

ANTHRAQUINONE AND ANTHRONE SERIES

Part V. Chlorinated 6-Aminoanthraquinoneacridones

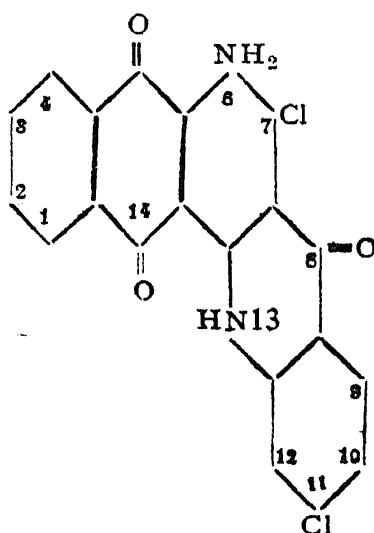
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INDANTHRENE Turquoise Blue GK and 3GK¹ are two vat dyes of the anthraquinone series, marketed by the I. G., which give turquoise blue shades with high fastness to light (7-8) and washing (4-5), but moderate fastness to chlorine (3) and soda boil (3). Both the dyes are dyed in the cold, but are distinguished from other dyes of the IK class in that they are applied from a long liquor (1:30) without the addition of common salt and the dyeings are oxidised in water, since the usual air oxidation gives redder and bluer shades.

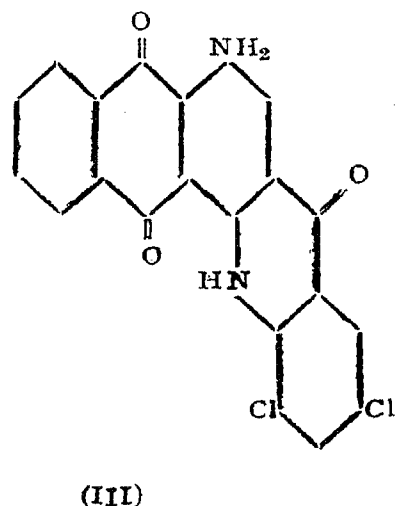
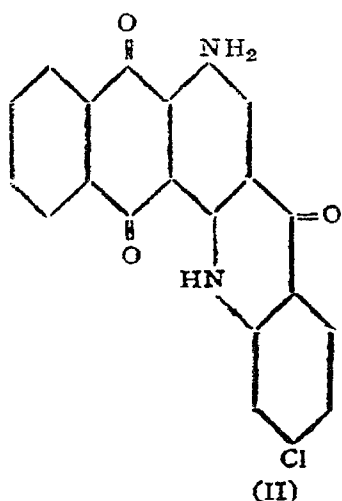
Rowe² has described Indanthrene Turquoise Blue GK and 3GK as aminoanthraquinoneacridones such as (I). The trivial name anthraquinoneacridone is used in this paper for the ring system (I) and the substituents are numbered as indicated. Indanthrene Turquoise Blue GK has been recently stated to be 6-amino-11-chloroanthraquinoneacridone (II).³



(I)

Elementary analysis of purified and crystallized Indanthrene Turquoise Blue GK indicated the presence of only one atom of chlorine, corresponding to the molecular formula $C_{21}H_{11}O_3N_2Cl$. Analysis of Indanthrene Turquoise Blue 3GK indicated the presence of two chlorine atoms and the molecular formula $C_{21}H_{10}O_3N_2Cl_2$. The present work deals with the syntheses of chloroaminoanthraquinoneacridones, firstly to determine the

constitution of Indanthrene Turquoise Blue GK and 3GK and secondly with a view to examine these compounds as vat dyes. Indanthrene Turquoise Blue GK and 3GK have now been shown to be 11-chloro-6-amino-

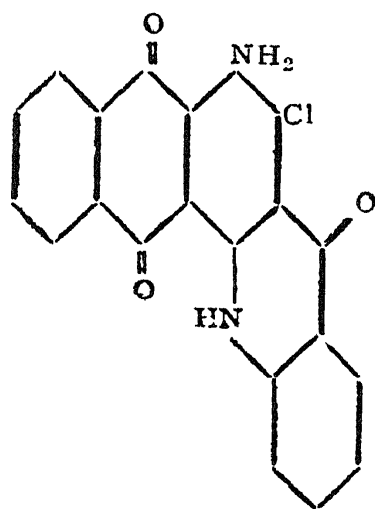


anthraquinoneacridone (II) and 10:12-dichloro-6-aminoanthraquinoneacridone (III) respectively.

