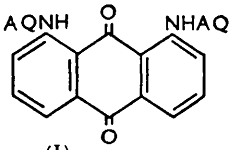
154. *The Cyclisation of* 1 : 8-*Di- and* 1 : 4 : 5 : 8-*Tetra-*(α-*anthraquinonylamino*)*anthraquinone to Derivatives of Carbazole.*

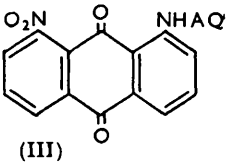
By William Bradley and P. N. Pandit.

On being heated with titanium tetrachloride or aluminium chloride 1 : 8-di-(α-anthraquinonylamino)anthraquinone (I) undergoes cyclisation to the compound (II), two carbazole nuclei being formed. Similar treatment of the 9 : 11-di-(α-anthraquinonylamino)-derivative of (II) affords a yellow substance believed to be (VII) which differs from the greenish-brown product that results by similar treatment of 1 : 4 : 5 : 8-tetra-(α-anthraquinonylamino)anthraquinone.

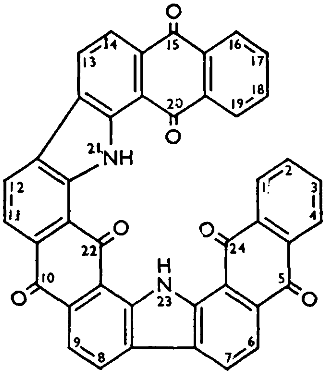
The present investigation continues that reported earlier.[1] Like 1 : 4- and 1 : 5-di-(α-anthraquinonylamino)anthraquinone the 1 : 8-isomer (I) is cyclised on being heated with titanium tetrachloride, and the reaction occurs more easily with aluminium chloride. The product is the hendecacylic triquinone (II). The formation of one carbazole nucleus in the ring-closure was confirmed in the following way. 1-α-Anthraquinonylamino-8-nitroanthraquinone (III) was cyclised to the nitrodiphthaloylcarbazole (IV; $R^1 = NO_2$, $R^2 = R^3 = H$) by means of titanium tetrachloride, and the structure of the product was



(I)



(III)



(II)

AQ = anthraquinonyl.

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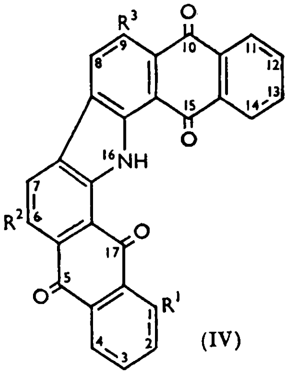
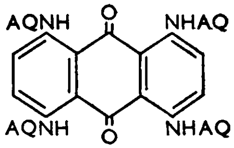
[1] Bradley and Pandit, *J.*, 1955, 3399.

proved by reduction to the amino-derivative and deamination; the end-product was 1 : 2-7 : 8-diphthaloylcarbazole (IV; $R^1 = R^2 = R^3 = H$) identical with an authentic sample.[2] This amino-derivative gave 1-α-anthraquinonylaminodiphthaloylcarbazole (IV; R^1 = NHAQ, $R^2 = R^3 = H$) on reaction with α-chloroanthraquinone, and the triquinone (II) was derived from the product by further treatment with titanium tetrachloride. The end-product was identical with that derived from the diamine (I) by treatment with aluminium chloride.

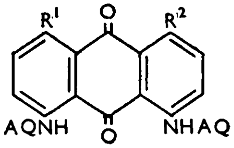
These experiments were extended in order to establish the structure of the product obtained by heating 1 : 4 : 5 : 8-tetra-(α-anthraquinonylamino)anthraquinone (V) with aluminium chloride. Chlorination of 1 : 8-dibenzamidoanthraquinone gave a mixture of 1 : 8-dibenzamido-4 : 5-dichloroanthraquinone with smaller amounts of the 2 : 5-dichloro-isomer. Each of the dichloro-derivatives gave a diamine on hydrolysis; that from the 4 : 5-dichloro-compound gave 1 : 8-dichloroanthraquinone on deamination, whilst that from the 2 : 5-isomer gave 1 : 6-dichloroanthraquinone. On being heated with α-amino-anthraquinone 1 : 8-dibenzamido-4 : 5-dichloroanthraquinone gave 1 : 8-di-(α-anthraquinonylamino)-4 : 5-dibenzamidoanthraquinone (VI; $R^1 = R^2$ = NHBz), hydrolysis of which affords 1 : 8-diamino-4 : 5-di-(α-anthraquinonylamino)anthraquinone (VI; $R^1 = R^2 = NH_2$). On being treated with sulphuric acid and sodium nitrite and then with hypophosphorous acid this 1 : 8-diamino-derivative gave the diamine (I). On being heated with α-chloroanthraquinone the 1 : 8-diamino-compound (VI) gave 1 : 4 : 5 : 8-tetra-(α-anthraquinonylamino)anthraquinone (V), identical with the products obtained by heating 1 : 4 : 5 : 8-tetrachloroanthraquinone with α-aminoanthraquinone or 1 : 4 : 5 : 8-tetra-aminoanthraquinone with α-chloroanthraquinone.



