Naphthoquinone Colouring Matters. Part 4.[1] Amino-substituted 1,2-Dimethylnaphth[2,3-*d*]imidazole-4,9-diones

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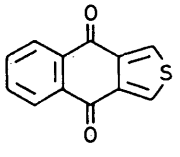
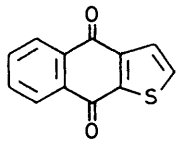
Synthetic routes to new 5- and 8-amino-substituted 1,2-dimethylnaphth[2,3-*d*]imidazole-4,9-dione dyes are described. The products are more hyposochromic than their 1,4-naphthoquinone counterparts, but are more bathochromic than the related 9,10-anthraquinone dyes. The bathochromic effect is enhanced by protonation or methylation of the heterocyclic ring to give the imidazolium derivatives. The PPP–SCF–MO procedure is used to interpret the visible absorption spectra of the dyes.

RECENTLY it has been shown that 1,4-naphthoquinones with electron donating groups in the benzenoid ring are, in spite of their smaller molecular size, more bathochromic than their 9,10-anthraquinone counterparts.[2] Annelation of a naphthoquinone to give an anthraquinone is thus disadvantageous from a colour point of view, but does improve the chemical and photochemical stability of the resultant dyes.[3] Heteroannelated 1,4-naphthoquinone dyes may, however, combine the high bathochromicity of the naphthoquinone system with the stability of anthraquinone dyes, and are thus worthy of investigation.

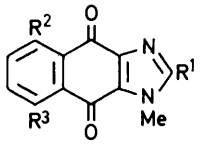
Although a large number of heteroannelated 1,4-naphthoquinones systems are known,[4] few derivatives containing auxochromes have been described. Little information is available concerning the electronic absorption spectra of such coloured compounds, and in only a few isolated instances has their potential as dyestuffs been tested. Peters and Walker have prepared dyes based on the thiophen-fused systems (1) and (2),



(1)



(2)



(3) $R^1 = R^2 = R^3 = H$
(4) $R^1 = Me$, $R^2 = R^3 = H$
(5a) $R^1 = Me$, $R^2 = NO_2$, $R^3 = H$
(5b) $R^1 = Me$, $R^2 = H$, $R^3 = NO_2$

and noted that on polymeric substrates they were slightly deeper in colour than the corresponding anthraquinone dyes.[5] Éfros *et al.* have examined dyes based on 1-methylnaphth[2,3-*d*]imidazole-4,9-dione (3), where amino-auxochromes were present in either the benzenoid ring,[6] or the heterocyclic ring.[7] The latter compounds were found to absorb at shorter wavelengths than the corresponding 1-aminoanthraquinones, but no spectral data were reported for the former, potentially more interesting compounds.

We now describe some new synthetic routes to dyes based on the 1,2-dimethylnaphth[2,3-*d*]imidazole-4,9-dione system (4). The absorption spectra have been measured and interpreted with the aid of PPP-MO calculations. The effects of protonation or quaternisation of the 3-nitrogen atoms to give the derived imidazolium systems have also been investigated.

RESULTS AND DISCUSSION

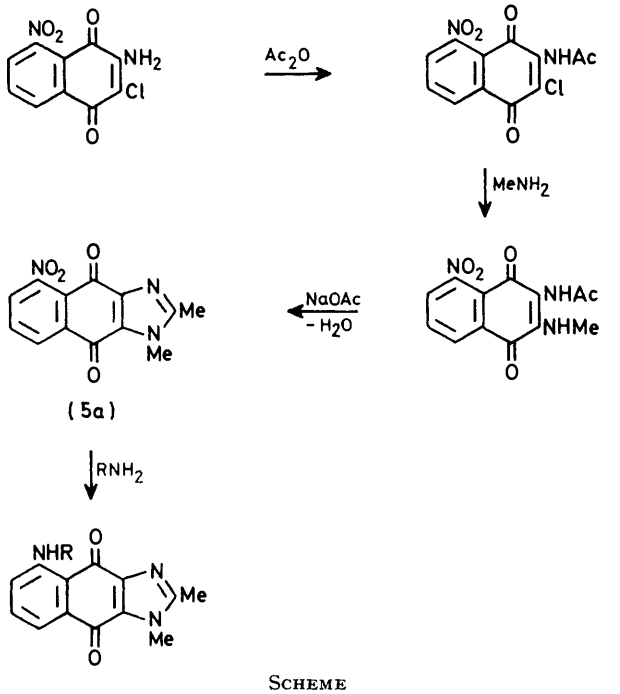
Synthesis of Amino-substituted 1,2-Dimethylnaphth[2,3-d]imidazole-4,9-diones.—The parent system (4) was prepared from 2-acetamido-3-methylamino-1,4-naphthoquinone by the base-catalysed procedure described by Hoover and Day for the preparation of various 1-H analogues.[8] The introduction of amino-auxochromes into the benzenoid ring of (4) was attempted by first nitrating the quinone with nitric acid–sulphuric acid. By analogy with the nitration of (3), described by Éfros *et al.*,[6] a mixture of the 5-, 6-, 7-, and 8-nitro-derivatives was expected. However, the nitration product, obtained in 89% yield after recrystallisation from benzene–petroleum, showed only two components on t.l.c. analysis, with almost identical R_F values. These were shown to be the 5- and 8-nitro-derivatives (5). Thus reduction of the mixture with tin(II) chloride gave two red amino-derivatives which could be resolved by t.l.c. only after several developments, and no other coloured products were detectable. The amino-compounds showed two carbonyl bands in the i.r. spectrum, at *ca.* 1 640 and 1 670 cm^{-1} [*cf.* 1-aminoanthraquinone, $\nu_{max.}$ (KBr) 1 635 and 1 665 cm^{-1}], indicating the intramolecularly hydrogen-bonded structures (6).

