylamine.*—A solution of 2-chloro-3-methoxy-1,4-naphthoquinone (2g)<sup>15</sup> (5.5 g) and methylamine (33% ethanolic solution, 5 ml) in absolute methanol (150 ml) was heated under reflux for 15 min. The solution was concentrated under reduced pressure to 30 ml and cooled. The orange-red crystals of 2-chloro-3-methylamino-1,4-naphthoquinone (2e) were filtered off and dried (5.3 g, 97%), m.p. 161–163 °C (lit.,<sup>16</sup> 150 °C). The product had an identical m.p. and i.r. spectrum to a purified sample of (2e) prepared from 2,3-dichloro-1,4-naphthoquinone and methylamine.

*2-Cyano-3-methylamino-1,4-naphthoquinone (2h).*—A suspension of 2,3-dicyano-1,4-naphthoquinone<sup>17</sup> (0.104 g) in a solution of methylamine (33% ethanolic solution, 0.2 ml) in absolute ethanol (10 ml) was heated under reflux for 1 h. The solvent was removed under reduced pressure and the residue digested with dichloromethane. Evaporation of the filtered extracts gave 2-cyano-3-methylamino-1,4-naphthoquinone (2h) (0.09 g, 85%), which formed fine yellow needles, m.p. 244–255 °C (decomp.), on recrystallisation from acetone (Found: C, 67.8; H, 3.9; N, 13.0. C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> requires C, 67.9; H, 3.8; N, 13.2%),  $\nu_{\text{max}}$  (KBr) 3 260 and 2 204 cm<sup>-1</sup>.

*2-Anilino-3-cyano-1,4-naphthoquinone (2i).*—A mixture of 2,3-dicyano-1,4-naphthoquinone (0.208 g) and aniline (0.205 g) in toluene (25 ml) was heated under reflux for 1 h. The dark yellow solution was evaporated to dryness under reduced pressure, and the residue chromatographed over alumina in benzene. The residue obtained from the main yellow fraction was triturated with a little light petroleum to remove soluble blue impurities, giving 2-anilino-3-cyano-

<sup>14</sup> T. Zincke, *Ber.*, 1879, **12**, 1641.

<sup>15</sup> W. L. Mosby and M. L. Silva, *J. Chem. Soc.*, 1964, 3990.

<sup>16</sup> A. Plagemann, *Ber.*, 1882, **15**, 484.

<sup>17</sup> G. A. Reynolds and J. A. VanAllan, *J. Org. Chem.*, 1964, **29**, 3591.

1,4-naphthoquinone (2i) as orange leaflets (0.08 g, 30%), m.p. 238—239 °C (Found: C, 74.4; H, 3.3; N, 10.1.  $C_{17}H_{10}N_2O_2$  requires C, 74.5; H, 3.6; N, 10.2%),  $\nu_{\max}$  (KBr) 3 265 and 2 206  $cm^{-1}$ .

2-Chloro-3-methylamino-5- and -8-nitro-1,4-naphthoquinones (2j) and (2k).—A solution of 2,3-dichloro-5-nitronaphthoquinone<sup>18</sup> (2.72 g) and methylamine (33% ethanolic solution; 5 ml) in ethanol (200 ml) was heated under reflux for 40 min and cooled. The red precipitate (2.3 g, 86%) was extracted with boiling toluene (250 ml) and the residue was recrystallised from toluene to give pure 2-chloro-3-methylamino-8-nitro-1,4-naphthoquinone (2k) as dark red crystals (0.6 g), m.p. 223—224 °C (Found: C, 49.7; H, 2.7; Cl, 13.4; N, 10.9.  $C_{11}H_7ClN_2O_4$  requires C, 49.5; H, 2.6; Cl, 13.3; N, 10.5%). A further crop of (2k) could be obtained from the mother liquors of the reaction and the toluene extracts, giving a total yield of 0.78 g.

Combination and evaporation of the various mother liquors gave a mixture of (2j) and (2k), which was separated by preparative t.l.c. (silica-benzene) to give a further quantity of (2k) (0.22 g) and red crystals of 2-chloro-3-methylamino-5-nitro-1,4-naphthoquinone (2j) (0.847 g, 32%), m.p. 262—263 °C (Found: C, 49.5; H, 2.5; Cl, 13.7; N, 10.75.  $C_{11}H_7ClN_2O_4$  requires C, 49.5; H, 2.6; Cl, 13.3; N, 10.5%).