(IV)



(V)



(VI)

With aluminium chloride and pyridine 1 : 8-di-(α-anthraquinonylamino)-4 : 5-dibenzamidoanthraquinone gave a product, not obtained crystalline, which on hydrolysis and deamination gave the crystalline product, (II); the non-crystalline product must, therefore, have been the 9 : 11-dibenzamido-derivative of (II), unless hydrolysis of the acyl groups had occurred during the cyclisation. When the cyclised product was hydrolysed and then caused to react with α-chloroanthraquinone an insoluble, non-crystalline product, presumably the 9 : 11-di-(α-anthraquinonylamino)-derivative of (II) was formed. On being heated with aluminium chloride or titanium tetrachloride this gave a yellow product, also insoluble, hygroscopic, and non-crystalline, which from the method of its preparation and analysis is believed to be the tetracarbazolepentaquinone (VII). Both the 9 : 11-diamino-derivative of (II), and (II) itself, were prepared crystalline and analysed.

An attempt was made to confirm the preparation of the C_{70}-compound (VII) by the following method. 1 : 5-Dibenzamidoanthraquinone was first converted into the 4 : 8-di-chloro-derivative. The structure of this was proved by hydrolysis with alkali to the known 1 : 5-diamino-4 : 8-dichloroanthraquinone; when the hydrolysis was attempted

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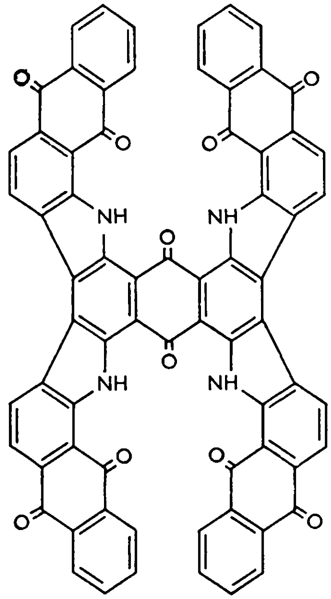
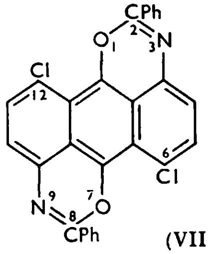
[2] Bradley and Thitchener, *J.*, 1953, 1085.

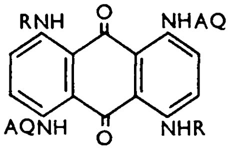
with concentrated sulphuric acid an unexpected reaction occurred, water was lost and a derivative $C_{28}H_{14}N_2Cl_2$ formed. This is considered to have structure (VIII) on the ground of composition and because it is quite unchanged on treatment with alkaline dithionite solution. On being heated with α-aminoanthraquinone 1 : 5-dibenzamido-4 : 8-dichloroanthraquinone gave 1 : 5-di-(α-anthraquinonylamino)-4 : 8-dibenzamidoanthraquinone (IX; $R = Bz$). This was recovered unaltered however after being heated in pyridine with aluminium chloride. It gave the corresponding diamino-derivative (IX; $R = H$) on hydrolysis, and 1 : 5-di(α-anthraquinonylamino)anthraquinone on further deamination.



(VII)



(VIII)



(IX)

The following additional observations were made during the work. 1 : 4-Diamino-2 : 3-dichloroanthraquinone and α-chloroanthraquinone react in the presence of sodium carbonate, copper, and nitrobenzene to form 1 : 4-di-(α-anthraquinonylamino)-2-chloro-3-hydroxyanthraquinone, one chlorine substituent having been replaced by hydroxyl. On being heated with titanium tetrachloride 4-nitro-1 : 1′-dianthraquinonylamine undergoes cyclisation and also replacement of the nitro-group by chlorine, the chlorodiphthaloylcarbazole (IV; $R^1 = R^3 = H$, $R^2 = Cl$) being formed. Analogously, 4 : 4′-dinitro-1 : 1′-dianthraquinonylamine gave the dichlorodiphthaloylcarbazole (IV; $R^1 = H$, $R^2 = R^3 = Cl$) with the same reagent.

EXPERIMENTAL

8-*Nitro*-1 : 1′-*dianthraquinonylamine* (III).—1-Chloro-8-nitroanthraquinone (28 g.), 1-aminoanthraquinone (22 g.), anhydrous sodium carbonate (6 g.), and copper bronze (1 g.), when refluxed for 12 hr. in nitrobenzene (500 c.c.), gave a product (28 g.) which crystallised (19 g.) from chlorobenzene (2 l.). 8-*Nitro*-1 : 1′-*dianthraquinonylamine* separates from *o*-dichlorobenzene in lustrous red needles (Found: C, 71·5; H, 2·3; N, 5·5. $C_{28}H_{14}O_6N_2$ requires C, 70·9; H, 2·9; N, 5·9%) which dissolve in concentrated sulphuric acid with a green colour, changed to blue on the addition of 40% aqueous formaldehyde.

