

ANTHRAQUINONE SERIES

Part II. Halogenated Aminanthraquinones and Indanthrones

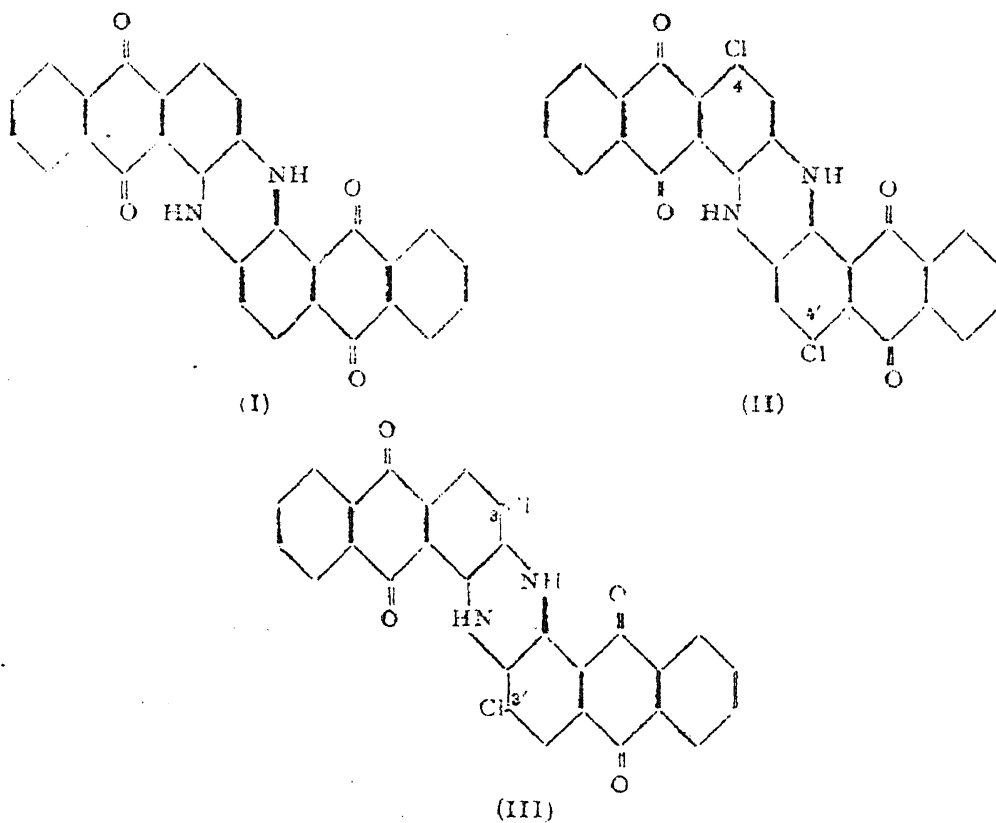
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ALTHOUGH indanthrone (I) was the first anthraquinone vat dyestuff discovered as early as 1901, indanthrone and its derivatives have continued to be among the most important anthraquinone vat dyes produced in large quantities by most of the dyemakers. Indanthrone possesses excellent fastness properties to all agencies other than chlorine, in which case it undergoes a greening of shade, probably due to oxidation to the azine. The halogenated derivatives of indanthrone, especially the dichloro derivatives, possess improved fastness to chlorine, and a series of halogenated indanthrones are now commercially available, examples being Caledon Blue RCS, GCD, BCD, GCPS and Alizanthrene Blue RC (ICI), and Indanthrene Blue GCD, BC, GC and RCL (I.G.).

Conflicting statements have been made in the literature regarding the constitution of the commercial chlorinated indanthrones and their methods of preparation. According to Fraser-Thomson¹ Caledon Blue GCD is



largely the 4:4'-dichloroindanthrone (II) obtained by chlorination of indanthrone with gaseous chlorine or with sulphuryl chloride. The 3:3'-orientation of the chlorine atoms is assigned by Rowe² who gives the following methods of preparation: (1) chlorination of indanthrone with sulphuryl chloride or benzoyl chloride, (2) the action of nitric and hydrochloric acids on indanthrone and (3) synthesis from 3-chloro-1-bromo-2-aminoanthraquinone. According to Fraser-Thomson¹ and Rowe,³ Caledon Blue RC is 3:3'-dichloroindanthrone (III) prepared synthetically, as it cannot be prepared by direct halogenation. In Colour Index² the dye is formulated as a trichloro-derivative of indanthrone, prepared by the action of antimony pentachloride or sulphuryl chloride on indanthrone. It is also prepared by the action of chlorine on indanthrone suspended in sulphuryl chloride, thionyl chloride or antimony pentachloride. Rowe³ has described the preparation of Soledon Blue 2RCS, which is the tetrasulphuric ester of 3:3'-dichlorotetrahydroindanthrone by the oxidation of 3-chloro-2-aminoanthrahydroquinone disulphuric ester with hypochlorite or lead peroxide. Indanthrene Blue GC and Caledon Blue GC are mentioned in Colour Index² as the 3:3'-dibromo-derivatives of indanthrone.

Indanthrene Blue GCD has been regarded as being identical with Caledon Blue GCD. According to Rowe³ the former is largely 4:4'-dichloroindanthrone (II) obtained by direct chlorination. Indanthrene Blue BC, stated⁴ to contain more chlorine atoms than the dichloro derivative and probably prepared by direct chlorination, has been described as identical with Caledon Blue RC in Colour Index.² The authentic methods for the preparation of the IG dyes are, however, now available.⁵ Indanthrene Blue GCD is prepared by direct chlorination by passing chlorine in a solution of indanthrone in 91.5% sulphuric acid at 50–55° in the presence of a small quantity of manganese dioxide till the chlorinated product has a chlorine content of 5–8%. Indanthrene Blue BC is the higher chlorinated product, obtained by carrying the chlorination further till the chlorine content is 13.8 to 14% chlorine (Calc. for dichloroindanthrone: Cl, 13.9%).

