Dyes and Pigments **6** (1985) 75–81

Reaction of 5-Amino-2,3-dicyano-1,4-naphthoquinone with Arylamines

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(Received: 17 January, 1984)

SUMMARY

The reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone (**1**) *with arylamines gave 5-amino-8-arylamino-* (**2**), *5,8-bis(arylamino)-* (**3**), *and 5-hydroxy-8-arylamino-2,3-dicyano-1,4-naphthoquinone* (**4**) *together with 5-amino-2-arylamino-3-cyano-* (**5**) *and 5-amino-2-cyano-3-arylamino-1,4-naphthoquinone* (**6**). *It is proposed that the initial quinone–quinoneimine tautomerism of* **1** *to 4-hydroxy-2,3-dicyano-5-imino-1,5-naphthoquinone* **7** *facilitates the 8-arylamination. Some derivatives of* **2** *have good properties as dyes for optical information-recording media for semiconductor lasers.*

1. INTRODUCTION

Deeply coloured naphthoquinonoid dyes have been anticipated as functional dyes for guest–host liquid crystal displays[1] or optical information-recording media. Recently some of the infrared dyes such as the squarylium and pentamethine dyes have been reported as dyes for optical information-recording media for semiconductor lasers.[2] 5-Amino-8-anilino-2,3-dicyano-1,4-naphthoquinone (**2a**), which has an absorption maximum in the near-infrared region (λ_{max} 759 nm in acetone)

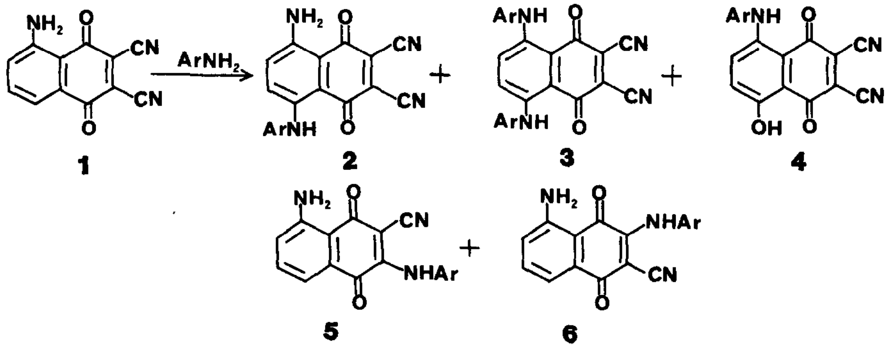
Dyes and Pigments 0143-7208/85/$03·30 © Elsevier Applied Science Publishers Ltd, England, 1985. Printed in Great Britain

was prepared for the first time by Chu and Griffiths[3] by the reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone (**1**) with aniline in ethanol. This novel 8-arylamination of **1** was re-examined by Kasai *et al.*[4] They studied this reaction in more detail and obtained 8-arylamino derivatives (**2**) together with 5-amino-2-arylamino-3-cyano-1,4-naphthoquinone (**5**) as CN-substitution product. They proposed that 8-arylamination was initiated by the formation of a π-complex between **1** and the arylamine, which was transferred to the σ-complex, and then the σ-complex was oxidized by **1** to give **2**. However, it is not known why the arylamination proceeds at the 8-position of **1**. In this paper, we wish to report the reaction of **1** with various arylamines and suggest a reaction mechanism based on the predictions of the PPP MO procedure.

2. RESULTS AND DISCUSSION

2.1. The reaction of 1 with arylamines

The reaction of **1** with 4-ethoxyaniline in ethanol was carried out under the conditions described in the literature,[4] and the products were carefully separated by silica gel column chromatography using chloroform as eluent. Products were eluted from the column in the following order: 5,8-bis(4-ethoxyanilino)-2,3-dicyano- (**3g**), 5-amino-2-(4-ethoxyanilino)-3-cyano- (**5g**), 5-amino-3-(4-ethoxyanilino)-2-cyano- (**6g**), 5-hydroxy-8-(4-ethoxyanilino)-2,3-dicyano- (**4g**), and 5-amino-8-(4-ethoxyanilino)-2,3-dicyano-1,4-naphthoquinone (**2g**). The results are shown in Scheme 1.



