

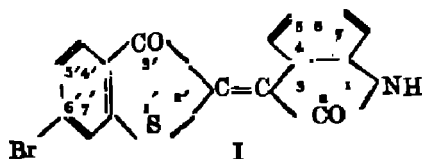
Indigoid Vat Dyes of the Isatin series. Part XIII. 3-Indole-2'-(6'-bromo) thionaphthene-Indigos

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3-Hydroxy-6-bromo-thionaphthene was condensed with isatin and some of its different types of substitution products. The resulting 3-indole-2'-(6'-bromo) thionaphthene-indigos are found lighter than those of the corresponding 7'-bromo compounds¹ from a comparative study of their colour, dyed shade and absorption maxima data.

Recently, Ciba Ltd² synthesised 3-hydroxy-6-bromo-thionaphthene and obtained from it "Thionaphtheneindole" which possesses antihistaminic, anaesthetic, and anti-fungal properties; but no attempt has hitherto been made to make a systematic study on the synthesis and properties of asymmetrical thioindigoid dyes derived from this hydroxy-thionaphthene.

Hence, the present authors prepared now a few 3-indole-2'-(6'-bromo) thionaphthene-indigos (general formula I) which are required for advancing their investigation on the four isomeric 3-indole-2'-(4', 5', 6', and 7'-bromo) thionaphtheneindigos from the point of view of examining colour in relation to their constitution.



The new compounds of this series are darkish brown, brownish-red, and darkish brown-red small crystalline dyes. But they are not so glistening as those of the 7'-Bromo compounds. These are obtained in 75-87% yield which are as high as those of the yield of the 7'-bromo dyes. All of them melt above 300°. These dyes are soluble in pyridine, aniline, and nitrobenzene; slightly soluble in ethanol, carbon tetrachloride, benzene and xylene. The parent dye (I), its 5-chloro- (II), 5-bromo-7-nitro- (VII), and 5,7-dinitro (VIII) derivatives are moderately soluble in acetic acid whereas the 5-bromo-(III), 5-iodo-(IV), 5-nitro-(V), and the 5,7-dibromo derivatives (VI) are sparingly soluble in the same.

The dyeing shades obtained on cotton from an alkaline hydrosulphite vat at 65-70° are very uniform and much better developed than those produced from the 7'-bromo compounds. The colour of the vat is similar to and slightly deeper than those obtained from

1. Guha and Mitra, *this Journal*, 1966, 43, 568.

2. Brit. patent, 830, 223. March 9, 1960.

compounds of the 6'-chloro³ series. The colour, dyed shade, and absorption maxima data (Table II) of some of the compounds of this 6'-bromo series with those of the corresponding substances of the 7'-bromo series indicate clearly that the 6'-bromo dyes are lighter in colour putting them in the order: 6-Br < 7-Br.

TABLE I

Dyes	Constituents	Appearance; Yield(%)	Shade on cotton	Action of H ₂ SO ₄	Formula	%Nitrogen Found	%Nitrogen Reqcd.
I. 3-Indole-2'-(6'-bromo)T	Isatin(0.147g) + A(0.23g)	Powdery darkish brown 0.31g(84%)	Brownish-red	Beautiful violet	C ₁₆ H ₈ O ₂ NBrS	4.34	3.91
II. 3-(5-chloro)indole-2'-(6'-bromo)T	5-chloro-isatin (0.181g)+A (0.229g)	Do 0.34g(87%)	Brownish-red	Darkish violet	C ₁₆ H ₇ O ₂ NCIBrS	3.81	3.56
III. 3-(5-bromo)indole-2'-(6'-bromo)T.	5-bromo-isatin (0.23g)+A (0.23g)	Powdery brownish red 0.35g (79%)	Brownish red deeper than I & II	Do	C ₁₆ H ₇ O ₂ NBr ₂ S	3.52	3.2
IV. 3-(5-iodo)indole-2'-(6'-bromo)T	5-Iodo-isatin (0.273g)+A (0.229g)	Silky darkish brownish red 0.4g (82%)	Brownish red	Do	C ₁₆ H ₇ O ₂ NBrIS	3.23	2.89
V. 3-(5-nitro)indole-2'-(6'-bromo)T	5-nitro-isatin (0.192g)+A (0.229g)	brownish red; 0.34g(85%)	Light brown violet	Do.	C ₁₆ H ₇ O ₄ N ₂ BrS	6.62	6.93
VI. 3-(5,7-dibromo)indole-2'-(6'-bromo)T.	5,7-dibromo-isatin (0.31g)+A (0.229g)	Silky brownish red, deeper than V; 0.4g(77.5%)	Brownish red, deeper than IV	Reddish violet	C ₁₆ H ₆ O ₂ NBr ₃ S	3.05	2.71
VII. 3-(5-bromo-7-nitro)indole-2'-(6'-bromo)T	5-bromo-7-nitroisatin (0.271g)+A(0.23g)	Brownish red 0.37g (76%)	Brownish red	Darkish violet	C ₁₆ H ₆ O ₄ N ₂ Br ₂ S	6.23	5.81
VIII. 3-(5,7-dinitro)indole-2'-(6'-bromo)T	5,7-dinitro-isatin (0.237g)+A (0.229g)	Silky dark brownish red 0.34g (75%)	Deep brown-red, deeper than VII	Light violet	C ₁₆ H ₆ O ₆ N ₂ BrS	9.71	9.37

T denotes thionaphtheneindigo and A 3-hydroxy-6-bromo-thionaphthene.

EXPERIMENTAL

The condensation products were obtained by boiling the glacial acetic acid solution of the constituents for 15-20 min. except the 5-iodo dye (IV) which was boiled for 30 min. only with the addition of HCl (conc. 2 ml.). For the preparation of dyes, II, IV, and VI, 50 ml of acetic acid were used and 40 ml for the rest. The separated crystalline dye was collected while the mother liquor was still hot and recrystallised from nitrobenzene, washed well with ethanol and water.

For convenience and ready comparison, the dyes prepared now are mentioned in a tabular form (I). The λ_{\max} were determined in xylene solution and values are recorded in Table II.

TABLE II

	λ_{\max}
3-Indole-2'-(6'-Bromo)-T	502 m μ
3-Indole-2'-(7'-Bromo)-T	508
3-(5,7-Dibromo)-Indole-2'-(6'-Bromo)-T	506
3-(5,7-Dibromo)-Indole-2'-(7'-Bromo)-T	512
3-(5,7-Dinitro)-Indole-2'-(6'-Bromo)-T	514
3-(5,7-Dinitro)-Indole-2'-(7'-Bromo)-T	523

T denotes thionaphthencindigo.

Further work for studying the preparation and various properties of 3-Indole-2'-(4'-Bromo)-thionaphtheneindigos has been undertaken.

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