As the 6- and 7-amino-derivatives would be expected to have much smaller R_F values than the 5- and 8-compounds, these are not present in the reduction mixture. Thus, in contrast to the observation of Éfros *et al.* for the nitration of (3),[6] the β-nitro-isomers cannot in the present case be formed in more than *ca.* 10% yield. In the former case, it was concluded that the α- and β-nitro-isomers were formed in the ratio of *ca.* 2 : 1.

The introduction of substituted amino-groups into the 5- and 8-positions of (4) could be achieved by direct nucleophilic replacement of the nitro-groups in (5). As separation of the nitro-isomers (5a and b) could not be

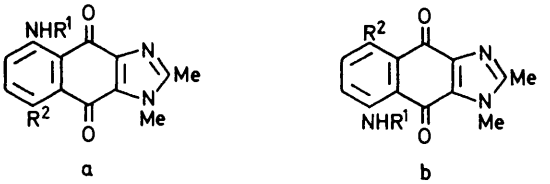
effected satisfactorily, the isomeric mixture was used for these reactions, and the resultant amino-isomers were separated chromatographically. With methylamine, isobutylamine, and cyclohexylamine, substitution of (5) occurred readily in boiling benzene, and the bluish red amino-derivatives (7)—(9), respectively, were formed in good yield. In each case, the 5- and 8-isomers were present in approximately equal proportions. Reaction of (5) with aniline proceeded much less readily, and required a temperature of *ca.* 150 °C. The anilino-derivatives (10) were isolated in low yield.

The isomers (7)—(9) were oriented by unambiguous synthesis of the 5-amino-isomer of each pair, as shown in the Scheme. Thus 2-amino-3-chloro-8-nitro-1,4-naphthoquinone of established orientation [9] was converted to 2-acetamido-3-methylamino-8-nitro-1,4-naphthoquinone, and the latter compound cyclised to give 1,2-dimethyl-5-nitronaphth[2,3-*d*]imidazole-4,9-dione (5a) by heating with fused sodium acetate. The nitro-group had an adverse effect on the cyclisation reaction, and the more usual base- or acid-catalysed solution procedures [8] were unsuccessful. Treatment of (5a) with the appropriate amine in boiling benzene gave the desired 5-amino-derivative.



SCHEME

In all cases the 5-amino-isomers had the higher R_F values on t.l.c. (Kieselgel–benzene), and absorbed at slightly longer wavelengths than their 8-amino-counterparts in the visible spectrum. The derivatives (7)—(9) showed two carbonyl bands in the i.r. spectrum, characteristic of quinones with α-amino-substituents, and the positions of these were very characteristic of the substitution pattern. The 5-amino-isomers showed an intense, sharp band at *ca.* 1 630 cm^{-1}, typical of intramolecularly hydrogen-bonded quinones, and a weaker overlapping band at 1 655 cm^{-1}, attributable to the non-bonded carbonyl group. In contrast, the two carbonyl bands of the 8-isomers were well separated, the hydrogen-bonded and free carbonyl groups absorbing at *ca.* 1 620 and 1 665 cm^{-1} respectively. These effects were well accounted for by the PPP-MO procedure. Thus the bond order (calculated assuming no intramolecular hydrogen bonding) for the 4-carbonyl group of the 5-isomers (*ca.* 0.76) was slightly higher than for the 9-

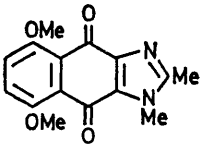


(6) $R^1 = R^2 = H$
(7) R^1 = Me, R^2 = H
(8) R^1 = Bu^i, R^2 = H
(9) $R^1 = C_6H_{11}$, R^2 = H
(10) R^1 = Ph, R^2 = H
(11) R^1 = H, R^2 = OH
(13) R^1 = Me, R^2 = OMe
(14) $R^1 = C_6H_{11}$, R^2 = OMe

carbonyl-group of the 8-isomers (*ca.* 0.74) (*cf.* $\nu_{max.}$ 1 630 and 1 620 cm^{-1}). The bond orders for the remaining carbonyl groups were 0.78 and 0.81 for the 5- and 8-amino-isomers respectively (*cf.* $\nu_{max.}$ 1 655 and 1 665 cm^{-1}). The structures of the anilino-derivatives (10) were assigned on the basis of these i.r. differences.