While a series of halogenated indanthrones have become commercially available and numerous processes for their preparation have been patented, the mode of action of different chlorinating agents is largely unknown. According to Fraser-Thomson⁴ and Rowe³ direct halogenation of indanthrone attacks both the 3:3'-and the 4:4'-positions, but chiefly the latter. The 3:3'-dihalogeno-derivatives cannot be prepared in pure form by direct halogenation and hence have to be obtained synthetically.³ Methods of direct chlorination of indanthrone which claim to lead to the 3:3'-dichloro

derivative have, however, been reported in patents.⁶ Substitution in the 3:3'-positions is stated to scarcely affect the shade of indanthrone, while substitution in the 4:4'-positions causes greening of the attractive reddish blue shade of indanthrone.

It is obvious that, while preparation from a halogenated intermediate, in which the orientation of the halogen atoms is definite, will give a chloroindanthrone of authentic constitution, the position of the chlorine atoms in a product obtained by the direct chlorination of indanthrone needs to be proved. The present work was undertaken with a view to determining the constitution of commercial chloroindanthrones and investigating the orientation of the dichloroindanthrones prepared by chlorination of indanthrone with antimony pentachloride and sulphuryl chloride.

Antimony pentachloride was found to be a vigorous chlorinating agent, two chlorine atoms being readily introduced in indanthrone by reaction in boiling nitrobenzene for 15 minutes. It was observed that even when excess of antimony pentachloride is used and the reaction carried out for 3 hours, no further chlorine could be introduced. It would appear that antimony pentachloride specifically attacks two positions in indanthrone, and no further chlorination can then be effected. When dichloroindanthrone prepared with antimony pentachloride (subsequently referred to as IIA), the dichloroindanthrone prepared through the azine which will be described later, and 3:3'-dichloroindanthrone obtained from its solubilised derivative Soledon Blue 2RCS, were treated with antimony pentachloride, no further chlorination took place, so that the presence of two chlorine atoms in the indanthrone molecule prevents further action of antimony pentachloride.

The action of sulphuryl chloride was found to be markedly different from that of antimony pentachloride. When excess of sulphuryl chloride was used, the chlorination did not stop with the introduction of two chlorine atoms but proceeded further. By carefully controlling the experimental conditions a dichloroindanthrone was prepared.

Scholl and Berblinger⁷ have prepared a dichloroindanthrone by the action of hydrochloric acid on anthraquinoneazine, the product being claimed to be 4:4'-dichloroindanthrone without conclusive supporting evidence. Seeking such proof, dichloroindanthrone prepared according to Scholl and Berblinger⁷ was treated with hydrazine, so that the dihydrazinoindanthrone may be produced, but the reaction was not successful.

Atack and Soutar⁸ have described the preparation of 3:3'-dichloroindanthrone by self-condensation of 3-chloro-1-bromo-2-aminanthraquinone

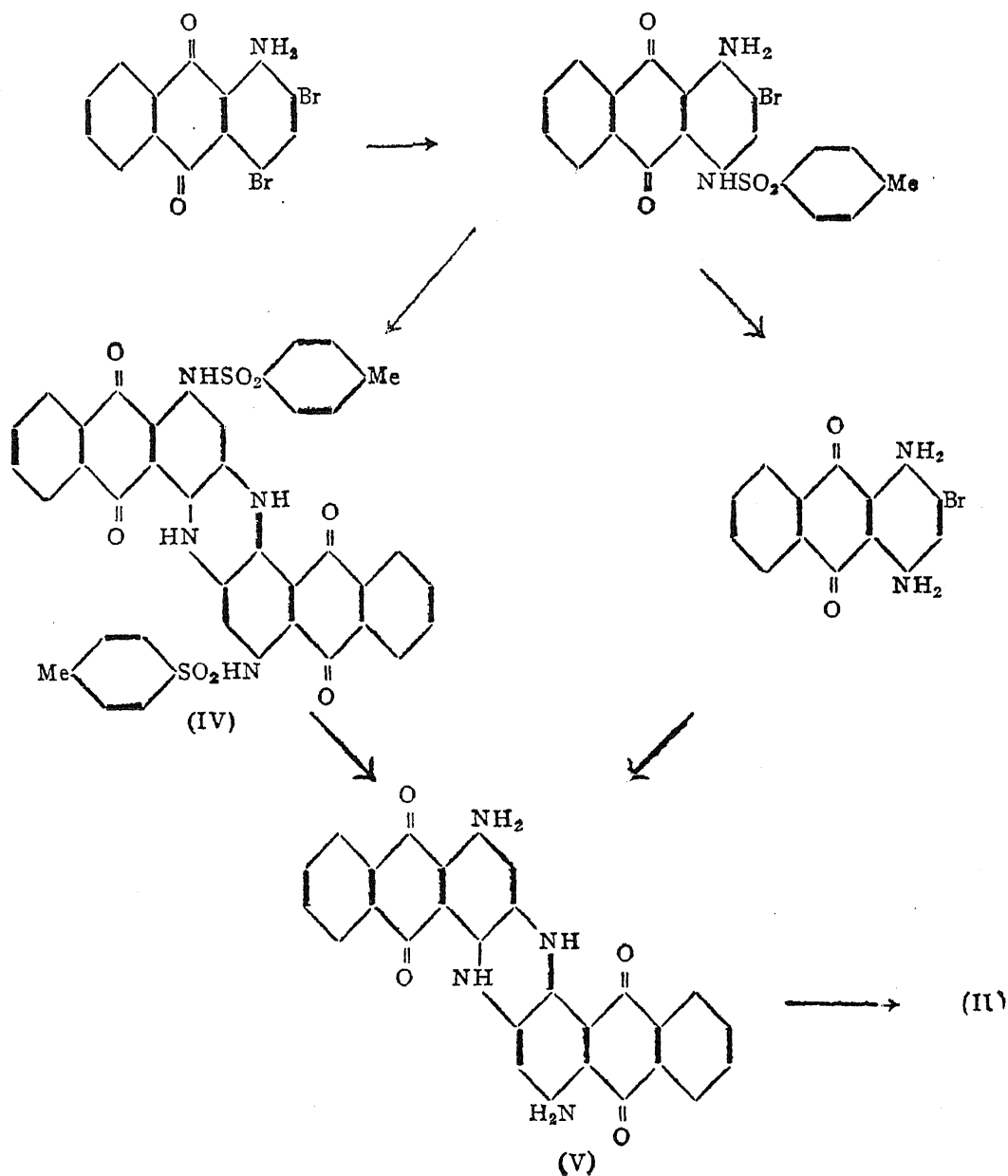
(m.p. 235°), which was obtained from 3-chloro-2-aminoanthraquinone by bromination in nitrobenzene. They prepared the latter, for which they have quoted m.p. of 221°, by chlorination of 2-aminoanthraquinone with gaseous chlorine in acetic acid or nitrobenzene. As 3-chloro-2-aminoanthraquinone prepared by unambiguous methods⁶ melts at 310°, while 1-chloro-2-aminoanthraquinone⁵ melts at 237°, it appeared likely that Attack and Soutar actually obtained the latter, rather than the 3-chloro-compound. Their chloro-bromo-2-aminoanthraquinone and its self condensation product would, therefore, be 1-chloro-3-bromo-2-aminoanthraquinone and 3:3'-dibromoindanthraquinone respectively. Direct chlorination of 2-aminoanthraquinone generally leads first to 3-chloro- and then to 1:3-dichloro-2-aminoanthraquinone, and to get 1-chloro-2-aminoanthraquinone it is necessary to acetylate 2-aminoanthraquinone before chlorination.^{9, 10} Fyfe¹¹ has, however, prepared 1-chloro-2-aminoanthraquinone by direct chlorination of 2-aminoanthraquinone in nitrobenzene, chlorobenzene and acetic acid without previously acetylating the amino group. When 2-aminoanthraquinone was chlorinated with sulphuryl chloride, 1-chloro-2-aminoanthraquinone (m.p. 237°) was obtained which was characterised by preparing its acetyl derivative (m.p. 241°) and comparison with authentic specimens of 1-chloro-2-aminoanthraquinone and its acetyl derivative.¹² Bromination of 1-chloro-2-aminoanthraquinone thus obtained gave 1-chloro-3-bromo-2-aminoanthraquinone, which melts at 238°, comparing well with the product prepared by Attack and Soutar⁷ (m.p. 235°) and claimed as 3-chloro-1-bromo-2-aminoanthraquinone. Self-condensation of 1-chloro-3-bromo-2-aminoanthraquinone now prepared gave 3:3'-dibromoindanthrone as expected.

