473. *Chemistry of Indanthrone. Part IV.* An Isomer of Indanthrone and the Constitution of Indanthren B.*

By William Bradley, Edward Leete, and Douglas S. Stephens.

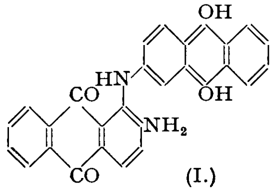
Whilst the reduction of 2-nitro-1 : 2′-dianthraquinonylamine with stannous chloride in acetic acid yields the related amine (A), reduction by means of sodium sulphide yields *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine (B), an isomer of indanthrone. The structure of the product is proved by its formation by condensing anthra-1 : 2-quinone with 2 : 3-diaminoanthraquinone, oxidising the resulting azine (C) to 1 : 2-2′ : 3′-anthraquinoneazine (D) and finally reducing this to the dihydro-azine. The azine (D) resembles indanthroneazine closely but 1 : 2-anthracene-2′ : 3′-anthraquinoneazine (C) is much more stable towards reduction.

The formation of (B) cannot involve the intermediate formation of (A) because (A) is known to form indanthrone on cyclisation (preceding paper). It is probable that 2-nitro-1 : 2′-dianthraquinonylamine becomes reduced to the related nitroso-compound which then cyclises to form the indanthrone isomer (B) before further reduction takes place.

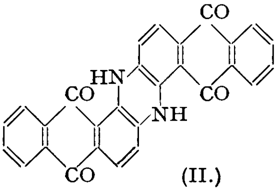
Indanthren B resembles (B) but the two colouring matters are not identical. The possibility that indanthren B is formed from (B) by the action of alkalis has been considered and shown to be improbable. It is suggested that indanthren B is a hydroxy- or dihydroxy-derivative of *NN*-dihydro-2 : 3-2′ : 3′-anthraquinoneazine.

A method of purifying indanthren B is described in which the reduced form is chromatographed on cellulose and the colouring matter regenerated by aeration.

After his original description of the preparation of indanthrone (G.P. 129,845) by alkali fusion of 2-aminoanthraquinone, Bohn referred in G.P. 135,407 to the simultaneous formation of a distinct colouring matter which resembled indanthrone and which he named " indanthren B." The formation of " indanthren B " was favoured by addition of alcohol and similar reducing agents to the alkali melt (G.P. 135,408). The new colouring matter was stated to be more soluble than indanthrone in quinoline, to give a brownish-red solution when reduced by means of alkaline dithionite (hydrosulphite), and to be regenerated from its reduced form on aeration with greater difficulty than was indanthrone. Like indanthrone it yielded a yellow azine on oxidation, from which the original colouring matter was re-formed on reduction. Maki (*J. Soc. Chem. Ind. Japan, Suppl.*, 1933, **36**, 44) showed that " indanthren B " resulted even when pure 2-aminoanthraquinone was used and that its formation could not be attributed to the presence of an initial impurity. Tanaka (*J. Chem. Soc. Japan*, 1935, **56**, 192) obtained a green product by heating 2-aminoanthraquinone with fused alkalis. He referred to it as " indanthren B " and stated that it was a quinol-quinone (I) and that it was converted into indanthrone (II) when heated again with fused alkali. " Indanthren B " cannot have the constitution (I), however, because of its colour, and because (I) dissolves readily in aqueous sodium hydroxide forming a brown solution (*J.*, 1951, 2161). In G.P. 347,692 a method of purifying crude indanthrone is described and it is stated that one of the impurities is a reduction product of indanthrone. Schwenk (*Chem.-Ztg.*, 1928, **52**, 45) held that " indanthren B " was a reduced form of indanthrone. This view does not accord with the known properties of " indanthren B,"



(I.)



(II.)