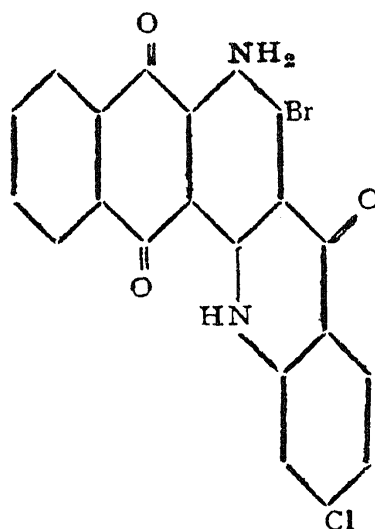
The general method for the synthesis of anthraquinoneacridones consists in the removal of a molecule of water from arylaminoanthraquinones in which there is an *ortho* carboxyl group, which may be present in the anthraquinone or in the aryl half. The cyclization of the intermediate carboxylic acids to the acridones can be brought about by treatment with concentrated sulphuric acid⁴ or with chlorosulphonic acid⁵ or by conversion of the carboxylic acid to the acid chloride and subsequent treatment with aluminium chloride.⁶ Aminoanthraquinoneacridones can be synthesized by the condensation of 4-bromo-1-aminoanthraquinone-2-sulphonic acid with anthranilic acid in aqueous solution in the presence of copper bronze or copper salts and sodium carbonate, the cyclization of the acid and the removal of the sulphonic group being effected simultaneously by treatment of the condensation product with chlorosulphonic acid or fuming sulphuric acid.⁷ Alternatively, 4-chloro-1-aminoanthraquinone or 2:4-dihalogeno-1-aminoanthraquinone can be condensed with anthranilic acid or its halogeno derivatives and the resulting intermediate acid cyclized to the desired acridone by means of sulphuric acid or chlorosulphonic acid.

The synthesis of monochloroaminoanthraquinoneacridones in which the chlorine atom is either in the anthraquinone or in the benzene half of the molecule was first undertaken. Condensation of 2:4-dichloro-1-aminoanthraquinone⁸ with anthranilic acid gave N-1'-(3'-chloro-4'-amino)-anthraquinonylanthranilic acid which was cyclized by means of chlorosulphonic acid

to 7-chloro-6-aminoanthraquinoneacridone (IV). Attempts to cyclize the carboxylic acid with sulphuric acid led to sulphonated products. The dye (IV) gave a greener shade on cotton than Indanthrene Turquoise Blue GK. Another distinction between the two dyes was the facile dehalogenation of (IV) to 6-aminoanthraquinoneacridone by treatment with caustic soda and sodium hydrosulphite at room temperature (29-30°) for an hour; under similar conditions Indanthrene Turquoise Blue GK was unaffected. The dye (IV) can, however, be applied to cotton by the cold-dyeing or



(IV)



(V)

IK process without danger of dehalogenation, if dyeing is commenced immediately after vatting. It has been noticed that 3:3'-dichloro-4:4'-diaminoindanthrone (Indanthrene Green 2B; Caledon Green 2B; Colour Index No. 1116) also undergoes dehalogenation by treatment with aqueous sodium hydroxide and hydrosulphite at 65-70°, but it is applicable by the hot-dyeing or IN process and continues to be in the commercial range of vat colours. A detailed examination of dehalogenation in the anthraquinone series will be reported later.