Treatment of the mixture of isomeric nitro-compounds (5) with sulphur in oleum gave the two violet amino-hydroxy-compounds (11a and b), which were separated by preparative t.l.c. These were oriented by similar reaction of (5a) with sulphur in oleum to give (11a). The large bathochromic shift accompanying the introduction of a hydroxy-group *para* to the amino-group of (6) is similar to that observed in the anthraquinone series.

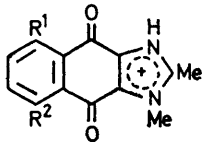
A potentially useful route to bathochromic dyes in this series involves photochemical substitution of 5,8-dimethoxy-1,2-dimethylnaphth[2,3-*d*]imidazole-4,9-dione (12) with primary alkylamines,[10] when one of the



methoxy-groups can be replaced. The parent dimethoxy-compound (12) was prepared from 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone by a procedure similar to that shown in the Scheme for the 5-nitro-analogue. Ring closure, however, was effected more readily and proceeded smoothly in ethanolic sodium hydroxide solution.

The dimethoxy-derivative (12) proved extremely sensitive to photosubstitution, and solutions containing primary alkylamines changed from yellow to violet even on exposure to diffuse daylight. With filtered u.v. light ($\lambda > 320$ nm) the reaction was rapid and the isomeric violet 5,8-methoxy-amino-derivatives were formed. The isomers obtained from the reactions with methylamine and cyclohexylamine were readily separable by chromatography. An unusual directing effect has been noted previously in these reactions.[10] Thus photochemical substitution occurs preferentially at the 5-position, and the 5-amino-isomers are formed in almost twice the amounts of the 8-amino-isomers. In contrast, thermal replacement of methoxy was extremely inefficient, and could only be achieved in boiling cyclohexylamine. The thermal reaction showed no significant differences in reactivity between the 5- and 8-positions. Orientation of the derivatives (13) and (14) was most easily achieved by i.r. spectroscopy, as the 5- and 8-amino-isomers showed the same characteristic differences in the carbonyl region as the derivatives (7)—(9).

The amino-substituted naphthimidazole-4,9-diones are dibasic, and thus may protonate in acid solution on the amino-auxochrome, which would result in a loss of colour, or on the 3-nitrogen atom to give an imidazolium cation. In the latter case minor spectral shifts should be observed, but there should be no colour loss. It was found that in dilute acids, protonation occurred preferentially in the heterocyclic ring, and the resultant cations (15) were more bathochromic than the parent molecule. Typically, the amino-derivatives (7)—(10) showed a reversible purple to deep violet colour change in ethanolic hydrochloric acid, and the amino-methoxy-compounds (13) and (14) showed a corresponding change from violet to blue. That protonation was occurring at the 3-nitrogen atom was confirmed by methylation of (9) and (13) with methyl iodide in the presence of sodium carbonate, when the 1,2,3-trimethylimidazolium iodides (16) and (17) were formed respectively. These had almost identical visible absorption spectra to those of the protonated analogues formed from (9) and (13). In more concentrated acidic solutions, addition of a second proton occurred, presumably at the amino-auxochrome, as indicated by the reversible loss of colour. The imidazolium derivatives (16) and (17) were water



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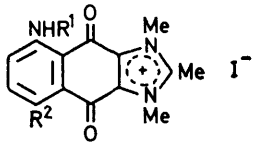


(16) $R^1 = C_6H_{11}$, $R^2 = H$
(17) $R^1 = Me$, $R^2 = MeO$

soluble, and could be applied to polyacrylonitrile fibres, when they showed outstanding resistance to photochemical fading.

