The Cyclisation of 1 : 4- *and* 1 : 5-*Di*-(α-*anthraquinonylamino*)-*anthraquinones to Derivatives of Carbazole.*

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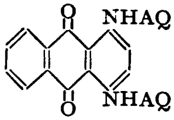
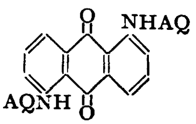
On being heated with aluminium chloride, titanium tetrachloride, or potassium hydroxide, 1 : 4-di-(α-anthraquinonylamino)anthraquinone (I) cyclises and yields the related hendecacyclic triquinone (III). The 1 : 5-isomer of (I) behaves analogously. The cyclised product (III) also results when 6-(α-anthraquinonylamino)dinaphtho(2 : 3-*a*, 2′ : 3′-*i*)carbazole-5 : 10 : 15 : 17-diquinone is heated with titanium tetrachloride. The second carbazole nucleus is formed more easily than the first. An isomeric triquinone (IV) derived from the 1 : 5-isomer is formed analogously by the action of titanium tetrachloride on the 4-(α-anthraquinonylamino)diquinone.

In previous communications Bradley and Thitchener (*J.*, 1953, 1085) and Bradley and Butcher (*J.*, 1954, 2311) discussed the cyclisation of 1 : 1′-dianthraquinonylamine and three isomeric dibenzamido-1 : 1′-dianthraquinonylamines into 1 : 2-7 : 8-diphthaloylcarbazole and its derivatives, and the present investigation is an extension of this work to derivatives of anthraquinone containing two α-anthraquinonylamino-substituent groups.

The formation of 1 : 4-di-(α-anthraquinonylamino)anthraquinone (I) and its conversion into a brown vat dye on being heated with potassium hydroxide, or a reddish-brown dye with aluminium chloride, were described in G.P. 208,969, 251,021, and 451,495, and the analogous conversion of 1 : 5-di-(α-anthraquinonylamino)anthraquinone (II) into brownish-yellow or orange dyes was described in G.P. 230,407, 240,080, 249,000, and 251,021. The structures of the products derived from (I) and (II) have not been established, but it has frequently been assumed that they are correctly represented by (III) and (IV) (see Cohn, " Die Carbazolgruppe," Georg Thieme, Verlag, Leipzig, 1919, p. 274; Thorpe's " Dictionary of Applied Chemistry," 4th edn., Vol. I, Longmans, London, p. 420; Kunz, *Melliand Textilber.*, 1952, **33**, 60), mainly because similar treatment of 1 : 1′-dianthraquinonylamine gives 1 : 2-7 : 8-diphthaloylcarbazole (literature: Bradley and Thitchener, *loc. cit.*).

(I)



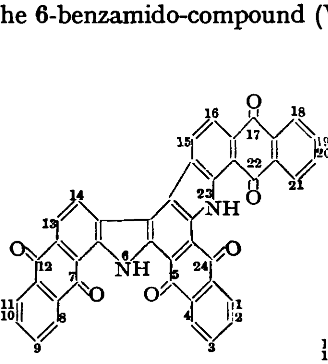


(II)

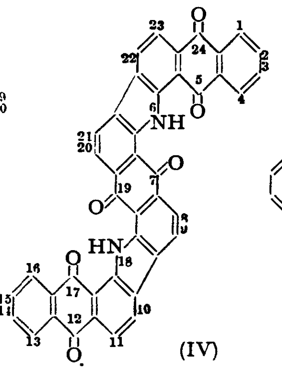
AQ = α-anthraquinonyl.

The present investigation has shown that treatment of the diamine (I) with potassium hydroxide, titanium tetrachloride, or aluminium chloride under conditions described in the Experimental part gives the hendecacyclic triquinone (III), and that treatment of the isomeric diamine (II) with titanium tetrachloride as described gives the isomeric triquinone (IV). There was no evidence of nuclear hydroxylation in the action of potassium hydroxide on the 1 : 4-diamine (I), which indicates how dominant is the cyclisation process in this case (cf. Bradley and Backhouse, *J.*, 1955, 849).