The parent aminoanthraquinoneacridone was prepared by a second route by condensing anthranilic acid with 4-chloro-1-aminoanthraquinone and subsequent cyclization of N-1'-(4'-amino)-anthraquinonylanthranilic acid by means of chlorosulphonic acid; the acridone can also be prepared from leuco-1:4-diaminoanthraquinone and *o*-chlorobenzoic acid,⁹ or by condensing 1:4-dichloroanthraquinone with anthranilic acid, cyclizing and replacing the chlorine atom by the amino group through the *p*-toluenesulphonamide.¹⁰

Monochloroanthraquinoneacridones having a chlorine atom in the benzene half of the molecule were then synthesized. 5-Chloroanthranilic acid, prepared by the chlorination of anthranilic acid with sulphuryl chloride

in the presence of anhydrous sodium acetate in carbon tetrachloride, was condensed with 4-chloro-1-aminoanthraquinone and the intermediate carboxylic acid was cyclized by sulphuric acid to 10-chloro-6-aminoanthraquinoneacridone. This dyed a greener shade than Indanthrene Turquoise Blue GK. The absorption spectra of the two dyes were also found to be different (Fig. 1). 4-Chloroanthranilic acid, prepared by oxidation of 4-chloro-N-acetyl-*o*-toluidine and subsequent deacetylation,¹¹ was condensed with 4-chloro-1-aminoanthraquinone and the product obtained was cyclized to give (II). The acridone (II) was found to be identical in all respects with pure Indanthrene Turquoise Blue GK. It was also prepared by condensing 1:4-diaminoanthraquinone with 2:4-dichlorobenzoic acid and cyclization of the intermediate acid. The absorption spectra of the

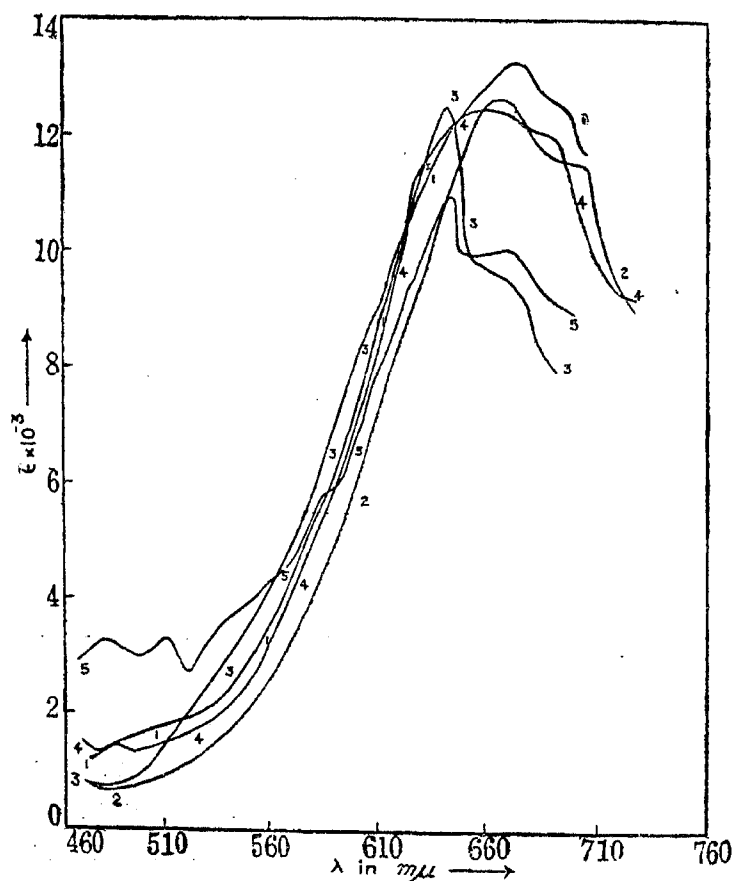


FIG. 1. Absorption Spectra of:

1. 6-Aminoanthraquinoneacridone
 2. 10-Chloro-6-aminoanthraquinoneacridone
 3. Indanthrene Turquoise Blue GK and 11-Chloro-6-aminoanthraquinoneacridone
 4. Indanthrene Turquoise Blue 3 GK and 10:12-dichloro-6-aminoanthraquinoneacridone
 5. 7-Chloro-6-aminoanthraquinoneacridone
- Solvent — quinoline.

synthetic dye (II) and of Indanthrene Turquoise Blue GK in quinoline in the visible range also showed their complete identity (Fig. 1).