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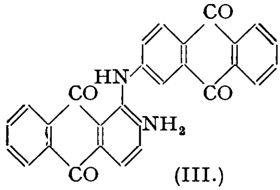
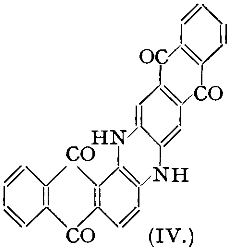
* Part III, preceding paper.

confirmed in the present experiments, that " indanthren B " and indanthrone cannot be interconverted by processes of oxidation and reduction. " Indanthren B " prepared by Maki's procedure (*loc. cit.*) was purified by dissolution in alkaline dithionite and passage of the solution through a column of cellulose prepared as in Part II (*J.*, 1951, 2147). " Indanthren B " was less strongly adsorbed than the indanthrone which was also present, and was easily eluted by means of alkaline dithionite as a brown solution from which aeration precipitated the purified " indanthren B " in the form of blue flocks. The properties of the product were similar to those of the original " indanthren B " described in G.P. 135,407. Oxidation with nitric acid or chromium trioxide gave a yellow product from which the original colouring matter was regenerated on reduction (see Fig. 1). The effect of alcohol in favouring the formation of " indanthren B " has been confirmed in the present work. In colour and absorption spectrum in concentrated sulphuric acid " indanthren B " resembled indanthrone closely, but analysis showed it to be richer in oxygen.

The present view that the formation of indanthrone from 2-aminoanthraquinone involves 2-amino-1 : 2′-dianthraquinonylamine (III) or a reduced form of this at an intermediate stage



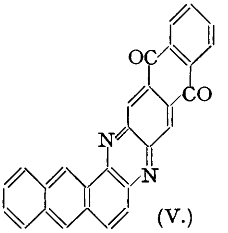
(III.)



(IV.)

(preceding paper) suggested the possibility that cyclisation might not have proceeded solely to give indanthrone but that an isomer (IV) might have resulted by ring-closure at the 3-position. There was the possibility that " indanthren B " was (IV) or a derivative of this.

Terres (*Ber.*, 1913, **46**, 1634) and G.P. 170,562 described a synthesis of indanthrone in which 1 : 2-diaminoanthraquinone was condensed with anthra-1 : 2-quinone, and the resulting 1 : 2-anthracene-1′ : 2′-anthraquinoneazine was oxidised to indanthroneazine and then reduced to indanthrone. We applied the same procedure to prepare the indanthrone isomer (IV). 2 : 3-Diaminoanthraquinone was condensed with anthra-1 : 2-quinone and the resulting 1 : 2-anthracene-2′ : 3′-anthraquinoneazine (V) was oxidised to 1 : 2-2′ : 3′-anthraquinoneazine



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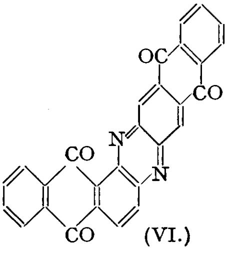


(VI.)

(VI) and the product reduced to (IV). Preparation of (IV) by condensation of alizarin with 2 : 3-diaminoanthraquinone in the presence of phenol and boric acid was described in G.P. 178,130, but we were unable to prepare (IV) satisfactorily by this method. The azine (VI) resembles indanthroneazine closely in that it is reduced to the related dihydro-azine merely by being heated with quinoline. The two dihydroazines, however, behave differently on reduction. Indanthrone dissolves in warm alkaline dithionite, forming a blue solution from which indanthrone is rapidly reprecipitated on exposure to air; (IV) dissolves to a deep reddish-brown solution from which the original colouring matter is precipitated more slowly than is indanthrone on aeration, and through a dull violet, and a greenish-yellow stage in succession. The final stage of change to blue colouring matter is slow in the case of (IV) because (IV) is a relatively strong acid which affords an alkali salt. When the greenish-yellow stage has been reached, addition of dilute acid precipitates the blue colouring matter. The alkali-salt forming properties of (IV) accord with the results described in Part I, in particular with the fact that

1-anilinoanthraquinone does not show any change in colour when methanolic potassium hydroxide is added to a solution in pyridine whilst 2-anilinoanthraquinone shows a colour change from orange to green (*J.*, 1951, 2129) and there can be little doubt that the potassium salt is the derivative (VII). *NN*-Dihydro-1 : 2-2′ : 3′-anthraquinoneazine affords a dimethyl derivative on methylation. This resembles *NN*-dimethylindanthrone in dissolving in pyridine with a blue colour which is unaltered by methanolic potassium hydroxide. It dissolves in alkaline dithionite, forming an orange-red solution from which the original colouring matter is regenerated in a single stage; in this respect the dimethyl derivative differs from the parent *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine. The dimethyl derivative resembles *NN*-dimethylindanthrone further in undergoing demethylation when heated with alumina, and in being more soluble in organic solvents than the unmethylated dihydro-azine. The isomer of indanthrone (IV) is probably the main constituent of the colouring matter obtained by heating 3-nitro-2 : 1′-dianthraquinonylamine with methanolic potassium hydroxide (G.P. 583,715).

