Naphthoquinone Colouring Matters. Part 3.[1] Synthesis and Electronic Absorption Spectra of 1,4-Naphthoquinones containing Electron Donor Groups in Both Rings

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The syntheses of several 1,4-naphthoquinones containing mesomeric electron donor groups (NH_2, NHR, or OMe) in both rings are described. The most convenient routes involve nucleophilic replacement of labile 2- or 3-substituents (Cl, OMe, CN) in appropriately substituted 5-donor- or 5,8-bis(donor)-1,4-naphthoquinones. The directing effects of 5-amino- and 5-nitro-groups in these reactions have been examined. The electronic absorption spectra of the derivatives show a broad, complex band system in the 350—600 nm region, and PPP–MO calculations indicate that this results from two overlapping $\pi \rightarrow \pi^*$ transitions, one involving electron density migration from the benzenoid donor-group(s) into the quinonoid system, and the other involving a similar transfer of negative charge from the quinonoid donor group(s).

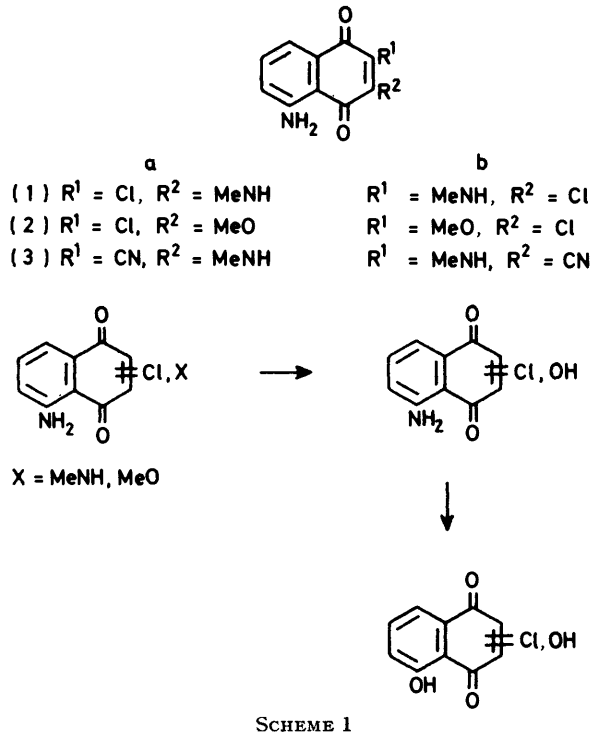
THE electron donor-substituted 1,4-naphthoquinones are a versatile group of colouring matters, and although they can provide a full range of colours, relatively little was known about their spectroscopic properties until recently.[1,2] Derivatives with electron donor ($+M$) groups in the benzenoid ring show a visible electronic transition which involves charge migration from the donor group into the quinonoid ring, and consequently electron-withdrawing groups in the latter ring cause bathochromic displacements.[1] In contrast, 1,4-naphthoquinones with donor groups confined to the quinonoid ring show a visible transition involving charge migration in the opposite direction, and thus electron acceptors in the benzenoid ring have a bathochromic effect.[2] It was thus of interest to see if the introduction of electron donor groups into both rings of 1,4-naphthoquinone would result in large hypsochromic shifts, owing to opposed directions of charge migration, or whether the more usual bathochromic effect accompanying multiplication of auxochromes would be observed.

We have examined the synthesis and electronic absorption spectra of 1,4-naphthoquinones of this type, bearing amino-, methylamino-, and methoxy-donor groups in the 2,5-, 3,5-, 2,3,5-, 2,5,8-, and 2,3,5,8-positions. The light absorption characteristics of these systems were interpreted with the aid of the PPP-SCF-MO method.

RESULTS AND DISCUSSION

Synthesis of Derivatives.—The lability of the halogen atoms in 2,3-dichloro-1,4-naphthoquinone towards nucleophilic displacement enables a wide range of derivatives to be prepared containing donor-groups in both rings. Thus reaction of 5-amino-2,3-dichloro-1,4-naphthoquinone with methylamine or methanol gave predominantly the 3-substituted derivatives (1a) and (2a), and only trace amounts of the 2-substituted isomers (1b) and (2b). The orientation of the products was established by the route summarised in Scheme 1, the resultant chlorodihydroxy-1,4-naphthoquinones being identified by comparison with authentic samples of established structure.[3]

