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Synthesis of Azoic Dyes from 7-Hydroxy-3-phenyl Quinoline Derivatives†

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SUMMARY

7-Hydroxy-3-(4-nitrophenyl)quinoline (**II**) *has been evaluated as an azoic coupler, together with several compounds derived from it, viz. by reduction and benzoylation to give* **III**, *by reaction with benzyl cyanide to give* **V**, and by azo coupling to give **VI**. *Azoic dyeings obtained from these couplers are evaluated with respect to their colour and fastness properties.*

1. INTRODUCTION

Azoic coupling components which yield brown hues are usually complex molecules and difficult to synthesise.[1–3] Attempts have been made to obtain cheaper azoic coupling components for brown shades.

We have synthesised recently a number of quinoline derivatives by condensing different malondialdehydes with *m*-aminophenol.[4] Thus, 4-nitrophenylmalondialdehyde (**I**) was reacted with *m*-aminophenol to yield the nitrophenylquinoline derivative (**II**).

Compound **II** and products derived from it (Scheme 1) have been studied as azoic couplers and the results are reported in the present paper.

† Abstracted from the Ph.D. Thesis of R. Krishnan, Bombay University, 1979.
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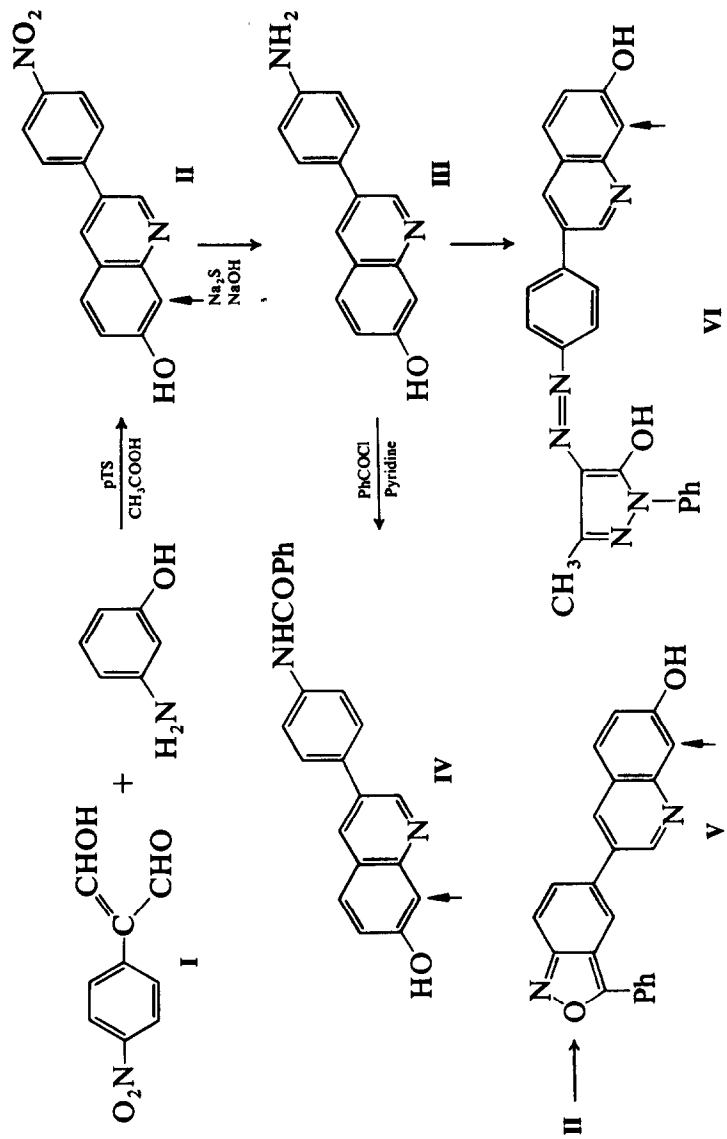


Scheme 1 (↓ indicates the site of coupling.)

2. RESULTS AND DISCUSSION

The nitrophenylquinoline (**II**) was reduced and the resulting amino derivative (**III**) benzoylated to give the benzamido derivative (**IV**). It was hoped that the presence of the benzamido group would result in a high substantivity when the compound was used as an azoic coupler.

Reaction of the nitrophenylquinoline (**II**) with benzyl cyanide under alkaline conditions led to the formation of the anthranil (**V**) as expected[5] and this compound was also studied as an azoic coupler.