FIG. 1.

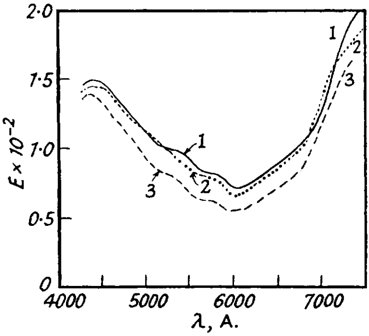


FIG. 2.

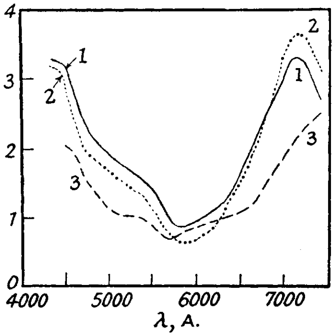


FIG. 3.

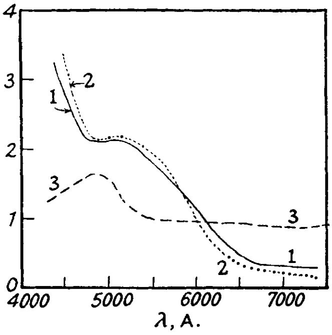


FIG. 1.—*Indanthren B in concentrated sulphuric acid.*

1, *Indanthren B obtained by fusion of* 2-*aminoanthraquinone in the presence of phenol, max. at* 4400 Å. (*E* = 147), *min. at* 6000 Å. (*E* = 74).
2, *Product obtain by oxidation of the above, followed by reduction.*
3, *Indanthren B obtained by fusion of* 2-*aminoanthraquinone in the presence of alcohol, max. at* 4400 Å. (*E* = 138), *min. at* 6000 Å. (*E* = 54).

FIG. 2.—*Solution of* NN-*dihydro*-2 : 1-2′ : 3′-*anthraquinonazine in concentrated sulphuric acid.*

1, NN′-*Dihydro*-1 : 2-2′ : 3′-*anthraquinoneazine prepared from* 2 : 3-*aminoanthraquinone, min. at* 5850 Å. (*E* = 87), *max. at* 7150 Å. (*E* = 330).
2, *Product obtained by reduction of* 2-*nitro*-1 : 2′-*dianthraquinonylamine with alcoholic sodium sulphide.*
3, *Product obtained by reduction of* 2-*nitro*-1 : 2′-*dianthraquinonyl*-N-*methylamine, min. at* 5700 Å. (*E* = 72).

FIG. 3.—*Solutions in sodium hydroxide–sodium dithionite of:*

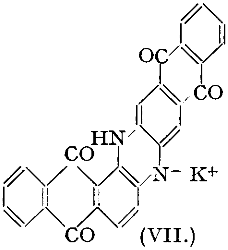
1, NN′-*Dihydro*-1 : 2-2′ : 3′-*anthraquinoneazine prepared from* 2 : 3-*diaminoanthraquinone, min. at* 4900 Å. (*E* = 206), *max. at* 5200 Å. (*E* = 212).
2, *Product obtained by reduction of* 2-*nitro*-1 : 2′-*dianthraquinolylamine with alcoholic sodium sulphide.*
3, *Indanthren B, max. at* 4850 Å. (*E* = 160).

" Indanthren B " resembles (IV) in colour, colour in sulphuric acid, and in dissolution in alkaline dithionite. It differs from (IV) in dissolving in pyridine with a blue colour which is changed to green by methanolic potassium hydroxide; with (IV) the corresponding colour change is from blue to greenish-brown.

The possibility that " indanthren B " is derived from (IV) by the further action of fused alkali hydroxides has been investigated. It was found that (IV) was recovered unaltered. When potassium acetate and potassium nitrate were added to the melt gross decomposition occurred resulting in the formation of a reddish-brown product.