The strong directing effect of the 5-amino-group, favouring substitution at the 3- rather than the 2-position, has been noted previously for reactions with secondary amines [4] and aniline,[5] and may be attributed to the $+M$ effect of the amino-group. This renders the



SCHEME 1

4-carbonyl group less electron attracting, and thus favours nucleophilic attack at the carbon atom β to the 1-carbonyl group, *i.e.* position 3. It was noted that with the weak nucleophile methanol, relatively higher proportions of the 2-substituted product were obtained, and the isolated yields were in the ratio (2a) : (2b) = 6 : 1. The 2-substituted isomers (1b) and (2b) were best prepared by condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with the appropriate nucleophiles. The nitro-group proved much less selective in its directing effect, and in both cases approximately equal amounts of the 2- and 3-substitution products were obtained. Reduction of the nitro-group with tin(II) chloride gave a mixture of the two 5-amino-substituted

isomers, which was separated chromatographically to give (1a) and (2a) and (1b) and (2b) in good yields.

Replacement of the chlorine atom in these derivatives by the cyano-group was of interest as the latter group would remove steric crowding in the quinonoid ring.[2] The cyano-compounds (3a and b) were prepared by reaction of 2,3-dicyano-5-nitro-1,4-naphthoquinone with methylamine, followed by reduction of the nitro-group, giving the 2- and 3-methylamino-replacement products in the ratio (3a) : (3b) = 2.5 : 1. In contrast, direct reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone [1] with methylamine gave the product ratio (3a) : (3b) = 24 : 1, paralleling the behaviour of 5-amino-2,3-dichloro-1,4-naphthoquinone. As noted previously, condensation of 5-amino-2,3-dicyano-1,4-naphthoquinone with aniline was anomalous, and resulted in substitution in the benzenoid ring.[1]

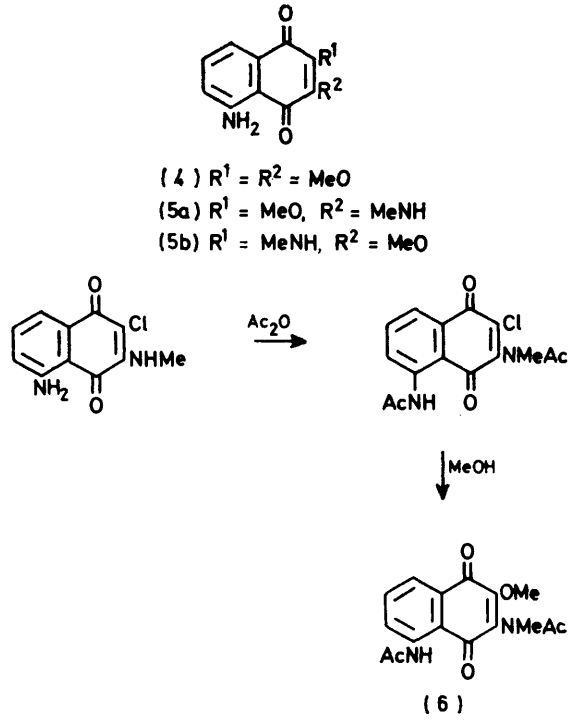
Orientation of (3a and b) by chemical means proved unsuccessful. Thus synthesis of (3a) from (1a), of established orientation, was attempted by successive *N*-acetylation, cyanodehalogenation, and hydrolysis. However, treatment of the bisacetyl derivative of (1a) with copper(I) cyanide in dimethylformamide gave no replacement products, whereas with aqueous potassium cyanide 5-acetylamino-2,3-dicyano-1,4-naphthoquinone was formed exclusively. The structures of (3a and b) were thus assigned on the basis of their visible absorption spectra, the 2-methylamino-derivative absorbing at longer wavelengths than the 3-isomer, as observed for the analogous methylaminochloro-compounds (1) (see Table).

Treatment of 5-amino-2,3-dichloronaphthoquinone with sodium methoxide in methanol gave 5-amino-2,3-dimethoxynaphthoquinone (4) in low yield. Better yields were obtained by reaction of 5-nitro-2,3-dichloronaphthoquinone with sodium methoxide, followed by reduction of the nitro-group of the resultant dimethoxy-compound. The product (4) provides an example of a 1,4-naphthoquinone with three $+M$ electron-donating groups, and was also a useful intermediate for the preparation of other related systems. Thus condensation of (4) with methylamine in ethanol gave predominantly 5-amino-2-methoxy-3-methylamino-1,4-naphthoquinone (5a) and trace amounts of the 2-methylamino-isomer (5b). 2,3-Dimethoxy-5-nitro-1,4-naphthoquinone gave with methylamine [2] somewhat larger amounts of the 2-replacement product, and the mixture could be reduced with tin(II) chloride and the amino-compounds (5a and b) separated in reasonable yield.

