NAPHTHOQUINONE SERIES—PART II

Brazanquinone Vat Dyes from 2:3-Dichloro-1:4-Naphtoquinone: Part II

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The synthesis of brazanquinone vat dyes obtained by the condensation of 2:3-dichloro-1:4-naphtoquinone (I) with 4-bromo-1-naphthol, 6-bromo-2-naphthol and 2-hydroxy-3-naphthanilide (Naphtol AS) has been described in the previous paper.\(^1\) The constitution of the condensation products as furan derivatives was also discussed. As against the poor substantivity of 1:2-benzobrazanquinone\(^2\) (II), the 4-carboxyanilide derivative\(^1\) (III) possessed good substantivity. The parent \(\beta\)-naphthol and Naphtol AS, from which

![Chemical Structures](image)

the above dyes were obtained, exhibit parallel substantivity to cotton, the latter being more substantive. In general the introduction of heterocyclic rings, carboxyamido groups, halogen atoms, methoxy groups and increase in structural complexity promote substantivity in the Naphtol AS series.\(^2\) A similar study has now been undertaken in the brazanquinone vat dyes which have been prepared by the condensation of (I) with compounds of the Naphtol AS series.

Naphtol AS-E (2-hydroxy-3-naphthoic-\(p\)-chloranilide) is one of the highly substantive Naphtols. In order to see whether the introduction of a chlorine atom in the anilide half of (III) has a similar effect, Naphtol AS-E was condensed with (I) to give the bright yellow dye, 1:2-benzobrazanquinone-4-carboxy-4'-chloranilide (IV); (III) and (IV), however, had nearly the same

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substantivitiy. The dye (III) from Naphtol AS was slightly superior in fastness to light than (IV), whereas fastness to washing and chlorine were the same. The azoic dyeings from Naphtol AS are likewise faster to light than the dyeings from Naphtol AS-E.

With a view to study the effect of the introduction of a bromine atom in the anilide and naphthalene half of (III), 2-hydroxy-3-naphthoic-p-bromanilide\(^3\) and 6-bromo-2-hydroxy-3-naphthylanilide\(^3\) were condensed with (I) to give 1:2-benzobrazanquinone-4-carboxy-4'-bromanilide (V) and 3'-bromo-1:2-benzobrazanquinone-4-carboxylanilide (VI) respectively. Whereas the parent bromonaphthols gave faster azoic shades than Naphtol AS, the brazanquinone vat dyes (V) and (VI) obtained from them did not show superior substantivity or fastness properties over the bromine-free dye (III). The increase in the substantivity by the introduction of bromine in brazanquinone dyes from \(\alpha\)- and \(\beta\)-naphthols\(^1\) was, therefore, not noticeable in dyes from the bromo derivatives of Naphtol AS.

Naphtol AS-D (2-hydroxy-3-naphthoic-\(\alpha\)-toluidide) has nearly the same substantivity as Naphtol AS and both give shades of nearly equal fastness. 1:2-Benzobrazanquinone-4-carboxy-2'-methylanilide (VII), obtained by the condensation of (I) with Naphtol AS-D, was however only weakly substantive to cotton and gave shades which were less fast than those given by (III). Introduction of a chlorine atom in the \(p\)-position to the anilide group in (VII) led to increase in substantivity. Thus 1:2-benzobrazanquinone-4-carboxy-4'-chloro-2'-methylanilide (VIII) obtained by condensation of (I) with 2-hydroxy-3-naphthoic-p-chloro-\(\alpha\)-toluidide (Naphtol AS-TR) had good affinity to cotton and gave bright yellow shades of good fastness. Introduction of chlorine in (VII), in common with other examples where halogen atoms were introduced, did not give dyes faster to light. The inferior fastness in general of the dye (VIII) compared to (IV) indicates the unfavourable influence of the introduction of a methyl group in (IV).