For the purposes of the present work 3:3'-dichloroindanthrone¹³ was then synthesised by the self-condensation of 3:3'-dichloro-2-aminoanthraquinone.⁹

One of the methods for the synthesis of 4:4'-dichloroindanthrone would be from the hitherto unknown 1:4-dichloro-2-aminoanthraquinone obtainable by the cyclisation of *o*-(2':5'-dichloro-4'-amino) benzoylbenzoic acid. Attempts to prepare the latter acid by condensation of phthalic anhydride with 2:5-dichloroacetanilide in the presence of anhydrous aluminium chloride proved unsuccessful as 2:5-dichlorophenylphthalamic acid was obtained instead of the desired acid. Another route explored was through 4-chloro-2-bromo-1-aminoanthraquinone. Attempts to brominate 2-bromo-1-aminoanthraquinone gave 2:4-dichloro-1-aminoanthraquinone instead of the desired product. The only recorded method for the preparation of 2:4-dichloro-1-aminoanthraquinone is due to Guhmann *et al.*¹⁵

who obtained it synthetically from *m*-dichlorobenzene and phthalic anhydride in four steps; they were unsuccessful in obtaining it by direct chlorination by methods analogous to those used for the preparation of 2:4-dibromo-1-aminoanthraquinone. It is remarkable that contrary to the experience of the above workers direct chlorination of 1-aminoanthraquinone in glacial acetic acid gave 2:4-dichloro-1-aminoanthraquinone in excellent yield.¹⁶ The constitution of the latter was confirmed by the preparation of 1:2:4-trichloroanthraquinone by the Sandmeyer reaction and by deamination to 1:3-dichloroanthraquinone.

The utility of 2:4-dichloro-1-aminoanthraquinone, which has now become readily available, as a dyestuff intermediate was investigated. Thus



the N-benzoyl derivative was prepared, but was found to have poor substantivity to cotton. Condensation with *p*-toluidine and aniline gave 2-chloro-1-amino-4-*p*-toluidinoanthraquinone and 2-chloro-1-amino-4-anilinoanthraquinone which on sulphonation would lead to acid dyes. 2:4-Dichloro-1-aminoanthraquinone on diazotisation and coupling with β -naphthol gave a reddish brown dye. Syntheses of anthraquinone-acridones from the dichloro derivative are also being studied.

4-Chloro-2-bromo-1-aminoanthraquinone was prepared by the bromination of 4-chloro-1-aminoanthraquinone, but it did not give 4:4'-dichloroindanthrone by self-condensation. Attempts to replace the hydroxyl groups in 4:4'-dihydroxyindanthrone (Indanthrene Blue 5G) by chlorine atoms by the action of phosphorus pentachloride were also unsuccessful.

Another route for the synthesis of 4:4'-dichloroindanthrone was then investigated. 2-Bromo-1-amino-4-*p*-toluenesulphonamidoanthraquinone¹⁷ on condensation with itself gave the new 4:4'-di-*p*-toluenesulphonamidoindanthrone (IV) in 76 per cent. yield. Hydrolysis of (IV) with concentrated sulphuric acid gave a bluish green vat dye similar in properties to 4:4'-diaminoindanthrone (V), but with 1.5% lower nitrogen content. It was, however, found that (V) could be readily synthesised through 1:4-diamino-2-bromoanthraquinone.¹⁸ Treatment of (V) with concentrated sulphuric acid also resulted in a loss in nitrogen indicating a partial hydrolysis of the amino groups during the hydrolysis of (IV). Attempts to replace the amino groups by chlorine by the Sandmeyer reaction proved unsuccessful.

When 2-aminoanthraquinone was chlorinated with gaseous chlorine in nitrobenzene a new trichloro-2-aminoanthraquinone (m.p. 216°) was obtained. Fries and Hartmann¹⁴ obtained 1:3:4-trichloro-2-hydroxyanthraquinone by treating 2-aminoanthraquinone with gaseous chlorine in fuming hydrochloric acid and acetic acid and subsequently treating the reaction product with sodium acetate. By analogy the trichloro derivative obtained can be formulated as 1:3:4-trichloro-2-aminoanthraquinone. Self-condensation of the trichloro derivative did not give 3:4:3':4'-tetrachloroanthraquinone, but a brown dye containing less chlorine content.