Experimental and calculated visible absorption spectra of polysubstituted 1,4-naphthoquinones [a]

	B Band		Q Band	
1,4-Naphthoquinone	$\lambda_{max.}$ [b,c]/nm	$10^{-3}\ \varepsilon_{max.}$ [d]	$\lambda_{max.}$ [b,c]/nm	$10^{-3}\ \varepsilon_{max.}$ [d]
(1a)	490s (451)	4.7 (0.23)	448 (393)	7.1 (0.27)
(1b)	500 (484)	4.4 (0.23)	454 (374)	3.6 (0.12)
(2a)	482 (465)	6.1 (0.23)	350—410 [e] (331)	*ca.* 1.5 (0.06)
(2b)	487 (483)	5.4 (0.20)	350—400 [e] (331)	*ca.* 1.5 (0.02)
(3a)	482 (470)	7.5 (0.28)	441 (422)	7.6 (0.25)
(3b)	504 (496)	6.5 (0.21)	445 (405)	4.5 (0.18)
(4)	471 (480)	5.3 (0.22)	410s (404)	2.2 (0.16)
(5a)	446 (431)	7.8 (0.23)	490s (554)	4.7 (0.18)
(5b)	452 (425)	4.1 (0.16)	504 (565)	4.7 (0.22)
(7)	400s (405)	2.2 (0.22)	360 (319)	4.3 (0.08)
(8)	460s (400)	4.2 (0.31)	414 (387)	6.9 (0.18)
(9)	320—350 [e] (390)	*ca.* 2.0 (0.23)	398 (407)	3.7 (0.21)
(10)	404 (382)	5.5 (0.23)	480s (503)	2.6 (0.21)
(11)	*f* (377)	(0.27)	430 (445)	6.9 [g] (0.11)
(12)	370 (385)	5.7 (0.26)	415s (424)	2.7 (0.29)

[a] Spectra recorded in cyclohexane. [b] s = shoulder. [c] Calculated wavelengths in parentheses. [d] Calculated oscillator strengths in parentheses. [e] Broad tail. [f] No detectable shoulder. [g] In acetone.



SCHEME 2

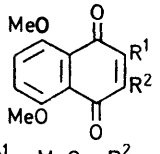
Orientation of the isomers was achieved by acetylation of (5a) to give (6), which was identified by i.r. and m.p. comparison with an authentic sample prepared by the route shown in Scheme 2.

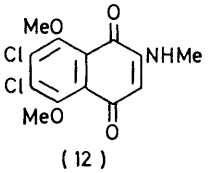
1,4-Naphthoquinones with two $+M$ groups in the 5,8-positions are exceptionally bathochromic, and range from red to blue-green in colour.[1] Attempts to prepare

5,8-diamino- or 5-amino-8-methoxy-systems with a third electron donor in the quinonoid ring were unsuccessful, although 5,8-dimethoxy-analogues proved more accessible. Thus 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone reacts readily with nucleophiles, and with methanol [6] or methylamine the substitution products (7) and (8) were formed respectively, by replacement of one of the halogen atoms. The methoxy-derivative (7) could be reacted further, and with methylamine gave 2-chloro-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone (8) in quantitative yield. The exclusive replacement of methoxy rather than chlorine parallels the behaviour of 2-chloro-3-methoxy-1,4-naphthoquinone noted previously.[2]

Under more severe conditions, using sodium methoxide in methanol, 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone gave the tetramethoxy-compound (9).[6] One of the quinonoid methoxy-groups could be replaced by nucleophiles, and, for example, on heating with methylamine, (9) gave (10). 2,3-Dicyano-5,8-dimethoxy-1,4-naphthoquinone [1] could also be substituted readily by nucleophiles, and with methylamine gave 2-cyano-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone (11).

As expected, the halogen atoms of 6,7-dichloro-5,8-dimethoxy-1,4-naphthoquinone [6] proved inert towards nucleophilic substitution, and it was found that nucleophilic addition to the quinonoid ring occurred preferentially. Thus on treating with methylamine in boiling ethanol, 6,7-dichloro-5,8-dimethoxy-2-methylamino-1,4-naphthoquinone (12) was formed.