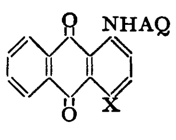
In an alternative synthesis of the triquinone (III), 4-benzamido-1 : 1′-dianthraquinonylamine (V; X = NHBz) was first prepared from 1-amino-4-benzamidoanthraquinone and 1-chloroanthraquinone, and from 1-benzamido-4-chloroanthraquinone and 1-aminoanthraquinone. Hydrolysis gave 4-amino-1 : 1′-dianthraquinonylamine (V; X = NH_2), and from this was derived 4-chloro-1 : 1′-dianthraquinonylamine (V; X = Cl). Treatment with titanium tetrachloride gave 6-chlorodinaphtho(2 : 3-*a*, 2′ : 3′-*i*)carbazole-5 : 10 : 15 : 17-diquinone (VI; X = Cl), and this afforded the 6-(α-anthraquinonylamino)-derivative on being heated with α-aminoanthraquinone. The end product was obtained also from 4-benzamido-1 : 1′-dianthraquinonylamine (V; X = NHBz) by cyclisation to the 6-benzamido-compound (VI; X = NHBz), hydrolysis to the 6-amino-compound (VI; X = NH_2), and condensation of this with 1-chloroanthraquinone. The end product was identical with that prepared by the first synthesis. On being heated with titanium tetrachloride the α-anthraquinonylaminodiphthaloylcarbazole was converted into a product which had the expected properties of the triquinone (III), and was identical with



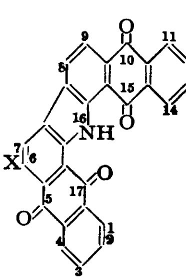
(III)



(IV)



(V)



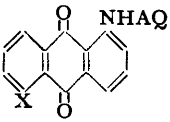
(VI)

the product obtained from the diaminoanthraquinone (I) directly by treatment with aluminium chloride.

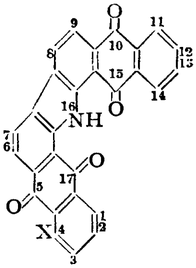
The correctness of the constitution (3-benzamido-1 : 2-7 : 8-diphthaloylcarbazole) assigned to the product from 4-benzamido-1 : 1′-di-anthraquinonylamine and aluminium chloride was established by deamination of the derived amine to 1 : 2-7 : 8-diphthaloylcarbazole, identical with the compound prepared by cyclisation of 1 : 1′-dianthraquinonylamine with aluminium chloride.

In a synthesis of the isomeric triquinone (IV), 1-benzamido-5-chloroanthraquinone and 1-aminoanthraquinone gave 5-benzamido-1 : 1′-dianthraquinonylamine (VII; X = NHBz). Treatment with aluminium chloride and pyridine gave the 4-benzamidodiquinone (VIII; X = NHBz), and thence the amino-compound (VIII; X = NH_2) by hydrolysis and the parent diphthaloylcarbazole (VIII; X = H) by subsequent deamination. The end-product was identical with 1 : 2-7 : 8-diphthaloylcarbazole prepared by the cyclisation of 1 : 1′-dianthraquinonylamine (Bradley and Thitchener, *loc. cit.*). On being heated with 1-chloroanthraquinone the amine (VIII; X = NH_2) gave the α-anthraquinonylamino-derivative (VIII; X = NHAQ), and from this was derived the triquinone (IV) by treatment with titanium tetrachloride. The end-product was identical with the product obtained directly from the diaminoanthraquinone (II) by treatment with aluminium chloride.

(VII)



(VIII)



Experimental

Absorption spectra refer to solutions in " AnalaR " concentrated sulphuric acid.

1 : 4-*Di-*(α-*anthraquinonylamino*)*anthraquinone*.—1 : 4-Diaminoanthraquinone (15 g.), 1-chloroanthraquinone (32 g.), anhydrous potassium acetate (9 g.), and cuprous chloride (5 g.) were stirred for 20 hr. with nitrobenzene (600 c.c.) under reflux. The cooled product was washed in turn with nitrobenzene, alcohol, hydrochloric acid, and water (yield, 36·5 g.). A portion (2·5 g.) afforded on crystallisation from nitrobenzene (1·5 l.) lustrous, dark blue needles, (1·3 g.), m. p. >400° (Found : C, 77·2; H, 3·5; N, 4·3. Calc. for $C_{42}H_{22}O_6N_2$: C, 77·5; H, 3·4; N, 4·3%). Light absorption : $\lambda_{max.}$ at 265, 475, and 600 mμ. This compound appeared to be similar to that (violet needles, m. p. 410°) obtained by Ullmann and Billig (*Annalen*, 1911, **381**, 20) from 1 : 4-dichloroanthraquinone and 1-aminoanthraquinone, and that described in G.P. 208,969 according to which it was prepared from 1-bromoanthraquinone and 1 : 4-diaminoanthraquinone or the reduced form of this.