Cyclisation.—The product (10·2 g.) obtained by refluxing 8-nitro-1 : 1′-dianthraquinonylamine (8 g.) and titanium tetrachloride (40 c.c.) in *o*-dichlorobenzene (150 c.c.) for 2·5 hr. was collected, washed with fresh solvent, then with alcohol, and finally with water. It was heated for 1 hr. with chromium trioxide (10 g.) in acetic acid (150 c.c.) and then crystallised from nitrobenzene. 1-*Nitrodinaphtho*[2,3-a, 2′,3′-i]*carbazole*-5 : 10 : 15 : 17-*diquinone* (IV; $R^1 = NO_2$, $R^2 = R^3 = H$) which resulted forms lustrous yellow needles (Found: C, 71·0; H, 2·7; N, 5·9. $C_{28}H_{12}O_6N_2$ requires C, 71·2; H, 2·5; N, 5·9%).

1-*Aminodinaphtho*[2,3-a, 2',3'-i]*carbazole*-5 : 10 : 15 : 17-*diquinone* (IV; $R^1 = NH_2$, $R^2 = R^3 = H$).—The 1-nitro-derivative (2·2 g.) was refluxed and vigorously stirred for 4 hr. with a solution of sodium sulphide crystals (8 g.) in water (10 c.c.) and alcohol (50 c.c.). The solid was collected, washed with water, dried (2 g.), and crystallised from 1 : 2 : 4-trichlorobenzene (2·8 l.). The 1-*amino-quinone* formed minute red needles (1·5 g.) (Found: C, 75·8; H, 3·3; N, 6·2. $C_{28}H_{14}O_4N_2$ requires C, 76·0; H, 3·2; N, 6·3%) which dissolve in concentrated sulphuric acid with a red colour, unchanged on the addition of 40% aqueous formaldehyde. Heating this amine (0·8 g.) with benzoyl chloride (1 c.c.) in nitrobenzene (10 c.c.) gave lustrous yellow needles of the 1-*benzamido-derivative* (Found: C, 77·1; H, 3·3; N, 5·2. $C_{35}H_{18}O_5N_2$ requires C, 76·9; H, 3·3; N, 5·1%). This gave a purple solution in concentrated sulphuric acid which changed to green on being kept, or on the addition of 40% aqueous formaldehyde.

Deamination. Sodium nitrite (0·25 g.) was added during 30 min. to a stirred solution of the 1-amino-derivative (0·5 g.) in concentrated sulphuric acid (10 c.c.) at 0°. After 4 hr. the resulting solution was added to ice, the precipitated diazonium compound was collected, washed, and then stirred with ice-cold 30% hypophosphorous acid (70 c.c.) for 3 hr., during which frothing occurred. The suspension which remained was filtered, the solid was washed, then dried (0·4 g.) and crystallised from nitrobenzene (300 c.c.). Yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole (II; $R^1 = R^2 = R^3 = H$) were obtained, identical with a sample prepared by cyclising di-α-anthraquinonylamine with aluminium chloride (light absorption in "AnalaR" concentrated sulphuric acid: $\lambda_{max.}$ at 226, 271, 508, and 650 mμ).

1-(α-*Anthraquinonylamino*)*dinaphtho*[2,3-a, 2',3'-i]*carbazole*-5 : 10 : 15 : 17-*diquinone*.—The 1-amino-derivative (0·5 g.), 1-chloroanthraquinone (0·3 g.), anhydrous sodium carbonate (0·1 g.), and a small proportion of copper bronze were refluxed for 20 hr. in nitrobenzene (6 c.c.). The solid was collected, washed in succession with nitrobenzene, alcohol, hydrochloric acid, and water, then dried (0·6 g.) and crystallised from trichlorobenzene. The 1-(α-*anthraquinonylamino*)-*quinone* formed red curved needles (Found: C, 77·2; H, 3·2; N, 4·2. $C_{42}H_{20}O_6N_2$ requires C, 77·8; H, 3·1; N, 4·3%), the deep red solution of which in concentrated sulphuric acid changed to pale violet on the addition of 40% aqueous formaldehyde.