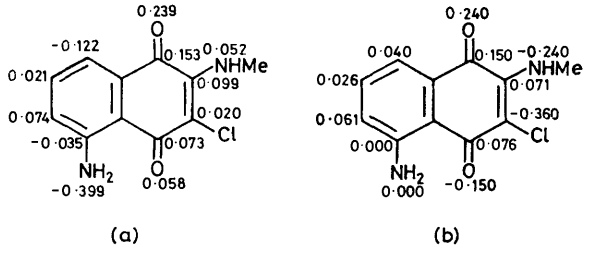




(7) R^1 = MeO, R^2 = Cl
(8) R^1 = MeNH, R^2 = Cl
(9) R^1 = R^2 = MeO
(10) R^1 = MeO, R^2 = MeNH
(11) R^1 = CN, R^2 = MeNH

(12)

Electronic Absorption Spectra.—The electronic absorption spectra of the derivatives (1a)—(5a), (1b)—(5b), and (7)—(12) were measured in cyclohexane. The relevant data for the 350—700 nm region of the spectrum are summarised in the Table. Whereas 1,4-naphthoquinones with electron donor groups confined to either the benzenoid or quinonoid ring show a single, symmetrical $\pi \rightarrow \pi^*$ band in the visible spectrum, the derivatives listed in the Table show a more complex band system. Thus one main band with a pronounced shoulder is often observed, or in some cases two discrete maxima can be seen. A typical example of the latter is provided by 5-amino-3-chloro-2-methylamino-1,4-naphthoquinone (1b), which has two absorption maxima, at 500 and 454 nm ($\varepsilon_{max.}$ 4 400 and 3 600 respectively). 5-Amino-1,4-naphthoquinone itself absorbs at 484 nm in cyclohexane ($\varepsilon_{max.}$ 5 400),[1] and 3-chloro-2-methylamino-1,4-naphthoquinone absorbs at 454 nm ($\varepsilon_{max.}$ 1 100).[2] Thus it is attractive to assume that the visible transitions of these parent chromogens are essentially preserved, with minor changes, in the hybrid molecule (1b). This simplistic argument was examined critically by molecular orbital calculations. The absorption spectrum of (1b) was calculated by the PPP method, using the parameters described previously,[1] and assuming a planar geometry. The transition energies were improved by a configuration interaction treatment involving the first nine singly excited singlet states. Two long wavelength bands were predicted for (1b), at 484 and 374 nm, with oscillator strengths of 0.23 and 0.12 respectively. The calculated electron density changes for the longer wavelength transition [Figure (a)] show a pronounced migration of electron density from the benzenoid amino-group (*i.e.* the 5-substituent) into the quinonoid ring, whereas the quinonoid methylamino-group is virtually unaffected. In this respect, the pattern is analogous to that found for the visible band of 5-amino-1,4-naphthoquinone.[1]



(a) (b)

π-Electron density changes for (a) the B transition, and (b) the Q transition of 5-amino-3-chloro-2-methylamino-1,4-naphthoquinone

Electron density changes for the second band of (1b) [Figure (b)] show that the quinonoid methylamino-group is the principal auxochrome, and the latter group transfers a significant degree of negative charge to the quinonoid ring. The 5-amino-group plays virtually no part in the transition. The situation parallels that found for 2-methylamino-1,4-naphthoquinone.[2] Thus, in this case, it is reasonable to assign the two bands of (1b) to the visible transitions shown separately by the two parent molecules. The agreement between the observed and calculated $\lambda_{max.}$ values for the first band of (1b) is reasonable, but is less satisfactory for the second (454 nm) band. The position and intensity of the visible band of 2-chloro-3-methylamino-1,4-naphthoquinone noted previously [2] suggests that the bulky halogen atom causes distortion of the quinonoid ring, and the bathochromic shift that would result from this in (1b) would not be taken into account in the calculations.

PPP calculations for other derivatives showed that the conclusions reached for (1b) were general, and in most cases the two long-wavelength transitions could be assigned as pure benzenoid (or B) bands, where auxochromes in the benzenoid ring only were involved, or as pure quinonoid (or Q) bands, where the quinonoid auxochromes were dominant. In some instances, distinction between the two transitions was less clear, when both types of auxochromes showed simultaneous involvement

in a particular transition. It was still possible, however, to recognise the dominant B- or Q-character of a transition from the molecular orbital calculations, and the assignments shown in the Table were made in this way.

