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Studies on the Use of 7-Amino-3-(4-aminophenyl)quinoline as a Benzidine Substitute

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SUMMARY

7-Amino-3-(4-aminophenyl)quinoline (**I**) *has been synthesised and its use as an alternative to benzidine investigated. Several disazo and trisazo acid and direct dyes have been prepared and their properties evaluated. The differential reactivity of the tetrazonium salt of* **I** *has been demonstrated and the diazo cation from the 4-aminophenyl substituent shown to be the more reactive.*

1. INTRODUCTION

In recent years there has been considerable interest in the synthesis of substantive dyes from various diamines used as an alternative to the carcinogenic benzidine,[1] and such structures that have been described reflect the continued interest in the synthesis of non-hazardous substantive dyes.

We have previously reported[2] the synthesis of 7-aminoquinoline derivatives by the reaction of *m*-phenylenediamines with different malondialdehydes, and also the synthesis of 3-(4-aminophenyl)-7-hydroxyquinoline and its use as an azoic coupler.[3] We report here the synthesis of 7-amino-3-(4-aminophenyl)quinoline (I) and its use in the preparation of disazo and trisazo colourants for wool and cotton.

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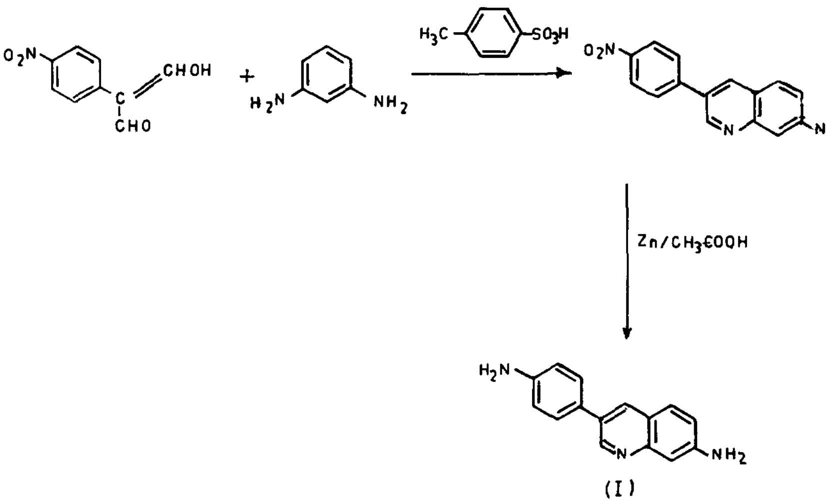
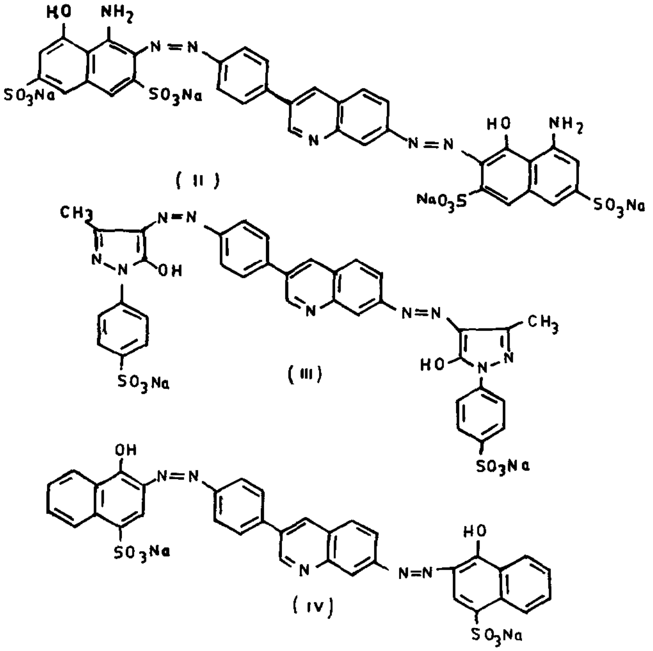
2. RESULTS AND DISCUSSION