A view that " indanthren B " is a mono- or di-hydroxy-derivative of (IV) accords with its composition and general properties but the failure to obtain it by further action of fused alkalis on *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine, alone or in the presence of oxidants, suggests that the view is incorrect.

A careful comparison of the stabilities towards hydrolysis of the colours produced when methanolic potassium hydroxide is added to pyridine solutions of numerous anthraquinone derivatives and related compounds has made it clear that " indanthren B " is a phenolic compound. The most acidic –NH– compounds encountered in the survey were the various anthraquinoneacridones but these did not approach " indanthren B " in the stability of their alkali salts. On the other hand " indanthren B " did resemble the hydroxyanthraquinones and 4 : 4′-dihydroxyindanthrone (VIII). The behaviour of the last-mentioned is especially interesting. It is very sparingly soluble in pyridine but on addition of methanolic potassium hydroxide a green solution is formed which in colour and stability towards hydrolysis closely resembles " indanthren B."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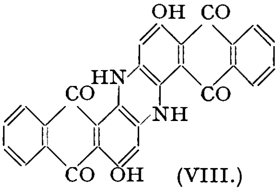
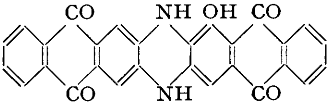
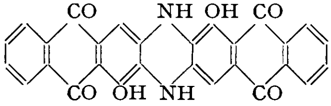
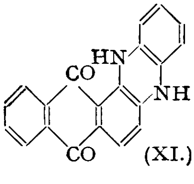

(VIII.)

The properties and composition of " indanthren B " accord best with its formulation as the mono- or di-hydroxy-derivative (IX or X), of *NN*-dihydro-2 : 3-2′ : 3′-anthraquinoneazine, the linear isomeride of indanthrone. This view accords with the properties of indanthrone and its isomers and derivatives, for " indanthren B," though phenolic, is redder than *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine, which in turn is redder than indanthrone. 4 : 4′-Dihydroxyindanthrone is the greenest member of the series. " Indanthren B " resembles *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine rather than indanthrone in its strongly acid character, and in the brown colour of its solution in alkaline dithionite. All indanthrone derivatives which are able to dissolve in this medium whilst still containing the grouping (XI) afford blue solutions, whereas *N*-methyl- and *NN*-dimethyl-indanthrone as well as fully reduced indanthrone which do not contain this grouping afford brown solutions. This relationship between structure and the colour of the alkaline solution of the reduced form, together with the close similarity of *NN*-dihydro-1 : 2-2′ : 3′-anthraquinoneazine and " indanthren B," supports the view that the latter is derived from the linear isomeride of indanthrone.


(IX.)


(X.)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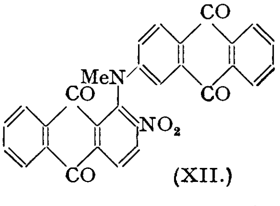
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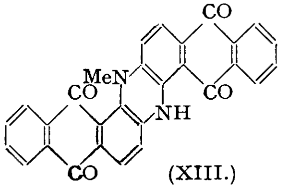
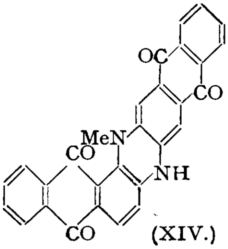
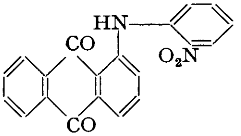

(XIII.)


(XIV.)

Whilst the reduction of 2-nitro-1 : 2′-dianthraquinonylamine with stannous chloride affords (III) (Part III, preceding paper), reduction with alcoholic sodium sulphide follows a different course and yields the isomer (IV) of indanthrone. The identity of the product with (IV) was confirmed by analysis, absorption spectrum in concentrated sulphuric acid, colour of its solution in alkaline dithionite (see Figs. 2 and 3), and by the greenish-brown colour developed when methanolic potassium hydroxide was added to a solution of the product in pyridine. When the reduction was carried out by aqueous sodium sulphide the yield of (IV) was smaller. The product contained unreduced nitro-compound but neither indanthrone nor 2-aminoanthraquinone.