Absolute agreement between the calculated wavelength values and experiment (Table) is not as good as for the simpler benzenoid-substituted systems,[1] but relative values are reasonable. Particularly interesting are those derivatives with a methylamino-auxochrome in the 2- or 3-position relative to a 5-amino-group, *i.e.* (1)—(3). In all cases the 3,5-isomers show the B and Q bands at shorter wavelengths than the corresponding bands of the 2,5-isomers, and this is predicted correctly by the PPP method. The absorption intensities for the B band of both isomers are generally similar, whereas the Q band intensity the 3,5-isomer is greater than that of the 2,5-isomer, as predicted.

In conclusion, then, one can regard the quinonoid- and benzenoid-substituted systems of a 1,4-naphthoquinone possessing auxochromes in both rings as two virtually independent chromogens, both retaining the basic characteristics of their parent chromogens. It can be predicted, therefore, that no dramatic spectral changes will occur in such polyauxochromic systems, and that these 'mixed' chromogens will show no colour advantages over the simpler dyes with auxochromes confined to one ring. This is confirmed by the data shown in the Table. The broadness and complexity of the visible spectra of these compounds result in compounds with dull colours (*i.e.* of low spectral purity) when applied to polymer substrates, and in this respect they are inferior to their simpler counterparts.

EXPERIMENTAL

Visible absorption spectra were recorded on a Unicam SP 800 spectrophotometer.

5-Amino-2-chloro-3-methylamino-1,4-naphthoquinone (1a).—A solution of 5-amino-2,3-dichloro-1,4-naphthoquinone (0.24 g) and methylamine (33% ethanolic solution; 0.6 ml) in absolute ethanol (20 ml) was heated under reflux for 3 h. The orange solution was concentrated to 15 ml and cooled. The deposited crystals were recrystallised from toluene, giving *5-amino-2-chloro-3-methylamino-1,4-naphthoquinone* (1a) as reddish brown needles (0.169 g, 72%), m.p. 240—241 °C (decomp.) (Found: C, 56.1; H, 3.65; N, 11.55; Cl, 14.9. $C_{11}H_9ClN_2O_2$ requires C, 55.8; H, 3.8; N, 11.8; Cl, 15.0%). Traces of the red 5-amino-3-chloro-2-methylamino-isomer (1b) were detectable by t.l.c. analysis.

Reaction of 5-Amino-2,3-dichloro-1,4-naphthoquinone with Methanol.—A mixture of 5-amino-2,3-dichloro-1,4-naphthoquinone (0.12 g), fused sodium acetate (0.3 g), and anhydrous methanol (60 ml) was heated under reflux for 3.5 h and filtered whilst hot. Concentration of the filtrate to 20 ml and cooling afforded dark needles. Recrystallisation of these from methanol gave pure *5-amino-2-chloro-3-methoxy-1,4-naphthoquinone* (2a). A further quantity could be obtained by preparative t.l.c. separation of the residue from the mother liquors (total yield 0.051 g, 43%), m.p. 187—189 °C (Found: C, 55.75; H, 3.5; N, 5.85; Cl, 15.0. $C_{11}H_8ClNO_3$ requires C, 55.6; H, 3.4; N, 5.9; Cl, 14.9%). Also obtained by preparative t.l.c. was the isomeric *5-amino-3-chloro-2-methoxy-1,4-naphthoquinone* (2b) (0.009 g, 7%), m.p. 167—168 °C (Found: C, 55.1; H, 3.4; N, 6.1; Cl, 14.9. $C_{11}H_8ClNO_3$ requires C, 55.6; H, 3.4; N, 5.9; Cl, 14.9%).

