# NAPHTHOQUINONE SERIES—PART III

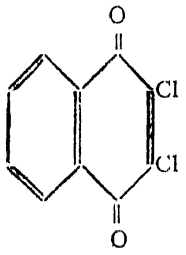
## Brazanquinone Vat Dyes from 2: 3–Dichloro–1: 4–Naphthoquinone: Part III

BY B. SURYANARAYANA AND B. D. TILAK, F.A.SC.

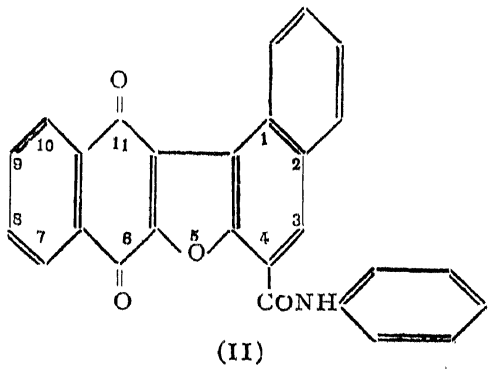
*(Department of Chemical Technology, University of Bombay, Bombay 19)*

Received October 1, 1952

SYNTHESIS of a series of brazanquinone vat dyes by the condensation of 2: 3-dichloro-1: 4-naphthoquinone (I) with 4-bromo-1-naphthol, 6-bromo-2-naphthol, 2-hydroxy-3-naphthanilide (Naphtol AS) and its derivatives has been described in previous communications.[1, 2] Whereas introduction of halogens, methyl, methoxy and nitro groups in Naphtol AS leads to the more substantive Naphtols, the brazanquinone vat dyes which resulted by the condensation of these Naphtol AS derivatives with (I) did not show superior substantivity or fastness than the parent 1: 2-benzobrazanquinone-4-carboxyanilide (II) which was obtained from Naphtol AS. Brazanquinone vat dyes described earlier gave yellow, orange-yellow and brownish-




(I)



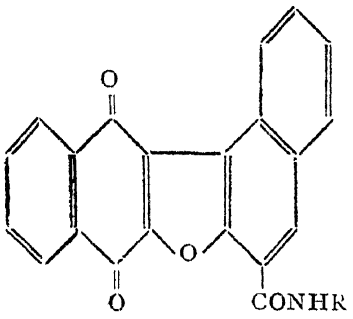

(II)

yellow shades on cotton. With the view to extend the range of shades and also with the view to synthesise dyes of higher substantivity and fastness, (I) was condensed with Naphtols in which the carboxyanilide half of Naphtol AS is replaced by arylides from naphthalene and dibenzofuran and with Naphtols derived from more complex *o*-hydroxycarboxyarylides. These Naphtols are highly substantive and give azoic shades of excellent fastness.

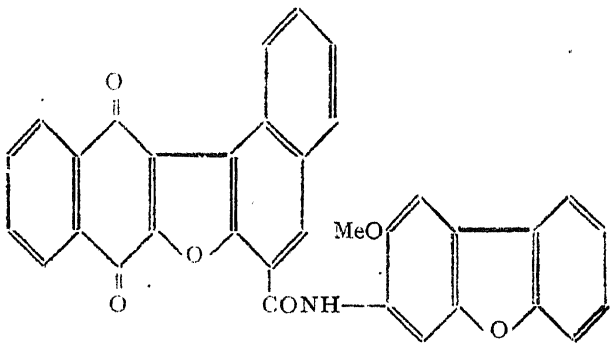
Reaction of (I) with 2-hydroxy-3-naphthoic-α-naphthalide (Naphtol AS-BO) and 2-hydroxy-3-naphthoic-β-naphthalide (Naphtol AS-SW) gave 1: 2-benzobrazanquinone-4-carboxy-α-naphthalide (III) and 1: 2-benzobrazanquinone-4-carboxy-β-naphthalide (IV) respectively. The substantivity of these dyes was very good and they gave bright orange yellow shades.

The dye (IV) containing the β-naphthalide group had good fastness to light and chlorine but was poor in washing fastness. The α-naphthalide was not so fast.

Naphtol AS-S [2-hydroxy-3-naphthoic-3′-(2′-methoxydibenzofurano)-amide] is highly substantive on account of the presence of the heterocyclic dibenzofuran ring system. However, 1 : 2-benzobrazanquinone-4-carboxy-3′-(2′-methoxydibenzofurano)-amide (V), a brown dye obtained by the

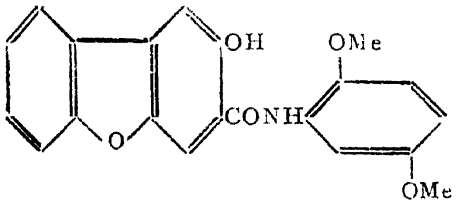



(III) R = α-Naphthyl
(IV) R = β-Naphthyl

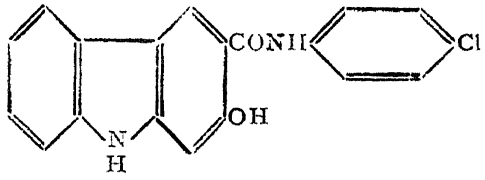



(V)

condensation of Naphtol AS-S with (I), had lower substantivity than (II) and the fastness properties were also poor.