Visible Absorption Spectra.—The visible absorption spectra of the dyes (7)—(14) recorded in cyclohexane and ethanol are summarised in Table 1. The absorption

TABLE 1

Visible absorption spectra of the 1,2-dimethylnaphth-[2,3-*d*]imidazole-4,9-diones

Derivative of (4)	$\lambda_{max.}$ (C_6H_{12})/nm	$\lambda_{max.}$ (EtOH)/nm	$\varepsilon_{max.}$ (C_6H_{12})	$\lambda_{max.}$ (EtOH)/nm (cation) [a]
(7a)	513	527	4 070	553
(7b)	509	527	5 830	553
(8a)	525	532	4 450	556
(8b)	520	530	6 100	556
(9a)	520	535	5 600	560
(9b)	519	535	5 940	560
(10a)	519	524	5 050	548
(10b)	515	523	5 000	548
(11a)	(562), 521 [b] (487)	(568), 528 [b]	4 800 [b]	(586), 544 [b]
(11b)	(560), 520 [b] (486)	(567), 528 [b]	7 125 [b]	(586), 544 [b]
(12)	410	440	5 250	471
(13a)	539	560	6 990	582
(13b)	535	557	7 910	582
(14a)	541	566	6 700	586
(14b)	539	563	7 380	586
(16) [c]				560
(17) [c]	564			584

[a] Formed by addition of concentrated hydrochloric acid to an ethanolic solution. [b] Main band. [c] As the imidazolium iodide.

TABLE 2

Comparison of visible spectra of naphthoquinone, anthraquinone, and naphth[2,3-*d*]imidazole-4,9-dione dyes

Compound	$\lambda_{max.}$ (C_6H_{12})/nm	$\varepsilon_{max.}$ (C_6H_{12})
5-Methylamino-1,4-naphthoquinone	529	5 700
1-Methylaminoanthraquinone	495	6 760
(7a)	513	4 070
(7b)	509	5 830
5-Methylamino-8-methoxy-1,4-naphthoquinone	556	5 200
1-Methylamino-4-methoxyanthraquinone	514	7 650
(13a)	539	6 990
(13b)	535	7 910

TABLE 3

Parameters used in the PPP-MO calculations

Residue	x—y	$VSIP_x$ [a]/eV	A_x [b]/eV	Z_x [c]	β_{x-y}/eV	r_{x-y} [d]/Å
MeNH—C	N—C	15.0	8.6	2	−2.75	1.36
Imidazole	N(1)—C(2)	21.0	10.0	2	−2.40	1.35
Imidazole	N(3)—C(2)	16.0	2.5	1	−2.60	1.33
Imidazolium	N—C(2)	18.0	2.9	2	−2.40	1.35
Carbonyl	O—C	18.0	2.5	1	−2.50	1.22

[a] Valence state ionisation potential. [b] Electron affinity. [c] Core charge. [d] Bond length.

maxima of the derived imidazolium ions in ethanol are also given. With the exception of the amino-hydroxy-derivatives (11), all the compounds showed a single, symmetrical absorption band in the visible region of the spectrum. The band intensities ($\varepsilon_{max.}$ *ca.* 5×10^3) and their positive solvatochromism indicate that the transitions are $\pi \longrightarrow \pi^*$ in character and have charge-transfer characteristics typical of other amino-substituted quinones. It is interesting to compare the absorption maxima of these compounds with those of the corresponding naphthaquinone and anthraquinone dyes, and it can be seen (Table 2) that in general the wavelength decreases in the sequence naphthoquinone > naphthimidazole-4,9-dione > anthraquinone. The absorption intensities

increase roughly in the same order. Thus the naphthimidazole-4,9-dione dyes occupy a position intermediate between the naphthoquinones and anthraquinones.

As can be seen from Table 1, the 5-amino-dyes always absorb at slightly longer wavelengths than the 8-isomers, whereas the 8-isomers have the greater intensity, with the exception of (10a and b). Although the wavelength differences are small, they are a useful indication of the substitution pattern. To examine these effects in more detail, the naphthimidazole-4,9-diones were subjected to PPP-SCF-CI molecular orbital calculations. For these calculations, planar structures were assumed, and, with the exception of the imidazole ring,[11] the geometry used previously for the naphthoquinones was adopted.[1,2] The other parameters used in the calculations were either as described previously,[1,2] or are as indicated in Table 3. The latter values were derived empirically. The carbonyl oxygen parameters differ slightly from those used for the naphthoquinones,[2] and give satisfactory results if hydrogen bonding between the 5- or 8-amino-groups and the adjacent carbonyl group is ignored, *i.e.* both carbonyl groups are treated as equivalent. This simplifies the calculations without detracting from the close agreement found between the theoretical and observed $\lambda_{max.}$ values. The transition energies calculated for representative compounds were improved by a configuration interaction treatment involving the first nine singly excited singlet states, and the results are summarised in Table 4.