The stability of both the chlorine atoms in Indanthrene Turquoise Blue 3GK to treatment with sodium hydroxide and hydrosulphite under the usual dyeing conditions indicated that there is no chlorine atom adjacent to the amino group in the anthraquinone nucleus as in (IV) and probably that both of these are in the benzene half of the anthraquinoneacridone. 3:5-Dichloroanthranilic acid¹² was condensed with 4-chloro-1-aminoanthraquinone and the intermediate N-1'-(4'-amino)-anthraquinonyl-3:5-dichloroanthranilic acid was cyclized with sulphuric acid to (III). This dye and pure Indanthrene Turquoise Blue 3GK were found to be identical in crystalline form, colour of the vat, shade on cotton yarn and colour reactions. The absorption spectra in the visible range of the synthetic dye (III) and pure Indanthrene Turquoise Blue 3GK were also identical (Fig. 1). The dye (III) was also synthesized by an alternative route starting from 4-bromo-1-aminoanthraquinone-2-sulphonic acid and 3:5-dichloroanthranilic acid; the condensation was effected in aqueous solution and the product was cyclized and desulphonated. 7:11-Dichloro- and 7:10-dichloro-6-aminoanthraquinoneacridones, isomers of (III), containing one chlorine atom in the anthraquinone half, were also synthesized, starting from 2:4-dichloro-1-aminoanthraquinone and 4-chloro- and 5-chloroanthranilic acid respectively. The dyes gave shades on cotton which were different from those given by Indanthrene Turquoise Blue 3GK and which had good fastness properties (light 7, chlorine 3-4, soda boil 3-4; and light 7-8, chlorine 3, soda boil 2-3 respectively). Indanthrene Blue 8GK, which is apparently not marketed at the present time, has been stated to be 7:10-dichloro-6-aminoanthraquinoneacridone.¹³

7:10:12-Trichloro-6-aminoanthraquinoneacridone, prepared from 2:4-dichloro-1-aminoanthraquinone and 3:5-dichloroanthranilic acid, gave a greenish blue shade possessing good fastness to light (7) and moderate fastness to chlorine (3) and soda boil (4). When this trichloro compound was treated with aqueous sodium hydroxide and hydrosulphite at 30° for one hour, the product on crystallization contained only two chlorine atoms and was identical with Indanthrene Turquoise Blue 3GK. A dihalogeno-aminoanthraquinoneacridone having a bromine atom in the anthraquinone nucleus and a chlorine in the benzene half (V) was synthesized in the usual manner by the condensation of 2:4-dibromo-1-aminoanthraquinone with 4-chloroanthranilic acid. It dyed cotton green-blue shade from a red-brown vat.

EXPERIMENTAL

Purification of Indanthrene Turquoise Blue GK:

The commercial dye (paste) (50 g.) was boiled with 5% hydrochloric acid (200 c.c.) for one hour and filtered. The residue (8 g.) crystallized from nitrobenzene in blue needles (Found: N, 7.1; Cl, 9.4. $C_{21}H_{11}O_3N_2Cl$ requires N, 7.4; Cl, 9.5%). The blue shade on cotton (I.K. process) has light fastness 7, chlorine 3, and soda boil 2-3. The vat is brown-violet in colour.

Purification of Indanthrene Turquoise Blue 3GK (powder fine for dyeing):

The commercial dye (5 g.) was boiled with 5% hydrochloric acid (100 c.c.) for one hour. After allowing the mixture to settle for two days, the acid extract was decanted off and the dye was isolated by centrifuging the suspension and washed. The purified dye (2.7 g.) crystallized from boiling nitrobenzene as long blue needles (Found; C, 61.5; H, 2.1; N, 7.3; Cl, 16.9. $C_{21}H_{10}O_3N_2Cl_2$ requires C, 61.6; H, 2.4; N, 6.9; Cl, 17.2%). The pure dye dyes a turquoise blue shade on cotton from a brown-violet vat (fastness to light 7; chlorine 3-4; soda boil 3).