Cyclisation. The 1-α-anthraquinonylamino-derivative (0·05 g.) and titanium tetrachloride (4 g.) were refluxed for 3 hr. in *o*-dichlorobenzene (15 c.c.). The solid was then collected, washed with fresh solvent, then with alcohol, and dried. After being heated for 6 hr. at 70° with alkaline sodium hypochlorite the dark solid changed in hue to brownish-yellow, and crystallisation from nitrobenzene then gave minute yellow needles of 21 : 23-*dihydrobisnaphtho*-[2', 3', 6, 7]*indolo*[2, 3-a, 2', 3'-j]*anthracene*-3 : 8 : 10 : 12 : 17 : 22-*triquinone* (II) (*A*) (Found: C, 77·8; H, 2·9; N, 4·5. $C_{42}H_{18}O_6N_2$ requires C, 78·0; H, 2·8; N, 4·3%). Light absorption in "AnalaR" concentrated sulphuric acid: $\lambda_{max.}$ at 275 and 570 mμ.

1 : 8-*Di*-(α-*anthraquinonylamino*)*anthraquinone* (I).—1 : 8-Dichloroanthraquinone (27·7 g.), 1-aminoanthraquinone (45·0 g.), anhydrous sodium carbonate (12·0 g.), and copper bronze (2 g.) were refluxed for 36 hr. in nitrobenzene (500 c.c.). The yield of purified product was 55 g. Crystallisation of a portion (4 g.) from nitrobenzene (1 l.) gave red minute needles (3·6 g.) (Found: C, 77·4; H, 3·1; N, 4·2. Calc. for $C_{42}H_{22}O_6N_2$: C, 77·5; H, 3·4; N, 4·3%). Light absorption in "AnalaR" concentrated sulphuric acid: $\lambda_{max.}$ at 265, 340—360 mμ. The green colour of the solution in concentrated sulphuric acid changed to deep blue on the addition of 40% aqueous formaldehyde. This description supplements that given in G.P. 240,080 in which a similar compound was prepared from 1-chloroanthraquinone and 1 : 8-diaminoanthraquinone.

Cyclisation. (*a*) 1 : 8-Di-(α-anthraquinonylamino)anthraquinone (2·0 g.) was refluxed for 1 hr. with titanium tetrachloride (5 c.c.) and *o*-dichlorobenzene (50 c.c.). The resulting solid was collected, washed in turn with *o*-dichlorobenzene and alcohol, and then crystallised from nitrobenzene (1·8 l.). Red minute needles (0·5 g.) separated which dissolved in concentrated sulphuric acid with a red colour, becoming deep blue on the addition of 40% aqueous formaldehyde solution. On being chromatographed on a filter paper between glass plates and then developed with a weak solution of alkaline dithionite the reduced dye gave a small central yellow zone and a larger outer red ring.

(*b*) 1 : 8-Di-(α-anthraquinonylamino)anthraquinone was refluxed for 17 hr. with titanium tetrachloride (20 c.c.) and *o*-dichlorobenzene (50 c.c.). The resulting solid was collected, washed in turn with *o*-dichlorobenzene and alcohol, and dried (3·4 g.). Chromatography of the solution of the reduced compound on a filter paper and development with weak alkaline dithionite gave a single central yellow zone. Crystallisation from boiling nitrobenzene gave yellow needles, whose light absorption in "AnalaR" concentrated sulphuric acid had max. at 275 and 570 mμ.

(*c*) 1 : 8-Di-(α-anthraquinonylamino)anthraquinone (2 g.) was powdered and mixed with aluminium chloride (18 g.), and then heated and stirred for 15 min. at 260°. The cooled melt was extracted with boiling, dilute hydrochloric acid, then collected and washed. Crystallisation from nitrobenzene gave yellow, minute needles of the triquinone (II) (Found : C, 77·9; H, 3·0; N, 4·4. Calc. for $C_{42}H_{18}O_6N_2$: C, 78·0; H, 2·8; N, 4·3%), identical with specimen (*A*). All the specimens of the triquinone (II) dissolved in concentrated sulphuric acid with a purple colour, unchanged on the addition of 40% aqueous formaldehyde.

1 : 4 : 5 : 8-*Tetra*-(α-*anthraquinonylamino*)*anthraquinone* (V)—(*a*) The product (5·2 g.) obtained by 24 hours' refluxing of 1 : 4 : 5 : 8-tetra-aminoanthraquinone (7 g.), 1-chloroanthraquinone (30 g.), cuprous chloride (5 g.), and anhydrous potassium acetate (24 g.) in nitrobenzene (600 c.c.) was washed with nitrobenzene, alcohol, dilute hydrochloric acid, and water; it crystallised from quinoline in dark blue needles (Found : N, 4·9. Calc. for $C_{70}H_{36}O_{10}N_4$: N, 5·1%). (*b*) The same compound (20·7 g.) resulted by 36 hours' refluxing of 1 : 4 : 5 : 8-tetrachloroanthraquinone (8·3 g.), 1-aminoanthraquinone (25 g.), anhydrous sodium carbonate (7 g.), and copper bronze (0·5 g.) in nitrobenzene (600 c.c.). After being washed and dried a portion (5 g.) of the product was crystallised from nitrobenzene (1·95 l.). Lustrous dark blue needles (3·6 g.) of 1 : 4 : 5 : 8-*tetra*-(α-*anthraquinonylamino*)*anthraquinone* (Found : C, 77·1; H, 3·1; N, 5·5. $C_{70}H_{36}O_{10}N_4$ requires C, 76·9; H, 3·3; N, 5·1%) were obtained. This description supplements that given in G.P. 262,788. On being heated with aluminium chloride the derivative gave a greenish-brown product as described in this patent.