TABLE 4

Comparison of observed [a] and predicted visible absorption spectra of the 1,2-dimethylnaphth[2,3-*d*]imidazole-4,9-diones

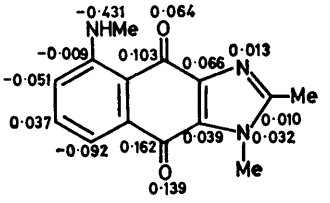
Compound	$\lambda_{max.}$(exp.)/nm	$\varepsilon_{max.}$ (exp.)	$\lambda_{max.}$ (calc.)/nm	f (calc.) [b]
(7a)	513	4 070	517	0.20
(7b)	509	5 830	509	0.26
(10a)	519	5 050	517	0.24
(10b)	515	5 000	505	0.24
(12)	410	5 250	414	0.33
(13a)	539	6 990	536	0.31
(13b)	535	7 910	528	0.38
(7) protonated)	553 [c]		550	0.36
(10) (protonated)	548 [c]		595	0.44
(12) (protonated)	471 [c]		439	0.48
(13) (protonated)	582 [c]		562	0.47
(17)	564 [a] (584) [c]		562	0.47

[a] Solvent cyclohexane unless otherwise stated. [b] Oscillator strength. [c] Solvent absolute ethanol.

As can be seen, the agreement between the experimental $\lambda_{max.}$ values (measured in cyclohexane) and theory is good, and in particular, the characteristic wavelength and intensity differences between the 5- and 8-amino-isomers are predicted accurately.

The electron density changes accompanying electronic excitation in the visible band are informative, and these are shown in the Figure for the 5-methylamino-derivative (7a). As observed for the 5-amino-1,4-naphthoquinones [2] and 1-aminoanthraquinones,[12] the transition involves a high degree of electron density migration from the methylamino-auxochrome to the carbonyl groups of the quinonoid system. There is an additional small, but significant increase in electron density in the imidazole ring, which suggests that factors increasing the electron-attracting properties of the ring should induce a bathochromic shift of the visible band. Thus one can understand qualitatively why the imidazolium cations absorb at longer wavelengths than the neutral dyes. The calculated wavelength values for representative cations are in reasonable agreement with experiment (Table 4) if it is borne in mind that the absorption spectra were, because of solubility difficulties, measured in ethanol. The large bathochromic shift of the bands in ethanol is indicated by the wavelength values for (17) in cyclohexane and ethanol (Table 4).

The bathochromic effect of the methoxy-group in dyes (13) and (14) can also be understood from the data of the Figure, as the carbon atom *para* to the amino-auxochrome shows a decrease in electron density in the excited state. The methoxy-group also increases the absorption intensity, and this is well predicted by the PPP method.



π-Electron density changes for the first electronic transition of (7a)

The amino-hydroxy-compounds (11a and b) appear to be exceptional in that they show two or three well defined absorption maxima in the visible region. This phenomenon is well known in the anthraquinone dyes, and has also been observed for the amino-hydroxy-1,4-naphthoquinones.[2] The complex band pattern is due to vibrational fine structure, which is generally enhanced when both quinone carbonyl groups are intramolecularly hydrogen bonded.

The amino-substituted naphth[2,3-*d*]imidazole-4,9-diones are potentially useful dyes, having a somewhat greater intensity than the corresponding 1,4-naphthoquinones and showing more bathochromic shades than the anthraquinones. They have the advantage of greater chemical stability than the 1,4-naphthoquinones, and can also be rendered water soluble by protonation or quaternisation. They would thus appear to be worthy of closer investigation as dyes for synthetic polymer fibres.

EXPERIMENTAL

1,2-*Dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (4).—Sodium hydroxide solution (25 ml, 2M) was added dropwise to a boiling solution of 2-acetylamino-3-methylamino-1,4-naphthoquinone (5 g) in ethanol (200 ml), and refluxed for 1 h. The crystalline deposit that formed on cooling was recrystallised from ethanol to give 1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (4) as pale yellow needles (3.6 g, 78%), m.p. 250—252 °C (Found: C, 68.7; H, 4.7; N, 12.5. $C_{13}H_{10}N_2O_2$ requires C, 69.0; H, 4.5; N, 12.4%).

5- *and* 8-*Nitro*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-

diones (5).—A solution of (4) (4.5 g) in concentrated sulphuric acid (23 ml) and fuming nitric acid (*d* 1.5, 1.5 ml) was heated at 100 °C for 1 h, and the cooled solution poured over crushed ice (450 g). The yellow suspension was extracted thoroughly with dichloromethane, and the extracts washed with 5% sodium carbonate solution until the washings were no longer red. The dichloromethane solution was washed with water and dried ($MgSO_4$). The yellow solid obtained after evaporation of the solvent was recrystallised from benzene–petroleum (b.p. 60—80 °C), giving a mixture of 5- and 1,2-*dimethyl*-8-*nitronaphth*[2,3-d]*imidazole*-4,9-*diones* as golden yellow needles (4.95 g, 89%), m.p. 262—264 °C (Found: C, 57.3; H, 3.4; N, 15.45. $C_{13}H_9N_3O_4$ requires C, 57.6; H, 3.3; N, 15.5%).

