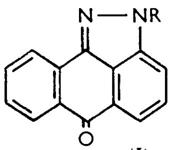
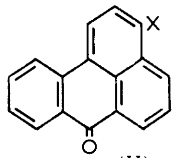
378. *Formation of Quinones by Union of Ketones. The Structure of Indanthrene Navy Blue R.*

By William Bradley and K. H. Shah.

The constitutions assigned to the products obtained by reaction of 1 : 9-pyrazoloanthrone with 3-bromo*meso*benzanthrone and subsequent cyclisation have been confirmed. The course of the reactions has been investigated and shown to be ionic in character.

B.I.O.S. Final Report No. 1493, p. 26, records the preparation of a compound (Indanthrene Navy Blue R) by the condensation of 1 : 9-pyrazoloanthrone (I; R = H) with 3-bromo*meso*benzanthrone (II; X = Br) and treatment of the product with ethanolic potassium hydroxide. The blue dye was assigned[1] structure (IV) on the grounds of


(I)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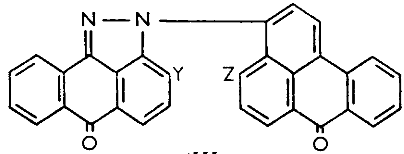
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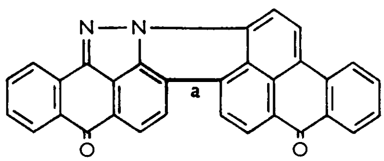
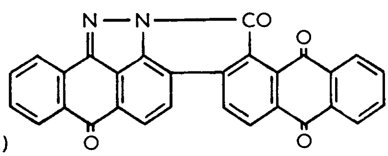
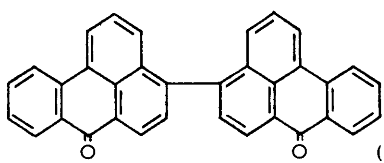

(IV)

composition and behaviour as a quinone, being reduced with alkaline sodium dithionite to an alkali-soluble product. This gave back the original compound on being oxidised in air. The purpose of the present work was to confirm structure (IV) and to study the reactions by which the dye had been formed.

It was found that the condensation of 1 : 9-pyrazoloanthrone with 3-bromo*meso*benzanthrone was much improved when the first was used as the potassium salt (I; R = K) and the reaction carried out in nitrobenzene. Purification gave 1′-(*meso*benzanthron-3-yl)pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (III; Y = Z = H), the structure of which follows from reactions to be described. For conversion of the compound (III; Y = Z = H) into the blue quinone, sodium hydroxide in pentyl alcohol at 110—120° was found to give the maximum yield. Sodium anilide was more active, but with this reagent degradation and substitution occurred even at 10°; at 60° side reactions were still more marked. The blue quinone was obtained crystalline and with the expected composition,

(V)


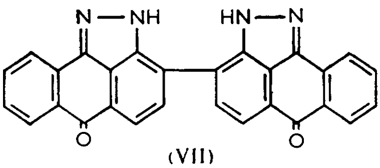

(VI)

$C_{31}H_{14}O_2N_2$. Reductive acetylation gave a magenta diacetyl derivative of a dihydro-compound, $C_{35}H_{20}O_4N_2$. On being oxidised with chromium trioxide in aqueous sulphuric acid the blue quinone gave a green lactam, $C_{29}H_{12}O_4N_2$ (V), which also behaved as a quinone towards alkaline sodium dithionite.