1 : 8-*Dibenzamido*-4 : 5-*dichloroanthraquinone*.—A current of dry chlorine was passed for 6 hr. through a vigorously stirred mixture of 1 : 8-dibenzamidoanthraquinone (40 g.), anhydrous sodium acetate (20 g.), acetic acid (320 c.c.), and nitrobenzene (350 c.c.) heated under reflux at 120—130°. The orange needles which separated on cooling were collected, washed with acetic acid, then with water, dried (35·5 g.; m. p. 300—310°), and recrystallised (26 g.) from *o*-dichlorobenzene (2 l.). 1 : 8-*Dibenzamido*-4 : 5-*dichloroanthraquinone* has m. p. 335° (Found : C, 65·9; H, 2·9% N, 5·3; Cl, 13·5. $C_{28}H_{16}O_4N_2Cl_2$ requires C, 65·2; H, 3·1; N, 5·4; Cl, 13·8%)

The *o*-dichlorobenzene mother-liquor gave on concentration yellow needles (6 g.) of 1 : 8-dibenzamido-2 : 5-dichloroanthraquinone, m. p. 280—285°. Recrystallisation from chlorobenzene gave yellow needles, m. p. 295° (Found : C, 65·01; H, 3·1; N, 5·7; Cl, 14·0%).

1 : 8-*Diamino*-4 : 5-*dichloroanthraquinone*.—A solution of 1 : 8-dibenzamido-4 : 5-dichloroanthraquinone (10·2 g.) in concentrated sulphuric acid (100 c.c.) was heated for 4 hr. on the water-bath, then cooled and added to ice-water. The precipitated 1 : 8-*diamino*-4 : 5-*dichloroanthraquinone* was collected, washed with dilute ammonia, then water, dried (6·0 g.), and crystallised from *o*-dichlorobenzene; shining red needles, m. p. 314°, were obtained (Found : C, 54·9; H, 2·6; N, 9·6; Cl, 23·5. $C_{14}H_8O_2N_2Cl_2$ requires C, 54·7; H, 2·6; N, 9·1; Cl, 23·1%).

Deamination. A solution of the compound, m. p. 314° (1 g.), in concentrated sulphuric acid (20 c.c.) was stirred in an ice-bath. Sodium nitrite (0·5 g.) was added during 30 min. and stirring was then continued for 5 hr. Addition of the mixture to ice then gave a light red solution which was added with stirring to 50% hypophosphorous acid (30 c.c.) at 0°. Foaming occurred and a light yellow precipitate formed. After being stirred for 4 hr. and then kept overnight the solid was collected, washed, dried (0·8 g.), and crystallised from acetic acid. The resulting yellow needles, m. p. 202°, did not depress the m. p. of authentic 1 : 8-dichloroanthraquinone,[3] m. p. 202°.

1 : 8-*Diamino*-2 : 5-*dichloroanthraquinone*.—A solution of 1 : 8-dibenzamido-2 : 5-dichloroanthraquinone (3 g.) in concentrated sulphuric acid (10 c.c.) was heated on a water-bath with stirring for 12 hr. The greenish-yellow solution so obtained was poured on crushed ice, and the precipitated diamino-derivative was collected, washed, and dried (1·7 g.). Crystallisation from *o*-dichlorobenzene gave minute red needles, m. p. 215°. A solution of the compound in chlorobenzene was chromatographed on alumina, and the lower main red band was eluted by means of fresh solvent; the chlorobenzene extract on concentration gave minute red needles of the *diamine*, m. p. 222° (Found : C, 54·4; H, 2·5; N, 8·9; Cl, 22·9. $C_{14}H_8O_2N_2Cl_2$ requires C, 54·7; H, 2·6; N, 9·1; Cl. 23·1%).

Deamination. A solution of the diamine, m. p. 222° (1 g.), in concentrated sulphuric acid (10 c.c.) was cooled in ice. Sodium nitrite (0·5 g.) was added to it with stirring, and stirring

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[3] Ullmann and Knecht, *Ber.*, 1911, **44**, 3125.

continued at 0° for 4 hr. On being poured on ice the mixture gave a light red solution, and this was added with stirring to 50% hypophosphorous acid (30 c.c.). Frothing occurred and a light grey precipitate separated. When the frothing had subsided (12 hr.), the resulting suspension was filtered, and the residual solid was washed and dried (0·6 g.; m. p. 200°). Two crystallisations from acetic acid gave material, m. p. 204·5°, mixed m. p. 170—175° with 1 : 8- and with 1 : 3-dichloroanthraquinone but not depressed on admixture with authentic 1 : 6-dichloroanthraquinone,[4] m. p. 203—204°.