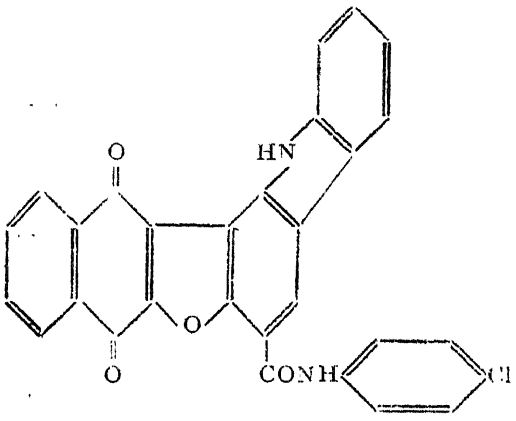

Naphtol AS-BT



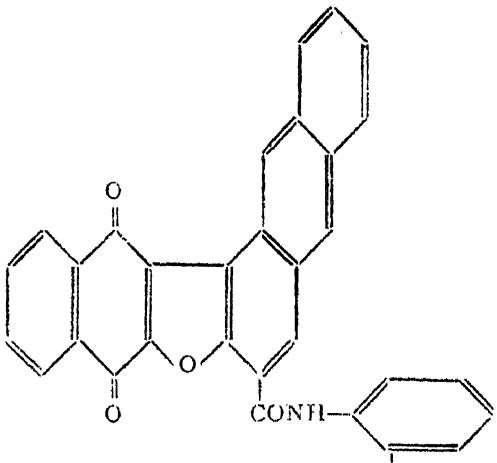

Naphtol AS-LB

Whereas Naphtol AS-BG (2-hydroxy-3-naphthoic-2′ : 5′-dimethoxy-anilide) readily reacts with (I) to give a brazanquinone vat dye,[2] Naphtol AS-BT (2-hydroxydibenzofurano-3-carboxy-2′ : 5′-dimethoxyanilide) does not condense with (I) in pyridine. Attempts to react (I) with 2-hydroxydibenzofuran were also unsuccessful. More complex brazanquinone vat dyes were, however, prepared by the condensation of (I) with compounds of the Naphtol AS series derived from other heterocyclic and higher polycyclic *o*-hydroxycarboxyarylides. Reaction of (I) with 2-hydroxycarbazole-3-carboxy-*p*-chloranilide (Naphtol AS-LB) and 2-hydroxyanthracene-3-carboxy-*o*-toluidide (Naphtol AS-GR) gave 1 : 2-(2′ : 3′-indolo)-brazanquinone-4-carboxy-*p*-chloranilide (VI) and 1 : 2-(2′ : 3′-naphtho)-brazanquinone-4-carboxy-*o*-toluidide (VII) respectively. These compounds were deeply coloured, the former being brick-red and the latter bright violet but they had poor affinity to cotton. The weak shades obtained had however excellent fastness to

light. Whereas Naphtol AS-LB reacted with (I), carbazole did not react under similar conditions.



(VI)



(VII)

In general in contrast to the Naphtol AS series where increase in structural complexity leads to increase in substantivity, brazanquinone vat dyes derived from the more complex Naphtols do not show higher substantivity or fastness and the parent member of the series 1 : 2-benzobrazanquinone-4-carboxyanilide (II) itself has better fastness, substantivity and brightness than these more complex dyes.

The above vat dyes were not readily reduced with alkaline hydrosulphite but after precipitation from sulphuric acid the finely divided dyes were easily vattable. However, the dye (VI) gave a different shade after precipitation from sulphuric acid (dull brownish red → dull brown). The range of shades obtainable from the brazanquinone dyes described in this and the previous papers[1, 2] varies from yellow to violet, although most of them dye bright yellow or orange-yellow shades. The substantivity in most cases is good and the fastness properties of the dyes are also satisfactory.

## Experimental

1 : 2-*Benzobrazanquinone*-4-*carboxy*-α-*naphthalide* (*III*)

Naphtol AS-BO (3·1 g.), 2 : 3-dichloro-1 : 4-naphthoquinone (I) (2·2 g.) and pyridine (30 c.c.) were refluxed for 3 hours. The crystalline product (2 g.), m.p. 328–29°, after two recrystallizations from nitrobenzene, gave lustrous red elongated plates, m.p. 328° (Found: N, 3·0. $C_{31}H_{17}NO_4$ requires N, 3·0%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-β-*naphthalide* (*IV*)

Naphtol AS-SW (3·1 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and cooled to room temperature. The crystalline

product (2·1 g.), m.p. 292–300°, after recrystallization from pyridine gav lustrous yellow needles, m.p. 292° (Found: N, 3·4. $C_{31}H_{17}NO_4$ requires N, 3·0%).