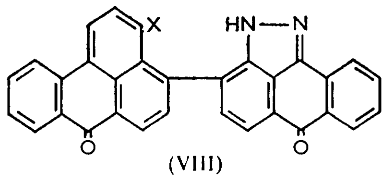
The main uncertainty in the structure of the blue quinone (IV) was of the bond (a) and to elucidate this point the union of *meso*benzanthrone with 1 : 9-pyrazoloanthrone in the

[1] "Colour Index," 2nd edn., 1956, Vol. III, No. 70,500.

presence of bases was studied. With alkaline reagents *meso*benzanthrone alone gives bi(*meso*benzanthron-4-yl) (VI) and violanthrone,[2] whilst 1 : 9-pyrazoloanthrone alone affords Pyrazoloanthrone Yellow [3] (VII). All these products were found in the reaction between the compounds (I; R = H) and (II; X = H) in the presence of sodium anilide, but a small proportion of 2-(*meso*benzanthron-4-yl)-1 : 9-pyrazoloanthrone (VIII; X = H) was formed also. This diketone resembles the diketone (VII) in physical and chemical



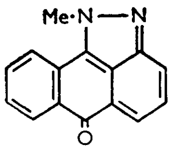
(VII)



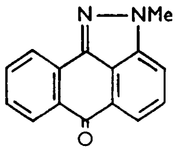
(VIII)

properties and differs considerably from (VI). It forms a red alkali-metal salt and an *N*-benzoyl derivative, and readily yields a turquoise-blue reduction product with alkaline sodium dithionite. In contrast, the compound (VI) shows no quinonoid properties. With bromine in chlorosulphonic acid containing iodine the compound (VIII) gave a monobromo-derivative, considered to be 2-(3-bromo*meso*benzanthron-4-yl)-1 : 9-pyrazoloanthrone (VIII; X = Br) for the reason that *meso*benzanthrone is most easily brominated in the 3-position [1] and because of the following reaction. Heating the bromo-derivative in nitrobenzene with anhydrous potassium carbonate gave a blue quinone identical with that of B.I.O.S. 1493, p. 26. It follows that the quinone possesses structure (IV) and that the intermediate product obtained by reaction of 1 : 9-pyrazoloanthrone with 3-bromo-*meso*benzanthrone is represented correctly by (III; Y = Z = H).

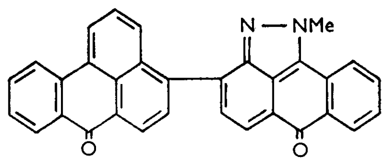
1 : 9-Pyrazoloanthrone forms two isomeric *N*-methyl derivatives of which (IX) is much more reactive towards nucleophilic substituting agents than is (X). In addition the isomer (IX) undergoes self-union in the presence of bases more readily than does (X).[4] Analogously, the latter was not observed to condense with *meso*benzanthrone in the



(IX)

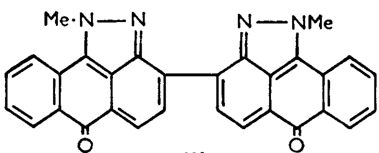


(X)



(XI)

presence of sodium anilide whilst the former condensed more readily than 1 : 9-pyrazoloanthrone itself, the product consisting of 2-(*meso*benzanthron-4-yl)-1′-methylpyrazolo-(3′ : 4′ : 5′-1 : 13 : 9)anthrone (XI) and other derivatives. With equimolar amounts of reactants the yield of compound (XI) was of the same order as that of the symmetrical derivative (XII) which is formed so readily when the derivative (IX) is used alone. The result indicates that the product (XI) cannot be formed by a radical type reaction, which should favour the symmetrical compound (XII). If on the contrary the coupling reaction



(XII)

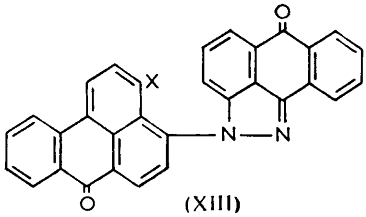
is ionic it remains to be decided whether *meso*benzanthrone or the pyrazoloanthrone (IX)

[2] Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259.
[3] Mayer and Heil, *Chem.-Ztg.*, *Fortschrittsber.*, 1929, p. 56.
[4] Bradley and Bruce, *J.*, 1954, 1894.