2-Hydroxy-3-naphthoic-\(\alpha\)-anisidide (Naphtol AS-OL), and \(p\)-anisidide (Naphtol AS-RL) and 2:5-dimethoxyanilide (Naphtol AS-BG) are more substantive than Naphtol AS and give faster azoic dyeings; the \(p\)-anisidide being more substantive than the \(\alpha\)-anisidide and the dimethoxyanilide being more substantive than the monomethoxyanilides. Condensation of Naphtol AS-RL, Naphtol AS-OL and Naphtol AS-BG with (I) gave 1:2-benzobrazanquinone-4-carboxy-4'-methoxyanilide (IX), 1:2-benzobrazanquinone-4-carboxy-2'-methoxyanilide (X) and 1:2-benzobrazanquinone-4-carboxy-2':5'-dimethoxyanilide (XI) respectively, but the dyes were inferior to (III) in substantive and fastness. In the condensation of (I) with
Naphtol AS-RL and Naphtol AS-BG, alkali-soluble by-products were isolated which are probably phenols obtained by demethylation of the methoxy groups by pyridine hydrochloride formed in the reaction. Attempts to isolate the hydroxy compounds in the pure form were however unsuccessful. The dye (X) had good substantivity, whereas (IX) and (XI) were less substantive. The fastness of these dyes was nearly of the same order.

Naphtol AS-BS (2-hydroxy-3-naphthoic-3'-nitranilide) is slightly more substantive than Naphtol AS but gives azoic shades of lower fastness. 1:2-Benzobrazanquinone-4-carboxy-3'-nitranilide (XII), obtained by condensation of Naphtol AS-BS with (I), was, however, inferior in substantivity and fastness to (III). The nitro group in (XII) is, however, reduced to the amino group during the dyeing from an alkaline hydrosulphite vat and the shade (brownish yellow) obtained from (XII) is different from the colour of (XII) in substance (red). When the dyed fibre was treated with a mixture of sodium nitrite and aqueous hydrochloric acid and then developed with an alkaline solution of β-naphtol, the shade changed to orange showing the presence of a diazotizable amino group in the dye on the fibre.

In contrast with the superior substantivity of Naphtol AS-E, AS-TR, AS-OL, AS-RL, AS-BG and AS-BS as compared with Naphtol AS, the brazanquinone vat dyes which were obtained by the condensation of these naphthols with (I) did not show higher substantivity than the parent 1:2-benzobrazanquinone-4-carboxyamidine (III) which was derived from Naphtol AS. The dye (III) was further found to possess the highest all-round fastness among the brazanquinone vat dyes prepared.

**Experimental**

1:2-Benzobrazanquinone-4-carboxy-4'-chloranilide (IV)

Naphtol AS-E (3·0 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and cooled when bright yellow needles (2·0 g.), m.p. 306–8°, separated. Recrystallization from pyridine did not raise the m.p. (Found: N, 3·3. C₂₋H₁₄ClNO₄ requires N, 3·1%).

1:2-Benzobrazanquinone-4-carboxy-4'-bromanilide (V)

2-Hydroxy-3-naphthoic-4'-bromanilide (3·4 g.), (I) (2·2 g.) and dry toluene (150 c.c.) were kept boiling under reflux and pyridine (3·2 c.c., 0·04 mols.) was added dropwise during 3 hours. The mixture was refluxed for 24 hours, toluene removed by steam distillation and the residue was extracted successively with boiling water (200 c.c.) to remove betaine, boiling
5% aqueous sodium hydroxide to remove unreacted naphthol and (I) as 2-chloro-3-hydroxy-1:4-naphthoquinone and finally washed with water. The product (4.45 g., yield 90%), m.p. 256–58°, was recrystallized from o-dichlorobenzene three times when it gave orange-yellow needles, m.p. 305–6°; unaltered by further recrystallization from the same solvent (Found: N, 2.8%. C_{27}H_{14}BrNO_{4} requires N, 2.8%).

3'-Bromo-1:2-benzobrazanquinone-4-carboxyanilide (VI)

The condensation of (I) (2.2 g.) and 6-bromo-2-hydroxy-3-naphthoic anilide (3.4 g.) was carried out as in the previous experiment and the crude product (4.4 g.), m.p. 260–65°, after three recrystallizations from xylene gave felted yellow needles, m.p. 332° (Found: N, 2.6. C_{27}H_{14}BrNO_{4} requires N, 2.8%).