Cyclisation. Formation of the Triquinone (III).—(*a*) The above compound (3 g.) was refluxed for 3 hr. with aluminium chloride (10 g.) and pyridine (25 c.c.) in an oil-bath at 180°. Addition to water, acidification, and subsequent treatment of the solid with chromium trioxide (5 g.) and acetic acid (150 c.c.) gave a product which crystallised from quinoline in minute, brown needles (A) (Found : C, 77·6; H, 2·8; N, 4·2. Calc. for $C_{42}H_{18}O_6N_2$: C, 78·0; H, 2·8; N, 4·3%), the properties of which resembled those of the products described in G.P. 208,969 and 451,495 except that these were not obtained pure or crystalline. The product (A), 6 : 23-dihydroanthra[2′,1′,4,5]pyrrolo[1,2-*c*]dinaphtho[2,3-*a*, 2′,3′-*i*]carbazole-5 : 7 : 12 : 17 : 22 : 24-triquinone, is very sparingly soluble in organic solvents; a saturated solution in 1·5 l. of boiling nitrobenzene affords 0·1 g. of (A) on being cooled.

(*b*) 1 : 4-Di-(α-anthraquinonylamino)anthraquinone (5 g.), potassium hydroxide (50 g.), and water (5 c.c.) were heated in a nickel crucible to 260° (temperature of metal bath) during 90 min., care being taken to avoid frothing caused by raising the temperature too quickly. The reactants were stirred at 260° for 3 hr. and then the product was cooled and added to water (1 l.). The resulting suspension was aerated, then filtered, and the residue was washed with water and then dried (5·2 g.). It showed the same properties as the crystalline material (A) prepared as in (*a*). Oxidation with chromium trioxide in acetic acid gave an unidentified yellow product, m. p. 260°, and phthalic acid. The alkaline medium from which the cyclised product was separated was deeply coloured, but no precipitate was formed on acidification.

4-*Benzamido*-1 : 1′-*dianthraquinonylamine.*—When crystallised from nitrobenzene 1-amino-4-benzamidoanthraquinone had m. p. 287° (Battegay and Bernhardt, *Bull. Soc. chim. France*, 1923, 33, 1510, state m. p. 278°). This derivative (34·2 g.), 1-chloroanthraquinone (24·2 g.), anhydrous sodium carbonate (6·0 g.), and copper bronze (2 g.) gave 4-*benzamido*-1 : 1′-*dianthraquinonylamine* (55 g.) after being refluxed in nitrobenzene (600 c.c.) for 24 hr. Recrystallisation from nitrobenzene gave a dark blue product (Found : C, 76·7; H, 3·6; N, 5·2. $C_{35}H_{20}O_5N_2$ requires C, 76·7; H, 3·7; N, 5·1%). Light absorption : $\lambda_{max.}$ at 257·5, 390—405, 625, 675—690 mμ. This compound was similar to that prepared from 1-benzamido-4-chloroanthraquinone and 1-aminoanthraquinone (shining dark blue needles from nitrobenzene and *o*-dichlorobenzene; Found: C, 76·5; H, 3·4; N, 5·2%) by a method similar to that of G.P. 220,581.

4-*Amino*-1 : 1′-*dianthaquinonylamine.*—The 4-benzamido-derivative (20 g.) was stirred and heated on a boiling-water bath for 4 hr. with concentrated sulphuric acid (200 c.c.). The cooled product was added to ice, and the precipitate was collected, washed with dilute aqueous ammonia, and dried (16·3 g.). Crystallisation from trichlorobenzene (1630 c.c.) gave 8·4 g. of blue needles. These were dissolved in concentrated sulphuric acid (40 c.c.), ice-cold water (15 c.c.) was added during 3 hr. with stirring, and the reddish-brown needles of the precipitated sulphate were collected, washed with 80% sulphuric acid, then hydrolysed by addition to water. 4-*Amino*-1 : 1′-*dianthraquinonylamine* crystallised from trichlorobenzene (450 c.c.) as lustrous blue needles (4·3 g.) (Found : C, 75·5; H, 3·4; N, 6·2. $C_{28}H_{16}O_4N_2$ requires C, 75·7; H, 3·6; N, 6·3%). Light absorption : $\lambda_{max.}$ at 265 and 360—365 mμ.