1 : 8-*Di*-(α-*anthraquinonylamino*)-4 : 5-*dibenzamidoanthraquinone*.—1 : 8-Dibenzamido-4 : 5-dichloroanthraquinone (24 g.), 1-aminoanthraquinone (24 g.), anhydrous sodium carbonate (18 g.), and copper bronze (5 g.) were refluxed for 24 hr. in nitrobenzene (400 c.c.). Filtration, washing with nitrobenzene, alcohol, dilute hydrochloric acid, and water, and drying gave a product (32·5 g.), of which a portion (16 g.) on being crystallised from nitrobenzene (7 l.) gave shining blue needles (12·5 g.) of 1 : 8-*di*-(α-*anthraquinonylamino*)-4 : 5-*dibenzamidoanthraquinone* (Found: C, 75·2; H, 3·5; N, 6·0. $C_{56}H_{32}O_8N_4$ requires C, 75·7; H, 3·6; N, 6·3%).

Cyclisation. The product (10 g.) was heated for 2·5 hr. at 150—160° with aluminium chloride (30 g.) and pyridine (75 c.c.). After being cooled the melt was added to water (600 c.c.) and concentrated hydrochloric acid (100 c.c.) and the resulting suspension which formed was boiled, then filtered. The resulting solid 9 : 11-dibenzamido-derivative of (II) could not be obtained crystalline (Found: N, 5·7. Calc. for $C_{56}H_{28}O_8N_4$: N, 6·3%). It dissolved in alkaline dithionite forming a deep red brown solution.

Hydrolysis. The preceding cyclised product (15 g.) was dissolved in concentrated sulphuric acid (100 c.c.) and heated on a water-bath with stirring for 12 hr. Addition to cold water gave a fine greenish precipitate and this was collected, washed with dilute ammonia, and then with water, and dried (11·5 g.). On being heated with boiling quinoline (1 l.) the substance (1 g.) partly dissolved and from the hot filtered solution minute greenish nodules (80 mg.) separated on cooling.

The resulting 9 : 11-*diamino-derivative* of (II) (10 g.) was purified by dissolution in concentrated sulphuric acid (50 c.c.), filtration, and progressive dilution of the filtrate with cold water (12 c.c.); a yellow, crystalline precipitate separated. This was collected, washed with dilute acid of the same strength as the mother-liquor, then with water, and dried (4·8 g.) (Found: N, 7·8. $C_{42}H_{24}O_6N_4$ requires N, 8·2%).

Deamination. The preceding diamine (1·5 g.) was dissolved in concentrated sulphuric acid (50 c.c.) at 0° and stirred whilst sodium nitrite (1 g.) was added during 30 min. After 6 hr. the solution was added to ice, then kept for 12 hr. at 0°, and the precipitate was collected and washed. It was suspended in water and added to 30% hypophosphorous acid (100 c.c.) at 0°. After 12 hr. the brown precipitate (1·3 g.) was collected and crystallised fron nitrobenzene. The yellow needles obtained (Found: C, 77·6; H, 3·1; N, 4·2%) were identical with the products (A) obtained as described above.

Condensation with 1-*chloroanthraquinone*. The 9 : 11-diamino-derivative (1 g) of (II), 1-chloroanthraquinone (1 g.), anhydrous potassium acetate (0·2 g.), copper bronze (0·1 g.), copper acetate (0·1 g.), and nitrobenzene (30 c.c.) were heated in a sealed tube at 170—230° for 24 hr. and then at 230° for 24 hr. The product was filtered, washed with alcohol, boiled with dilute hydrochloric acid, washed, and dried (0·9 g.). It was dark brown and dissolved in alkaline dithionite to a red-brown solution. It was almost insoluble in high-boiling solvents.

Cyclisation. The above product (0·5 g.) was heated under reflux with titanium tetrachloride (5 c.c.) in *o*-dichlorobenzene (30 c.c.) for 2 hr. On being cooled the mixture was filtered, and the residue, presumed to be the *pentaquinone* (VII), was washed with acetone, boiled with dilute hydrochloric acid and then with water, and dried (Found, N, 5·1. $C_{70}H_{28}O_{10}N_4$ requires N, 5·2%). It was almost insoluble in high-boiling solvents but dissolved in warm alkaline dithionite giving a red solution which dyed a yellowish shade on cotton and gave a single band when allowed to diffuse down a column of cellulose.