Scheme 1

Compound **3g** might be obtained by the further 5-arylamination of **2g**, and **4g** might be obtained by the further 5-hydroxylation of **2g**. Compounds **5g** and **6g** were the substitution products of the cyano group at the 2- and 3-positions, respectively. Some other products were detected by column chromatography but the isolation and identification of these were unsuccessful because of their insufficient amounts. Reactions of **1** with other substituted anilines were carried out under similar conditions. The yields and some properties of **2** are summarized in Table 1. The yields of **2** were not affected significantly either by the number or by the chain length of alkyl or alkoxyl substituents on the benzene ring. Kasai *et al.* have reported that *p*-nitroaniline did not react with **1**, but *p*-dimethylamino-aniline gave the corresponding 8-arylamino derivative **2** in 38 % yield.[4] On the other hand, 4-*tert*-butylaniline gave **2e** in 35·6 % yield in spite of its bulky substituent (Run 5). It is proposed that 8-arylamination of **1** is not affected significantly either by the electron donating effect or by the steric effect of substituents on the benzene ring. These results are not consistent with the suggestion that the initial formation of the π-complex between **1** and the arylamine plays an important role in the 8-arylamination of **1**.

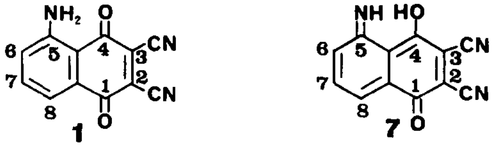
TABLE 1
Reaction of **1** with Substituted Anilines

Run	*X-PhNH$_2$*	2	*Yield* (%)[a]	*M.p.* (°C)[b]	λ_{max} (*nm*) ($\varepsilon \times 10^{-4}$)[c]
1	H	**2a**	37·0[d]	283 (dec.)[d]	768 (1·52)[e]
2	3,4-$(Me)_2$	**2b**	37·2	279 (dec.)	770 (1·66)
3	3,5-$(Me)_2$	**2c**	38·9	>300	768 (1·76)
4	3-Et	**2d**	36·4	232–235	771 (1·51)
5	4-Bu^t	**2e**	35·6	279 (dec.)	772 (1·64)
6	3-EtO	**2f**	35·8	220–223	769 (1·66)
7	4-EtO	**2g**	27·2	254–256	774 (1·67)
8	4-Pr^nO	**2h**	40·1	268 (dec.)	772 (1·71)
9	4-Bu^nO	**2i**	25·6	243–244	774 (1·76)
10	3,4,5-$(OMe)_3$	**2j**	42·0	257–258	773 (1·50)

[a] Isolated yield from column chromatography. Yield based on **1** reacted.
[b] Recrystallized from chloroform.
[c] Measured in chloroform in a concentration of 1×10^{-4} mol l^{-1}.
[d] Cited from Ref. 4.
[e] Acetonitrile, 758 nm (1·73),[4] acetone, 759 nm.[3]

2.2. Reaction mechanism

The reactions of **1** with alkylamines and arylamines proceed by different mechanisms. Reaction of **1** with *n*-butylamine gave 2-cyano-3-butylamino- and 2-butylamino-3-cyano-5-amino-1,4-naphthoquinone in yields of 76% and 6%, respectively, and none of the 8-butylamino derivative was obtained.[5] Similar results have been reported for the reaction of **1** with methylamine.[6] The orientation of the reaction sites between **1** and an alkylamine is well rationalized by the aid of the PPP MO procedures. The π-electron densities for the lowest unoccupied molecular orbital (LUMO) of **1** were calculated and the results are shown in Fig. 1. It is proposed that the alkylamination of **1** proceeds via nucleophilic substitution by the alkylamine and that substitution occurs predominantly at the position which has the highest π-electron density in the LUMO. The results of Fig. 1 suggest that the reaction occurs preferentially at the 3- and 2-positions, and the 3-position is much more favoured than the 2-position. These observations are well reproduced by the experimental results. On the other hand, in the case of the reaction of **1** with arylamines, arylamination occurred at the 8-, 2- and 3-positions. The reaction process differs markedly from that of the reaction between **1** and alkylamines. The 8-arylamination cannot be anticipated from the calculated π-electron density of **1** but can be rationalized if **1** tautomerizes to **7**, 4-hydroxy-2,3-dicyano-5-imino-1,5-naphthoquinone, in the first stage of the reaction