4-*Chloro*-1 : 1′-*dianthraquinonylamine.*—Sodium nitrite (3 g.) was added during 1 hr. to a solution of 4-amino-1 : 1′-dianthraquinonylamine (6 g.) in concentrated sulphuric acid (60 c.c.) which was stirred at 0°. After 6 hr. the resulting solution was kept 12 hr. at 0° and then added to ice. The precipitated yellow-brown diazonium compound was collected, washed with dilute hydrochloric acid at 0°, and then vigorously stirred with a solution of cuprous chloride (10 g.) in hydrochloric acid (100 c.c.). The temperature was raised to 70° during 4 hr., and then the product was collected, washed with hydrochloric acid, then with water, and finally dried (5·5 g.). Crystallisation from nitrobenzene gave lustrous, dark red needles of 4-*chloro*-1 : 1′-*dianthraquinonylamine* (Found : C, 72·5; H, 3·1; N, 2·7; Cl, 7·1. $C_{28}H_{14}O_4NCl$ requires C, 72·5; H, 3·0; N, 3·0; Cl, 7·7%). Light absorption : $\lambda_{max.}$ at 265·5 and 373·5 mμ.

4-*Nitro*-1 : 1′-*dianthraquinonylamine.*—1-Chloro-4-nitroanthraquinone (14·5 g.), 1-aminoanthraquinone (11·1 g.), anhydrous sodium carbonate (2·6 g.), and copper bronze (2·5 g.), refluxed in nitrobenzene (300 c.c.) for 24 hr., gave 4-*nitro*-1 : 1′-*dianthraquinonylamine* (21 g.) which crystallised as dark red needles (13·5 g.) from *o*-dichlorobenzene (Found : C, 71·4; H, 2·5; N, 5·4. $C_{28}H_{14}O_6N_2$ requires C, 71·9; H, 2·5; N, 5·9%). Light absorption : $\lambda_{max.}$ at 260, 430 mμ.

6-*Chlorodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone.*—4-Chloro-1 : 1′-dianthraquinonylamine (2 g.) was refluxed for 3 hr. with titanium tetrachloride (8 c.c.) in *o*-dichlorobenzene (40 c.c.). The cooled product was collected, washed with *o*-dichlorobenzene, then with acetone, and dried (3·2 g.). Purification from nitrobenzene (2 l.) gave a yellow solid (1·1 g.), and this was boiled for 30 min. with chromium trioxide (1·5 g.) and glacial acetic acid (100 c.c.). Crystallisation from nitrobenzene (400 c.c.) gave the 6-*chloro-compound* as lustrous yellow needles (Found : C, 72·9; H, 2·6; N, 3·2; Cl, 7·5. $C_{28}H_{12}O_4NCl$ requires C, 72·8; H, 2·6; N, 3·0; Cl, 7·7%). Light absorption : $\lambda_{max.}$ at 226, 271, and 505 mμ.

6-*Benzamidodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone.*—This *compound* was obtained essentially by the method of G.P. 451,495, 4-benzamido-1 : 1′-dianthraquinonylamine being cyclised by means of aluminium chloride in pyridine. The crude brown-red product was heated with alkaline sodium hypochlorite and then crystallised from nitrobenzene, giving lustrous red needles (Found : C, 76·4; H, 3·5; N, 5·6. $C_{35}H_{18}O_5N_2$ requires C, 76·9; H, 3·3; N, 5·1%). Light absorption : $\lambda_{max.}$ at 222·5—225, 264—266, 355—360, 560 mμ.

6-*Aminodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone.*—The above 6-benzamido-derivative (3·7 g.) was heated for 3 hr. on a boiling-water bath with concentrated sulphuric acid (15 c.c.). The cooled product was added to ice, and the resulting precipitate was collected, washed in succession with dilute aqueous ammonia and water, and dried (2·5 g.). This material crystallised from trichlorobenzene in blue needles. Another portion (1·5 g.) was dissolved in concentrated sulphuric acid (8 c.c.). Water (2 c.c.) was added slowly and the minute yellow needles of precipitated sulphate were hydrolysed by stirring them with water. Crystallisation of the regenerated base from quinoline gave the 6-*amine* as lustrous blue needles (Found : C, 76·3; H, 3·2; N, 6·2. $C_{28}H_{14}O_4N_2$ requires C, 76·0; H, 3·2; N, 6·3%). Light absorption : $\lambda_{max.}$ at 267, 485 mμ.