5-Chloroanthranilic acid:

Anthranilic acid (1.37 g.) and anhydrous sodium acetate (0.9 g.) were suspended in carbon tetrachloride (20 c.c.) and a solution of sulphuryl chloride (1.49 g.; 1.1 mol.) in carbon tetrachloride (2 c.c.) was added slowly under stirring. After 3 hours, the suspension was filtered, the residue suspended in water and neutralised by the addition of sodium acetate. The crude 5-chloroanthranilic acid (1.3 g.), m.p. 205°, crystallized from alcohol in needles, m.p. 211-2° (Found: Cl, 20.5. Calc. for $C_7H_6O_2NCl$: Cl, 20.7%).

7-Chloro-6-aminoanthraquinoneacridone (IV):

2:4-Dichloro-1-aminoanthraquinone (2.92 g.), anthranilic acid (2.05 g.) anhydrous potassium acetate (1.96 g.) and copper bronze (0.06 g.) were refluxed under stirring with amyl alcohol (20 c.c.) for 8 hours. The blue mass was filtered hot, washed with alcohol, boiled with dilute hydrochloric acid (100 c.c.) for 30 minutes, filtered and washed. On crystallization from glacial acetic acid, N-1'-(3'-chloro-4'-amino)-anthraquinonylanthranilic acid was obtained as long blue needles (3.4 g.), m.p. 291-2° (Found: N, 6.9; Cl, 8.9. $C_{21}H_{13}O_4N_2Cl$ requires N, 7.1; Cl, 9.0%). It dissolves in alcoholic ammonia giving a blue solution. On treating the carboxylic acid with concentrated sulphuric acid at 98-100° or with 20% fuming sulphuric acid at room temperature, a water-soluble sulphonic acid was obtained.

The carboxylic acid (1.5 g.) was dissolved in chlorosulphonic acid (12.7 c.c.); after keeping in a stoppered flask for 24 hours, the red-brown solution was poured into a porcelain dish and allowed to stand in moist air for 10 days, when a red-violet product separated. This was filtered, and washed with hot alcohol until the washings were colourless. The residue (1.0 g.) crystallized from nitrobenzene in blue plates. The dye (IV) does not melt up to 360° (Found: N, 7.4; Cl, 9.4. $C_{21}H_{11}O_3N_2Cl$ requires N, 7.4; Cl, 9.5%). The vat is red-brown in colour and the green-blue shade on cotton has fastness grades of light 7, chlorine 3, and soda boil 2.

10-Chloro-6-aminoanthraquinoneacridone:

4-Chloro-1-aminoanthraquinone (2.4 g.), 5-chloroanthranilic acid (7.1 g.), anhydrous sodium acetate (1.0 g.), copper bronze (0.05 g.), anhydrous copper sulphate (0.1 g.) and amyl alcohol (40 c.c.) were heated at 140° for 24 hours. After removal of the solvent by steam-distillation, the product was filtered off and washed successively with sodium carbonate solution and hot dilute hydrochloric acid. N-1'-(4'-Amino)-anthraquinonyl-5-chloroanthranilic acid crystallized from glacial acetic acid in blue needles (2.1 g.), m.p. 265–6° (Found: Cl, 9.0. $C_{21}H_{13}O_4N_2Cl$ requires Cl, 9.0%). The above acid (1.02 g.), boric acid (0.05 g.) and concentrated sulphuric acid (12 c.c.) were heated at 150° for 15 minutes. The resultant acridone was isolated (0.6 g.) and it crystallized from nitrobenzene in blue needles which did not melt up to 360° (Found: N, 7.6; Cl, 9.3. $C_{21}H_{11}O_3N_2Cl$ requires N, 7.4; Cl, 9.5%). The fastness grades of the blue-green shade on cotton were light 7, chlorine 3, and soda boil 3.