7-Amino-3-(4-aminophenyl)quinoline (**I**) was readily obtained by the reaction of *m*-phenylenediamine with 4-nitrophenylmalondialdehyde and subsequent reduction as shown in Scheme 1. This diamine was tetrazotised and coupled with various coupling components such as naphthionic acid, NW-acid, J-acid and H-acid, giving dyes typified by structures **II**–**IV**. In order to obtain evidence for the structure of the unsymmetrical disazo dye **II**, the diamine **I** was tetrazotised and coupled with 1 mole of 1-phenyl-3-methylpyrazol-5-one to give the monoazo derivative **V**. Hydrolysis of **V** in dilute sulphuric acid yielded the 7-hydroxyquinoline azo dye **VI**. This dye **VI** was also prepared by diazotising 3-(4-aminophenyl)-7-hydroxyquinoline[3] and coupling with 1-phenyl-3-methylpyrazol-5-one. The dyes thus obtained were found to be identical (m.p., mixed m.p., IR spectra) and this indicates that the phenyldiazonium moiety is more reactive than the diazo residue in the quinoline ring and couples initially to give the monoazo derivative **V**. The structure of the unsymmetrical disazo dye from H-acid is thus formulated as **II**.



Scheme 1.

All the dyes thus obtained showed the expected substantivity for cellulose but only the unsymmetrical disazo dye from H-acid (**II**) and the disazo dye from 1-(4-sulphophenyl)-3-methylpyrazol-5-one (**III**) gave



(II)

(III)

(IV)

bright shades, but the fastness properties were not satisfactory. These disazo dyes were also evaluated on wool.

The visible absorption maxima and the hues of the direct dyeings and wool dyeings and their fastness properties are shown in Table 1.

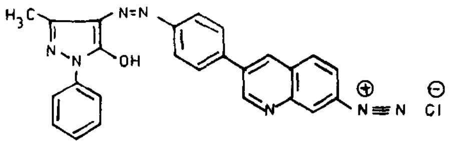
To investigate the values of the diamine **I** further, a series of

TABLE 1

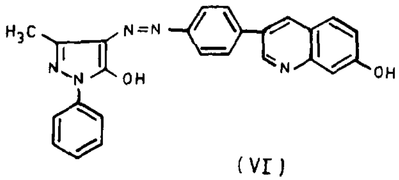
Properties of Dyes **II**, **III** and **IV**

Dye	λ_{max} (*nm*)	*Shade*		*Dyeing properties*[a]				
				PU	*LF*	*WF*	*SC*	*SW*
II	540	Cotton:	Violet	1/1	2–3	3	4–5	4–5
		Wool:	Violet	2/1	4–5	3	4–5	4–5
III	442	Cotton:	Yellow	3/4	3–4	2–3	4–5	4–5
		Wool:	Orange	1/6	3–4	2–3	4–5	4–5
IV	455	Cotton:	Scarlet	1/1	1–2	2	4–5	4–5
		Wool:	Scarlet	1/6	2–3	2–3	4–5	4–5

[a] PU, pick-up; LF, lightfastness; WF, washfastness; SC, staining on cotton; SW, staining on wool.



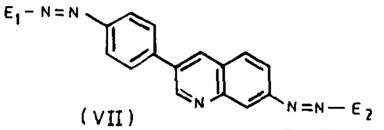
(V)



(VI)

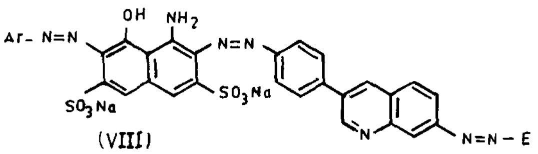
unsymmetrical disazo dyes (**VII**) and trisazo dyes (**VIII**) were synthesised. The various coupling components used, the visible absorption maxima of the resultant dyes, the hues of the disazo dyes **VII** obtained on wool and the fastness properties are shown in Table 2. These dyes **VII** did not show any substantivity for cellulose. The trisazo dyes **VIII** were evaluated on cotton and the hues obtained, on fastness properties and visible absorption maxima of the dyes are shown in Table 3.