1 : 2-*Benzobrazanquinone*-4-*carboxy*-3′-(2′-*methoxydibenzofurano*)-*amide* (*V*)

Naphtol AS-S (3·0 g.), (I) (1·8 g.) and pyridine (35 c.c.) were boiled under reflux and the brownish orange crystalline residue (1·6 g.), m.p. 348–49°, was recrystallized from nitrobenzene when it gave elongated brick-red needles, m.p. 348–49° (Found: C, 75·8; H, 3·9; N, 2·7. $C_{34}H_{19}NO_6$ requires C, 75·9; H, 3·5; N, 2·6%).

1 : 2-(2′ : 3′-*indolo*) *brazanquinone*-4-*carboxy*-p-*chloranilide* (*VI*)

Naphtol AS-LB (3·4 g.), (I) (2·2 g.) and pyridine (30 c.c.) were boiled under reflux for 3 hours and the violet-red crystalline product (0·5 g.), m.p. 350–54°, which separated was collected and recrystallized from *o*-dichlorobenzene when it gave brick-red needles, m.p. 354–55° (Found: C, 70·3; H, 3·2; N, 5·8. $C_{29}H_{15}ClN_2O_4$ requires C, 70·9; H, 3·1; N, 5·7%).

1 : 2-(2′ : 3′-*naphtho*) *brazanquinone*-4-*carboxy*-o-*toluidide* (*VII*)

Naphtol AS-GR (1·4 g.), (I) (1·0 g.) and pyridine (15 c.c.) were boiled under reflux. The mixture became viscous owing to separation of a red coloured product. It was, therefore, diluted with pyridine (20 c.c.) and refluxing continued for 3 hours more. The mixture was cooled and filtered. The residue was washed with alcohol and ether, when lustrous violet-red flat needles (1·5 g.), m.p. 345–46°, were obtained. Recrystallization from *o*-dichlorobenzene gave lustrous violet elongated needles, m.p. 346–47° (Found: C, 79·4; H, 3·8; N, 2·6. $C_{32}H_{19}NO_4$ requires C, 79·8; H, 3·9; N, 2·9%).

*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 severe washing and chlorine were determined by the I.C.I. method[4] and fastness to light was determined using the Atlas Fade-O-Meter and following the standards of the Society of Dyers and Colourists.[5]

With the exception of (III) and (VII), which were dyed by the IN process (at 50–60°), the other dyes were dyed at 70–80°. The dyes gave yellow to violet shades which had good fastness to light and chlorine and moderate to good fastness to washing.

TABLE I

| Compound | Colour in sulphuric acid | Colour of the vat | Shade on cotton | Fastness | | |
|---|---|---|---|---|---|---|
| | | | | Light | Severe washing | Chlorine |
| (II) | Blue-black | Deep red brown | Bright orange yellow | 5–6 | 5 | 5 |
| (III) | Blue-black | Brownish violet | Reddish orange | 5 | 3–4 | 4 |
| (IV) | Blue-black | Brownish violet | Bright orange yellow | 6 | 2–3 | 4 |
| (V) | Brown | Dirty red | Brownish yellow | 4–5 | 4 | 4–5 |
| (VI) | Bright greenish blue | Red-brown | Dull brownish red | 6–7 | 3 | 4–5 |
| (VII) | Olive green | Olive green | Dull violet | 6–7 | 5 | 3–4 |


## SUMMARY

Naphtols AS-BO, AS-SW, AS-S, AS-LB and AS-GR were condensed with 2 : 3-dichloro-1 : 4-naphthoquinone (I) with the view to prepare brazanquinone vat dyes of higher substantivity and fastness than 1 : 2-benzobrazanquinone-4-carboxyanilide (II). Whereas the above Naphtols are highly substantive, the brazanquinone vat dyes obtained from them were less substantive than (II). The dyes gave yellow to violet shades which had good fastness to light and chlorine and moderate fastness to washing.


We are indebted to the Council of Scientific and Industrial Research for a Fellowship awarded to one of us (B.S.) and to Dr. T. S. Gore for the microanalyses recorded in the paper.

## REFERENCES


1. Suryanarayana and Tilak .. See previous paper.
2. Dikshit, Suryanarayana and Tilak *Ibid.*
3. Venkataraman .. *The Chemistry of Synthetic Dyes* (Academic Press), 1952, p. 650.
4. *Fastness Assessment of Textile Dyestuffs*, Imperial Chemical Industries Limited, London, p. 47.
5. *J. Soc. Dyers and Col.*, 1940, **56**, 273.