1: 2-Benzobrazanquinone-4-carboxy-2'-methylanilide (VII)

Naphtol AS-D (2.8 g.), (I) (2.3 g.) and pyridine (30 c.c.) were heated under reflux for 3 hours and the crystalline compound, m.p. 307–10°, which separated was collected and recrystallized from pyridine when it gave bright orange felted needles, m.p. 307° (Found: C, 77.8; H, 3.2; N, 3.2. C_{28}H_{17}NO_{4} requires C, 77.9; H, 4.0; N, 3.2%).

1: 2-Benzobrazanquinone-4-carboxy-4'-chloro-2'-methylanilide (VIII)

Naphtol AS-TR (3.1 g.), (I) (2.25 g.) and pyridine (30 c.c.) were heated under reflux for 3 hours. The crystalline product (2.2 g.), m.p. 331–33°, when recrystallized from nitrobenzene gave yellow needles, m.p. 333°; raised to 336–37° by further crystallization from pyridine (Found: N, 3.0. C_{28}H_{19}ClNO_{4} requires N, 3.0%).

1: 2-Benzobrazanquinone-4-carboxy-4'-methoxyanilide (IX)

Naphtol AS-RL (2.9 g.), (I) (2.2 g.) and pyridine (30 c.c.) were refluxed for 3 hours and cooled. The crystalline product (1.35 g.), m.p. 298–300°, was washed with alcohol and it gave after two recrystallizations from pyridine yellow needles, m.p. 299° (Found: C, 75.2; H, 4.0; N, 3.6. C_{28}H_{17}NO_{5} requires C, 75.2; H, 3.8; N, 3.2%).

The pyridine mother-liquor was poured into ice and hydrochloric acid and the precipitate obtained was extracted with boiling water. The residue (1.95 g.) was dissolved in benzene and passed through a column of activated alumina. The red band at the top of the column was eluted with benzene and on concentration it gave a red compound which after recrystallization from benzene gave red needles, m.p. 255°. It was soluble in
alcoholic alkali giving a red solution which gave an orange-yellow precipitate on acidification.

1: 2-Benzobrazanquinone-4-carboxy-2′-methoxyanilide (X)

Naphtol AS-OL (2.9 g.) and (I) (2.2 g.) were heated under reflux in pyridine (30 c.c.) and the crystalline product (1.7 g.), m.p. 300–05°, was recrystallized twice from pyridine when it gave yellow needles, m.p. 300° (Found: C, 74.6; H, 3.9; N, 3.3. C_{23}H_{17}NO_{4} requires C, 75.1; H, 3.8; N, 3.1%).

1: 2-Benzobrazanquinone-4-carboxy-2′:5′-dimethoxyanilide (XI)

Naphtol AS-BG (3.2 g.), (I) (2.2 g.) and pyridine (30 c.c.) were refluxed for 4 hours, cooled and filtered. The reddish violet product (1.55 g.) was washed with alcohol, dried and crystallized from nitrobenzene four times. It gave shining violet hexagonal plates, m.p. 290–91° (Found: C, 72.6; H, 4.1; N, 3.2. C_{29}H_{18}NO_{4} requires C, 72.9; H, 4.0; N, 2.95%).

The pyridine mother-liquor on pouring into crushed ice and hydrochloric acid gave a dark coloured precipitate which was collected, extracted with boiling water to remove the betaine and dried (1.6 g.). Since this was found to be alkali-soluble, it was extracted with 10% sodium hydroxide (50 c.c.). The extracts were treated with Norit and filtered. Carbon dioxide was then bubbled through this solution, when a red brown precipitate (1.1 g.), m.p. 230–32°, separated. Attempts to purify this substance further proved unsuccessful.