Deamination to 1 : 2-7 : 8-*diphthaloylcarbazole*. Sodium nitrite (0·25 g.) was added during 30 min. to a stirred solution of the 6-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 for 3 hr. with ice-cold 30% hypophosphorous acid (70 c.c.), during which frothing occurred. The suspension which remained was filtered, and the solid was washed, then dried (0·4 g.), and crystallised from nitrobenzene (350 c.c.). Yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole were obtained, identical with authentic material prepared by cyclising 1 : 1′-dianthraquinonylamine with aluminium chloride (light absorption : $\lambda_{max.}$ at 226, 271, 508, and 650 mμ).

6-*Nitrodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone*.—A solution of the 6-amine (4 g.) in concentrated sulphuric acid (25 c.c.) was cooled to 0°. Sodium nitrite (2 g.) was added during 20 min. and stirring was continued for 4 hr. The resulting solution was added to crushed ice, the precipitated diazonium sulphate was collected, washed with ice-water, and then stirred 12 hr. with a suspension of copper sulphate in sodium nitrite [prepared by mixing aqueous solutions of sodium sulphite (10 g.) and copper sulphate (8 g.), collecting the brown precipitate, washing it free from sulphite ions, and finally suspending it in water containing sodium nitrite (20 g.)]. The suspension was heated to boiling, then filtered, and the yellow product was washed and dried (3·8 g.). After short heating with chromium trioxide in acetic acid, the product was recovered and then recrystallised several times from nitrobenzene. The 6-*nitro-compound* forms brownish-yellow needles (Found : C 71·4; H, 2·6; N, 5·8. $C_{28}H_{12}O_6N_2$ requires C, 71·2; H, 2·7; N, 5·9%).

6-(α-*Anthraquinonylamino*)*dinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone*.—(*a*) The 6-amino-compound (1·8 g.), 1-chloroanthraquinone (0·9 g.), anhydrous sodium carbonate (0·23 g.), and copper bronze (0·2 g.) were refluxed 24 hr. with nitrobenzene (30 c.c.). The solid was collected from the cooled product and washed in turn with nitrobenzene, alcohol, hydrochloric acid, and water (yield 1·8 g.). Crystallisation from quinoline gave blue needles of the 6-α-*anthraquinonylamino-derivative* (Found : C, 77·4; H, 3·2; N, 4·6. $C_{42}H_{20}O_6N_2$ requires C, 77·8; H, 3·1; N, 4·3%). Light absorption : $\lambda_{max.}$ at 267 and 490—495 mμ. (*b*) An identical product resulted by similar condensation of the 6-chloro-compound with 1-aminoanthraquinone.

Cyclisation. The above derivative (0·5 g.) was refluxed for 3 hr. with titanium tetrachloride (1 c.c.) in *o*-dichlorobenzene (9 c.c.). The resulting solution was filtered hot, and the residue was washed in succession with *o*-dichlorobenzene and acetone, and then dried. Further treatment with alkaline sodium hypochlorite and crystallisation from quinoline gave brown needles identical in properties with compound (A).

1 : 5-*Di*-(α-*anthraquinonylamino*)*anthraquinone*.—1 : 5-Dichloroanthraquinone (27·7 g.), 1-aminoanthraquinone (45 g.), anhydrous sodium carbonate (11 g.), and copper bronze (2 g.) were heated 36 hr. under reflux in nitrobenzene (500 c.c.). The product (61 g.) was very sparingly soluble in nitrobenzene; 0·11 g. crystallised on cooling from a saturated solution in 2 l. of boiling nitrobenzene. 1 : 5-*Di*-(α-*anthraquinonylamino*)*anthraquinone* forms bright red, minute needles (Found : C, 76·4; H, 3·5; N, 4·3. $C_{42}H_{22}O_6N_2$ requires C, 77·5; H, 3·4; N, 4·3%). This description supplements the reference to the preparation of the compound which is given in G.P. 230,407.