The specific α -chlorinating action of antimony pentachloride has been observed by Steiner¹⁹ who obtained 1:4:5:8-tetrachloroanthraquinone by chlorination of anthraquinone with this reagent. While substitution of the α -positions (4, 5, 8, 4', 5' and 8') in indanthrone in direct chlorination can be regarded as more likely than the β -positions on account of the higher activity of the α -positions, there is no reason to assume, as Fraser-Thomson⁴ and Rowe³ have done, that the 4:4'-positions are first substituted and then

the 3:3'-positions, leaving the other available α -positions unsubstituted. Since antimony pentachloride unlike sulphuryl chloride is specific in introducing two atoms of chlorine, it is reasonable to regard the dichloroindanthrone (IIA) as a pure α : α' -disubstituted derivative, and probably the 4:4'-dichloro derivative, on the basis of its greater resistance to azine formation on treatment with oxidising agents as discussed later. The chlorinated indanthrones obtained by direct halogenation with sulphuryl chloride or gaseous chlorine are probably indanthrones substituted chiefly in the 5, 8, 5' and 8'-positions. Since a halogen atom substituted in the α -position in the anthraquinone molecule is much more reactive than a β -chlorine atom, chlorine atoms substituted in the α -positions in indanthrone should be more reactive than those in the β -positions. The lability of the chlorine atoms in dichloroindanthrones prepared by direct chlorination, 3:3'-dichloroindanthrone, and the commercial chloroindanthrones, towards boiling alkaline sodium hydrosulphite solution was then tested. It was found that the chlorine atoms in (IIA) were the least stable, as much as 57% of chlorine being lost after this treatment. At the other end of the scale was the synthetic 3:3'-dichloroindanthrone which lost about 24% chlorine, under identical conditions. Dehalogenation of (IIA) and 3:3'-dichloroindanthrone by heating with copper bronze resulted in a loss of 32% and 25% chlorine respectively. The above experiments give some supporting evidence to the exclusive α -orientation in (IIA).

Attempts to synthesise 4:4'-dichloroindanthrone unambiguously which could then be compared with (IIA), have so far been unsuccessful, and another approach to a solution of the problem was to convert (IIA) into di-*p*-toluenesulphonamidoindanthrone or diaminoindanthrone for comparison with the synthetic specimens (IV) or (V) respectively. Ammonolysis of (IIA) to give the diamino derivative in the presence of arsenic trioxide under pressure proved unsuccessful. Reaction of (IIA) with *p*-toluenesulphonamide resulted in partial substitution of the chlorine atoms by *p*-toluenesulphonamido groups. 3:3'-Dichloroindanthrone did not react with *p*-toluenesulphonamide under these conditions. While the synthesis of the *p*-toluenesulphonamido derivative from (IIA) could not be accomplished, the higher reactivity of the chlorine atoms in (IIA) as compared to 3:3'-dichloroindanthrone has given further evidence as regards their α -orientation in (IIA).

Pure chloroindanthrones were isolated from commercial Caledon Blue RC and GCD, Soledon Blue 2RCS and Indanthrene Blue BC and GCD, which represent the more important members of the group of commercial

chloroindantrones. The purified dyes were compared with the chloroindantrones now prepared, the comparison relating to (1) the shade on cotton yarn, (2) colour reactions,^{20, 21} (3) fastness to chlorine, (4) chlorine content, and (5) stability of chlorine to alkali and sodium hydrosulphite.

The crystallised dyes isolated from Caledon Blue RC and GCD, Soledon Blue 2RCS, and Indanthrene Blue BC analysed for dichloroindanthrone (Cl = 13.9%), but purified Indanthrene Blue GCD contained only 5.8% chlorine (calc. for monochloroindanthrone 7.5%). Although most of the properties of the different chlorinated indantrones were practically identical they could nevertheless be distinguished by the different reactivity of the chlorine atoms and by the colour reaction recently described by Derrett-Smith and Gee.²¹

The chlorine atoms in (IIA) were least stable to treatment with alkaline hydrosulphite, while those in the 3:3'-dichloroindanthrone were most stable, all the other chloroindantrones, occupying intermediate positions between these two extremes. The dichloroindanthrone obtained through the anthraquinoneazine does not appear to be the 4:4'-dichloro derivative as claimed by Scholl and Berblinger,⁶ being comparable in the stability of the chlorine to 3:3'-dichloroindanthrone. While the greater lability of the chlorine atoms in (IIA) in comparison with 3:3'-dichloroindanthrone suggests α -orientation, the test is beset with experimental difficulties and for the present can only be regarded as a rough distinction between α - and β -orientation of chlorine atoms in indanthrone.

Derrett-Smith and Gee²¹ have recently reported a colour reaction, involving treatment of the dyed yarn successively with acid permanganate and acid hydrogen peroxide, for distinguishing vat dyes such as halogenated indantrones, dibenzanthrones and certain grey and black dyes which could not be distinguished by their earlier tests.²⁰ The chlorinated indantrones are oxidised to different extents to the yellowazine by treatment with the potassium permanganate and hydrogen peroxide solutions, and it is possible to distinguish them by the colour changes observed in this test. Thus Indanthrene Blue RSN, GCD, BC and 3GT, Caledon Blue RN, 3GCT and GCPS which give greenish yellow to green colour changes are distinguished from Indanthrene Blue GT, BCD and BCS, Indanthrene Brilliant Blue RCL and Caledon Blue GCS, GCDS, RCS, BCD, 2R, Caledon Brilliant Blue 2RC, Soledon Blue 2RC and Alizanthrene Blue RC which give a bluish green to greenish blue colour change. On examination of the chlorinated indantrones by this test, it was found that Indanthrene Blue GCD and BC, which are dichloroanthrones prepared by the action of chlorine in sulphuric

