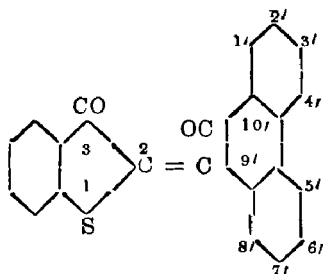


## Indigoid Dyes Derived from Phenanthraquinone. Part I. Thionaphthene-phenanthrene Indigos.

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It has been shown by Friedlander, Herzog and Voss (*Ber.*, 1922, 55, 1591) that phenanthraquinone condenses very easily with 3-hydroxythionaphthene in acetic acid solution containing traces of hydrochloric acid and a violet dye is produced. Later on Luther (*Ber.*, 1931, 64, 831) prepared the same substance in a pure crystalline form by a slight modification of the above method. The present author got the substance as a chocolate brown crystalline mass and he has further extended this reaction to study the effect of different elements or groups on the colour of the substances. The condensation products with bromo- and nitrophenanthraquinones are violet in colour whereas those with amino- and hydroxyphenanthraquinones, black or brownish black. The substances dissolve in concentrated sulphuric acid with a green, violet green or violet brown colour and the original dyes are reprecipitated by treatment with water. The freshly precipitated compounds are found to be quite suitable for dyeing on wool from an acid bath, yielding even and deep shades. Except the bromo compounds which are very feebly soluble, they dissolve in hydrosulphite vat with a yellowish brown colour from which the original substances are reprecipitated by oxidation with air. The shades obtained on cotton from hydrosulphite vat were not very deep, but quite even and fast. Generally speaking, these substances are sparingly soluble in alcohol, moderately so in amyl alcohol and acetic acid and easily soluble in nitrobenzene, xylene and pyridine and they generally melt above 295° and some of them sublime at higher temperatures, yielding a reddish violet vapour. In the monosubstituted phenanthraquinones, it has not been determined which, of the two ketonic groups, actually, takes part in the reaction. Further work in this line is in progress.

The structure of these compounds can be represented by the following general formula.



For the sake of abbreviation, the preparation of only one of these compounds is given in the experimental portion, the rest being prepared in similar manners, their properties are recorded in the Table.

#### EXPERIMENTAL.

*2-Thionaphthene- 9'(2'-nitro)-phenanthrene indigo.*—Solutions of 2-nitrophenanthraquinone (1.26 g.) in hot acetic acid (100 c.c.) and 3-hydroxythionaphthene (0.8 g.) in 2 c.c. of the same solvent were freed from dissolved air by passing carbon dioxide and mixed together, thoroughly agitated and the mixture treated with 0.5 c.c. of hydrochloric acid in 5 c.c. of acetic acid. On boiling the mixture for ten minutes a brownish violet crystalline precipitate separated out. It was filtered hot and washed with a little acetic acid and then with alcohol. For purification, it was boiled with alcohol for sometime and filtered hot. The residue was dissolved in pyridine and reprecipitated as a violet crystalline precipitate by the cautious addition of hot water. It crystallises from amyl alcohol in small rectangular plates melting above 290°. It is sparingly soluble in alcohol, moderately in amyl alcohol and acetic acid and easily soluble in nitrobenzene, xylene and pyridine in the cold. It dissolves in concentrated sulphuric acid with a green colour and dyes wool in violet shades from an acid bath and dyes cotton in light violet shades from hydrosulphite vat.

*Indigoid Dyes Derived from Phenanthraquinone.*

(T = Thionaphthene, P = Phenanthrene, p = Phebanthraquinone, I = Idigo).								
Name.	Prepared from 3-hydroxy-T. and 2-nitro-p	Appearance.	Crystallised from	M.p.	Colour in sulphuric acid.	Shade on wool from acid bath.	Shade on cotton from hydro-sulphite vat.	Analysis.
			pyridine	Above 290°	Green	Violet	Light violet	Found. Calc.
2-T-9'(2'-nitro)-PI		Violet crystalline mass.	pyridine	Above 290°	Green	Violet	Light violet	C, 65.23 68.57 H, 3.01 2.85
2-T-9'(4'-nitro)-PI		"	"	"	"	Pinkish violet	Light pinkish violet.	H, 3.11 2.85
2-T-9'(3':7'-dinitro)-PI		"	"	"	"	Blackish violet	Light pink	N, 6.45 6.51
2-T-9'(4':5'-dinitro)-PI		"	"	"	"	Violet	"	N, 6.58 6.51
2-T-9'(2':4'-bromo)-PI		Violet brown prismatic needles.	"	279°	Greenish brown	Reddish brown	—	Br, 18.91 19.09
2-T-9'(4'-dibromo)-PI		Violet crystalline mass.	"	Above 295°	" violet	Violet	—	Br, 31.98 32.12
2-T-9'(dibromonitro)-PI		Violet needles.	"	Above 300°	Green	Deep violet	—	Br, 29.91 29.46
2-T-9'(bromodinitro)-PI		Deep violet prismatic needles.	nitro-benzene	281°	"	Violet blue	Pink	Br, 15.65 15.71
2-T-9'(2' amino)-PI		Violet brown microscopic needles.	pyridine	Above 295°	Greenish brown	Chocolate brown.	Light pink	C, 74.14 74.96 H, 3.61 3.66
2-T-9'(4' amino)-PI		Black crystalline mass.	"	Above 300°	"	Deep violet	"	C, 74.08 74.36 H, 3.88 3.66
2-T-9'(2':7'-diamino)-PI		Blackish-brown crystalline mass.	"	"	Brown red	Chocolate brown	Light pinkish brown	N, 7.38 7.56
2-T-9'(4':5'-diamino)-PI		Violet-black crystalline mass.	"	Above 295°	Violet black	Blackish violet	—	N, 7.24 7.56
2-T-9'(2'-hydroxy)-PI		Violet microscopic needles.	acetic acid	200°	Bottle green	Violet	Violet	C, 73.66 74.15 H, 3.46 3.37
2-T-9'(4'-hydroxy)-PI		Violet-brown needles.	"	Above 300°	Violet brown	Blackish brown	Blackish brown	C, 73.81 74.15 H, 3.57 3.37
2-T-9'(2':7'-dihydroxy)-PI		Brownish black plates.	"	"	"	Greenish brown	Greenish brown	C, 70.57 70.96 H, 3.45 3.22

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