5-Amino-3-chloro-2-methylamino-1,4-naphthoquinone (1b).—Condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with methylamine, as described previously,[2] gave a mixture of 2-chloro-3-methylamino- and 3-chloro-2-methylamino-5-nitro-1,4-naphthoquinones. The crude solid (0.8 g) was dissolved in a mixture of acetic acid (20 ml), concentrated hydrochloric acid (15 ml), and tin(II) chloride dihydrate (3.5 g) and heated with stirring at 70 °C for 30 min. The pale yellow solution was poured into a solution of iron(III) chloride (4 g) in water (100 ml), and after 30 min the red precipitate was filtered off. The products were separated by chromatography over neutral alumina in benzene–light petroleum (b.p. 60—80 °C) (1 : 1). The dark red band eluted first afforded *5-amino-3-chloro-2-methylamino-1,4-naphthoquinone* (1b) (0.175 g, 25%), m.p. 214—216 °C (decomp.) (Found: C, 55.75; H, 3.65; N, 11.85; Cl, 14.75. $C_{11}H_9ClN_2O_2$ requires C, 55.8; H, 3.8; N, 11.8; Cl, 15.0%). The second orange band gave the isomer (1a) (0.21 g, 30%), m.p. 187—189 °C.

Orientation of the Derivatives (1a *and* b) *and* (2a *and* b).—The appropriate methylamino-derivative (1a or b) (0.100 g) was dissolved in a mixture of concentrated sulphuric acid (3 ml) and water (1.5 ml) and heated at 105 °C for 15 min. Water (35 ml) was added and the red suspension boiled and cooled. The red crystals of the appropriate 5-amino-2(or 3)-chloro-3(or 2)-hydroxy-1,4-naphthoquinone were filtered off. In the case of the methoxy-derivatives (2a and b) hydrolysis was effected with a mixture of aqueous sodium hydroxide solution (5%, 25 ml) and ethanol (5 ml) under reflux for 1 min. The samples of 5-amino-2-chloro-3-hydroxy-1,4-naphthoquinone obtained from (1a) and (2a) were identical by i.r., m.p., and mixed m.p. comparison, as were the samples of 5-amino-3-chloro-2-hydroxy-1,4-naphthoquinone from (1b) and (2b).

The 5-amino-2(or 3)-chloro-3(or 2)-hydroxy-compounds (0.05 g) were dissolved in concentrated sulphuric acid (1.3 g) and cooled to *ca.* 2 °C. Sodium nitrite (0.023 g) was added, and after 1 h at this temperature the mixture was heated at 130—135 °C for 45 min and poured into ice–water. The yellow solid was filtered off and dried. The products from (1a) and (2a) were recrystallised from acetic acid to give yellow needles, m.p. 182—183 °C. These were identical to an authentic sample of 2-chloro-3,5-dihydroxy-1,4-naphthoquinone (prepared from 5-amino-2-chloro-3-hydroxy-1,4-naphthoquinone), m.p. 182—183 °C (lit.,[3] 193 °C) (Found: C, 53.1; H, 2.1. Calc. for $C_{10}H_5ClO_4$: C, 53.45; H, 2.2%) and repeated recrystallisation gave no increase in m.p.

The products from (1b) and (2b) were recrystallised from acetic acid, giving lustrous golden yellow plates, m.p. 216—218 °C, identical to an authentic sample of 3-chloro-2,5-dihydroxy-1,4-naphthoquinone (prepared from 5-amino-3-chloro-2-hydroxy-1,4-naphthoquinone), m.p. 216—218 °C (lit.,[3] 224 °C).

5-Amino-2-cyano-3-methylamino- and 5-Amino-3-cyano-2-methylamino-1,4-naphthoquinones.—Ethanolic methylamine solution (33%, 1 ml) was added to a solution of 2,3-dicyano-5-nitro-1,4-naphthoquinone[7] (0.5 g) in benzene (60 ml), and the mixture stirred at room temperature for 45 min. Removal of the solvent under reduced pressure gave a mixture of the 2(or 3)-cyano-3(or 2)-methylamino-

5-nitronaphthoquinones as a yellow solid (0.44 g, 87%), m.p. 102—112 °C. The solid was dissolved in acetic acid (10 ml) containing concentrated hydrochloric acid (10 ml) and tin(II) chloride dihydrate (2 g), and heated at 70 °C for 30 min. The suspension was oxidised by addition to a 3% aqueous solution (100 ml) of iron(III) chloride, and the red solid purified by chromatography over neutral alumina in benzene–dichloromethane (2 : 1). The first bluish red band afforded *5-amino-3-cyano-2-methylamino-1,4-naphthoquinone* (3b) (0.056 g, 16%), m.p. 318 °C (decomp.) (Found: C, 63.3; H, 4.0; N, 18.2. $C_{12}H_9N_3O_2$ requires C, 63.5; H, 4.0; N, 18.5%). The second red band gave *5-amino-2-cyano-3-methylamino-1,4-naphthoquinone* (3a), which was recrystallised from acetone as orange crystals (0.13 g, 37%), m.p. 292 °C (decomp.) (Found: C, 63.45; H, 3.75; N, 18.95. $C_{12}H_9N_3O_2$ requires C, 63.5; H, 4.0; N, 18.5%).

Reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone [1] (0.05 g) with methylamine (33% ethanolic solution, 0.1 ml) in acetone at room temperature gave 5-amino-2-cyano-3-methylamino-1,4-naphthoquinone (0.036 g, 71%) and 5-amino-3-cyano-2-methylamino-1,4-naphthoquinone (0.002 g, 3%), separated by preparative t.l.c. (silica–benzene).

5-Amino-2,3-dimethoxy-1,4-naphthoquinone (4).—2,3-Dimethoxy-5-nitro-1,4-naphthoquinone [2] (0.526 g) was dissolved in a mixture of acetic acid (15 ml), concentrated hydrochloric acid (10 ml), and tin(II) chloride dihydrate (2 g) and heated at 70 °C for 25 min. The solution was added to iron(III) chloride solution (4%, 100 ml) and stirred at room temperature for 30 min. Extraction with dichloromethane gave the crude product, which was recrystallised from benzene–light petroleum to give *5-amino-2,3-dimethoxy-1,4-naphthoquinone* (4) as reddish brown lustrous plates (0.4 g, 86%), m.p. 109—111 °C (Found: C, 61.6; H, 4.8; N, 6.0. $C_{12}H_{11}NO_4$ requires C, 61.8; H, 4.7; N, 6.0%).

Treatment of 5-amino-2,3-dichloro-1,4-naphthoquinone with excess of sodium methoxide in methanol at 40 °C for 1 h gave the same compound in 26% yield.

5-Amino-2-methoxy-3-methylamino-1,4-naphthoquinone (5a).—5-Amino-2,3-dimethoxy-1,4-naphthoquinone (4) was heated under reflux with methylamine (33% ethanolic solution, 2.5 ml) in ethanol (40 ml) for 40 min, and the solution was concentrated to *ca.* 10 ml. *5-Amino-2-methoxy-3-methylamino-1,4-naphthoquinone* (5a) deposited as a dark solid (0.55 g, 92%) and was recrystallised from ethanol as black lustrous needles, m.p. 209—210 °C (Found: C, 61.9; H, 5.0; N, 11.6. $C_{12}H_{12}N_2O_3$ requires C, 62.1; H, 5.2; N, 12.0%). Trace amounts of the 3-methoxy-2-methylamino-isomer (5b) were detectable in the mother liquors by t.l.c.

5-Amino-3-methoxy-2-methylamino-1,4-naphthoquinone (5b).—The crude mixture of 2(or 3)-methoxy-3(or 2)-methylamino-5-nitro-1,4-naphthoquinones (0.22 g), prepared from 2,3-dimethoxy-5-nitro-1,4-naphthoquinone and methylamine as described previously,[2] was reduced with tin(II) chloride dihydrate (1 g) in a mixture of acetic acid (8 ml) and concentrated hydrochloric acid (5 ml) at 70 °C for 25 min. The clear solution was added to a solution of iron(III) chloride (4 g) in water (100 ml) and stirred at room temperature for 30 min. The red precipitate was filtered off and recrystallised from ethanol to give pure 5-amino-2-methoxy-3-methylamino-1,4-naphthoquinone (5a) (0.112 g). The aqueous filtrate was extracted with dichloromethane and the residue from the extracts combined with the material in the ethanolic mother liquors. The combined materials were then purified by preparative t.l.c. (silica–benzene) to give more (5a) (0.025 g) and the bluish red *5-amino-3-methoxy-2-methylamino-1,4-naphthoquinone* (5b) (0.022 g, 11%), m.p. 167.5—169 °C (Found: C, 61.8; H, 5.25; N, 12.4. $C_{12}H_{12}N_2O_3$ requires C, 62.1; H, 5.2; N, 12.0%).