1 : 8-*Diamino*-4 : 5-*di*-α-*anthraquinonylaminoanthraquinone*.—4 : 5-Di-(α-anthraquinonylamino)-1 : 8-dibenzamidoanthraquinone (16 g.) was stirred with concentrated sulphuric acid (100 c.c.) for 12 hr. The solution was slowly diluted with water (35 c.c.) and then stirred for 12 hr. longer. The sulphate that separated as reddish needles was filtered off and neutralised with dilute aqueous ammonia, and the resulting solid was washed with water and then dried (8·4 g.). The *product* crystallised from boiling quinoline and then trichlorobenzene in dark bluish-violet needles (Found: C, 73·4; H, 3·4; N, 8·0. $C_{42}H_{24}O_6N_4$ requires C, 74·1; H, 3·5; N, 8·3%).

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[4] Goldberg, *J.*, 1931, 1771.

Deamination. A portion (1·5 g.) of the above derivative was dissolved in concentrated sulphuric acid (15 c.c.) at 0° and stirred whilst sodium nitrite (1 g.) was added during 30 min. After being stirred for 6 hr. the solution was added to ice and kept for 12 hr. at 0°, and the precipitate was then collected and washed with ice-water. It was suspended in water and added with stirring to 30% hypophosphorous acid (100 c.c.) at 0°. After 12 hr. a dark-red precipitate was collected (1·3 g.) and crystallised from nitrobenzene. The dark-red needles so obtained were identical with 1 : 8-di-(α-anthraquinonylamino)anthraquinone (light absorption in " AnalaR " concentrated sulphuric acid : $\lambda_{max.}$ at 265 and 340—360 mμ).

Condensation of 1 : 8-*Diamino*-4 : 5-*di*-α-*anthraquinonylaminoanthraquinone with* 1-*Chloroanthraquinone.*—The diamino-derivative (1·2 g.), 1-chloroanthraquinone (1·2 g.), anhydrous sodium carbonate (0·2 g.), nitrobenzene (100 c.c.), and copper bronze (0·1 g.) were heated under reflux with stirring for 48 hr. The product was obtained as minute crystals which made filtration of the product very slow. Nitrobenzene was removed by steam-distillation and the residue boiled with dilute hydrochloric acid and then filtered off, extracted with 1 : 2 : 4-trichlorobenzene to remove unchanged reactants, washed, and dried (1·1 g.) (Found : N, 6·1. Calc. for $C_{70}H_{36}O_{10}N_4$: N, 5·1%). It was identical with 1 : 4 : 5 : 8-tetra-(α-anthraquinonylamino)anthraquinone prepared from 1 : 4 : 5 : 8-tetra-aminoanthraquinone.

1 : 5-*Dibenzamido*-4 : 8-*dichloroanthraquinone.*—Dry chlorine was passed for 3·5 hr. at 150° through a vigorously stirred mixture of 1 : 5-dibenzamidoanthraquinone (6 g.), anhydrous sodium acetate (3 g.), acetic acid (50 c.c.), and nitrobenzene (100 c.c.). On being cooled, the *product* (5·5 g.) separated. Crystallisation from *o*-dichlorobenzene (500 c.c.) gave lustrous, orange needles, m. p. 340° (Found : C, 65·4; H, 3·3; N, 5·7; Cl, 13·7. $C_{28}H_{16}O_4N_2Cl_2$ requires C, 65·2; H, 3·1; N, 5·4; Cl, 13·8%).

Hydrolysis. On being refluxed for 12 hr. with 20% alcoholic potassium hydroxide (50 c.c.) the above derivative (1 g.) afforded 1 : 5-diamino-4 : 8-dichloroanthraquinone as lustrous red plates (from *o*-dichlorobenzene), m. p. 305°, not depressed on admixture by authentic material.[5]

Cyclisation. A solution of 1 : 5-dibenzamido-4 : 8-dichloroanthraquinone (2·5 g.) in concentrated sulphuric acid (15 c.c.) was stirred at the room temperature for 2 hr. On addition to water the resulting green solution gave a precipitate of 6 : 12-*dichloro*-2 : 8-*diphenylanthra*-[9, 1-d'e', 10, 5-ed]*di*-m-*oxazine* which crystallised from 1 : 2 : 4-trichlorobenzene as bright red needles, m. p. >400° (Found : C, 70·0; H, 3·0; N, 5·5; Cl, 14·6. $C_{28}H_{14}O_2N_2Cl_2$ requires C, 70·1; H, 2·9; N, 5·8; Cl, 14·8%).

1 : 5-*Di*-(α-*anthraquinonylamino*)-4 : 8-*dibenzamidoanthraquinone.*—1 : 5-Dibenzamido-4 : 8-dichloroanthraquinone (4 g.), 1-aminoanthraquinone (3·7 g.), sodium carbonate (1 g.), and copper bronze (0·5 g.) were refluxed for 18 hr. in nitrobenzene (50 c.c.). The product (6·0 g.) crystallised from nitrobenzene as lustrous dark blue needles, 1 g. of which was soluble in 130 c.c. of the boiling solvent (Found : N, 6·3. $C_{56}H_{32}O_8N_4$ requires N, 6·3%). This *compound* was recovered unaltered after having been heated at 140° for 1 hr. with a solution of aluminium chloride in pyridine.