6-Aminoanthraquinoneacridone:

4-Chloro-1-aminoanthraquinone (2.58 g.), anthranilic acid (6.8 g.), anhydrous sodium acetate (1.0 g.), copper bronze (0.1 g.), anhydrous copper sulphate (50 mg.) and amyl alcohol (40 c.c.) were refluxed for 24 hours. Amyl alcohol was removed by steam-distillation and the residue was washed with hot sodium carbonate and dilute hydrochloric acid, and dried (3.7 g.). Crystallization from glacial acetic acid gave N-1'-(4'-amino)-anthraquinonylanthranilic acid in blue needles, m.p. 263° (Found: N, 7.4. $C_{21}H_{14}O_4N_2$ requires N, 7.8%). The acid (0.5 g.) was dissolved in chlorosulphonic acid (6.0 c.c.) and the solution warmed to 35–40° for 5 minutes. The red-brown solution was poured on crushed ice, and the blue precipitate collected (0.4 g.). The acridone crystallized from nitrobenzene in plates (Found: N, 8.3. Calc. for $C_{21}H_{12}O_3N_2$: N, 8.2%). The dye gives a light blue shade on cotton from a brown vat (fastness to light 6, chlorine 3, soda boil 2).

11-Chloro-6-aminoanthraquinoneacridone (II):

(a) 4-Chloro-1-aminoanthraquinone (1.2 g.), 4-chloroanthranilic acid (0.9 g.), anhydrous copper sulphate (0.1 g.), copper bronze (20 mg.), anhydrous sodium acetate (0.8 g.) and amyl alcohol (40 c.c.) were refluxed for 24 hours and N-1'-(4'-amino)-anthraquinonyl-4-chloroanthranilic acid was isolated as usual and crystallized in blue needles from acetic acid (Found: Cl, 8.9. $C_{21}H_{13}O_4N_2Cl$ requires Cl, 9.0%).

The acid (0.5 g.) was treated with concentrated sulphuric acid (5 c.c.) at 98° for 20 minutes, during which the colour of the solution changed from blue to bottle green. On cooling and pouring on ice, the product (II; 0.3 g.) was obtained which crystallized from nitrobenzene in blue needles (Found: N, 7.4; Cl, 9.3. $C_{21}H_{11}O_3N_2Cl$ requires N, 7.4; Cl, 9.5%). The above dye and pure Indanthrene Turquoise Blue GK showed identical dyeing properties and colour reactions.¹⁴

(b) Sublimed 1:4-diaminoanthraquinone (2.38 g.; 1 mol.), potassium 2:4-dichlorobenzoate (2.3 g.; 1 mol.), anhydrous sodium acetate (2.0 g.), anhydrous copper sulphate (0.5 g.), copper bronze (20 mg.) and nitrobenzene (40 c.c.) were refluxed for 24 hours at 230°. Nitrobenzene was steam-distilled, the residue filtered, washed with dilute hydrochloric acid and 10% sodium carbonate solution, and extracted with ammonia. The blue solution was acidified with hydrochloric acid and the precipitate of N-1'-(4'-amino)-anthraquinonyl-4-chloroanthranilic acid was washed and dried (0.7 g.). The acid was cyclized as above and the acridone (II) crystallized from nitrobenzene (Found: N, 7.4%).

10:12-Dichloro-6-aminoanthraquinoneacridone (III):

(a) 4-Chloro-1-aminoanthraquinone (2.57 g.), 3:5-dichloroanthranilic acid (3.0 g.), anhydrous sodium acetate (1.0 g.), copper bronze (20 mg.), anhydrous copper sulphate (0.05 g.) and amyl alcohol (35 c.c.) were refluxed at 150° for 28 hours. Isolated as usual, N-1'-(4'-amino)-anthraquinonyl-3:5-dichloroanthranilic acid (2.0 g.) crystallized from acetic acid in blue needles, m.p. 280° (Found: N, 6.7. $C_{21}H_{12}O_4N_2Cl_2$ requires N, 6.5%). The acid (0.2 g.) was heated with concentrated sulphuric acid (2 c.c.) at 98–100° for 20 minutes and the acridone (III; 0.18 g.) crystallized from nitrobenzene in long blue needles which did not melt up to 400° (Found N: 6.9; Cl, 16.9. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6.9; Cl, 17.2%). The dye (III) was identical in all properties with purified Indanthrene Turquoise Blue 3GK.