Reduction of the mixed nitro-isomers (5) was effected by heating a solution of (5) (2 mmol) in a mixture of acetic acid (7 ml) and concentrated hydrochloric acid (4 ml) containing tin(II) chloride dihydrate (1.8 g) at 80 °C for 20 min, and oxidising the product with iron(III) chloride. The red-brown solid was recrystallised from benzene–petroleum (b.p. 60—80 °C) to give the mixed 5- and 8-amino-isomers (6) (45%), m.p. 244—248 °C (Found: M^+, 241. Calc. for $C_{13}H_{11}N_3O_2$: *M*, 241).

Reaction of 5- *and* 8-*Nitro*-1,2-*dimethylnaphth*[2,3-d]-*imidazole*-4,9-*diones* (5) *with Alkylamines*.—The mixture of nitro-isomers (5) (2 g) in benzene (200 ml) was heated under reflux and the appropriate amine [cyclohexylamine (10 ml); isobutylamine (24 ml); methylamine, as a 33% solution in ethanol (40 ml)] added to the boiling solution over 30 min. Heating was continued for 24 h and the solution cooled and diluted by the addition of dichloromethane (200 ml). The solution was washed thoroughly with dilute hydrochloric acid and water, and dried ($MgSO_4$). The residue obtained after removal of the solvent was chromatographed over neutral alumina, using benzene–dichloromethane as eluant. The two isomers separated as deep purple bands, the 5-amino-isomer being eluted first.

1,2-*Dimethyl*-8-*methylaminonaphth*[2,3-d]*imidazole*-4,9-*dione* (7b) formed red-brown crystals from benzene–petroleum (b.p. 60—80 °C) (0.72 g, 38%), m.p. 219—220 °C (Found: C, 66.0; H, 5.25; N, 16.1. $C_{14}H_{13}N_3O_2$ requires C, 65.9; H, 5.1; N, 16.5%); $\nu_{max.}$(KBr) 1 618 and 1 662 cm^{-1}. The 5-methylamino-isomer (7a) formed red-brown crystals (0.8 g, 42%), m.p. 215—217 °C (Found: M^+, 255. Calc. for $C_{14}H_{13}N_3O_2$: *M*, 255); $\nu_{max.}$ (KBr) 1 630s and 1 655 cm^{-1}.

8-*Isobutylamino*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (8b) was obtained as bright red plates (0.56 g, 25%), m.p. 180—181 °C (Found; C, 68.4; H, 6.1; N, 14.5. $C_{17}H_{19}N_3O_2$ requires C, 68.7; H, 6.4; N, 14.1%); $\nu_{max.}$ (KBr) 1 620 and 1 663 cm^{-1}. The 5-isobutylamino-isomer (8a) was obtained in a similar form (0.64 g, 29%), m.p. 216—218 °C (Found: M^+, 297. Calc. for $C_{17}H_{19}N_3O_2$: *M*, 297); $\nu_{max.}$ (KBr) 1 628s and 1 655 cm^{-1}.

5-*Cyclohexylamino*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (9a) formed bright red plates (0.75 g, 31%), m.p. 192—194 °C (Found: C, 70.6; H, 6.4; N, 12.5. $C_{19}H_{21}N_3O_2$ requires C, 70.6; H, 6.55; N, 13.0%); $\nu_{max.}$ (KBr) 1 625s and 1 645 cm^{-1}. The 8-*cyclohexylamino-isomer* (9b) was also isolated as red plates (0.70 g, 29%), m.p. 195—197 °C (Found: C, 69.9; H, 6.5; N, 12.7. $C_{19}H_{21}N_3O_2$ requires C, 70.6; H, 6.55; N, 13.0%); $\nu_{max.}$ (KBr) 1 620 and 1 660 cm^{-1}.

5- *and* 8-*Anilino*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*diones* (10a and b).—A mixture of the nitro-isomers (5) (2 g) and aniline (6 ml) in benzene (150 ml) was heated in an autoclave at 150—160 °C for 8 h. The solution was extracted thoroughly with dilute hydrochloric acid to remove aniline, and evaporated to dryness. The residue was dissolved in a small volume of dichloromethane and applied to several thick-layer chromatography plates (Kieselgel), and the plates were eluted with benzene. The faster moving band afforded the 5-*anilino-derivative* (10a) (0.33 g, 14%), m.p. 178—179 °C (Found: C, 71.8; H, 4.6; N, 12.9. $C_{19}H_{15}N_3O_2$ requires C, 71.9; H, 4.8; N, 13.2%); $\nu_{max.}$ (KBr) 1 630s and 1 655 cm^{-1}. The second band gave the 8-*anilino-isomer* (10b) (0.21 g, 9%), m.p. 196—198 °C (Found: M^+, 317. Calc. for $C_{19}H_{15}N_3O_2$: *M*, 317); $\nu_{max.}$ (KBr) 1 620 and 1 660 cm^{-1}.

