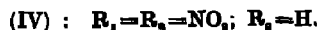
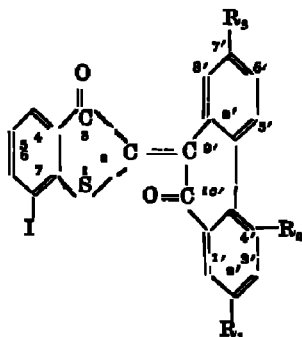


## Studies on Indigoid Dyes. Part VIII. 2-(7-Iodo)thionaphthene-9'-phenanthrene Indigos

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Several dyes have been prepared by the condensation of 7-iodothioindoxyl with phenanthraquinone and substituted phenanthraquinones with the object of comparing the colour and chemical constitution of these dyes with analogous dyes derived from 5-iodothioindoxyl, reported earlier.

Many variations have been effected by variously substituting and the thioindoxyl moiety with a view to studying the consequent changes in absorption of thioindigoid dyes. The present investigation deals with the preparation of 7-iodophenanthrene indigos and comparison with their 5-iodo analogues.<sup>1</sup> These dyes have been prepared by condensing the 7-iodothioindoxyl with phenanthraquinone (Dye I), 2-bromophenanthraquinone (II), 4-nitrophenanthraquinone (III), and 2, 7-dinitrophenanthraquinone (IV), and can be represented as:



### 2-(7-Iodo)thionaphthene-9'-phenanthrene indigos.

The dyes after preparation were boiled with ethanol to remove the unchanged components and were then crystallised from suitable solvents.

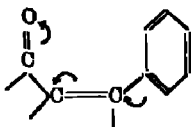
The dyes are dark reddish violet in colour and are soluble in high boiling solvents such as nitrobenzene and pyridine. The solution of the dyes in concentrated sulphuric acid develops characteristic colour and the original dyes are reprecipitated unchanged on dilution with water. These 2-(7-iodo) thionaphthene-9'-phenanthrene indigos are decidedly much lighter in colour than the analogous 5-iodo derivatives<sup>1</sup> in conformity with Martinet's rule.<sup>2</sup>

1. Sinha, *this Journal*, 1962, 39, 163.

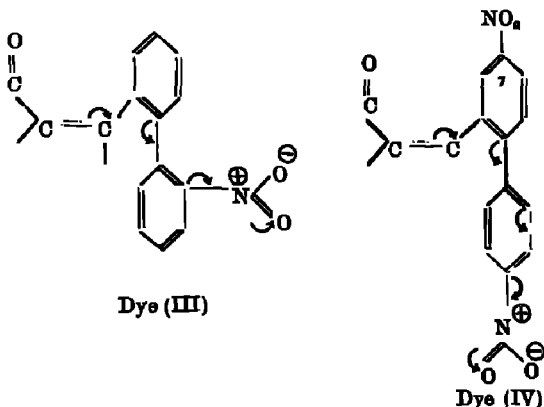
2. *Rev. Gen. Mat. Col.*, 1921, 23, 17.

The reducibility of these dyes in alkaline vat presents an interesting study. As in cases of some analogous dyes reported earlier<sup>1</sup>, presence or absence of a suitably placed substituent materially affects the external electron accession to the carbonyl carbon undergoing reduction by causing either electron accession or recession internally.

Thus in the cases of the four dyes now reported, (I) may be taken as the standard. Here too, some internal electron accession to the carbonyl carbon atom may be envisaged due to the participation of structures like



and similar others. This state of affairs is, however, common to all the dyes referred. Reducibility of dye (II) may be expected to be almost equal to that of (I) because of the Br atom being capable of donating as well as abstracting electrons by inductive and mesomeric effects respectively. Dyes (III) and (IV) should be distinctly more reducible than (I) because of electron-recession and consequent increase in the cationoid property of the relevant carbon atom caused by the *o*- and *p*-placed nitro groups, thus :



The 7-nitro group in (IV) may of little effect being placed *m*- to the relevant carbon chain.

The reducibility of the dyes under report, has indeed been found to be of the order expected.

#### EXPERIMENTAL

*2-(7-Iodo)thionaphthene-9'-phenanthrene Indigo*.—7-Iodothioindoxyl (0.414 g.) and phenanthraquinone (0.312 g.) were dissolved in glacial acetic acid (20 ml.). To the resulting red solution, HCl (conc., 1.5 ml.) was added and the mixture was boiled for 10 min. The dye (0.22 g.) was purified by recrystallisation from benzene, m.p. 253-54° (shrinking from

248°). It dissolves in  $H_2SO_4$  cold, (conc.) producing deep green colour. It dyes cotton in reddish violet shade. (Found: I, 27.5; S, 6.8.  $C_{22}H_{11}O_4IS$  requires I, 27.25; S, 6.86%).

2-(7-Iodo)thionaphthene-9'-(2'-bromo) phenanthrene Indigo.—On refluxing a solution of 2-bromophenanthraquinone (0.431 g.), 7-iodothioindoxyl (0.414 g.) in glacial acetic acid (30 ml.) and HCl (conc., 3 ml.) for 10 minutes, the dye was deposited as deep reddish violet crystals (0.64 g.). It was recrystallised from xylene and did not melt till 310°. Solution of the dye in  $H_2SO_4$  (conc.) was deep yellowish green in colour. The dye developed on cotton a reddish violet shade. (Found: Br+I, 38.2.  $C_{22}H_{10}O_4BrIS$  requires Br+I, 37.98%).

2-(7-Iodo)thionaphthene-9'-(4'-nitro) phenanthrene Indigo was obtained by refluxing for 10 min. a mixture of 4-nitrophenanthraquinone (0.38 g.) and 7-iodothioindoxyl (0.414 g.), glacial acetic acid (25 ml.) and HCl (conc. 2.5 ml.). The precipitated dye (0.55 g.) was recrystallised from xylene, m.p. 259-60° (shrinking from 245°). The colour of the dye in  $H_2SO_4$  was deep yellowish green and developed a bluish violet shade on cotton. (Found: I, 25.05.  $C_{22}H_{10}O_4NIS$  requires I, 24.85%).

2-(7-Iodo)thionaphthene-9'-(2', 7'-dinitro) phenanthrene Indigo.—A solution of 2, 7-dinitrophenanthraquinone (0.298 g.) and 7-iodothioindoxyl (0.276 g.) in boiling glacial acetic acid (30 ml.) was treated with HCl (conc., 4 ml.) when the condensation product immediately separated. The reaction mixture was refluxed for 20 min. The dye (0.34 g.) was crystallised from nitrobenzene, m.p. 284-86°. It dissolves in  $H_2SO_4$  (conc.) producing deep green colour and developed a brownish chocolate shade on cotton. (Found: I, 22.95.  $C_{22}H_8O_6N_2IS$  requires I, 22.84%).