(b) 4-Bromo-1-aminoanthraquinone-2-sulphonic acid (2.02 g.), 3:5-dichloroanthranilic acid (1.12 g.), anhydrous potassium carbonate

(0.8 g.), copper bronze (0.5 g.) and water (25 c.c.) were heated together at 95° for 6 hours. The blue mass was diluted with water (100 c.c.), acidified with hydrochloric acid, heated to 80° for 30 minutes and filtered hot. The residue was washed with water till the washings were pink in colour and dried (2.0 g.). The N-1'-(4'-amino-3'-sulpho)-anthraquinonyl-3:5-dichloro-anthranilic acid (0.5 g.) thus obtained was added slowly to chlorosulphonic acid (2 c.c.) at 35°. After two hours the mixture was poured into crushed ice and the blue precipitate collected (0.25 g.) and washed with hot water. Crystallization from nitrobenzene gave (III) in blue needles (Found: C, 61.5; H, 2.5; N, 6.8. $C_{21}H_{10}O_3N_2Cl_2$ requires C, 61.6; H, 2.4; N, 6.9%), which were identical with purified and crystallized Indanthrene Turquoise Blue 3GK.

7:11-Dichloro-6-aminoanthraquinoneacridone:

2:4-Dichloro-1-aminoanthraquinone (2.92 g.), 4-chloroanthranilic acid (2.74 g.), copper bronze (0.05 g.), copper acetate (20 mg.), anhydrous potassium acetate (1.96 g.) and amyl alcohol (20 c.c.) were refluxed for 15 hours with stirring. The mixture was filtered, washed repeatedly with hot methylated spirit, 10% sodium carbonate and dilute hydrochloric acid. The crude N-1'-(3'-chloro-4'-amino)-anthraquinonyl-4-chloroanthranilic acid (3.0 g.) crystallized from nitrobenzene in blue needles, m.p. 310-11° (Found N, 6.3. $C_{21}H_{12}O_4N_2Cl_2$ requires N, 6.5%). The acridone crystallized in blue needles from nitrobenzene (Found: N, 6.6; Cl, 17.0. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6.9; Cl, 17.2%). It dyes a blue green shade on cotton from a brown vat (fastness to light 7, chlorine 3-4, and soda boil 3-4).

7:10-Dichloro-6-aminoanthraquinoneacridone:

Prepared as usual from 2:4-dichloro-1-aminoanthraquinone and 5-chloroanthranilic acid, the intermediate N-anthraquinonylanthranilic acid crystallized from nitrobenzene in blue needles, m.p. 308-9° (Found: Cl, 16.4. $C_{21}H_{12}O_4N_2Cl_2$ requires Cl, 16.6%). The acridone crystallized from *o*-dichlorobenzene in blue needles (Found: N, 7.0; Cl, 17.0. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6.9; Cl, 17.2%). The turquoise blue shade on cotton is greener than the shade from Indanthrene Turquoise Blue 3GK (fastness to light 7-8, chlorine 3, and soda boil 2-3).

7:10:12-Trichloro-6-aminoanthraquinoneacridone:

The condensation product of 2:4-dichloro-1-aminoanthraquinone and 3:5-dichloroanthranilic acid crystallized from glacial acetic acid in long blue needles, m.p. 267-8° (Found N, 5.8. $C_{21}H_{11}O_4N_2Cl_3$ requires N, 6.0%).

The acridone crystallized from *o*-dichlorobenzene in long blue needles not melting up to 370° (Found: N, 6.3; Cl, 23.8. $C_{21}H_9O_3N_2Cl_3$ requires N, 6.3; Cl, 24.0%). The product dyes a bright green-blue shade from a violet brown vat (fastness to light 7, chlorine 3, and soda boil 4).