Orientation of the Derivative (5a).—5-Amino-2-chloro-3-methylamino-1,4-naphthoquinone (5a) (0.11 g) of established structure was dissolved in acetic anhydride (1 ml) and one drop of concentrated sulphuric acid was added. After 5 min the solution was diluted with ice–water (50 ml) and the suspension stirred for 3 h. The yellow solid was filtered off and dried (0.134 g, 90%) to give the N^3N^5-*bis-acetyl derivative*, which was recrystallised from benzene–light petroleum as yellow crystals, m.p. 203—204 °C. The product (0.05 g) was heated under reflux in anhydrous methanol (30 ml) containing fused sodium acetate (0.1 g) for 1.5 h, and after removal of the solvent the residue was washed with water and recrystallised from benzene–ligroin. 5-Acetylamino-3-*N*-methylacetylamino-2-methoxy-1,4-naphthoquinone (6) was obtained as yellow leaflets (0.047 g, 95%), m.p. 199—201 °C.

The product (5a) (0.11 g) from the reaction of 5-amino-2,3-dimethoxy-1,4-naphthoquinone with methylamine was acetylated at room temperature in acetic anhydride (1 ml) containing 1 drop of concentrated sulphuric acid, and the product recrystallised from benzene–light petroleum as yellow leaflets (0.089 g, 65%), m.p. 199—201 °C, identical by i.r., m.p., and mixed m.p. to (6) of known orientation.

2-Chloro-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone (8).—2,3-Dichloro-5,8-dimethoxy-1,4-naphthoquinone [6] (0.1 g) was heated under reflux with methylamine (33% ethanolic solution, 0.2 ml) in ethanol (20 ml) for 30 min. The red solution was concentrated to *ca.* 10 ml, and on cooling lustrous red needles of *2-chloro-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone* (8) deposited (0.085 g, 87%), m.p. 214—215 °C (Found: C, 55.2; H, 4.35; N, 5.2; Cl, 12.7. $C_{13}H_{12}ClNO_4$ requires C, 55.4; H, 4.3; N, 5.0; Cl, 12.6%). The same product was formed in similar yield by replacing 2,3-dichloro-5,8-dimethoxynaphthoquinone by 2-chloro-3,5,8-trimethoxy-1,4-naphthoquinone.

3-Methylamino-2,5,8-trimethoxy-1,4-naphthoquinone (10).—A mixture of 2,3,5,8-tetramethoxy-1,4-naphthoquinone [6] (0.10 g), methylamine (33% ethanolic solution, 0.2 ml), and ethanol (20 ml) was heated under reflux for 30 min, and more methylamine solution (0.3 ml) was added. After a further 40 min, the solution was diluted with water (100 ml), and the suspension extracted with dichloromethane. The extracts were washed with 1N-sodium hydroxide solution and water, and dried ($MgSO_4$). Removal of the solvent gave a dark solid that was recrystallised from light petroleum to give *3-methylamino-2,5,8-trimethoxy-1,4-naphthoquinone* (10) as lustrous black leaflets (0.082 g, 82%), m.p. 142—144.5 °C (Found: C, 60.6; H, 5.25; N, 5.0. $C_{14}H_{15}NO_5$ requires C, 60.7; H, 5.4; N, 5.05%).

2-Cyano-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone (11).—2,3-Dicyano-5,8-dimethoxy-1,4-naphthoquinone [1] (0.020 g) was dissolved in dichloromethane (20 ml) and methylamine (33% ethanolic solution, 0.07 ml) was added. The purple solution rapidly turned yellow, and after 15 min the solvent was removed under reduced pressure. The residue was recrystallised from benzene to give yellow crystals of *2-cyano-5,8-dimethoxy-3-methylamino-1,4-naph-*

thoquinone (11) (0.015 g, 74%), m.p. 254—258 °C (Found: M^+, 272. $C_{14}H_{12}N_2O_4$ requires M, 272).

6,7-*Dichloro*-5,8-*dimethoxy*-2-*methylamino*-1,4-*naphthoquinone* (12).—6,7-Dichloro-5,8-dimethoxy-1,4-naphthoquinone [6] (0.050 g) was heated under reflux with excess of methylamine in dichloromethane (30 ml) for 2 h. After removal of the solvent under reduced pressure, the residue was recrystallised from benzene–light petroleum, giving 6,7-*dichloro*-5,8-*dimethoxy*-2-*methylamino*-1,4-*naphthoquinone* (12) as fine orange needles (0.032 g, 58%), m.p. 235—237 °C (decomp.) (Found: C, 49.55; H, 3.6; N, 4.8; Cl, 22.2. $C_{13}H_{11}Cl_2NO_4$ requires C, 49.4; H, 3.5; N, 4.4; Cl, 22.5%).

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