The reduction of 2-nitro-1 : 2′-dianthraquinonyl-*N*-methylamine (XII) by aqueous sodium sulphide yielded a blue colouring matter which was not identical with *N*-methylindanthrone (XIII). By analogy with the product obtained from 2-nitro-1 : 2′-dianthraquinonylamine and sodium sulphide that derived from (XII) should be (XIV), a *N*-methyl derivative of the indanthrone isomer (IV). This conclusion is supported by the absorption spectrum of (XIV) in sulphuric acid which closely resembles that of (IV) (see Fig. 3).

In this connection reference must be made to the proof by Ullmann and Fodor (*Annalen*, 1911, **380**, 324) that 1-*o*-nitroanilinoanthraquinone (XV) is reduced by alcoholic sodium sulphide to *NN*-dihydro-3 : 4-phthaloylphenazine (XVI). In the present work it was found



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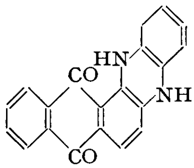
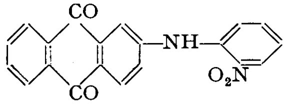


(XVI.)



(XVII.)

that 2-*o*-nitroanilinoanthraquinone (XVII), similarly reduced, did not yield the dihydrophenazine (XVI), but a product, probably the related amine, which proved to be stable towards ring closure with alkali and sodium sulphide. Evidently the cyclisation of (XV) to (XVI) occurs before the related amine is formed, and a similar conclusion must be reached regarding the sodium sulphide reduction of 2-nitro-1 : 2′-dianthraquinonylamine. In this instance it is known that the related amine (III) yields indanthrone on ring closure, whereas the product obtained by reducing the nitro-compound with sodium sulphide is the indanthrone isomer (IV), neither the related amine nor indanthrone being formed.

2-Nitro-1 : 2′-dianthraquinonylamine forms a stable salt with potassium hydroxide (Part I, *J.*, 1951, 2139) but is not otherwise easily changed by this reagent. The effect of sodium sulphide added to the alkali is probably to reduce the nitro- to the related nitroso-compound which then undergoes cyclisation with formation of (IV). Probably the related nitroso-compounds are the intermediates which cyclise when 2-nitro-1 : 2′-dianthraquinonyl-*N*-methylamine (XII) and 2-*o*-nitroanilinoanthraquinone are reduced by sodium sulphide.

EXPERIMENTAL.

" *Indanthren B.*"—(*a*) The product obtained by heating 2-aminoanthraquinone (10 g.) with potassium hydroxide (34 g.), water (6 c.c.) and phenol (6·0 g.) at 220° according to Maki's procedure (*loc. cit.*) weighed 0·35 g. It was dissolved in water (20 c.c.) containing sodium dithionite (1·0 g.) and sodium hydroxide (5 c.c. of 20%), and the brown solution was mixed with water containing sodium dithionite (1%) and sodium hydroxide (2%) and then passed through a column of cellulose pulp. A strongly adsorbed blue zone was succeeded by a lower, dull brownish-grey zone. The column was extruded and cut into thin sections and the adsorbed material was allowed to oxidise in air. The blue, strongly adsorbed zone yielded indanthrone. The brownish-grey zone became green and finally blue as oxidation proceeded; the blue product, extracted by *o*-dichlorobenzene, afforded 0·1 g. of blue needles (Found : C, 71·8; H, 3·4; N, 4·2. $C_{28}H_{14}O_5N_2$ requires C, 72·9; H, 3·5; N, 6·1. $C_{28}H_{14}O_6N_2$ requires C, 70·5; H, 3·4; N, 5·9%).

(*b*) 2-Aminoanthraquinone (10 g.) was added during 20 minutes to a molten mixture of potassium hydroxide (50 g.) and ethyl alcohol (25 c.c.) at 150°. The mass was stirred for 3 hours at this temperature and then added to water. The resulting deep violet solution was aerated and the precipitate (8·0 g.) collected. Extraction of the precipitate by alcohol gave a blue insoluble portion (2·7 g.). This was extracted by boiling nitrobenzene (200 c.c.); a portion (1·0 g.), which showed the reactions of indanthrone, remained undissolved. The filtrate afforded indistinct blue crystals (0·55 g.) on cooling; these differed from indanthrone in dissolving in alkaline dithionite with a brown colour. The brown solution in alkaline dithionite was passed through a column of cellulose pulp. As in (*a*), two zones formed, the upper blue zone yielded indanthrone, the lower greyish-brown zone afforded " indanthren B " which, extracted from the cellulose by pyridine and precipitated therefrom by alcohol, was obtained as an amorphous blue powder (0·19 g.). The blue pyridine solution of this product became bright green when methanolic potassium hydroxide was added, and the colour was stable towards dilution with alcohol or even water; on storage a green precipitate was formed. Addition of a drop of hydrochloric acid restored the original blue colour.