Both disazo and trisazo dyes exhausted well from acidic and neutral dyebath respectively. The wool dyeings showed good washfastness whereas the cotton dyeings showed only moderate washfastness. The lightfastness of all the dyeings was moderate. The bright orange dye **VIIb** on wool, the dull green dye **VIIId** on cotton and the attractive



(VII)

E$_1$, E$_2$ ARE COUPLING COMPONENTS CONTAINING -SO$_3$Na GROUPS



(VIII)

Ar IS ARYL
E IS A COUPLING COMPONENT CONTAINING SO$_3$Na GROUP

TABLE 2
Disazo Dyes **VII** on Wool

Dye	E_1	E_2	λ_{max}[a] *(nm)*	*Shade on wool*	*Dyeing properties*[b]				
					PU	*LF*	*WF*	*SC*	*SW*
VIIa	Naphthionic acid	Schaeffer's acid	479	Orange	1/6	2	3–4	5	5
VIIb	Naphthionic acid	1-(4-Sulphophenyl)-3-methylpyrazol-5-one	420	Orange	1/1	3	4–5	5	5
VIIc	Gamma acid	NW-acid	514	Reddish violet	1/6	3	3	5	4
VIId	Gamma acid	Schaeffer's acid	516	Reddish violet	1/6	3	4	5	4–5
VIIe	H-acid	NW-acid	560	Bluish violet	1/6	2–3	2–3	5	5
VIIf	H-acid	1-(4-Sulphophenyl)-3-methylpyrazol-5-one	545	Reddish brown	1/6	2–3	4	5	5
VIIg	Gamma acid	J-acid	515	Reddish violet	1/6	2	3	5	4–5

[a] λ_{max}, visible absorption maximum. The dyes used in recording the visible spectra and in dyeing were resalted and the purity was checked by thin layer chromatography using the following solvent system: 4·0 ml *n*-butanol, 1·5 ml ethanol, 2·0 ml 28% aqueous ammonia, 2·0 ml pyridine and 1·5 ml water.

[b] Abbreviations as in Table 1.

TABLE 3
Trisazo Dyes **VIII** on Cotton

Dye	*E*	*Ar*	λ_{max}[a] (*nm*)	*Shade on cotton*	*Dyeing properties*[b]				
					PU	*LF*	*WF*	*SC*	*SW*
VIIIa	Schaeffer's acid	*p*-Nitroaniline	514	Olive	1/25	2	1	5	5
VIIIb	Schaeffer's acid	2,5-Dichloroaniline	510	Reddish olive	1/25	2–3	1–2	5	5
VIIIc	NW-acid	*p*-Anisidine	536	Reddish violet	1/12	2	1–2	5	5
VIIId	NW-acid	*p*-Nitroaniline	525	Dull green	1/1	3–4	2–3	5	4–5
VIIIe	1-(4-Sulphophenyl)-3-methylpyrazol-5-one	2,5-Dichloroaniline	540	Greenish grey	1/12	2–3	2–3	5	5
VIIIf	1-(4-Sulphophenyl)-3-methylpyrazol-5-one	*p*-Anisidine	552	Dull violet	1/12	2	1	5	5
IIIg	J-acid	*p*-Nitroaniline	552	Reddish brown	1/1	4	1–2	5	4
VIIIh	J-acid	2,5-Dichloroaniline	512	Dull brown	1/12	2	1–2	5	4–5

[a] λ_{max}, visible absorption maximum. The dyes used in recording visible spectra and in dyeing were resalted and the purity was checked as described in Table 2.

[b] Abbreviations as in Table 1.

reddish brown dye **VIIIg** on cotton gave the most satisfactory colourations.

3. EXPERIMENTAL

Visible spectra were recorded using a Uvikon spectrophotometer. 4-Nitrophenylmalondialdehyde[4] and 3-(4-nitrophenyl)-7-aminoquinoline[3] were prepared as previously described.

3.1. 7-Amino-3-(4-aminophenyl)quinoline (I)

A mixture of 3-(4-nitrophenyl)-7-aminoquinoline (2·65 g, 0·01 mol) and zinc dust (2·6 g, 0·04 mol) was added to glacial acetic acid (15 ml) and the mixture refluxed for 3 h. Completion of the reaction was indicated by the appearance of a green fluorescence without yellow colour in the reaction mixture. The reaction mixture was filtered hot and was used directly to prepare the dyes.

3.2. Preparation of the dye II

The above filtrate containing the diamino compound **I** was added to thoroughly cooled (0–5°C) concentrated hydrochloric acid (20 ml) with stirring. It was then tetrazotised with sodium nitrite (1·65 g, 0·021 mol) and excess of nitrous acid destroyed by the addition of urea.