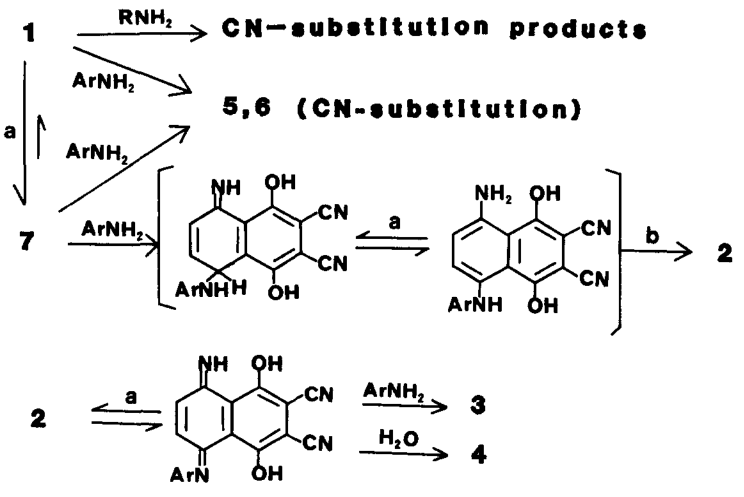
1 Quinone form		**7** Quinoneimine form	
C(1)	0·129	C(1)	0·084
C(2)	0·346*	C(2)	0·299†
C(3)	0·352*	C(3)	0·234†
C(4)	0·121	C(4)	0·097
C(5)	0·022	C(5)	0·043
C(6)	0·043	C(6)	0·138
C(7)	0·028	C(7)	0·031
C(8)	0·043	C(8)	0·208†

Fig. 1. Quinone–quinoneimine tautomerism and calculated π-electron densities for the LUMO of **1** and **7**. * Observed reaction site for alkylamination. † Observed reaction site for arylamination.

scheme. From the π-electron densities for the LUMO of **7** shown in Fig. 1, nucleophilic arylamination can be anticipated to occur at the 8-, 2- and 3-positions, as observed experimentally. Recently we observed many examples of the quinone–quinoneimine tautomerism of some amino-naphthoquinones in solution[7] and the tautomerism of **1** to **7** could possibly occur under these reaction conditions.

Solvent effects for this 8-arylamination have also been reported; 8-arylamination occurs readily in protic polar solvents such as ethanol but is retarded markedly in aprotic polar solvents such as acetonitrile.[4] It is reasonable to assume that the tautomerism occurs more readily in protic polar than in aprotic solvents.

The difference in the reaction course between **1** with alkylamines and arylamines may be due to the difference in the basicity of the amines. A possible reaction mechanism is shown in Scheme 2.



Scheme 2. (a) Tautomerism, (b) Oxidation with **1** or atmospheric oxygen. R = alkyl, Ar = aryl.

3. EXPERIMENTAL

All the melting points are uncorrected. The visible spectra in chloroform solution were measured using a Shimadzu UV-240 spectrophotometer. The mass spectra were recorded on a Hitachi RMU-6E spectrometer operating at 80 eV. Elemental analyses were recorded on a Yanako CHN recorder MT-2. Column chromatography was carried out on silica gel (Wako-gel C-300) using chloroform as eluent. Values of R_f were determined on TLC (Wako silica gel spotfilm) using benzene/acetone (9:1 v/v) as developing solvent.

3.1. Reaction of 1 with 4-ethoxyaniline

A mixture of **1** (1·0 g) and 4-ethoxyaniline (1·1 g) in ethanol (400 ml) was heated under reflux for 15 min. The reaction mixture was filtered immediately with a glass filter to recover unreacted **1** (50 mg). The filtrate was cooled and the separated products (fraction A) were collected on a glass filter. The filtrate was concentrated and the separated products (fraction B) were collected. Each of the fractions A and B were separated by column chromatography on silica gel (Wako-gel C-300) using chloroform as eluent. From the fraction A, **3g**, **4g** and **2g** were obtained. From the fraction B, products were eluted in the order **3g**, **5g**, **6g**, **4g** and **2g**. Reaction of **1** with other substituted anilines were carried out in the same manner and the main product **2** was isolated.