acid,⁵ and dichloroindanthrone prepared by sulphuryl chloride gave a greenish yellow to yellow colour change while Caledon Blue GCD, RC, the dichloroindanthrone from Soledon Blue RC and 3:3'-dichloroindanthrone synthesised by us gave greenish blue to bluish green colour changes. The resistance to colour changes in 3:3'-dichloroindanthrone in this test is probably due to the proximity of chlorine atoms to the imino groups of indanthrone which retard oxidation of the latter to the azine. Caledon Blue RC, GCD and the parent vat dye from Soledon Blue RC are likewise resistant to oxidation and are probably 3:3'-dichloroindanthrone. The dichloroindanthrone (IIA) is distinguished from the other dichloroindanthrones obtained by direct chlorination by its similarity to 3:3'-dichloroindanthrone in this test. It is, however, different from the latter in the greater activity of the chlorine atoms which has been referred to earlier. If (IIA) is constituted as 4:4'-dichloroindanthrone and the other direct chlorinated indanthrones as indanthrones substituted largely in the 5, 8, 5', 8'-positions, the similarity of (IIA) to 3:3'-dichloroindanthrones in Derret-Smith and Gee's test can be readily accounted for, as the substitution of chlorine atoms in the 4:4'-positions should retard the oxidation of indanthrone to the azine to a greater extent than substitution in the more remote 5, 8, 5', 8'-positions, although to a less extent than substitution in the 3:3'-positions. The reactivity of the chlorine atoms in (IIA) and the other direct chlorinated indanthrones should be of the same order as they are all chiefly α -substituted derivatives.

Further and more conclusive evidence regarding the orientation of chlorine in the chlorinated indanthrones is being sought by a study of the degradation products²² and by a synthesis of 4:4'-dichloroindanthrone.

EXPERIMENTAL

Chlorination of indanthrone with antimony pentachloride.—Antimony pentachloride (3.2 c.c.; 4.4 mols) was added to a suspension of indanthrone (2.5 g.; 1 mol) in nitrobenzene (20 c.c.), and the mixture was boiled for 15 minutes. After cooling, the mixture was filtered and the residue was washed with alcohol and benzene and then treated with hot 1:1 hydrochloric acid to remove residual antimony. The residue was washed with water, dried (2.8 g.) and then crystallised from quinoline when blue needles of dichloroindanthrone (IIA) were obtained (Found: N, 5.4; Cl, 13.8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5.5; Cl, 13.9%).

Dichloroindanthrone prepared from Soledon Blue 2RCS, the dichloroindanthrone obtained through the azine which will be described later and

(IIA), when further treated with antimony pentachloride as above, remained unaffected.

Chlorination of indanthrone with sulphuryl chloride.—The action of sulphuryl chloride on indanthrone under various conditions was studied in order to determine the conditions for obtaining dichloroindanthrone. It was found that the optimum conditions were to heat a suspension of indanthrone (2 g.) in nitrobenzene (15 c.c.) with sulphuryl chloride (1 c.c.; 2.7 mols) with mechanical agitation for 2 hours. The mixture was cooled, filtered and the residue was washed with alcohol and then with water. Since the chloroindanthrone was partly oxidised to the azine it was treated with a solution of sodium hydrosulphite, filtered, washed and dried. Crystallisation from high boiling pyridine bases (b. p. 235–245°) gave dichloroindanthrone as blue needles (Found: Cl, 14.0. $C_{28}H_{12}O_4N_2Cl_2$ requires Cl, 13.9%). The dichloroindanthrone was similar to (IIA) in its properties and colour reactions although there were certain minor differences which will be described later. When the molar proportion of sulphuryl chloride was increased to 3.2 and 3.8 mols., the chlorine content of the product increased to 15.9 and 16.9% respectively; trichloroindanthrone requires Cl, 19.5%).

Action of hydrochloric acid on anthraquinoneazine.—Indanthrone (5 g.) was treated with potassium nitrate (4.5 g.) and concentrated sulphuric acid (41 c.c.) for 75 minutes and then diluted with acetic acid (166 c.c.) at 0°. The precipitated golden yellow anthraquinoneazine was washed successively with glacial acetic acid, 5% caustic soda solution and water. The azine (4.5 g.) was boiled with concentrated hydrochloric acid (50 c.c.) for 6 hours, during which the yellow azine changed to the blue chloroindanthrone. The chloroindanthrone obtained was washed free from hydrochloric acid and dried (4.5 g.) (Found: Cl, 3.7. $C_{28}H_{13}O_4N_2Cl$ and $C_{28}H_{12}O_4N_2Cl_2$ require Cl, 7.5 and 13.9% respectively). The chloroindanthrone was again subjected to the above treatment when the chlorine content increased to 8%. A third treatment gave a product containing 12.3% chlorine which, on further treatment, gave dichloroindanthrone crystallising from high boiling pyridine bases as blue needles (Found: N, 5.4; Cl, 13.8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5.5; Cl, 13.9%).

1-Chloro-2-aminoanthraquinone.—A solution of sulphuryl chloride (1.2 c.c.) in nitrobenzene (25 c.c.) was added dropwise during 4 hours to a boiling solution of 2-aminoanthraquinone (2 g.) and anhydrous sodium acetate (0.9 g.) in nitrobenzene (15 c.c.). After further boiling under reflux for 1 hour the mixture was worked up as usual. The crude product (2.3 g.),

m.p. 225°, when crystallised from alcohol, gave orange needles of 1-Chloro-2-aminoanthraquinone (VI), m.p. 237–238°, undepressed when mixed with a specimen (m.p. 236–38°) prepared by hydrolysis of 1-chloro-2-acetamidoanthraquinone (VII) (m.p. 240–42°) obtained by the chlorination of 2-acetaminoanthraquinone.^{1,2} The acetyl derivative, m.p. 241–242°, prepared from (VI) was identical with (VII).

