# ANTHRAQUINONE AND ANTHRONE SERIES*

## Part III. Constitution of Dinitrodibenzanthrone and Some Derivatives of 3 : 3′-Dibenzanthronyl

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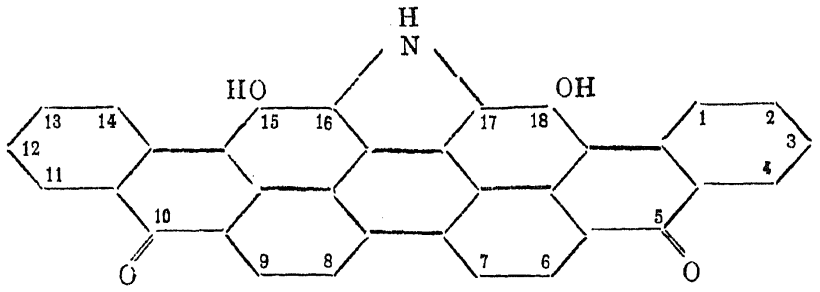
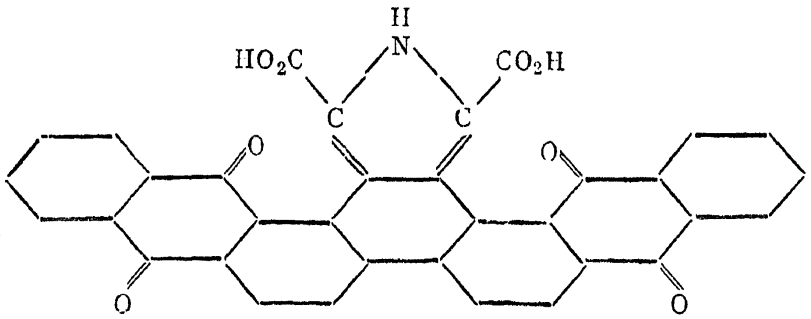
NITRATION of dibenzanthrone with nitric acid in acetic acid, nitrobenzene or chloracetic acid (the last being used in one of the I. G. processes)[1] at 20–35° gives a mixture of mono- and dinitrodibenzanthrone, dyeing an unlevel green (Indanthrene Green B) of no practical value.[2] Since the nitro groups are reduced during vatting, the product on the fibre is a mixture of aminodibenzanthrones. When the green dye is oxidized on the fibre with hypochlorite (about 0·5% available chlorine) at room temperature, a deep fast black is produced.[3] Nitrodibenzanthrone is marketed under the name of Indanthrene Black B, BB, BGA, and is an important and largely used dye. Other examples of commercial nitrodibenzanthrones are Caledon Green BP and Caledon Black NB and 2B. The position of the nitro groups and the constitution of the black dye produced on the fibre are still undetermined. The nitrogen content (4·0%) of purified Caledon Black 2B indicates that it is approximately a 50% mixture of the mononitro and the dinitro derivatives (Calc. N, 2·8% and 5·1% respectively).

The available data on the constitution of dinitrodibenzanthrone, obtained by nitration of dibenzanthrone, is conflicting and inconclusive. Maki[4] considers that the nitro groups are in the 16: 17-positions, since the corresponding diamino compound, on oxidaton with chromic acid and sulphuric acid, gave first a brown alkali-soluble product (I) and ultimately a dicarboxylic acid (II); the proposed structures (I and II), however, were based mainly on nitrogen estimation. On the assumption of the 16: 17-orientation for the nitro groups, Maki concludes that the black dye, produced by hypochlorite oxidation of the diamine on the fibre, is the pyridazine derivative (III). Bennett, Pritchard and Simonsen[5] have obtained a carboxylic acid containing nitrogen by the chromic acid oxidation of dinitrodibenzanthrone, and this rules out the 16: 17-orientation since the oxidation of benzanthrone leads to anthraquinone-1-carboxylic acid. By analogy with other substitution reactions in the benzanthrone series, they regard dinitrodibenzanthrone as the 3: 12-compound. Oxidation gave a dinitro-

* Parts I and II of the Series have appeared as 'Anthraquinone Series, Parts I and II' in the *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 467 and 1948, **28 A**, 236, respectively.