Cyclisation. Titanium tetrachloride (40 g.) and 10 g. of the above derivative were refluxed 3 hr. in *o*-dichlorobenzene (300 c.c.). The solid (12·5 g.) was then separated, and washed with fresh solvent and finally with alcohol. It became yellow when heated at 70° with sodium hydroxide and sodium hypochlorite, and it was then similar (Found : C, 77·0; H, 2·7; N, 4·4. Calc. for $C_{42}H_{18}O_6N_2$: C, 78·0; H, 2·8; N, 4·3%) to 6 : 18-dihydrobisanthra[2′,1′,4,5]pyrrolo-[2,3-*a*, 2′,3′-*h*]anthra-5 : 7 : 12 : 17 : 19 : 24-triquinone, obtained from 1 : 5-di-(α-anthraquinonylamino)anthraquinone and potassium hydroxide (G.P. 230,407) or aluminium chloride (G.P. 240,080) after the same purification (G.P. 251,021) (substance B).

5-*Nitro*-1 : 1′-*dianthraquinonylamine*.—1-Chloro-5-nitroanthraquinone (29 g.), 1-aminoanthraquinone (23 g.), anhydrous sodium carbonate (11 g.), and copper bronze (2 g.), when refluxed for 20 hr. in nitrobenzene (500 c.c.), gave a product (34 g.). Crystallisation from nitrobenzene (1·9 l.) gave red minute needles (22 g.) (Found : C, 71·2; H, 2·7; N, 5·2. $C_{28}H_{14}O_6N_2$ requires C, 71·9; H, 2·5; N, 5·4%) of 5-*nitro*-1 : 1′-*dianthraquinonylamine*. This derivative did not yield a homogeneous product when heated with titanium tetrachloride in *o*-dichlorobenzene or with aluminium chloride in pyridine.

5-*Chloro*-1 : 1′-*dianthraquinonylamine*.—A solution of the 5-amino-derivative (2 g.) in concentrated sulphuric acid (10 c.c.) was diazotised at 0° by the addition of sodium nitrite (1 g.), and the resulting diazonium salt was isolated and stirred with cuprous chloride (5 g.) and hydrochloric acid (30 c.c.) for 4 hr. whilst the temperature was raised slowly from 0° to 40°. 5-*Chloro*-1 : 1′-*dianthraquinonylamine* (2 g.) crystallised from *o*-dichlorobenzene in red needles, m. p. *ca.* 384° (Found : C, 72·0; H, 3·2; N, 3·3; Cl, 7·8. $C_{28}H_{14}O_4NCl$ requires C, 72·47; H, 3·0; N, 3·0; Cl, 7·7%).

Cyclisation. The chloro-compound (0·7 g.) was refluxed 2 hr. with titanium chloride (4 c.c.) in *o*-dichlorobenzene (15 c.c.). The solid was collected, washed, and boiled 1 hr. with chromium trioxide (4 g.) in acetic acid (30 c.c.) containing concentrated sulphuric acid (0·5 c.c.). The resulting 4-*chlorodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone* (VII; X = Cl) (0·5 g.) crystallised from nitrobenzene in yellow needles (Found : C, 72·4; H, 2·8; N, 2·8; Cl, 7·4. $C_{28}H_{12}O_4NCl$ requires C, 72·8; H, 2·6; N, 3·0; Cl, 7·7%).

5-*Benzamido*-1 : 1′-*dianthraquinonylamine*.—1-Chloro-5-benzamidoanthraquinone (18 g.), 1-aminoanthraquinone (11·5 g.), anhydrous sodium carbonate (2·6 g.), and copper bronze (1 g.), refluxed for 24 hr. in nitrobenzene (350 c.c.), gave 5-*benzamido*-1 : 1′-*dianthraquinonylamine* (27·4 g.), which formed lustrous red needles (Found : C, 76·4; H, 3·7; N, 6·0. $C_{35}H_{20}O_5N_2$ requires C, 76·7; H, 3·7; N, 5·4%).

Cyclisation. The 5-benzamido-derivative (10 g.) was vigorously stirred for 90 min. with aluminium chloride (25 g.) and pyridine (75 c.c.) in an oil-bath at 140°. The product which separated on addition to water and acidification was heated for 2 hr. at 70° with alkaline sodium-hypochlorite. The bright yellow solid was collected (9·5 g.) washed, dried, and then crystallised from nitrobenzene (6 l.). 4-*Benzamidodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone* (VII; X = NHBz) (6 g.) formed glistening yellow needles (Found : C, 76·9; H, 3·3; N, 4·6. $C_{35}H_{18}O_5N_2$ requires C, 76·9; H, 3·3; N, 5·1%).