H-Acid (7·6 g, 0·021 mol) was dissolved in 20% sodium carbonate solution (18·0 ml) and to this stirred solution, the tetrazo liquor was added slowly and the reaction mixture maintained at pH 6·0 (0–5°C) by intermittently adding sodium acetate for 1 h and then at pH 8·0–9·0 at 5–10°C for 1 h. The disazo dye which separated was filtered and dried. Yield 7·2 g (80%).

3.3. Preparation of the dye III

This was prepared by adapting the same procedure as described for the preparation of **II** but employing 1-(4-sulphophenyl)-3-methylpyrazol-5-one (6·0 g, 0·021 mol) at pH 8·0–9·0 and at 5–10°C. The disazo dye which separated was filtered and dried. Yield 6·5 g (85%).

3.4. Preparation of the dye IV

The dye **IV** was prepared by adapting the same procedure described above but employing NW-acid (5·5 g, 0·021 mol) at pH 8·0–9·0 and at 5–10°C. Yield 5·3 g (75%).

3.5. Preparation of the disazo dye VIIa

Naphthionic acid (4·68 g, 0·021 mol) was dissolved in 20% sodium carbonate solution (9·0 ml). To the stirred solution of the tetrazonium salt prepared from **I** (equivalent to 0·02 mol) at 0–5°C was added slowly the naphthionic acid solution. The mixture was stirred for 3 h at pH 2·0–3·0 and at 0–5°C. A red colour developed when the clear run out of a spot of the reaction mixture came into contact with an adjacent spot of H-acid on a filter paper. The intensity of this colour remained constant after 3 h, indicating completion of the coupling reaction.

The pH of this monoazo diazonium salt mixture was gradually raised to 6·5–7·0. To this, Schaeffer's acid (5·4 g, 0·021 mol) dissolved in 20% sodium carbonate (18·0 ml) was added and the pH was adjusted to 8·5–9·0 by the addition of further 20% sodium carbonate solution. The coupling was complete in about 1 h at 5–10°C.

The mixture was heated at 85–90°C and 12 g of salt was added (12% w/v) slowly with stirring when the dye separated out. The liquor was cooled to 55–50°C and filtered. Yield 12 g (homogeneous as shown by TLC).

The other dyes **VIIb–VIIg** (Table 2) were prepared by following the above procedure.

3.6. Preparation of the trisazo dye VIIIa

A solution of H-acid (7·6 g, 0·021 mol) dissolved in 20% sodium carbonate solution (18 ml) was added to the tetrazonium salt solution prepared from **I** (equivalent to 0·02 mol) at 0–5°C. The mixture was stirred for 3 h at pH 2·0–3·0 and at 0–5°C (the test for completion of the coupling was carried out as described above). The pH of the monoazo diazonium salt was gradually raised to 6·0 by addition of 20% sodium carbonate solution and to the solution was then added Schaeffer's acid (5·4 g, 0·021 mol) dissolved in 20% sodium carbonate (9·0 ml) and the pH adjusted to 7·5. The coupling was complete in 2 h at 5–10°C.

p-Nitrobenzenediazonium chloride [prepared from 2·76 g (0·02 mol) of *p*-nitroaniline] was added to the above disazo dye and the pH of the mixture was raised to 9·0 by addition of 20% sodium hydroxide and 20% sodium carbonate solutions. The diazonium salt was consumed in 30 min at 5–10°C. The mixture was heated to 85–90°C, 18 g of salt was added slowly and after stirring for 30 min the dye was precipitated. The liquor was cooled to 50–55°C and filtered.

The crude dye was dissolved in about 150 ml of water by boiling and 4–5 g of salt was added at 90–95°C. The mixture was cooled to 50–55°C and the separated dye was filtered. Yield 17·7 g.

All the other trisazo dyes **VIIIb–VIIIh** (Table 3) were similarly prepared.

4. SUMMARY

7-(Amino)-3-(4-aminophenyl)quinoline (**I**) yields acid dyes and direct dyes when diazotised and coupled to suitable coupling components. The resultant dyes gave dyeings which in general had fairly good washfastness but the tinctorial power was, on the whole, unsatisfactory and the lightfastness below average. It was very difficult to obtain a black dye by the use of this intermediate.

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