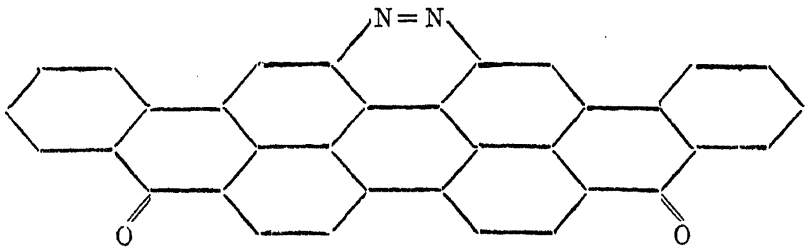


(I)



(II)

dianthraquinonyldicarboxylic acid, which on reduction and deamination *via* the diazonium salt gave 2:2′-dianthraquinonyl-1:1′-dicarboxylic acid, identical with the product of the oxidation of dibenzanthrone itself. We have now synthesized authentic 3:12-diaminodibenzanthrone (IV) by two routes, and found that it is different from the reduction product of dinitrodibenzanthrone. Dehalogenation of 3-bromo-9-aminobenzanthrone by



(III)

treatment with palladium and hydrazine hydrate[6] gave a mixture of the hitherto difficultly accessible 9-aminobenzanthrone as the major product, together with a small quantity of a vat dye which analysed for diaminodibenzanthrone and is obviously the 3:12-compound (IV).[7] The possibility of isodibenzanthrone formation during this dehalogenation is discounted by the fact that Busch and others[6] have noticed exclusive dibenzanthrone formation in such dehalogenations. The constitution (IV) for the new diaminodibenzanthrone was also confirmed by its unambiguous synthesis from 9:9′-dinitro-3:3′-dibenzanthronyl (VI) described later.

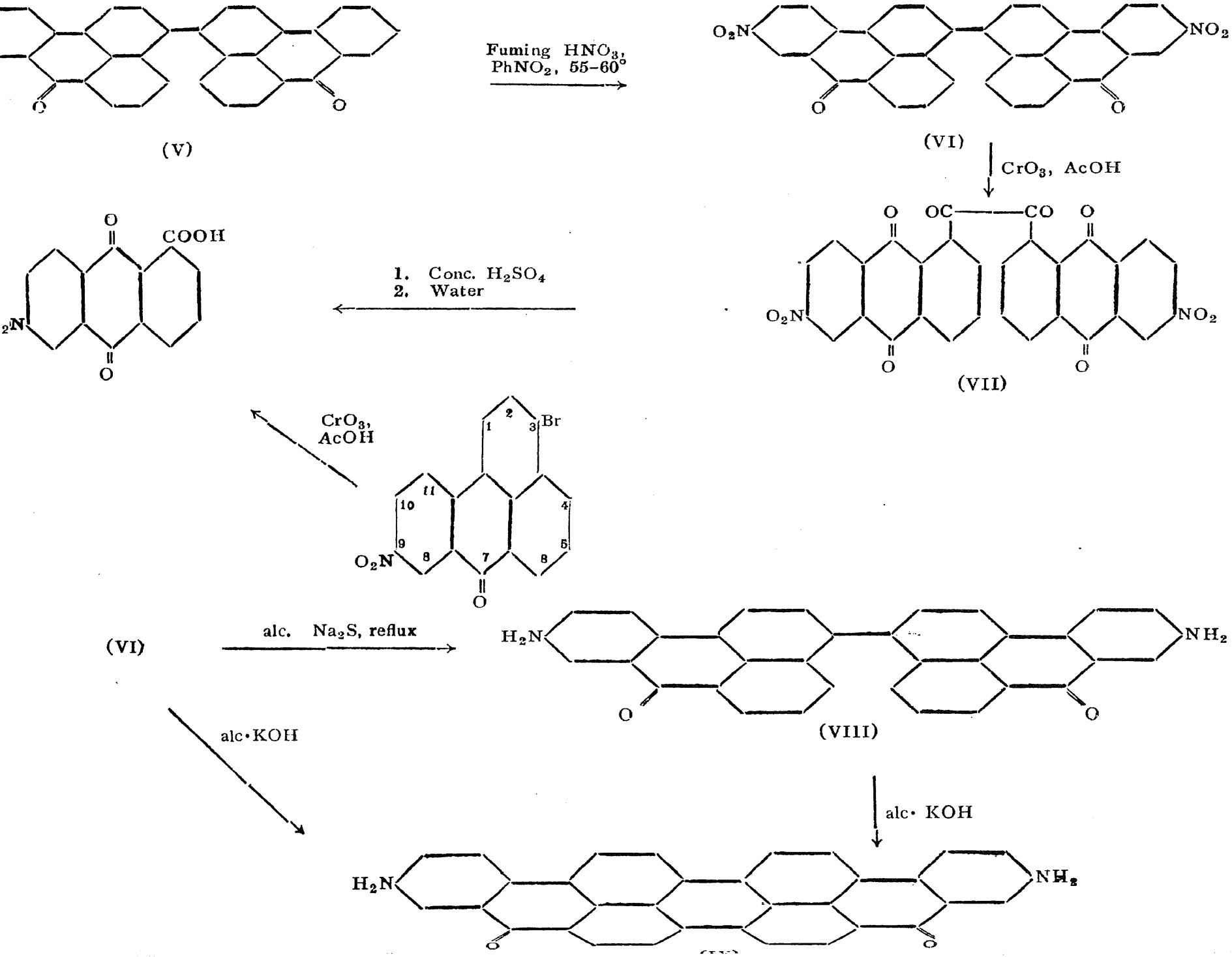
Dibenzanthrone, which forms the essential tinctorial constituent of the important vat dye Indanthrene Dark Blue BO (Bally, 1904; Colour Index No. 1099) (Caledon Dark Blue BM),[8] is prepared technically by the alkali fusion of benzanthrone, and it is somewhat difficult to isolate in pure form from the commercial product. One of the methods of obtaining pure