In a modification of the test, " indanthren B " was heated with boiling pyridine, and two volumes of water were added and finally potassium hydroxide; a green colour developed and on storage a green precipitate. Even when heated with aqueous sodium hydroxide " indanthren B " dissolved to a slight extent forming a brownish-green solution.

Oxidation. (*a*) A solution of chromium trioxide (0·05 g.) in 80% sulphuric acid (2 c.c.) was added at 0° to one of " indanthren B " (0·05 g.) in concentrated sulphuric acid (1 c.c.). The mixture was stirred for an hour during which the colour of the solution changed from dull brown to reddish-brown. On addition of the mixture to water a blue-green precipitate formed; this was collected (centrifuge) and washed with very dilute sodium hydroxide containing sodium dithionite. Finally, it was washed thoroughly with water and dried. The product was identical with the starting material.

(*b*) " Indanthren B " (0·04 g.) was added at 0° to concentrated nitric acid (*d* 1·4; 1 c.c.). The orange-yellow solution was stirred for 15 minutes and then added to water. A yellow precipitate resulted; in contact with dilute sodium hydroxide it became blue; on addition of alkali and sodium dithionite and warming to 50° it dissolved with a brown colour. Oxidation by aeration and neutralisation by acid caused a greenish-blue precipitate (0·015 g.) to be formed. This was shown to be identical with the starting material by means of the absorption spectrum of the brown solution in concentrated sulphuric acid (see Fig. 1).

1 : 2-*Anthracene-2′* : *3′-anthraquinoneazine.*—1 : 2-Anthraquinone was obtained in small yield by reducing alizarin to 1 : 2-dihydroxyanthracene (Graebe, *Annalen*, 1906, **349**, 207; Hall and Perkin, *J.*, 1923, 2029) and oxidising the product by chromic acid. A better method consisted in preparing anthracene-2-sulphonic acid (cf. Ferrero and Conzetti, *Helv. Chim. Acta*, 1928, **11**, 1152), converting this in turn into 2-anthrol, 2-hydroxy-1-nitrosoanthracene, and 1-amino-2-hydroxyanthracene, and finally oxidation to 1 : 2-anthraquinone (Lagodzinski, *Annalen*, 1905, **342**, 87). After isolation of 2-anthrol the successive yields were almost quantitative.

A solution of 1 : 2-anthraquinone (2·0 g.) in glacial acetic acid (50 c.c.) was added to one of 2 : 3-diaminoanthraquinone (2·1 g.) in glacial acetic acid (500 c.c.). A product began to separate almost at once. After 30 minutes the suspension was cooled and the golden-yellow leaflets (2·9 g.) were collected. Recrystallisation from nitrobenzene gave 1 : 2-*anthracene-2′* : *3′-anthraquinoneazine* as golden-yellow plates, m. p. 415—417° (Found: C, 82·2; H, 3·6; N, 6·5. $C_{28}H_{14}O_2N_2$ requires C, 81·9; H, 3·4; N, 6·8%). It dissolved in concentrated sulphuric acid with a deep green colour; on storage a reddish-blue solid (sulphate ?) separated; this decomposed when added to water, and a violet solution resulted and then a brownish-yellow precipitate. The azine was recovered unaltered when 1 g. was heated under reflux for 14 hours with 10 c.c. of quinoline. This stability is in sharp contrast with that of 1 : 2 : 1′ : 2′-anthraquinoneazine (indanthroneazine) which becomes reduced to indanthrone even when it is heated with nitrobenzene (Scholl and Berblinger, *Ber.*, 1903, **36**, 3427). In another experiment the azine (0·5 g.) was warmed with a solution of sodium hydroxide (2·0 g.) and sodium dithionite (2·0 g.) in water (50 c.c.). A portion dissolved with a reddish-brown colour, but after a short time a brown substance was precipitated. The filtered solution exposed to air gave a red precipitate. This was collected (centrifuge; 0·04 g.) and heated with nitrobenzene. It dissolved with a yellow colour and the solution afforded yellow plates of the original azine, m. p. 417°, on cooling. The brown precipitate, collected (0·35 g.) and then crystallised from nitrobenzene, afforded a yellow solution having a green fluorescence and on cooling golden-yellow plates of the azine, m. p. 416—417°.