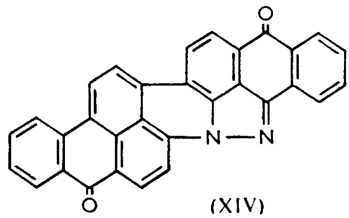
initiates the reaction. *N*-Methyl-1 : 9-pyrazoloanthrone (IX) undergoes self-union more rapidly than *meso*benzanthrone in the presence of bases, and for this reason it is probable that the formation of (VIII; X = H) is initiated by ionisation of (IX), the anion of which then attacks a molecule of *meso*benzanthrone.

A decision as to the course of the cyclisation (III; Y = Z = H) $\longrightarrow$ (IV) is less easy because compound (III; Y = Z = H) belongs to the same chemical class as (X) which undergoes self-union only with difficulty. Indeed it appears more probable that with compound (III) cyclisation begins with the ionisation of the *meso*benzanthrone portion.

An attempt to prepare the diketone (VIII; X = H) by Ullmann condensation of 4-chloro*meso*benzanthrone and 2-chloro-1 : 9-pyrazoloanthrone was unsuccessful, as also were several attempts to prepare its derivatives.



(XIII)



(XIV)

Reaction of 4-chloro*meso*benzanthrone with the potassium derivative (I; R = K) gave 1′-(*meso*benzanthron-4-yl)pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (XIII; X = H) (XIII) (cf. U.S.P. 1,873,925) which did not cyclise to a quinone with sodium hydroxide in pentyl alcohol or sodium anilide. Bromination of 4-chloro*meso*benzanthrone gave a mono(3?)-bromo-derivative, which with the potassium derivative (I; R = K) afforded a bromo-derivative (XIII; X = Br?), the 4-chloro-substituent being eliminated. Further treatment with sodium anilide gave a crystalline reddish-brown quinone but this was not obtained free from bromine. Nitration of 4-chloro*meso*benzanthrone gave the 3-nitro-derivative[5] and this gave the derivative (XIII; X = NO_2) from which the nonacyclic product (XIV) resulted on treatment with alcoholic potassium hydroxide.

Experimental

1′-(meso*Benzanthron-3-yl)pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone* (III; Y = Z = H).—A solution of potassium hydroxide (1 g.) in methanol (5 ml.) was added to one of 1 : 9-pyrazoloanthrone (4·4 g.) in hot pyridine (40 ml.). After 30 min. benzene was added and the potassium salt which separated was collected and dried (4·4 g.). A mixture of the potassium salt (10 g.), 3-bromo*meso*benzanthrone (10 g.), and nitrobenzene (150 ml.) was stirred for 24 hr. under reflux. The suspension which was formed was filtered and the residue washed with alcohol, extracted with boiling water, and then dried (12 g.). Crystallisation from nitrobenzene gave yellow *needles* which dissolved in concentrated sulphuric acid to form a non-fluorescent orange-red solution (Found: C, 82·7; H, 3·6; N, 6·5. $C_{31}H_{16}O_2N_2$ requires C, 83·0; H, 3·6; N, 6·3%). The procedure is an improvement on that described,[6] which also does not record an analysis of the product.

5 : 10-*Dihydro*-5 : 10-*dioxoanthra*[9,1,2-jkl]*benz*[6,7]*indazolo*[4,3,2-cde]*acridine* (IV) (cf. Ring Index No. 3919).—The yellow needles (10 g.) obtained in the preceding preparation were stirred for 5 hr. at 110° with sodium hydroxide (30 g.) and pentyl alcohol (120 ml.). The resulting suspension was distilled in steam, then acidified, and the solid was collected, dried (10 g.), and extracted (Soxhlet) with acetone, then pyridine. The residue was extracted with alkaline sodium dithionite, and the blue solution which was formed was filtered and aerated. A precipitate formed, was collected, was hed, dried, and crystallised from nitrobenzene. It gave blue needles (Found: C, 82·9; H, 3·2; N, 6·2. Calc. for $C_{31}H_{14}O_2N_2$: C, 83·4; H, 3·1; N, 6·3%) which dissolved in concentrated sulphuric acid with a blue colour.