dibenzanthrone is the mild alkali fusion of 3 : 3′-dibenzanthronyl (V), which is obtained in good yield by the action of manganese dioxide and concentrated sulphuric acid on benzanthrone.[9] 3 : 3′-Dibenzanthronyl (V) can be readily isolated and crystallized from nitrobenzene, and it is of considerable interest as a starting material for the synthesis of dibenzanthrone derivatives of definite structure; but the orientation of substituents in 3 : 3′-dibenzanthronyl and the preparation of vat dyes from derivatives of (V) do not appear to have been studied.

Since in general the first substitution in benzanthrone takes place in the 3-position and subsequent substitution in the 9-position, it was anticipated that 3 : 3′-dibenzanthronyl (V), which can be regarded as a 3-substituted benzanthrone, would be attacked in the 9 : 9′-positions. Dinitration of (V) gave in fact the 9 : 9′-derivative (VI), the orientation of the nitro groups being established by oxidative degradation of (VI) to 6-nitroanthraquinone-1-carboxylic acid (see Chart 1).

Nitration of 3 : 3′-dibenzanthronyl to a dinitro-3 : 3′-dibenzanthronyl has been claimed in the patent literature,[10] but it has not been possible to obtain a homogeneous dinitro derivative under the conditions described. Nitration by means of concentrated nitric acid for 12 hours, according to the method of Maki[4] for dinitrodibenzanthrone, likewise gave an intractable mixture. A homogeneous dinitro-3 : 3′-dibenzanthronyl (VI) was finally obtained in good yield by the addition of fuming nitric acid (*d.*, 1·55) to a suspension of 3 : 3′-dibenzanthronyl in nitrobenzene. When (VI) was finely divided by precipitaton from sulphuric acid solution and then oxidized by means of chromic anhydride in boiling acetic acid, a light yellow crystalline powder, m.p. 420° (decomp.), was obtained, which analysed for dinitrodianthraquinonylglyoxal (VII). The glyoxal (VII) could not be converted into a nitroanthraquinone-carboxylic acid by the methods which are successful for dianthraquinonyl-1 : 1′-glyoxal and its 4 : 4′-dichloro derivatives;[11] hydrolysis with alcoholic sodium ethoxide gave a red product which was soluble in alkali, but not identifiable as a nitroanthraquinonecarboxylic acid. Fission by means of dimethyl sulphate was also unsuccessful. It was then found that concentrated sulphuric acid, in which (VII) does not dissolve initially, gradually dissolves it with the formation of a deep red solution, from which 6-nitroanthraquinone-1-carboxylic acid, m.p. 276–77°, identical with the product of oxidation of 3-bromo-9-nitrobenzanthrone with chromic acid in acetic acid,[12] was isolated. The dinitroglyoxal is, therefore, constituted as 6 : 6′-dinitrodianthraquinonyl-1 : 1′-glyoxal (VII), and the dinitrodibenzanthronyl obtained by the nitration of 3 : 3′-dibenzanthronyl as the 9 : 9′-dinitro derivative (VI).