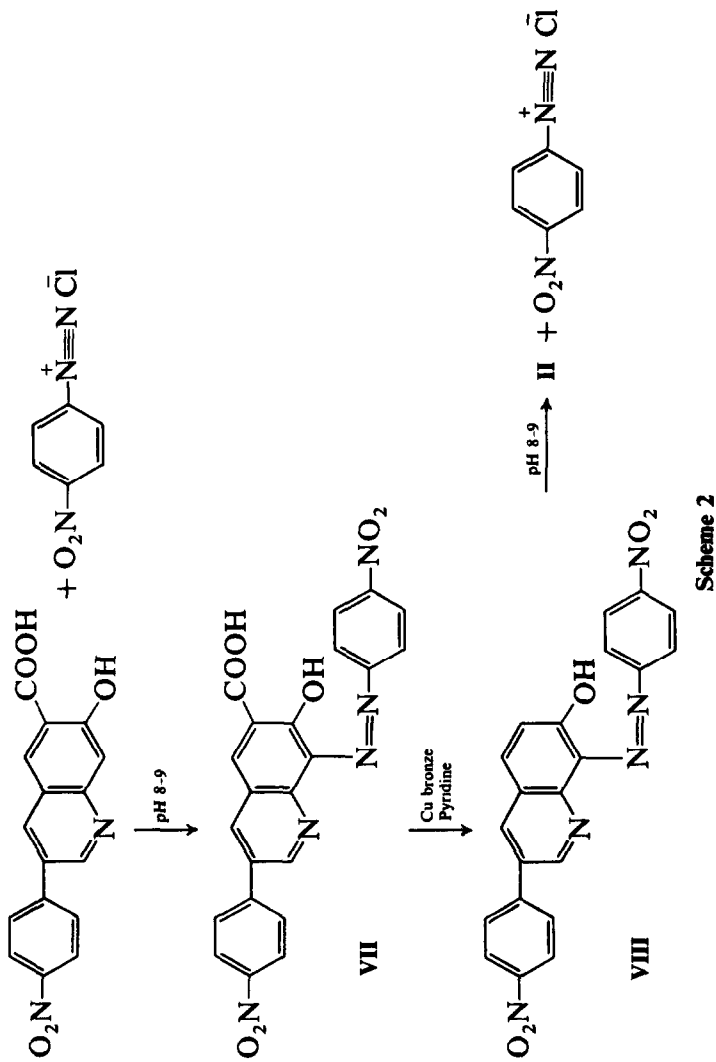
In order to obtain higher substantivity for the azoic coupler, the aminophenylquinoline (**III**) was diazotised and coupled with 1-phenyl-3-methylpyrazol-5-one to yield the monoazo dye (**VI**), which was also evaluated as an azoic coupler. The shades of the azoic dyeings obtained and their fastness properties are given in Table 1.

The azoic dyeings obtained from the 7-hydroxyquinolines are constituted as the 8-arylazo-7-hydroxy compounds by analogy with the behaviour of 2-naphthol and also by an unambiguous synthesis of the azo dye from 4-nitroaniline and the 4-nitrophenylquinoline derivative (**II**). This was effected by the reaction sequence shown in Scheme 2, which involved:

(a) Coupling diazotised 4-nitroaniline with 7-hydroxy-3-(4-nitrophenyl)-quinoline-6-carboxylic acid to obtain the corresponding azo dye (**VII**), and
(b) decarboxylation of **VII** to yield **VIII**.

The decarboxylated product was identical with the product obtained from diazotised 4-nitroaniline and **II**, as was established by m.p., mixed m.p., TLC and superimposable infrared spectra.

Whilst it had been anticipated that the anilide of the 7-hydroxyquinoline-6-carboxylic acid derivative would behave like Naphtol AS and result in good azoic dyeings, when applied on cotton it possessed only moderate substantivity and gave unsatisfactory shades with various diazonium salts. Table 1 outlines the results of the azoic dyeings: whilst the hues obtained are in some cases close to the desired browns, they are generally reddish-brown and not the darker browns which had been anticipated. The lightfastness of the dyeings varied from poor to moderate and none of the new azoic coupling components derived from **II** can thus be regarded as satisfactory.


COOH
OH
N
O_2N
+ O_2N
$\overset{+}{N}\equiv N\ \bar{Cl}$
pH 8-9
NO_2
N=N
VII
Cu bronze
Pyridine
VIII
pH 8-9
II
+ O_2N
$\overset{+}{N}\equiv N\ \bar{Cl}$

Scheme 2

TABLE 1
Shades and Fastness Properties of Azoic Dyeings

Coupler	*Base*	*Concentration of naphthol (g litre^{-1})*	*Shade*	*Pick-up*[a]	*Light-fastness*[b]
II	4-Nitroaniline	2	Yellowish-brown	M	3–4
II	2-Methoxy-4-nitroaniline	2	Reddish-brown	S	3–4
II	2,5-Dichloroaniline	2	Yellowish-orange	M	1–2
IV	4-Nitroaniline	2	Reddish-brown	S	2–3
IV	2,5-Dichloroaniline	1·3	Brownish-yellow	M	2–3
V	4-Nitroaniline	2	Yellowish-orange	S	2–3
V	2,5-Dichloroaniline	1·3	Brownish-orange	M	2–3
VI	4-Nitroaniline	2	Reddish-brown	S	1–2

[a] S, equal to standard; M, slightly less than standard.
[b] Xenotest lightfastness on the 1–8 scale.