4-*Aminodinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone*.—A solution of the 4-benzamido-derivative (1·2 g.) in concentrated sulphuric acid (10 c.c.) was heated for 4 hr. on the water-bath. The cooled solution was added to ice, and the red solid (1 g.) was crystallised from trichlorobenzene. The *amine* forms brownish-red needles (Found : C, 75·7; H, 3·4; N, 6·1. $C_{28}H_{14}O_4N_2$ requires C, 76·0; H, 3·2; N, 6·3%).

Deamination. Sodium nitrite (0·2 g.) was added during 15 min. to a solution of the 4-amine (0·35 g.) in concentrated sulphuric acid (10 c.c.) which was stirred in an ice-bath. After being stirred for 1 hr. longer the resulting solution was added to ice and kept at 0° for 2 hr., and then the precipitated diazonium salt was collected, washed (ice-water), and suspended in water (100 c.c.). Hypophosphorous acid (50 c.c. of 30%) was added; foaming occurred and a yellow precipitate was formed. The suspension was stirred overnight, the solid was collected, washed, and dried (0·32 g.), giving yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole (light absorption : $\lambda_{max.}$ at 226, 271, and 508 mμ) from nitrobenzene.

4-(α-*Anthraquinonylamino*)*dinaphtho*(2 : 3-a, 2′ : 3′-i)*carbazole*-5 : 10 : 15 : 17-*diquinone*.—The above 4-amino-derivative (0·16 g.), 1-chloroanthraquinone (0·08 g.), anhydrous sodium carbonate (0·02 g.), and a small amount of copper bronze were refluxed for 24 hr. in nitrobenzene. The solid was collected from the hot suspension, and washed in turn with nitrobenzene, alcohol, hydrochloric acid, and water. The *product* crystallised from quinoline in small red needles (Found : C, 75·7; H, 3·4; N, 4·3. $C_{42}H_{20}O_6N_2$ requires C, 77·8; H, 3·1; N, 4·3%).

Cyclisation. Titanium tetrachloride (0·15 g.), and the 4-α-anthraquinonylamino-derivative (0·06 g.) were refluxed for 3 hr. in *o*-dichlorobenzene (2 c.c.). The solid was collected and then washed in turn with *o*-dichlorobenzene (2 c.c.) and alcohol. After being dried it was heated with sodium hydroxide and sodium hypochlorite; it was then identical with the product (B) prepared directly from 1 : 5-di-(α-anthraquinonylamino)anthraquinone and titanium tetrachloride.

The following Table shows colour reactions of derivatives of 1 : 1′-dianthraquinonylamine in comparison with corresponding derivatives of 1 : 2-7 : 8-diphthaloylcarbazole.

The hendecacyclic triquinone (III) derived from either 1 : 4-di-(α-anthraquinonylamino)-anthraquinone or 3-(α-anthraquinonylamino)-1 : 2-7 : 8-diphthaloylcarbazole dissolved in concentrated sulphuric acid with a dull brownish-yellow colour, unchanged on the addition of aqueous formaldehyde. The isomeric quinone (IV) gave a violet colour in concentrated

1 : 1′-Dianthraquinonylamine and its derivatives		
Substituent	Colour in conc. H_2SO_4 (*a*)	Colour on addition of 40% CH_2O to (*a*)
—	Green	Dark blue
4-Chloro	Green	Royal blue
4-Nitro	Green-yellow	Royal blue
4-Amino	Green (red fluor.)	Deep green
4-Benzamido	Green	Green
4-(α-Anthraquinonylamino)	Green	Green
5-Chloro	Yellow	Blue
5-Nitro	Yellow	Blue
5-Amino	Yellow	Blue
5-Benzamido	Yellow	Blue
5-(α-Anthraquinonylamino)	Greenish-yellow	Blue

1 : 2-7 : 8-Diphthaloylcarbazole and its derivatives		
Substituent	Colour in conc. H_2SO_4 (*b*)	Colour on addition of 40% CH_2O to (*b*)
—	Red	Red
3-Chloro	Red	Red
3-Nitro	Red	Red
3-Amino	Red	Red
3-Benzamido	Red	Red
3-(α-Anthraquinonylamino)	Red	Red
14-Chloro	Red	Red
—	—	—
14-Amino	Purple	Purple
14-Benzamido	Blue	Blue
14-(α-Anthraquinonylamino)	Red-brown	Green

sulphuric acid, unchanged on the addition of aqueous formaldehyde. In 35% oleum the former product dissolved to a violet, and the latter to a deep blue solution.

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