## CHART 1


Fuming $HNO_3$, $PhNO_2$, 55–60°
(V)
(VI)
$CrO_3$, AcOH
(VII)
1. Conc. $H_2SO_4$
2. Water
$CrO_3$, AcOH
alc. $Na_2S$, reflux
(VI)
(VIII)
alc·KOH
alc· KOH

Cyclization of 9 : 9′-dinitro-3 : 3′-dibenzanthronyl with alcoholic potassium hydroxide gave a diaminodibenzanthrone which is unambiguously constituted as 3 : 12-diaminodibenzanthrone (IV) and is identical with the dye obtained by the dehalogenation of 3-bromo-9-aminobenzanthrone described later.[7] While the green shade from nitrated dibenzanthrone, such as Indanthrene Black B, changes to a full black by hypochlorite oxidation, (IV) gave a dull green shade on cotton, which changed to blue by treatment with hypochlorite. Thus, the nitration of dibenzanthrone does not yield the 3 : 12-dinitro compound as suggested by Bennett, Pritchard and Simonsen.

The dinitrodibenzanthronyl (VI) gave 9 : 9′-diamino-3 : 3′-dibenzanthronyl (VIII) by reduction with alcoholic sodium sulphide; the diamine crystallized readily from quinoline and was characterized as its acetyl and benzoyl derivatives.

Chlorination of 3 : 3′-dibenzanthronyl with gaseous chlorine in boiling trichlorobenzene and chlorination by means of antimony pentachloride in nitrobenzene gave mixtures of products. A homogeneous dichloro derivative (IX), m.p. 420°, was obtained by passing chlorine through a suspension of the dinitro derivative (VI) in trichlorobenzene at 220° till a clear solution resulted. The chlorine atoms in (IX) are in the 9 : 9′-positions as proved by the oxidative degradation of (IX) to 6-chloroanthraquinone-1-carboxylic acid (XI) through the intermediate 6 : 6′-dichlorodianthraquinonyl-1 : 1′-glyoxal (X) (see Chart 2).

When 9 : 9′-dichloro-3 : 3′-dibenzanthronyl (IX) was heated in a sealed tube with methanolic caustic potash, the product was 3 : 12-dichlorodibenzanthrone (XII); dimethoxydibenzanthronyl and the corresponding dimethoxydibenzanthrone were not isolated.[13]

## Experimental

### 9 : 9′-*Dinitro*-3 : 3′-*dibenzanthronyl* (*VI*)

3 : 3′-Dibenzanthronyl (V) (30 g.) was suspended in dry nitrobenzene (300 c.c.), nitric acid (*d.*, 1·55; 30 c.c.) added in the course of 30 minutes under stirring at 55–60°, and the mixture further stirred at this temperature for one and a half hours. After the addition of half the quantity of nitric acid, the suspended dibenzanthronyl went into solution, and as the reaction continued the nitro derivative gradually separated. It was collected, washed successively with nitrobenzene and benzene, and dried (22 g.). The nitro derivative crystallized from a large volume of nitrobenzene in shining minute orange-yellow needles which did not melt up to 550°. (Found: C, 74·2; H, 3·0; N, 5·1. $C_{34}H_{16}N_2O_6$ requires C, 74·4; H, 2·9; N, 5·1%.)