Orientation of 5-*Amino-derivatives* (7a)—(9a).—Authentic 2-acetamido-3-chloro-8-nitro-1,4-naphthoquinone (0.2 g) was suspended in boiling toluene (25 ml), and dry methylamine was bubbled through for 45 min. The residue obtained after evaporation of the solvent was recrystallised once from ethanol, giving 2-acetamido-3-methylamino-8-nitro-1,4-naphthoquinone as red-brown needles (0.18 g, 92%), m.p. 202—204 °C. A portion of the solid (0.05 g) was ground intimately with fused sodium acetate (0.05 g), and the mixture heated in a tube fitted with a silica-gel drying tube at 160—180 °C for 1.5 h. The solid residue was extracted with boiling benzene, and the extracts concentrated to give 1,2-dimethyl-5-nitronaphth[2,3-*d*]imidazole-4,9-dione (5a) as fine yellow needles (0.012 g, 26%), m.p. 266—269 °C (Found: M^+, 271. Calc. for $C_{13}H_9N_3O_4$: *M*, 271). The nitro-derivative (5a) was heated in boiling benzene with a large excess of the appropriate amine (methylamine, isobutylamine, or cyclohexylamine) for several hours. In each case only one red product was formed, and this, the 5-amino-isomer, was used to identify (7a)—(9a) by t.l.c. comparison.

5-*Amino*-8-*hydroxy- and* 8-*Amino*-5-*hydroxy*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*diones* (11a *and* b).—The mixture of nitro-isomers (5) (2.71 g) and sulphur (0.7 g) were added to concentrated sulphuric acid (5 ml), and 20% oleum (15 ml) was added dropwise to the stirred suspension at room temperature. After addition, the temperature was raised to 35 °C and maintained for 2 h. The mixture was poured onto crushed ice (300 g) and the suspension neutralised with calcium carbonate. The precipitated calcium sulphate was filtered off and extracted with boiling benzene. The benzene extracts were combined with the red solution obtained from continuous extraction of the filtrate with benzene, and after concentration, the solution deposited deep red crystals of the amino-hydroxy-isomers (11) (0.79 g, 38%). T.l.c. analysis (Kieselgel–benzene) showed the product to consist of two red components of very similar R_F value. A small amount of each isomer could be obtained by preparative t.l.c., and in each case the mass spectrum indicated the correct molecular formula (Found: M^+, 257. Calc. for $C_{13}H_{11}N_3O_3$: *M*, 257); (11a), m.p. 258—260 °C; (11b), m.p. 219—222 °C. Reaction of the 5-nitro-derivative (5a) with sulphur and oleum gave only the 5-amino-8-hydroxy-compound, which was used to identify (11a) by comparison of their R_F values on t.l.c.

5,8-*Dimethoxy*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (12).—A solution of 2,3-dichloro-5,8-dimethoxy-1,4-naphthoquinone [13] (7.5 g) in the minimum volume of dichloromethane was added to ethanol (1 l), and ammonia was bubbled through for 20 min. The solution was sealed in a stoppered flask and maintained at room temperature

in the dark for 15 h. Concentration of the solution under reduced pressure to a volume of *ca.* 250 ml gave orange-brown plates of 2-amino-3-chloro-5,8-dimethoxy-1,4-naphthoquinone (5.1 g, 72%), m.p. 247—249 °C. The solid was heated under reflux in a mixture of acetic acid (100 ml) and acetic anhydride (100 ml) for 4 h. The residue, obtained after evaporation of the solvent under reduced pressure, was chromatographed over neutral alumina in dichloromethane to give the *N*-acetyl-derivative (3.75 g, 63%) as orange plates, m.p. 225—227 °C. The product was heated under reflux in toluene (400 ml) and methylamine was bubbled through the solution for 2 h. The solvent was removed under reduced pressure, and the residue recrystallised from benzene–petroleum (b.p. 60—80 °C) to give 2-acetamido-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone as brown needles (3.1 g, 85%), m.p. 214—217 °C. This was dissolved in absolute ethanol (650 ml) containing 6 drops of 2M-sodium hydroxide solution, and the solution heated under reflux. After 10 min a similar quantity of sodium hydroxide solution was added, and heating continued for 1.5 h. The solvent was removed under reduced pressure, and the residue dissolved in dichloromethane. The solution was extracted with dilute hydrochloric acid until no more colour was removed, and the washings neutralised and extracted with dichloromethane. The residue obtained after evaporation of the dichloromethane extracts was recrystallised from benzene–petroleum (b.p. 60—80 °C), giving 5,8-*dimethoxy*-1,2-*dimethylnaphth*[2,3-d]*imidazole*-4,9-*dione* (12) as lustrous orange needles (2.2 g, 75%), m.p. 210 °C (Found: C, 62.7; H, 9.5; N, 4.8. $C_{15}H_{14}N_2O_4$ requires C, 62.9; H, 9.8; N, 4.9%).