[5] G.P. 450,445, 492,248.
[6] B.I.O.S. Final Report, No. 1493, p. 26.

The same quinone (IV) was obtained when the product (III; Y = Z = H) was stirred for 2 hr. at 0—5° with a solution of sodium anilide in aniline.

5 : 10-*Diacetoxyanthra*[9,1,2-jkl]*benz*[6,7]*indazolo*[4,3,2-cde]*acridine*.—Zinc dust (5 g.) was added gradually to a suspension of the quinone (IV) (1 g.) in acetic anhydride (20 ml.) which was stirred under reflux. After the addition was complete refluxing was continued for 5 hr. and then the suspension was filtered, the filtrate was added to dilute hydrochloric acid, the precipitate was collected, dried, and extracted with pyridine, and the solution so obtained added to water. The precipitate was collected, washed with acetone, and dried (Found: C, 78·4; H, 4·0; N, 5·7. $C_{35}H_{20}O_4N_2$ requires C, 78·9; H, 3·8; N, 5·3%). This *diacetoxy-derivative* dissolved readily in pyridine forming a magenta solution.

Oxidation of Quinone (IV) *to the Lactam* (V).—A solution of the quinone (IV) (5·5 g.) in concentrated sulphuric acid (150 ml.) was added slowly to a boiling solution of chromium trioxide (22·5 g.) in water (695 ml.) through which air was passed. After 4 hr. a further portion of chromium trioxide (7·5 g.) was added and refluxing continued for 12 hr. Water was then added and the precipitate formed was collected and dissolved in alkaline sodium dithionite. The red-violet solution which resulted was filtered and the filtrate aerated. The solid which separated was collected, heated in concentrated sulphuric acid for 1 hr., and recovered by addition to water. After being dried it crystallised from nitrobenzene as green needles (Found: C, 76·9; H, 2·7; N, 6·1. $C_{29}H_{12}O_4N_2$ requires C, 77·0; H, 2·7; N, 6·2%). This *lactam* of 2-(2′-anthraquinonyl)-1 : 9-pyrazoloanthrone-1′-carboxylic acid dissolves in alkaline sodium dithionite forming a reddish-brown solution.

N-*Benzoyl-2-*(meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* (N-*Benzoyl Derivative of* VIII; X = H).—1 : 9-Pyrazoloanthrone (10 g.), *meso*benzanthrone (10 g.), and glucose (10 g.) were refluxed with stirring for 7 hr. in alcohol (150 g.) containing potassium hydroxide (100 g.). Water was then added, air was passed through the resulting suspension, and finally this was acidified. The solid formed (23 g.) was collected, washed, dried, and extracted with acetone and then with hot trichlorobenzene. The latter extract was chromatographed on alumina, and the bands were developed with trichlorobenzene. The column was washed with alcohol and dried, and the adsorbate eluted from the main band with pyridine (Soxhlet). The pyridine solution so obtained was added to dilute hydrochloric acid, and the precipitate (1·4 g.) was collected, dried, and heated with benzoyl chloride for 4 hr. The *N*-benzoyl derivative was then isolated by the addition of ether, filtration, and warming of the filtrate with aqueous sodium carbonate. A solid was formed and this was taken up in chlorobenzene and chromatographed on alumina. The principal band was yellow; it was eluted with pyridine, and the solute separated by addition of the extract to dilute hydrochloric acid. N-*Benzoyl-*(2-meso-*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* crystallised from aniline–tetralin in yellow plates (Found: C, 82·6; H, 3·6; N, 5·0. $C_{38}H_{20}O_3N_2$ requires C, 82·6; H, 3·6; N, 5·1%).