1-Chloro-3-bromo-2-aminoanthraquinone.—A solution of bromine (1·2 c.c.) in glacial acetic acid (10 c.c.) was added gradually to a solution of 1-chloro-2-aminoanthraquinone (2 g.) in acetic acid (100 c.c.) at room temperature under stirring. After addition of more glacial acetic acid (50 c.c.), the mixture was boiled under reflux for 2 hours. The crystalline compound (2·35 g.), which separated on cooling the mixture to 0°, was recrystallised from glacial acetic acid when 1-chloro-3-bromo-2-aminoanthraquinone separated in yellowish brown needles, m.p. 238° (Found: N, 4·0; Cl, 10·4; Br, 23·9. $C_{14}H_7O_2NClBr$ requires N, 4·2; Cl, 10·6; Br, 23·8%). A solution of the amine (2g.) in acetic anhydride (10 c.c.) was acidified with a drop of concentrated sulphuric acid, vigorously shaken for 15 minutes and then diluted with water. The product after crystallisation from alcohol gave 1-chloro-3-bromo-2-acetamidoanthraquinone as shining yellow plates, m.p. 185–186° (Found: Cl, 9·5; Br, 20·8. $C_{16}H_9O_3NClBr$ requires Cl, 9·4; Br, 21·0).

3:3'-Dibromoindanthrone.—1-Chloro-3-bromo-2-aminoanthraquinone (1·7 g.), anhydrous sodium acetate (0·5 g.), anhydrous copper sulphate (0·1 g.) and nitrobenzene (20 c.c.) were boiled under reflux for 4 hours. After cooling, the mixture was filtered, washed with nitrobenzene, alcohol and hot water and dried (0·9 g.). On crystallisation from high boiling pyridine bases (b.p. 235–245°), 3:3'-dibromoindanthrone separated as lustrous blue needles with a copper reflex.

1:3:4-Trichloro-2-aminoanthraquinone.—Dry chlorine was passed through a suspension of 2-aminoanthraquinone (15 g.) in nitrobenzene (40 c.c.) at room temperature under vigorous stirring for 3 hours. The amine gradually dissolved and the golden yellow solution obtained was steam distilled to remove nitrobenzene and the residue obtained was dried and washed with ether. The product (6·6 g.) was crystallised from glacial acetic acid when 1:3:4-trichloro-2-aminoanthraquinone separated as pale yellow needles, m.p. 216° (Found: N, 4·3; Cl, 32·6. $C_{14}H_6O_2NCl_3$ requires N, 4·2; Cl, 32·5%). The amine (2 g.) when boiled with acetic anhydride (10 c.c.) for 2 hours gave 1:3:4-trichloro-2-acetamidoanthraquinone which crystallised from glacial acetic acid in pale yellow needles, m.p. 263° (Found;

N, 3.7; Cl, 29.0. $C_{16}H_8O_3NCl$ requires N, 3.8; Cl, 28.9%.) Self-condensation of the trichloroaminoanthraquinone gave noncrystallisable brown dye containing 12.5 per cent. chlorine as against the required value of 24.5 per cent. for tetrachloroindanthrone.

3:3'-Dichloroindanthrone.—1: 3-Dichloro-2-aminoanthraquinone⁹ (2 g.), anhydrous sodium acetate (1 g.), anhydrous copper sulphate (20 mg.) and nitrobenzene (15 c.c.) were boiled together for 24 hours. The mixture was cooled, filtered, and the residue was washed successively with boiling glacial acetic acid, alcohol and water. The product (0.4 g.) on crystallisation from high boiling pyridine bases gave blue needles of 3:3'-dichloroindanthrone (Found: N, 5.6; Cl, 13.8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5.5; Cl, 13.9%).

2:5-Dichlorophenylphthalamic acid.—2:5-Dichloroacetanilide (2 g., 1 mol) and phthalic anhydride (1.5 g., 1 mol) were added to a molten mixture of anhydrous aluminium chloride (10 g.) and sodium chloride (3 g.). The reaction mixture was heated for one hour under stirring at 180°, cooled, mixed with dilute hydrochloric acid and then filtered. The residue was extracted with 5% sodium hydroxide solution and the extract on acidification gave 2:5-dichloro-phenylphthalamic acid as a white precipitate. On crystallisation from dilute alcohol, colourless needles, m.p. 169° were obtained (Found: N, 4.4; Cl, 23.1. Acid equivalent, 312. $C_{13}H_8ONCl_2 \cdot CO_2H$ requires N, 4.5; Cl, 22.9%. Acid equivalent, 310). On hydrolysis with concentrated sulphuric acid at 100° phthalic acid was obtained.

2:4-Dichloro-1-aminoanthraquinone.—(1) Dry chlorine prepared from potassium permanganate (2 g.) and concentrated hydrochloric acid (20 c.c.) was passed at a moderate rate through a suspension of 2-bromo-1-aminoanthraquinone¹⁷ in glacial acetic acid (100 c.c.) kept vigorously stirred at 100°. As a test portion contained insufficient halogen, the mixture was further treated with the same amount of chlorine under similar conditions. The reaction mixture was poured into water and the precipitate was collected, washed, dried and crystallised from alcohol, when reddish brown needles of 2:4-dichloro-1-aminoanthraquinone were obtained, m.p. 205°. Guhelmann *et al.*¹⁵ give m.p. 205–6° (Found: N, 4.9; Cl, 24.2. Calculated for $C_{14}H_7O_2NCl_2$ N, 4.8; Cl, 24.3%).

(2) Dry chlorine from potassium permanganate (10 g.) and concentrated hydrochloric acid (75 c.c.) was passed in a suspension of 1-aminoanthraquinone (13.5 g.) in glacial acetic acid (140 c.c.) at such a rate that the reaction was completed in 3 hours. During the reaction the mixture was kept well agitated and the temperature was maintained at 100°. The reaction mixture was finally boiled for a short time and then cooled to 0°. The

product which separated was washed with a little acetic acid and dried, m.p. 202° (15 g.). The mother liquor on concentration gave a second crop of the product (1 g.). On recrystallisation from alcohol reddish brown needles of 2:4-dichloro-1-aminoanthraquinone were obtained, m.p. 205°.

A solution of 2:4-dichloro-1-aminoanthraquinone (2 g.) in acetic anhydride (30 c.c.) and concentrated sulphuric acid (2 drops) was vigorously shaken for 30 minutes and then diluted with water, when the *acetyl* derivative was obtained. Crystallisation from glacial acetic gave orange needles which did not melt upto 360° (Found: N, 4.3; Cl, 21.2. $C_{18}H_9O_3NCl_2$ requires N, 4.2; Cl, 21.3%).