2-Anilino-3-methylamino-1,4-naphthoquinone (5b).—2-Chloro-3-(*N*-nitrosomethylamino)-1,4-naphthoquinone (1.25 g) and aniline (0.5 g) were heated under reflux in benzene (15 ml) for 10 min. The solvent was removed under reduced pressure, and the residue chromatographed over alumina in benzene. The main yellow band afforded a dark brown solid (0.95 g) which was denitrosated by heating with zinc dust (0.95 g) and concentrated hydrochloric acid (5 ml) in ethanol (10 ml) at 70 °C for 40 min. The solution was neutralised with aqueous ammonia and the suspension agitated in air for 30 min. The blue precipitate was filtered off and purified by column chromatography (alumina-benzene). 2-Anilino-3-methylamino-1,4-naphthoquinone (5b) formed deep blue needles (0.68 g, 51%), m.p. 158—159 °C (Found: C, 73.35; H, 5.35; N, 9.8.  $C_{17}H_{14}N_2O_2$  requires C, 73.4; H, 5.0; N, 10.1%).

2-Methoxy-3-methylamino-1,4-naphthoquinone (5c).—A solution of 2,3-dimethoxynaphthoquinone (5e)<sup>19</sup> (0.1 g) and methylamine (33% ethanolic solution, 0.1 ml) in ethanol (20 ml) was heated under reflux for 40 min. After concentration of the solution to ca. 5 ml and cooling, the dark red solid was filtered off. Recrystallisation from light petroleum (b.p. 60—80 °C) gave 2-methoxy-3-methylamino-

<sup>18</sup> K. Fries, W. Pense, and O. Peeters, *Ber.*, 1928, **61**, 1401.

1,4-naphthoquinone (5c) as dark red needles (0.1 g, 92%), m.p. 158—160 °C (Found: C, 66.45; H, 5.3; N, 6.65.  $C_{12}H_{11}NO_3$  requires C, 66.4; H, 5.1; N, 6.45%).

2-Anilino-3-methoxy-1,4-naphthoquinone (5d).—A solution of (5e) (0.645 g) in glacial acetic acid (30 ml) was treated with aniline (0.6 g) and the mixture heated under reflux for 16 h. Water (100 ml) was added, and the crystals that separated after several hours were filtered off. Recrystallisation from petroleum-benzene gave 2-anilino-3-methoxy-1,4-naphthoquinone (5d) as dark red plates (0.7 g, 85%), m.p. 79 °C (Found: C, 72.9; H, 4.7; N, 5.1.  $C_{17}H_{13}NO_3$  requires C, 73.1; H, 4.7; N, 5.0%).

2,3-Dimethoxy-5-nitro-1,4-naphthoquinone (5f).—2,3-Dichloro-5-nitronaphthoquinone (1.36 g) was added in portions to a solution of sodium methoxide (prepared from 0.4 g of sodium in 20 ml dry methanol), with stirring at room temperature. When addition was complete, a clear orange-red solution resulted which on further stirring deposited a copious yellow precipitate. After 40 min the solid was filtered off, dried, and recrystallised from methanol to give yellow needles of 2,3-dimethoxy-5-nitro-1,4-naphthoquinone (5f) (1.09 g, 82%), m.p. 154—156 °C (Found: C, 54.95; H, 3.6; N, 5.45.  $C_{12}H_9NO_6$  requires C, 54.75; H, 3.4; N, 5.3%).

Reaction of 2,3-Dimethoxy-5-nitro-1,4-naphthoquinone (5f) with Methylamine.—A solution of (5f) (1.7 g) and methylamine (33% ethanolic solution, 4 ml) in absolute ethanol (100 ml) was heated under reflux for 45 min. The solution was concentrated under reduced pressure to ca. 50 ml and cooled. The purple solid that deposited with time was filtered off and recrystallised twice from benzene, giving a mixture of the 2-methoxy-3-methylamino-5- and -8-nitro-1,4-naphthoquinones (5g) (1.2 g, 71%), m.p. 197—199 °C (Found: C, 54.9; H, 3.8; N, 11.1.  $C_{12}H_{10}N_2O_5$  requires C, 55.0; H, 3.8; N, 10.7%).

The ethanol and benzene mother liquors were combined and evaporated to dryness. The mixture of isomeric 2,5- and 2,8-bismethylamino-3-methoxy-1,4-naphthoquinones was obtained as black rectangular plates (0.17 g), m.p. 140—141 °C after purification by preparative t.l.c. (silica-benzene) ( $M^+$  246; calc. for  $C_{13}H_{14}N_2O_3$ ,  $M$  246).

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<sup>19</sup> L. F. Fieser and R. H. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 3614.