3.2. Characterization and identification of products

2g Yield, 27·2 %; m.p. 254–256 °C (chloroform); mass (rel. intensity), 358(M^+, 71), 330(51), 329(100); Analysis (%), Found: C, 67·03; H, 3·54; N, 15·34; Calc. for $C_{20}H_{14}N_4O_3$: C, 67·03; H, 3·94; N, 15·64; $R_f = 0·64$.

3g Yield, 2 %; m.p. 248–251 °C (chloroform); mass, 478(M^+, 100), 453(47), 449(47); UV, λ_{max}(nm), ($\varepsilon \times 10^{-4}$), 798(1·77); Analysis (%), Found: C, 69·32; H, 4·22; N, 10·58; Calc. for $C_{28}H_{22}N_4O_4$: C, 70·28; H, 4·63; N, 11·71; $R_f = 0·90$.

4g Yield, trace; m.p. 218–222 °C (chloroform); mass, 359(M^+, 100), 330(99), 314(10); UV, 584(1·40); Analysis (%), Found: C, 66·52; H, 3·33; N, 11·99; Calc. for $C_{20}H_{13}N_3O_4$: C, 66·85; H, 3·65; N, 11·70; $R_f = 0·49$.

5g Yield, trace; m.p. 249–251 °C (chloroform); mass, 333(M^+, 100), 304(67); UV, 522(0·50); Analysis (%), Found: C, 67·26; H, 4·54; N, 10·39; Calc. for $C_{19}H_{15}N_3O_3$: C, 68·46; H, 4·54; N, 12·61; $R_f = 0·74$.

6g Yield, 8 %; m.p. 243–246 °C (chloroform); mass, 333(M^+, 100), 305(61), 304(53); UV, 472(0·90); Analysis (%), Found: C, 68·38;

H, 4·25; N, 12·26; Calc. for $C_{19}H_{15}N_3O_3$: C, 68·46; H, 4·54; N, 12·61; R_f = 0·65.

2b Mass, 342(M^+, 100), 327(14); Analysis (%), Found: C, 69·34; H, 3·59; N, 16·22; Calc. for $C_{20}H_{14}N_4O_2$: C, 70·16; H, 4·12; N, 16·37.

2c Mass, 342(M^+, 100), 327 (11); Analysis (%), Found: C, 70·10; H, 3·79; N, 16·37; Calc. for $C_{20}H_{14}N_4O_2$: C, 70·16; H, 4·12; N, 16·37.

2d Mass, 342(M^+, 100), 327(14); Analysis (%), Found: C, 70·62; H, 3·70; N, 16·38; Calc. for $C_{20}H_{14}N_4O_2$: C, 70·16; H, 4·12; N, 16·37.

2e Mass, 370(M^+, 54), 355(100), 345(29); Analysis (%), Found: C, 71·15; H, 4·78; N, 15·16; Calc. for $C_{22}H_{18}N_4O_2$: C, 71·33; H, 4·90; N, 15·13.

2f Mass, 358(M^+, 100), 330(31), 313(29); Analysis (%), Found: C, 66·67; H, 3·46; N, 15·45; Calc. for $C_{20}H_{14}N_4O_3$: C, 67·03; H, 3·94; N, 15·64.

2h Mass, 372(M^+, 80), 330(100); Analysis (%), Found: C, 67·05; H, 4·10; N, 15·21; Calc. for $C_{21}H_{16}N_4O_3$: C, 67·73; H, 4·33; N, 15·05.

2i Analysis (%), Found: C, 68·36; H, 4·34; N, 14·42; Calc. for $C_{22}H_{18}N_4O_3$: C, 68·38; H, 4·70; N, 14·50.

2j Mass, 404(M^+, 91), 389(100), 379(79); Analysis (%), Found: C, 62·30; H, 3·73; N, 13·62; Calc. for $C_{21}H_{16}N_4O_5$: C, 62·37; H, 3·99; N, 13·86.

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