11-Chloro-7-bromo-6-aminoanthraquinoneacridone (V):

2:4-Dibromo-1-aminoanthraquinone (1.9 g.), 4-chloroanthranilic acid (0.85 g.), anhydrous sodium acetate (0.8 g.), copper bronze (0.3 g.), and amyl alcohol (35 c.c.) were refluxed for 14 hours. The product was worked up as usual. N-1-(3'-Bromo-4'-amino)anthraquinonyl-4-chloroanthranilic acid (2.2 g.) crystallized from glacial acetic acid in blue needles, m.p. 285° (Found N, 5.6; Cl+Br, 24.2. $C_{21}H_{12}O_4N_2ClBr$ requires N, 5.9; Cl+Br, 24.4%). The acridone (V) crystallized from *o*-dichlorobenzene in long blue needles, which did not melt up to 360° (Found: N, 5.8. $C_{21}H_{10}O_3N_2ClBr$ requires N, 6.1%). The green-blue shade on cotton from a red-brown vat has fastness to light 7-8, chlorine 3, and soda boil 2-3.

Dechlorination of 7-chloro-6-aminoanthraquinoneacridone by aqueous sodium hydroxide and hydrosulphite:

The chloroacridone (0.18 g.) was pasted with a little Turkey Red Oil, 10% sodium hydroxide (5 c.c.) and hydrosulphite (0.5 g.) were added, and the solution was diluted to 50 c.c. The violet-brown vat was kept under alkaline and reduced condition at 28° (room temperature) for one hour, after which it was oxidised by passing air. The finely divided blue precipitate was centrifuged, repeatedly washed with water and dried (0.14 g.). The product did not contain chlorine, and crystallized from nitrobenzene, in blue plates (Found: N, 8.3. Calc. for $C_{21}H_{12}O_3N_2$: N, 8.2%). It dyes a blue shade on cotton which is identical with the shade of 6-aminoanthraquinoneacridone, and is different from the shade of the original chloroacridone.

Indanthrene Turquoise Blue GK and 3GK, when treated as described above, remained unaffected and gave their original shades on dyeing. (Indanthrene Turquoise Blue GK:—Found: Cl, 9.2. $C_{21}H_{11}O_3N_2Cl$ requires Cl, 9.5%) (Indanthrene Turquoise Blue 3GK:—Found: Cl, 16.8. $C_{21}H_{10}O_3N_2Cl_2$ requires Cl, 17.2%).

7:10:12-Trichloro-6-aminoanthraquinoneacridone gave 10:12-dichloro-6-aminoanthraquinoneacridone (Indanthrene Turquoise Blue 3GK) by treatment with alkali and hydrosulphite at room temperature for one hour (Found: N, 6.9; Cl, 16.9. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6.9; Cl, 17.2%).

SUMMARY

Indanthrene Turquoise Blue GK and 3GK have been shown to be 11-chloro-6-aminoanthraquinoneacridone (II) and 10:12-dichloro-6-aminoanthraquinoneacridone (III) respectively by unambiguous synthesis. The absorption spectra of the commercial and the synthetic dyestuffs have been determined. Chloro derivatives of 6-aminoanthraquinoneacridone, substituted by chlorine in the anthraquinone nucleus, in the benzene half of the molecule, and in both the anthraquinone and the benzene halves, have been synthesised, and the fastness properties of the shades on cotton determined. 6-Aminoanthraquinoneacridone has been prepared by a new route; the various chloro derivatives of 6-aminoanthraquinoneacridone which have been synthesised are the 7-, 10-, and 11-monochloro, 7:10-, 7:11- and 10:12-dichloro, the 7:10:12-trichloro and 11-chloro-7-bromo-compounds. It is found that the acridones containing a chlorine atom in the 7-position, adjacent to the amino group, are dehalogenated by treatment with aqueous alkali and hydrosulphite at room temperature (28°) for about one hour.

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