2-(meso*Benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* (VIII; X = H).—(*a*) On being refluxed for 12 hr. with potassium hydroxide in *tert.*-butyl alcohol the foregoing *N*-benzoyl derivative gave 2-(meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* which crystallised from nitrobenzene in greenish-yellow plates (Found; C, 83·2; H, 3·7; N, 6·2. $C_{31}H_{16}O_2N_2$ requires C, 83·0; H, 3·6; N, 6·3%). It formed a red potassium salt and dissolved in alkaline sodium dithionite with a turquoise-blue colour. (*b*) 2-(*meso*Benzanthron-4-yl)-1 : 9-pyrazoloanthrone was prepared directly by the interaction of *meso*benzanthrone and 1 : 9-pyrazoloanthrone under the following conditions. *meso*Benzanthrone (10 g.), 1 : 9-pyrazoloanthrone (10 g.), and aniline (60 g.) were added at 40—45° to a stirred solution of sodium anilide prepared by refluxing sodium (5 g.), copper bronze (0·2 g.), and nickel oxide (0·2 g.) with " AnalaR " aniline (150 ml.) under nitrogen. After 2 hr. the resulting suspension was cooled and added to dilute hydrochloric acid containing ice, and the solid (22 g.) formed was collected, washed, and dried. It was then extracted (Soxhlet) with acetone, and the insoluble part (11 g.) was extracted with hot trichlorobenzene. The residue (5 g.) consisted mainly of bi-(1 : 9-pyrazoloanthron-2-yl). The extract was chromatographed on alumina at 160—170° and the bands were developed further with trichlorobenzene. A red substance passed through the column followed by bi-(*meso*benzanthron-4-yl) as a greenish-yellow band. After washing of the column with alcohol the material which remained was eluted with pyridine and separated by addition of the eluate to dilute hydrochloric acid. The precipitate so formed was collected, washed, and extracted with alkaline sodium dithionite. On being aerated the extract afforded a precipitate which after being extracted with acetone was dissolved in nitrobenzene and chromatographed on alumina at 140°.

A main band consisting of 2-(*meso*benzanthron-4-yl)-1 : 9-pyrazoloanthrone was formed. Violanthrone also was formed in the sodium anilide reaction, the amount increasing with the temperature at which the condensation was carried out.

Two other experiments were carried out, with sodium anilide at 40—45° in which the proportions of the reactants were varied. The results obtained were:

*meso*Benzanthrone (g.)	1 : 9-Pyrazoloanthrone (g.)	Na (g.)	Yield (g.) of (VIII; X = H)
34·5	6·6	10	0·02
6·9	33·0	10	0·03

It was not possible to prepare compound (VIII; X = H) by heating a mixture of 2-chloro-1 : 9-pyrazoloanthrone and 4-chloro*meso*benzanthrone, or by the action of sodium anilide on a mixture of 1 : 9-pyrazoloanthrone and 4-chloro*meso*benzanthrone at 45—50° (3 hr.). None was formed when *meso*benzanthrone-4-carboxylic acid [7] (3 g.) was heated with 1 : 9-pyrazoloanthrone (12·5 g.) at 300—320° for 5 hr.

Reaction of meso*Benzanthrone with* 1′-*Methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone*.—*meso*-Benzanthrone (4·5 g.) and 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (4·5 g.) were stirred for 2 hr. at 45—50° with sodium anilide prepared from sodium (2·4 g.) and aniline (75 ml.). The product was worked up as in (*b*) (above) and finally purified by dissolution in alkaline sodium dithionite solution, filtration, and reprecipitation by aeration of the filtrate. The solid (3 g.) so obtained was extracted with acetone, and the residue (2 g.) taken up in nitrobenzene and chromatographed on alumina at 100—120°; a small orange-red fraction consisting of bi-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl] remained undissolved.[4] The main band was eluted with nitrobenzene, and the solute recovered by concentration of the extract. 2-(meso*Benzanthron-4-yl*)-1′-*methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone* (XI) crystallised from nitrobenzene as orange needles (Found: C, 82·7; H, 4·0; N, 6·3. $C_{32}H_{18}O_2N_2$ requires C, 83·1; H, 3·9; N, 6·1%), which dissolved in concentrated sulphuric acid with an orange-red colour and in alkaline sodium dithionite forming a blue solution.