2:4-Dichloro-1-benzamidoanthraquinone.—The amine (2 g.) was dissolved in benzoyl chloride (10 c.c.) and at 100° the solution was acidified with two drops of concentrated sulphuric acid. After agitation for 30 minutes, the *benzoyl* derivative was obtained on dilution with water, and it crystallised from solvent naphtha in yellow needles, m.p. 217° (Found: N, 3.4; Cl, 17.8. $C_{21}H_{11}O_3NCl_2$ requires N, 3.5; Cl, 17.9%). The red alkali-hydro-sulphite vat had practically no affinity for cotton.

2:4-Dichloroanthraquinone-1-azo-β-naphthol.—2:4-Dichloro-1-aminoanthraquinone (1.5 g.) was dissolved in glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (1 c.c.) was added and the mixture was boiled for a few minutes. After cooling to room temperature, sodium nitrite (0.4 g.) was added and the mixture was left for 15 minutes and then coupled with an alkaline solution of β-naphthol (0.9 g.) below 25°. After leaving overnight the *azo dye* was filtered, precipitated from concentrated sulphuric acid and finally crystallised from pyridine, when reddish brown needles were obtained, m.p. 241° (Found: N, 6.1. Cl, 15.7. $C_{24}H_{12}O_3N_2Cl_2$ requires N, 6.3; Cl, 15.9%).

2-Chloro-1-amino-4-(p-toluidino)-anthraquinone.—2:4-Dichloro-1-aminoanthraquinone (3.0 g., 1 mol), p-toluidine (5 g.; 5 mols), anhydrous sodium acetate (1 g.), anhydrous copper sulphate (50 mg.), precipitated copper (50 mg.) and amyl alcohol (30 c.c.) were boiled under reflux for 7 hours, and the mixture was worked up as usual. The crude product (2.9 g.; yield 81%), m.p. 231–33°, crystallised from solvent naphtha in violet plates, m.p. 238–39°.

2-Chloro-1-amino-4-anilinoanthraquinone.—2:4-Dichloro-1-aminoanthraquinone (1.45 g.), aniline (2.3 c.c.), anhydrous sodium acetate (0.5 g.), anhydrous copper sulphate (50 mg.), precipitated copper (50 mg.) and amyl alcohol (30 c.c.) when boiled under reflux for 10 hours gave the *anilino derivative* which crystallised from solvent naphtha in reddish blue plates, m.p.

232–33° (Found: N, 8.1; Cl, 10.3. $C_{20}H_{13}O_2N_2Cl$ requires N, 8.0; Cl, 10.2%).

4-Chloro-2-bromo-1-aminoanthraquinone.—A solution of bromine (1.2 c.c.; 1 mol) in glacial acetic acid (10 c.c.) was gradually added to a solution of 4-chloro-1-aminoanthraquinone (5 g.; 1 mol) in acetic acid (100 c.c.) at room temperature with mechanical agitation. The mixture was boiled under reflux for 2 hours and then cooled to 0°. The product which separated (6.1 g.) was recrystallised from glacial acetic acid when the *bromo derivative* separated as red needles, m.p. 209° (Found: N, 4.0; Cl, 10.5; Br, 24.0. $C_{14}H_7O_2NCl$ requires N, 4.2; Cl, 10.6; Br, 23.8%). A solution of the compound (1.5 g.) in benzoyl chloride (10 c.c.) when treated with a drop of concentrated sulphuric acid at 100° and agitated for 15 minutes gave the *benzoyl derivative* which crystallised from solvent naphtha in pale yellow needles, m.p. 228° (Found: N, 3.0; Cl, 8.2; Br, 18.0. $C_{21}H_{11}O_3NClBr$ requires N, 3.2; Cl, 8.1; Br, 18.2). The benzoyl derivative gave a red alkaline hydrosulphite vat which had very little substantivity for cotton.

4-Chloro-1-benzamidoanthraquinone.—4-Chloro-1-aminoanthraquinone was benzoylated in the presence of sulphuric acid. The benzoyl derivative crystallised in golden yellow needles from solvent naphtha, m.p. 240° (Found: N, 3.7, Cl, 9.7. $C_{21}H_{12}O_3NCl$ requires N, 3.9; Cl, 9.8).

4:4'-di-p-toluenesulphonamidoindanthrone (IV).—2-Bromo-1-amino-4-*p*-toluenesulphonamidoanthraquinone (2.81 g.), prepared according to Ullmann and Eiser,¹⁷ fused sodium acetate (0.6 g.), anhydrous copper sulphate (0.12 g.) and nitrobenzene (40 c.c.) were boiled under reflux for 48 hours. The mixture was filtered while hot and then washed successively with nitrobenzene, boiling toluene, benzene and finally with methyl alcohol. The residue was extracted with hot water, leaving 4:4'-*di-p*-toluenesulphonamidoindanthrone as dark greenish blue needles possessing a reddish blue lustre (1.76 g.; yield 76%) (Found: N, 7.0%. $C_{42}H_{28}O_8N_4S_2$ requires N, 7.2%). The compound gave a pale blue shade on cotton from a blue alkaline hydrosulphite vat which was only partly exhausted at the end of 45 minutes of dyeing. When the compound (1.4 g.) was treated with concentrated sulphuric acid (25 c.c.) at 50° for 3 hours it gave 4:4'-diaminoindanthrone as a greenish blue precipitate which dyed a bluish green shade on cotton. The latter, however, contained only 10.3% nitrogen as against 11.9% required for diaminoindanthrone indicating a loss of nitrogen during the hydrolysis of the *p*-toluenesulphonamido derivative.

4:4'-Diaminoindanthrone.¹⁸—A mixture of 2-bromo-1:4-diaminoanthraquinone¹⁷ (1.0 g.), copper bronze (0.1 g.), fused sodium acetate (0.5 g.)

and nitrobenzene (8.4 c.c.) was vigorously boiled under reflux for 6 hours at 230–240°. The mixture was filtered while hot and the residue was extracted repeatedly with boiling toluene till the filtrate was nearly colourless. The residue was washed with methyl alcohol with water and then boiled with concentrated hydrochloric acid. It was washed free from acid and dried, when 4:4'-diaminoindanthrone was obtained as an olive black product (0.62 g.) giving a bluish green shade on cotton (Found: N, 11.9. $C_{28}H_{16}O_4N_4$ requires N, 11.9%). On treatment with concentrated sulphuric acid at 50–60° for 3 hours the nitrogen content of the product decreased to 9.2%.