3. EXPERIMENTAL

All melting points are uncorrected and are expressed in °C.

3.1. 7-Hydroxy-3-(4-nitrophenyl)quinoline (II)

A mixture of **I** (3·85 g, 0·02 mol), *m*-aminophenol (2·2 g, 0·02 mol) and *p*-toluenesulphonic acid (3·45 g, 0·02 mol) was added to glacial acetic acid (35 ml). The reaction mixture was refluxed for 3 h. It was then cooled and poured on to crushed ice, when a yellow solid separated. The solid was filtered off, suspended in water (75 ml) and neutralised with sodium carbonate to pH 7·5–8. The solid was filtered, washed with water and dried to yield **II**, 4·25 g (80%), m.p. > 360°. It was crystallised from chlorobenzene in yellow needles. Yield: 4 g, m.p. > 360°.

$C_{15}H_{10}N_2O_3$ requires: C, 67·8; H, 3·8; N, 10·5%.
Found: C, 67·7; H, 3·9; N, 10·4%.

3.2. 3-(4-Aminophenyl)-7-hydroxyquinoline (III)

7-Hydroxy-3-(4-nitrophenyl)quinoline (**II**) (2·65 g, 0·01 mol) was dissolved in 5% sodium hydroxide solution (20 ml) and to it was added

sodium sulphide flakes (3·9 g, 0·0055 mol). The reaction mixture was refluxed for 4 h, cooled and filtered. The filtrate was carefully neutralised to pH 8 with concentrated hydrochloric acid (40 ml), when a grey solid separated. This was filtered, washed with water and dried to yield **III**, 1·42 g (60%), m.p. > 360°. It was crystallised from dioxane in almost quantitative yield, m.p. > 360°.

$C_{15}H_{12}N_2O$ requires: C, 76·2; H, 5·0; N, 11·8%.
Found: C, 76·1; H, 5·1; N, 11·7%.

3.3. 3-(4-Benzamidophenyl)-7-hydroxyquinoline (IV)

The aminophenylquinoline (**III**) (2·35 g, 0·01 mol) was dissolved in pyridine (10 ml) and the solution stirred at 0–5 °C. Benzoyl chloride (1·5 ml, 0·013 mol) was slowly added and the temperature was not allowed to rise above 5 °C during the addition. After about 2 h, the mass was allowed to come to room temperature, gently refluxed for 1 h and then allowed to stand overnight. It was then added to a mixture of ice and hydrochloric acid to remove excess pyridine and the brown solid which separated was filtered, washed with dilute sodium bicarbonate solution and dried to yield **IV**, 1·87 g (55%), m.p. > 360°. It crystallised from DMF in brown needles. Yield: 0·84 g, m.p. > 360°.

$C_{22}H_{16}N_2O_2$ requires: C, 77·6; H, 4·7; N, 8·3%.
Found: C, 77·6; H, 4·6; N, 8·2%.

3.4. 7-Hydroxy-3-[5-(7-phenylanthranil)yl]quinoline (V)

Potassium hydroxide pellets (assay 85%) (6·2 g, 0·11 mol) was added to methanol (25 ml) and the resulting mixture was further stirred for 20 min. A solution of **II** (2·65 g, 0·01 mol) in methanol (30 ml) was added and the reaction mixture was stirred for one hour at 0 °C. It was then heated over a water bath at 55 °C for 5 h and added to ice water (150 ml). The mixture was acidified with concentrated hydrochloric acid (30 ml) to precipitate a yellow solid. This was filtered, washed with water and dried to yield **V**, 2·4 g (75%), m.p. 340–341°. It was recrystallised from dioxane in quantitative yield, m.p. 343–344°.

$C_{21}H_{14}N_2O_2$ requires: C, 77·1; H, 4·3; N, 8·6%.
Found: C, 77·0; H, 4·3; N, 8·5%.