When the isomeric 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone was used in the preceding experiment no union with *meso*benzanthrone was observed.

2-(3-*Bromo*meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* (VIII; X = Br).—A solution of 2-(*meso*benzanthron-4-yl)-1 : 9-pyrazoloanthrone (0·4 g.) in chlorosulphonic acid (7 ml.) was stirred with bromine (0·2 ml.) and a trace of iodine for 24 h. at the room temperature. Sulphuric acid was then added and the whole added to water. The product which separated was stirred with sodium metabisulphite solution, collected, and washed with water. It was a green solid which was not obtained pure (Found: Br, 19. Calc. for $C_{31}H_{15}O_2N_2Br$: Br, 15%). It dissolved in alkaline sodium dithionite forming a green solution.

Cyclisation. A solution of the bromo-derivative (0·3 g.) in nitrobenzene (10 ml.) containing anhydrous potassium carbonate (0·3 g.) was refluxed for 12 hr. On being cooled, this gave a greenish-blue precipitate. This was collected and extracted with nitrobenzene, and the solution so obtained was chromatographed on alumina at 160—170°. A blue band formed. This was eluted with nitrobenzene, the eluate steam-distilled, and the residue chromatographed in alkaline sodium dithionite and on cellulose powder with alcoholic alkaline sodium dithionite to develop the bands. A small green fraction passed through the column first, followed by a large blue band. The latter was collected, and the colouring matter was precipitated by aeration and crystallised from nitrobenzene (Found: N, 6·0. Calc. for $C_{31}H_{14}O_2N_2$: N, 6·3%). It was identical with the quinone (IV) formed by cyclisation of (III; X = Y = H); like this it showed no reaction when a drop of 30% methanolic potassium hydroxide was added to its blue solution in dry pyridine.

N-(meso*Benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone*.—The potassium salt of 1 : 9-pyrazoloanthrone (1 g.) and 4-chloro*meso*benzanthrone (1 g.) were refluxed for 24 hr. with stirring in dry nitrobenzene (10 ml.). The precipitate formed was collected, washed with alcohol, extracted with hot water, and then dried. N-meso*Benzanthron-4-yl*-1 : 9-*pyrazoloanthrone* crystallised from nitrobenzene in greenish-yellow needles (Found: C, 83·0; H, 3·7; N, 6·4. $C_{31}H_{16}O_2N_2$ requires C, 83·0; H, 3·6; N, 6·2%). It dissolved in concentrated sulphuric acid with a red colour. This derivative did not cyclise to a quinonoid compound when 1 g. was heated with sodium hydroxide (3 g.) and pentyl alcohol (12 ml.) at 110° for 24 hr. with stirring. Similarly no cyclisation was observed with sodium anilide in aniline at 80°.

[7] Bradley and Shah, following paper.

*Bromination of 4-Chloro*meso*benzanthrone.*—(*a*) A solution of bromine (1 ml.) in nitrobenzene (5 ml.) was added dropwise during 2 hr. to a suspension of 4-chloro*meso*benzanthrone (4·4 g.) in nitrobenzene (20 ml.) containing iodine (0·01 g.) which was stirred at 100°. The reaction was continued for 16 hr. and then the suspension was cooled. Benzene was added, and the precipitate was collected, washed with alcohol, and crystallised from xylene (norite). 3-*Bromo-4-chloro*meso*benzanthrone* forms yellow needles, m. p. 220° (Found: C, 57·5; H, 2·6. $C_{17}H_8OClBr$ requires C, 59·4; H, 2·3%. 5·699 mg. gave 5·527 mg. of mixed silver halides; calc. for $C_{17}H_8OClBr$, 5·499 mg.). (*b*) In a similar experiment in which the reactants were bromine (0·6 ml.), iodine (0·05 g.), and 4-chloro*meso*benzanthrone (1 g.) stirred in nitrobenzene (15 ml.) at 130° for 4 hr. the product was chromatographed on alumina at 60° from a solution in chlorobenzene. The main fraction crystallised from chlorobenzene as yellow, flat needles, m. p. 259—260° (Found: C, 47·9; H, 1·7. $C_{17}H_7OClBr_2$ requires C, 47·2; H, 1·7%. 6·443 mg. gave 7·405 mg. of mixed silver halides. Calc. for $C_{17}H_7OClBr_2$: 7·884 mg.).