NN-*Dihydro*-1 : 2-2′ : 3′-*anthraquinoneazine.*—(*a*) A solution prepared from chromium trioxide (1·0 g.) and water (2 c.c.) was mixed with concentrated sulphuric acid (10 c.c.) and then added at 0° to one of 1 : 2-anthracene-2′ : 3′-anthraquinoneazine (1·0 g.) in concentrated sulphuric acid (25 c.c.). There was an immediate change in colour from green to reddish-brown. The mixture was stirred for 15 minutes, then added to water, and the resulting greenish-yellow suspension warmed to 50° and then filtered. The green residue (1·35 g.) extracted for 3 hours by boiling quinoline (300 c.c.) yielded a greenish-blue solution from which on cooling very small blue needles (0·15 g.) separated (Found: C, 75·7; H, 3·5; N, 5·9. $C_{28}H_{14}O_4N_2$ requires C, 76·0; H, 3·2; N, 6·3%). The *dihydro-azine* afforded a bright blue solution in pyridine; on addition of methanolic potassium hydroxide the colour changed to dull greenish-brown. The brown colour is stable towards dilution with methanol or even water; a brown precipitate slowly forms. Addition of a drop of hydrochloric acid to the diluted solution restores the original blue colour.

The dihydro-azine can also be prepared from the sulphuric acid solution of the oxidised anthracene-anthraquinoneazine by addition to water, basification with sodium hydroxide, and then warming to 50° with the addition of 20% sodium hydroxide (8 c.c.) and sodium dithionite (2·0 g.). A brown solution formed; this was filtered off and the filtrate aerated. The resulting suspension was made neutral, and the fine precipitate collected, and washed with water and finally with dilute hydrochloric acid. The crude dihydro-azine (0·7 g.) so obtained dissolved in concentrated sulphuric acid with a greenish-brown colour; on addition of water it was reprecipitated as a dull blue solid. Nitric acid added to a solution of the dihydro-azine in concentrated sulphuric acid gave an orange-brown colour.

(*b*) Finely powdered 2-nitro-1 : 2′-dianthraquinonylamine (2·0 g.) was heated under reflux for 30 minutes with a solution of sodium sulphide crystals (5·0 g.) in alcohol (100 c.c.). A transient reddish-brown colour formed but this soon became bluish-green. The cooled product was filtered off and washed with alcohol and water. The blue residue was dissolved in alkaline sodium dithionite, and the resulting brown solution chromatographed on cellulose. A uniform brown zone was obtained which was less strongly adsorbed than reduced indanthrone but more strongly than reduced " indanthren B."

Recovered from the cellulose and recrystallised from 250 parts of boiling quinoline the NN-*dihydro-1 : 2-2′ : 3′-anthraquinoneazine* was obtained as blue needles (Found : C, 76·1; H, 3·4; N, 6·35. $C_{28}H_{14}O_4N_2$ requires C,76·0; H, 3·2; N, 6·3%). When the dihydro-azine is reduced by alkaline dithionite and the brown solution is adsorbed on cellulose in contact with air the colour changes rapidly to dull bluish-violet and then almost at once to dull green. The final transition to blue occurs slowly unless acid is added, whereupon it takes place immediately. The same behaviour is shown by the dihydro-azine prepared by method (*a*).

The same dihydro-azine was obtained less conveniently by reducing 2-nitro-1 : 2′-dianthraquinonylamine with a solution of sodium sulphide in aqueous sodium hydroxide.

Alkali fusion. (*a*) The finely powdered dihydro-azine (1·0 g.) was stirred for an hour at 200° with a melt of potassium hydroxide (10·0 g.) and water (1·0 c.c.). The dark product added to water afforded a brown solution; there was no residue. The filtered solution when acidified yielded a dull blue precipitate (0·9 g.) consisting of the unchanged dihydro-azine. A portion of it was dissolved in alkaline dithionite and chromatographed on cellulose; only a single bright brown zone resulted.