3.5. Azo dye (VI) from 3-(4-aminophenyl)-7-hydroxyquinoline (III) and 1-phenyl-3-methylpyrazol-5-one

3-(4-Aminophenyl)-7-hydroxyquinoline (**III**) (2·35 g, 0·01 mol) was dissolved in hydrochloric acid (25 ml) with stirring, and the solution cooled to 0–5 °C and diazotised with sodium nitrite (0·83 g, 0·012 mol). The excess nitrous acid was destroyed by the addition of urea. The diazo liquor was added slowly to a solution of 1-phenyl-3-methylpyrazol-5-one (2 g, 0·012 mol) in the minimum amount of 5% sodium hydroxide solution, the reaction mixture being maintained at pH 8–9 by intermittent addition of 25% sodium hydroxide solution. The solution was then stirred at 10–15 °C for 3 h and then at room temperature for 1 h when the red coloured azo derivative separated. This was filtered, washed with water and dried to yield **VI**, 2·9 g (70%), m.p. 233–234°. It crystallised from DMF in red needles. Yield: 1·8 g, m.p.|238–239°.

$C_{25}H_{19}N_5O_2$ requires: C, 71·2; H, 4·5; N, 16·6%.
Found: C, 71·0; H, 4·3; N, 16·5%.

3.6. 7-Hydroxy-3-(4-nitrophenyl)quinoline-6-carboxylic acid

A mixture of **I** (3·85 g, 0·02 mol), *p*-aminosalicylic acid (3·4 g, 0·02 mol) and *p*-toluenesulphonic acid (3·45 g, 0·02 mol) was added to glacial acetic acid (35 ml). The reaction mixture was refluxed for 3 h. It was then cooled and poured on crushed ice when a yellow solid separated. The solid was filtered, suspended in water (75 ml) and neutralised with sodium carbonate to pH 7·5–8.

The solid was filtered, washed with water and dried to yield 7-hydroxy-3-(4-nitrophenyl)quinoline-6-carboxylic acid, 4·6 g (80%), m.p. > 360°.

The compound obtained was sufficiently pure for further use without any purification. For analytical purposes a small portion was crystallised from *o*-dichlorobenzene as yellow needles, m.p. > 360°.

$C_{16}H_{10}N_2O_5$ requires: C, 61·9; H, 3·2; N, 9·0%.
Found: C, 61·8; H, 3·1; N, 8·9%.

3.7. Azo dye (VII) from 4-nitroaniline and 7-hydroxy-3-(4-nitrophenyl)-quinoline-6-carboxylic acid

A mixture of 4-nitroaniline (1·4 g, 0·01 mol) and sodium nitrite (0·83 g, 0·12 mol) was added to cooled (0–5 °C) concentrated hydrochloric acid

(5 ml) with stirring. To this mixture ice cold water (100 ml) was added and the excess of nitrous acid was destroyed by adding urea.

7-Hydroxy-3-(4-nitrophenyl)quinoline-6-carboxylic acid (3·7 g, 0·12 mol) was dissolved in the minimum amount of 5% sodium hydroxide solution and the diazo liquor was added slowly to it whilst maintaining pH 8–9 by intermittent addition of 25% sodium hydroxide solution. The solution was stirred at 10–15 °C for 2 h and at room temperature for 1 h.

The red dye (**VII**) which separated was filtered, washed with water and dried. Yield: 3·2 g (70%), m.p. 340–343 °. It crystallised from DMF in red granules. Yield: 1·9 g, m.p. > 360 °.

3.8. Decarboxylation of VII to VIII

A mixture of the azo dye **VII** (2·3 g, 0·05 mol) and copper bronze (catalytic amount) was added to pyridine (5 ml). The reaction mixture was heated at 180 °C for 4 h, cooled, filtered and the filtrate added to ice cold concentrated hydrochloric acid (10 ml). The red dye (**VIII**) which separated was filtered, washed with water and dried. Yield: 1·65 g (50%), m.p. 300–302 °.

The residue was heated in pyridine (5 ml), filtered and the filtrate added to ice cold concentrated hydrochloric acid (15 ml) to yield a further 0·41 g (25%) of product, m.p. 300–302 °. It crystallised from DMF in red needles. Yield: 1·25 g, m.p. 304–305 °.

This dye and the azo dye prepared from 4-nitrophenyldiazonium chloride and 7-hydroxy-3-(4-nitrophenyl)quinoline (**II**) were found to be identical on the basis of TLC, m.p. and mixed m.p.

3.9. Azo dye (VIII) from 4-nitroaniline and 7-hydroxy-3-(4-nitrophenyl)-quinoline

The azo dye was prepared by adopting the procedure described above for the preparation of **VII**, employing 4-nitroaniline (1·4 g, 0·01 mol), sodium nitrite (0·83 g, 0·012 mol) and 7-hydroxy-3-(4-nitrophenyl)quinoline (3·2 g, 0·012 mol). Yield: 2·9 g (70%), m.p. 301–302 °. It crystallised from DMF as red needles. Yield: 2 g, m.p. 304–305 °.

$C_{21}H_{13}N_5O_5$ requires: C, 60·7; H, 3·1; N, 16·8%.
Found: C, 60·5; H, 3·1; N, 16·8%.

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