CHART II


Cl
O
O
Cl
(IX)
$Cl_2$, trichlorobenzene, 220°
$CrO_3$, AcOH
Cl
O
O
CO
OC
O
O
Cl
(X)
1. Conc. $H_2SO_4$
2. Water
(IX)
COOH
O
O
Cl
Methanolic KOH, 150°
Cl
O
O
(XII)

6 : 6′-*Dinitrodianthraquinonyl*-1 : 1′-*glyoxal* (*VII*)

The dinitro derivative (VI) (0·5 g.) was dissolved in concentrated sulphuric acid and reprecipitated with water. After washing the finely divided product free from sulphuric acid, it was washed with acetic acid and treated in boiling glacial acetic acid (25 c.c.) under reflux with chromic acid (4 g.) in the course of four hours. Refluxing was continued for two hours longer and the reaction mixture filtered hot. The residue was washed with acetic acid and water; the glistening mass of light yellow needles (0·25 g.) was crystallizable from nitrobenzene and trichlorobenzene, but the yield in the recrystallizations was poor. The crystalline reaction product itself, however, melted sharply at 420° (decomp.) and analysed for dinitrodianthraquinonyl-1 : 1′-glyoxal (VII). (Found: C, 64·2; H, 2·1; N, 5·2. $C_{30}H_{12}N_2O_{10}$ requires C, 64·2; H, 2·4; N, 5·2%.) The product (VII) darkens in colour on exposure to air.

6-*Nitroanthraquinone*-1-*carboxylic acid*

The glyoxal (VII) (0·1 g.) was suspended in concentrated sulphuric acid (2 c.c.). In the course of one hour a dark red solution was obtained which on dilution with ice gave a greenish coloured product (0·1 g.), m.p. 255–60°. The latter gave a red solution in dilute aqueous ammonia and caustic soda, and the alkali solution on acidification gave the parent substance as a light yellow precipitate. The purified product on recrystallizing twice from dilute acetic acid was obtained as pale yellow needles, m.p. 276–77°, alone or admixed with authentic 6-nitroanthraquinone-1-carboxylic acid, m.p. 277–78°, prepared by oxidation of 3-bromo-9-nitrobenzanthrone with chromic acid in acetic acid.

3 : 12-*Diaminodibenzanthrone* (IV)

A mixture of crystalline dinitrodibenzanthronyl (VI) (1 g.), caustic potash (8 g.) and methyl alcohol (15 c.c.) was heated to 120° under vigorous stirring for 2 hours, during which it darkened in colour. On dilution with water a red-violet solution of the reduced vat dye was obtained. The dye was recovered by aeration, filtered, washed with water and dried (0·9 g.). It was purified by vatting, filtering and reoxidizing when a green flocculent precipitate separated. Crystallization from quinoline gave a blue substance. (Found: C, 83·5; H, 4·0; N, 5·2. $C_{34}H_{18}N_2O_2$ requires C, 83·9; H, 3·7; N, 5·7%.) It dyes from a violet vat a dull green shade which turns to bright blue on hypochlorite oxidation.

9 : 9′-*Diamino*-3 : 3′-*dibenzanthronyl* (*VIII*)

Finely powdered dinitrodibenzanthronyl (VI) (4·16 g.) was refluxed under stirring with 10% alcoholic sodium sulphide (110 c.c.) for four hours.

The reaction mixture, which turned deep red in colour, was filtered, and the residue washed with hot water and alcohol and dried (3·7 g.). The diamine (VIII) crystallized from quinoline (280 c.c.) in brownish red needles (3 g.), which did not melt up to 550°. (Found: C, 83·9; H, 4·2; N, 5·4. $C_{34}H_{20}N_2O_2$ requires C, 83·6; H, 4·1; N, 5·7%.) The substance gives a red solution with concentrated sulphuric acid from which a yellow coloured sulphate separates on dilution with water.

9 : 9′-*Bis-acetamido*-3 : 3′-*dibenzanthronyl*

The crystallized diamine (VIII) (0·2 g.) was refluxed with glacial acetic acid (10 c.c.), acetic anhydride (10 c.c.) and 3 drops of pyridine for two hours. After cooling, the reaction mixture was filtered, and the residue washed with acetic acid and water. The scarlet product (0·23 g.) on crystallization from quinoline (50 c.c.) gave the diacetyl derivative as small disc-shaped crystals. (Found: N, 5·1. $C_{38}H_{24}N_2O_4$ requires N, 4·9%.)