(*b*) In a similar experiment potassium acetate (0·5 g.) and potassium nitrate (0·2 g.) were added to the melt before introduction of the dihydro-azine. On addition to water a brown solution was obtained and from this a reddish-brown product (0·7 g.).

9 : 10-*Dihydro*-9 : 10-*dimethyl*-1 : 2-6 : 7-*diphthaloylphenazine*.—The dihydro-azine (1·0 g ; prepared by reducing 2-nitro-1 : 2′-dianthraquinonylamine with alcoholic sodium sulphide) was heated under reflux with methyl toluene-*p*-sulphonate (4·0 g.) and potassium carbonate (2·0 g.) in trichlorobenzene (100 c.c.) for 48 hours. The blue solution was filtered hot and the filtrate evaporated to 40 c.c. On cooling, crystals (0·7 g.) separated. Two recrystallisations from quinoline afforded the *phenazine* derivative as blue needles (0·3 g.) (Found : C, 74·1; H, 3·8; N, 6·0. $C_{30}H_{18}O_4N_2$ requires C, 76·6; H, 3·8; N, 6·0%). It dissolved readily in pyridine with a violet-blue colour which was unaltered by methanolic potassium hydroxide, whether in the cold or on heating. It dissolved in alkaline dithionite with an orange-red colour. Exposure to air regenerated the original violet-blue colour. Unlike the behaviour of the parent dihydro-azine there was no indication of a stable intermediate stage in the process of reoxidising the reduced methyl derivative.

When the *NN*-dimethyl derivative (0·05 g.) was heated under reflux for 10 hours in *o*-dichlorobenzene containing alumina (0·5 g.) and the suspension was allowed to cool, all the colouring matter was adsorbed on the alumina. Extracted from the alumina by means of pyridine, the adsorbed product afforded a deep blue solution which became olive-brown on addition of methyl-alcoholic potassium hydroxide. When the product was dissolved in alkaline dithionite the resulting brown solution yielded first a pale green solution and finally a blue colour on exposure to air. Both these reactions are characteristic of the demethylated amine.

Alkali Fusion of Indanthrone.—Indanthrone was recovered almost completely unaltered when 2·0 g. was heated for 30 minutes with potassium hydroxide (40 g.) and ethyl alcohol (20 c.c.) at 140—150°. The product, reduced and then chromatographed on cellulose, afforded a main blue zone consisting of dihydroindanthrone and a faint brown zone containing only a negligible amount of material (cf. Maki, *J. Soc. Chem. Ind. Japan, Suppl.*, 1929, **32**, 300).

2-o-*Nitroanilinoanthraquinone.*—2-Iodoanthraquinone (3·0 g.) was heated under reflux for 3 hours in nitrobenzene (20 c.c.) with *o*-nitroaniline (2·0 g.), lead monoxide (2·0 g.), and cupric acetate (0·05 g.). The hot suspension was filtered; on cooling the filtrate gave 2·25 g. of the product, m. p. 243—244°. Recrystallisation from acetic acid afforded orange-yellow needles, m. p. 247—248° (Found : C, 69·6; H, 3·6; N, 8·3. $C_{20}H_{12}O_4N_2$ requires C, 69·7; H, 3·5; N, 8·2%). 2-o-*Nitroanilinoanthraquinone* dissolved in pyridine with a yellow colour; addition of methanolic potassium hydroxide changed the colour to green and this was stable to considerable dilution with alcohol.

Reduction. 2-*o*-Nitroanilinoanthraquinone (1·0 g.) was heated under reflux for 30 minutes in alcohol (50 c.c.) containing sodium sulphide crystals (3·0 g.). The product added to water (300 c.c.) afforded a red crystalline precipitate, m. p. 220—230°. This was readily soluble in water and quite different in this respect from *NN*-dihydro-1 : 2-phthaloylphenazine (Ullmann and Fodor, *Annalen*, 1911, **380**, 324) obtained by the similar reduction of 1-*o*-nitroanilinoanthraquinone. Like the *o*-aminodianthraquinonylamines it dissolved in concentrated sulphuric acid with a deep violet-blue colour. In similar circumstances anthraquinonedihydroazines afford brown solutions.

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