Purification of commercial chloroindanthrones.—The general method of purification was to remove water-soluble diluents (mainly sodium bicarbonate), then boil with 5% hydrochloric acid wash and crystallise from high boiling pyridine bases, when the pure dye usually separated as blue needles. Soledon Blue 2RCS was oxidised with hydrochloric acid and sodium nitrite to dichloroindanthrone which was then purified by crystallisation. Estimation of sulphuric acid liberated by hydrolysis indicated the dye to be the sodium salt of the tetrasulphuric ester of dichlorotetrahydroindanthrone.

Comparison of chloroindanthrones.—The pure chloroindanthrones isolated from the commercial dyes and the pure dyes now prepared were compared with regard to the properties mentioned earlier, as well as the following, and the results are summarised in Table I.

TABLE I

Dye	% Chlorine content	% Chlorine content after alkali hydro-sulphite treatment	% Chlorine loss	Colour reactions. 20' 21				Acid $KMnO_4$ and H_2O_2
				Acid vat	Alkaline vat	Sulphuric acid	Nitric acid group	
Indanthrone Blue GCD	5.8	4.94	14.8	Violet	Blue	Brown		Green-yellow
Indanthrone Blue BC	13.0	5.83	55.1	Blue	Blue	Greenish Brown	D	Yellow-green
Caledon Blue GCD	13.9	8.64	37.8	do	do	do	do	Blue-green
Caledon Blue RC	13.9	8.62	38.0	do	do	do	do	do
Vat dye from Soledon Blue 2RCS	13.9	10.42	25.0	do	Greenish blue	do	do	do
3:3'-Dichloroindanthrone	13.9	10.60	23.7	do	do	do	do	do
Dichloroindanthrone (IIA)	13.8	5.91	57.2	do	Blue	do	do	do
Dichloroindanthrone from sulphuryl chloride	14.0	7.58	45.8	do	do	do	do	Yellow-green
Dichloroindanthrone from the azine	13.9	10.61	23.7	do	Greenish blue	do	do	Blue-green

Colour reactions.—The colour reactions described by Bradley and Derrett-Smith²⁰ and Derrett-Smith and Gee²¹ for the characterisation of vat dyes were examined (Table I).

Stability of the chlorine in the dyes.—The pure, finely powdered dye (0.5 g.) was treated with a solution of sodium hydroxide (3.0 g.) and sodium hydrosulphite (2.5 g.) in water (250 c.c.) at 60–65° for 3 hours. After cooling, the dye was recovered by air-oxidation, washed till free from chlorides and sulphates, dried and its chlorine content was then determined.

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SUMMARY

Attempts to determine the orientation of the chlorine atoms in some of the commercial chlorinated indantrones and in the dichloroindantrones prepared by the action of antimony pentachloride and sulphuryl chloride on indanthrone and by the action of hydrochloric acid on anthraquinone-azine are described. The higher reactivity of the chlorine atoms in the direct chlorinated indantrones suggests α -orientation. The dichloroindanthrone (IIA) from antimony pentachloride is distinguished from the other chloroindantrones obtained by direct chlorination by its greater resistance to azine formation on treatment with oxidising agents. The 4:4'-orientation is, therefore, suggested for the chlorine atoms in (IIA), and substitution in the 5, 8, 5', 8' positions in the other direct chlorinated indantrones. Antimony pentachloride was found to be specific in introducing two chlorine atoms in indanthrone. 4:4'-Di-*p*-toluenesulphonamidoindanthrone (IV) has been synthesised.

2:4-Dichloro-1-aminoanthraquinone has been prepared by an improved method and its utility as a dyestuff intermediate has been studied. A few other halogenated aminoanthraquinones and their acyl derivatives which do not appear to have been described in literature have been synthesised.

REFERENCES

1. Fraser-Thomson .. *J. Soc. Dyers Col.*, 1936, 52, 240.
2. Rowe .. *Colour Index*, 1924.
3. .. *The Development of the Chemistry of Commercial Synthetic Dyes* (1856-1938), 76, 85.
4. Fraser-Thomson .. *Thorpe's Dict. App. Chem.*, 4th Ed., I, 414.
5. .. *B. I. O. S. Final Rep.*, 987, 11.
6. .. U.S.P., 2,205,418 ; 2,413,483; 2,413,514.
7. Scholl and Berblinger .. *Ber.*, 1903, 36, 3434.
- , — and Mansfield .. *Ibid.*, 1907, 40, 322.
8. Atack and Soutar .. *J. Soc. Chem. Ind.*, 1922, 41, 170 A ; B.P. 134,166 ;
 F.P. 774,702.
9. Ullmann and Junghans .. *Annalen*, 1913, 399, 316.
10. Houben .. *Das Anthracen und die Anthrachinone*, Georg Thieme,
 Leipzig, 1929.
11. Fyfe .. *App. Chem. Rep.*, 1922, 7, 88; B.P. 173,166.
12. .. D.R.P., 199,758.
13. .. U.S.P., 2,126,456.
14. Fries and Hartmann .. *Ber.*, 1921, 54 B, 193.
15. Guhelmann *et al.* .. *Ind. Eng. Chem.*, 1929, 21, 1231.
16. Bedekar and Venkataraman .. *Indian Pat.* 34211.
17. Ullmann and Eiser .. *Ber.*, 1916, 49, 2156.
18. .. D.R.P. 193,121.
19. Steiner .. *Monatsh*, 1915, 36, 825.
20. Bradley and Derrett-Smith .. *J. Soc. Dyers Col.*, 1940, 56, 97.
21. Derrett-Smith and Gee .. "Recent Advances in the Theory and Practice of
 Dyeing," *Soc. Dyers Col. Symposium*, 1947, 37.
22. Scholl and Edlbacher .. *Ber.*, 1911, 44, 1727.