9 : 9′-*Bis-benzamido*-3 : 3′-*dibenzanthronyl*

The diamine (VIII) (0·4 g.) was refluxed with benzoyl chloride (15 c.c.) for one hour, during which the colour of the reaction mixture changed from brownish red to yellow. After pouring in ice-water (600 c.c.), the mixture was left overnight, and the benzoyl derivative was washed with dilute ammonia and water, dried and crystallized from nitrobenzene (150 c.c.) when minute yellow needles were obtained. (Found: N, 3·9. $C_{48}H_{28}N_2O_4$ requires N, 4·0%.)

9 : 9′-*Dichloro*-3 : 3′-*dibenzanthronyl* (*IX*)

Dinitrodibenzanthronyl (VI) (0·5 g.) was suspended in trichlorobenzene (40 c.c.) kept at 220° by heating in an oil-bath, and dry chlorine gas was passed through the suspension for one hour. The dinitro derivative (VI), which was initially undissolved, went into solution at the end of the reaction. After removal of trichlorobenzene by steam distillation, a nitrogen-free chloro-compound (0·48 g.), m.p. 410–18°, was obtained. Two crystallizations from nitrobenzene gave yellow plates, m.p. 420–22°. (Found: C, 77·0; H, 3·1; Cl, 14·1. $C_{34}H_{16}Cl_2O_2$ requires C, 77·4; H, 3·1; Cl, 13·5%.)

3 : 12-*Dichlorodibenzanthrone* (*XII*)

The dichlorodibenzanthronyl (XI) (0·5 g.) was obtained in a finely divided form by precipitation from sulphuric acid solution, and after washing with water and methanol was suspended in methanolic potassium hydroxide (7 g. in 50 c.c.). The suspension was heated in a sealed tube for 7 hours at 150°.

The red reaction mixture was poured into water (400 c.c.), the suspension boiled and the precipitate collected (0·47 g.). The greyish blue product was sparingly soluble in boiling nitrobenzene, from which it crystallized in minute greyish blue needles. (Found: Cl, 13·4. $C_{34}H_{14}Cl_2O_2$ requires Cl, 13·5%.)

6 : 6′-*Dichlorodianthraquinonyl*-1 : 1′-*glyoxal* (*X*)

9 : 9′-Dichloro-3 : 3′-dibenzanthronyl (IX) (0·5 g.) was refluxed with glacial acetic acid (25 c.c.), and chromic anhydride (4 g.) was added in five lots during three hours. After refluxing for two hours, the mixture was filtered hot, washed with acetic acid and then with water. The residue (0·23 g.) was a light yellow crystalline powder, m.p. 310° (decomp.). (Found: Cl, 12·8. $C_{30}H_{12}Cl_2O_6$ requires Cl, 13·1%.)

6-*Chloroanthraquinone*-1-*carboxylic acid from* (*IX*)

The compound (IX) (0·1 g.) was treated with concentrated sulphuric acid (3 c.c.) when it dissolved with a red colouration. After leaving overnight the solution was poured into water, when a green precipitate separated (0·1 g.), m.p. 280–90°. It dissolved in alkali with a light red colouration and a light yellow substance (0·06 g.) precipitated on acidification. Two crystallizations from dilute acetic acid gave light yellow needles, m.p. 305-06°. The mixed m.p. with authentic 6-chloroanthraquinone-1-carboxylic acid was unaltered; Maki records the m.p. 307–08° (corr.).[14]

## Summary

The orientation of the nitro groups in dinitrodibenzanthrone produced by nitration of dibenzanthrone has not been established so far. The suggestion of Simonsen *et al.*[5] that the nitro groups are in the 3 : 12-positions has been disproved by the unambiguous synthesis of 3 : 12-diaminodibenzanthrone (IV), which was found to be different from the diamino derivative obtained by the reduction of the above dinitrodibenzanthrone. The diaminodibenzanthrone (IV) was synthesized from 3 : 3′-dibenzanthronyl (V) by nitration to 9 : 9′-dinitro-3 : 3′-dibenzanthronyl (VI) and conversion of the latter in one step to (IV). The 9 : 9′-orientation of the nitro groups in (VI) was shown by its oxidation to 6-nitroanthraquinone-1-carboxylic acid.

Derivatives of 3 : 3′-dibenzanthronyl of definite orientation are useful as intermediates for the corresponding dibenzanthrone derivatives. Thus the dinitrodibenzanthronyl (VI) has been converted to 3 : 12-dichloro- and 3 : 12-diaminodibenzanthrone.

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