1 : 5-*Diamino*-4 : 8-*di*-(α-*anthraquinoylamino*)*anthraquinone.*—A solution of the preceding dibenzamido-derivative (2 g.) in concentrated sulphuric acid (15 c.c.) was stirred on the water-bath for 6 hr. On the addition of water (4 c.c.) minute needles separated. These were collected and washed with sulphuric acid of the same concentration as the mother-liquor, and then with water. Crystallisation of the dried *product* from trichlorobenzene gave fine, blue needles (Found : C, 73·1; H, 3·5; N, 8·1. $C_{42}H_{24}O_6N_4$ requires C, 74·1; H, 3·5; N, 8·2%).

Deamination. The diamino-derivative (0·5 g.) was prepared in a finely divided state by dissolution in concentrated sulphuric acid (5 c.c.) and addition of the solution to water and ice. On the addition of sodium nitrite (0·2 g.) in water the colour of the suspension changed from blue to green. After 30 min. 50% hypophosphorous acid (30 c.c.) was added and the suspension was stirred for 12 hr.; the colour changed to red during this period. The suspension was filtered and the solid was crystallised from nitrobenzene. It formed minute red needles (0·2 g.) (Found : C, 76·9; H, 3·1; N, 4·2. Calc. for $C_{42}H_{22}O_6N_2$: C, 77·5; H, 3·4; N, 4·3%) which gave the reactions of 1 : 5-di-(α-anthraquinonylamino)anthraquinone.

Condensation of 1-*Chloroanthraquinone with* 1 : 4-*Diamino*-2 : 3-*dichloroanthraquinone.*—A sample of the 1 : 4-diamino-derivative was purified by recrystallisation and obtained as violet needles, m. p. 296° (Brass and Heide[6] state m. p. 288°) (Found : C, 54·9; H, 2·65;

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[5] Scholl and Wanka, *Ber.*, 1929, **62**, 1424.

[6] Brass and Heide, *Ber.*, 1924, **57**, 104.

N, 9·2; Cl, 23·2. Calc. for $C_{14}H_8O_2N_2Cl_2$: C, 54·7; H, 2·6; N, 9·1; Cl, 23·1%). The 1 : 4-diamino-derivative (3·1 g.), 1-chloroanthraquinone (4·9 g.), anhydrous sodium carbonate (1·1 g.), copper bronze (0·2 g.), and nitrobenzene (50 c.c.) were stirred together for 18 hr. under reflux. The product (3·8 g.) was purified by dissolving it (2·5 g.) in concentrated sulphuric acid (15 c.c.) and gradually adding water (4 c.c.) to the solution. On being stirred for 12 hr. the solution afforded crystals; these were collected, washed with sulphuric acid of the same strength, then with water, dried, and recrystallised from nitrobenzene. Long slender needles of 1 : 4-*di-α-anthraquinonylamino*-2-*chloro*-3-*hydroxyanthraquinone* separated (Found: C, 71·7; H, 3·0; N, 4·0; Cl, 5·15. $C_{42}H_{21}O_7N_3Cl$ requires C, 71·8; H, 3·0; N, 4·0; Cl, 5·1%).

Action of Titanium Tetrachloride on 4-*Nitro*-1 : 1′-*dianthraquinonylamine. Formation of* (IV; $R^1 = R^3 = H$, $R^2 = Cl$).—The nitro-derivative (5 g.) was gently heated with titanium tetrachloride (12 c.c.) in *o*-dichlorobenzene (120 c.c.). Brown fumes (nitrogen oxides?) appeared above the reactants and a yellow crystalline sublimate formed. A vigorous reaction occurred at the b. p. and when this had subsided heating was resumed for 3 hr. The resulting suspension was cooled and filtered, and the residue was washed with alcohol, then heated with hot dilute hydrochloric acid. After being washed and dried, the sparingly soluble 6-*chlorodinaphtho*-[2,3-a, 2′,3′-i]*carbazole*-5 : 10 : 15 : 17-*diquinone* (5·2 g.) crystallised from nitrobenzene as minute orange needles (Found: C, 72·1; H, 2·6; N, 3·2; Cl, 7·9. $C_{28}H_{12}O_4NCl$ requires C, 72·8; H, 2·6; N, 3·0; Cl, 7·7%).

6 : 9-*Dichlorodinaphtho*[2,3-a, 2,′3′-i]*carbazole*-5 : 10 : 15 : 17-*diquinone* (IV; $R' = H$, $R^2 = R^3 = Cl$).—In a similar preparation in which 4 : 4′-dinitro-1 : 1′-dianthraquinonylamine (5 g.) was used instead of the 4-nitro-derivative a *product* (4·2 g.) resulted which crystallised from nitrobenzene as brown needles (Found: N, 3·2; Cl, 13·8. $C_{28}H_{11}O_4NCl_2$ requires N, 3·0; Cl, 14·3%).

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