Photosubstitution of (12) *with Methylamine.*—The dimethoxy-compound (12) (0.06 g) was dissolved in dichloromethane (100 ml) containing methylamine (33% ethanolic solution, 2 ml), and the solution was irradiated in a Pyrex vessel with a medium pressure mercury lamp (100 W) for 3 h. Strong water cooling was maintained throughout the irradiation period. The solution was washed thoroughly with dilute hydrochloric acid and water, and dried ($MgSO_4$). The concentrated solution was applied to thick-layer plates of Kieselgel, and these were developed with dichloromethane. The faster moving violet band afforded 8-*methoxy*-1,2-*dimethyl*-5-*methylaminonaphth*[2,3-d]*imidazole*-4,9-*dione* (13a), which formed bronze needles from cyclohexane (0.03 g, 50%), m.p. 208 °C (Found: C, 63.0; H, 5.4; N, 14.2. $C_{15}H_{15}N_3O_3$ requires C, 63.15; H, 5.3; N, 14.7%), $\nu_{max.}$ 1 625s and 1 650 cm^{-1}. The second violet band gave the 5-methoxy-8-methylamino-isomer (13b) as bronze needles from cyclohexane (0.018 g, 30%), m.p. 198—200 °C (Found: M^+, 285. Calc. for $C_{15}H_{15}N_3O_3$: *M*, 285); $\nu_{max.}$ 1 620 and 1 660 cm^{-1}.

Photosubstitution of (12) *with Cyclohexylamine.*—A solution of (12) (0.06 g) and cyclohexylamine (2.5 ml) in dichloromethane (100 ml) was irradiated as described for the reaction with methylamine. The crude reaction product was worked up in the usual way, and the isomeric components isolated by column chromatography (neutral alumina–dichloromethane). The first intense purple band afforded 5-*cyclohexylamino*-2,3-*dimethyl*-8-*methoxynaphth*[2,3-d]*imidazole*-4,9-*dione* (14a), which formed bronze needles from cyclohexane (0.014 g, 19%), m.p. 226—228 °C (Found: C, 67.6; H, 6.4; N, 11.7. $C_{20}H_{23}N_3O_3$ requires C, 68.0; H, 6.5; N, 11.9%); $\nu_{max.}$ 1 625s and 1 645 cm^{-1}. The second and third pale bands were discarded, and the fourth intense purple band gave the 8-cyclohexylamino-5-methoxy-isomer (14b) as bronze needles from cyclohexane (0.006 g, 8%), m.p. 210—211 °C (Found: M^+, 353. Calc. for $C_{20}H_{23}N_3O_3$: *M*, 353); $\nu_{max.}$ 1 620 and 1 660 cm^{-1}.

5-*Cyclohexylamino*-1,2,3-*trimethyl*-4,9-*dioxonaphth*[2,3-d]-*imidazolium Iodide* (16).—A suspension of the isomers (9a and b) (0.10 g) was added to a suspension of anhydrous sodium carbonate (0.3 g) in a mixture of ethanol (0.1 ml), water (5 ml), and methyl iodide (0.4 g). The mixture was heated under reflux for 3 h, and the product extracted into dichloromethane. The dried dichloromethane extracts were percolated down a short neutral alumina column, and the slow moving intense blue band was isolated. The residue obtained after removal of the solvent was recrystallised from ethanol to give the imidazolium iodide (16) as metallic blue needles (0.07 g, 48%), m.p. 249—251 °C (Found: M^+, 337. Calc. for $C_{20}H_{24}IN_3O_2$ -- HI: *M*, 337).

5-*Methoxy*-1,2,3-*trimethyl*-8-*methylamino*-4,9-*dioxonaphth*-[2,3-d]*imidazolium Iodide* (17).—A mixture of the isomers (13a and b) (0.20 g) was heated under reflux in a mixture of methanol (40 ml), methyl iodide (7 ml), and sodium carbonate (0.02 g) for 2 h. More methyl iodide (1 ml) was added and heating continued for a further 4 h. The solution was diluted with water (50 ml) and extracted thoroughly with dichloromethane. The residue from the extracts was chromatographed over neutral alumina in dichloromethane, and the intense blue band collected. The *imidazolium iodide* (17) was obtained as fine purple needles (0.04 g), 13%), m.p. 250 °C (decomp.) (Found: C, 45.5; H, 4.1; N, 9.8. $C_{16}H_{18}IN_3O_3$ requires C, 45.1; H, 4.2; N, 9.8%).

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