1: 2-Benzobrazanquinone-4-carboxy-3′-nitranilide (XII)

Naphtol AS-BS (3.1 g.), (I) (2.2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours. The orange-yellow compound (1.4 g.) obtained gave on recrystallization from quinoline orange-yellow needles, m.p. 332° (Found: N, 6.2. C_{25}H_{14}NO_{4} requires N, 6.1%).

Colour Reactions and Dyeing Properties

The colour in sulphuric acid, the colour of the vats, the shades on cotton, and the fastness properties of the dyes are given in Table I. Fastness to light was determined using the Atlas Fade-O-Meter and following the standards of the Society of Dyers and Colourists and fastness to washing and chlorine have been determined by the I.C.I. method. The brazanquinone vat dyes gave purple, blue and bluish black coloured solutions in concentrated sulphuric acid, although majority of them gave blue solutions in common with other brazanquinone derivatives.
Naphthoquinone Series—II

**TABLE 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour in sulphuric acid</th>
<th>Colour of the vat</th>
<th>Shade on cotton</th>
<th>Fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(III)</td>
<td>Blue-black</td>
<td>Deep red-brown</td>
<td>Bright orange yellow</td>
<td>5-6</td>
</tr>
<tr>
<td>(IV)</td>
<td>Bright-blue</td>
<td>Red-brown</td>
<td>Bright yellow</td>
<td>3-4 5 5</td>
</tr>
<tr>
<td>(V)</td>
<td>Bright-blue</td>
<td>Violet-red</td>
<td>Bright orange yellow</td>
<td>3-4 5 4-5</td>
</tr>
<tr>
<td>(VI)</td>
<td>Purple</td>
<td>Deep red</td>
<td>Bright orange yellow</td>
<td>4-5 3-4 4</td>
</tr>
<tr>
<td>(VII)</td>
<td>Bright-blue</td>
<td>Violet-red</td>
<td>Pale orange</td>
<td>4-5 3-4 4-5</td>
</tr>
<tr>
<td>(VIII)</td>
<td>Blue</td>
<td>Brownish violet</td>
<td>Bright yellow</td>
<td>5 3 4-5</td>
</tr>
<tr>
<td>(IX)</td>
<td>Bluish black</td>
<td>Violet-red</td>
<td>Dull yellow</td>
<td>5-6 3 4</td>
</tr>
<tr>
<td>(X)</td>
<td>Bluish black</td>
<td>Brownish violet</td>
<td>Orange-yellow</td>
<td>5 3 3</td>
</tr>
<tr>
<td>(XI)</td>
<td>Bluish black</td>
<td>Dirty violet</td>
<td>Dull brown-orange</td>
<td>4 5 4</td>
</tr>
<tr>
<td>(XII)</td>
<td>Bright-blue</td>
<td>Dark brown-violet</td>
<td>Brownish yellow</td>
<td>4-5 2-3 2-3</td>
</tr>
</tbody>
</table>

The dyes (III), (IV) and (XII) were difficult to reduce, but after precipitation from sulphuric acid they vatted readily. The dyes (VII) to (XI) were dyed by the IN process (50–60°), (III) was dyed at 70–80° and the other dyes were dyed at 60–70°. Higher temperatures employed in the case of the latter dyes are due to the difficulty in vatting at lower temperatures. The shades obtained were yellow, orange-yellow or brownish yellow. The dyestuffs had moderate to good light fastness and had good fastness to severe washing and chlorine. Comparison of the substantivity of the dyestuffs was made on the basis of the depth of the shade and the exhaustion of the dye-baths.

**SUMMARY**

Brazanquinone vat dyes have been prepared by the condensation of 2:3-dichloro-1:4-naphthoquinone (I) with compounds of the Naphtol AS series. Whereas the introduction of halogens and methoxy groups in the anilide half of Naphtol AS gives more substantive naphthols, derivatives of 1:2-benzobrazanquinone-4-carboxyanilide (III) which contain the substituents in the carboxyanilide part do not show higher substantivity than (III). The dyestuffs gave yellow, orange-yellow and brownish yellow shades which are moderately fast to light and had good fastness to severe washing and chlorine.
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REFERENCES

1. Suryanarayana and Tilak --- See previous paper.