N-(*3-Bromo*meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone.*—Potassium 1 : 9-pyrazoloanthrone (1·3 g.) and 3-bromo-4-chloro*meso*benzanthrone [1·7 g.; prepared as in (*a*) above] were refluxed together in nitrobenzene (25 ml.) for 24 hr. The resulting suspension was cooled, and the solidwas collected (1·5 g.) and crystallised from nitrobenzene. N-(*3-Bromo*meso*benzanthron-4-yl*-1 : 9-*pyrazoloanthrone* formed greenish-yellow needles (Found: C, 70·8; H, 3·0; N, 5·2; Br, 15·3. $C_{31}H_{15}O_2N_2Br$ requires C, 70·6; H, 2·8; N, 5·3; Br, 15·2%) which dissolved in concentrated sulphuric acid with a red colour.

N-(*3-Nitro*meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone.*—4-Chloro-3-nitro*meso*benzanthrone [5] (5 g.) and potassium 1 : 9-pyrazoloanthrone (5 g.) were refluxed in nitrobenzene (50 ml.) for 24 hr. The product was isolated as for the 3-bromo-derivative and crystallised from nitrobenzene. N-(*3-Nitro*meso*benzanthron-4-yl*)-1 : 9-*pyrazoloanthrone* forms orange-yellow plates (Found: N, 8·8. $C_{31}H_{15}O_4N_3$ requires N, 8·5%).

Conversion into the Quinone (XIV).—The 3-nitro-derivative (5 g.) was stirred for 7 hr. with potassium hydroxide (30 g.) in ethanol (50 g.). Water was then added and the resulting suspension aerated. The solid formed was collected and dissolved in alkaline sodium dithionite, and the solution so obtained was filtered and again aerated. The precipitate was crystallised from nitrobenzene and the *quinone* (XIV) was obtained as reddish-brown needles (Found: C, 83·2; H, 3·1; N, 6·0. $C_{31}H_{14}O_2N_2$ requires C, 83·4; H, 3·1; N, 6·3%) which dissolved with a blue colour both in concentrated sulphuric acid and in alkaline sodium dithionite solution.

2-Chloro-1 : 9-*pyrazoloanthrone.*—99—100% Hydrazine hydrate (4·5 ml.) was added dropwise to a refluxing solution of 1 : 2-dichloroanthraquinone (13·5 g.) in pyridine (150 ml.). Heating was then continued for 6 hr. The solution formed was cooled and added to water, and the *2-chloro*-1 : 9-*pyrazoloanthrone* so obtained was crystallised from chlorobenzene (norite) as pale greenish-yellow needles, m. p. 286° (Found: C, 66·2; H, 2·8; N, 11·0; Cl, 14·0. $C_{14}H_7ON_2Cl$ requires C, 66·1; H, 2·7; N, 11·0; Cl, 13·9%). The red potassium salt separated when potassium hydroxide (0·5 g.) in methanol (5 ml.) was added to a solution of the derivative (2·5 g.) in pyridine (40 ml.). Attempts to bring the salt into reaction with 3-bromo*meso*benzanthrone and 4-chloro*meso*benzanthrone were unsuccessful.

2-Amino-1 : 9-*pyrazoloanthrone.*—Reaction of 2-amino-1-chloroanthraquinone (5 g.) with 99—100% hydrazine hydrate (2·5 ml.) in pyridine (50 ml.) under reflux for 12 hr. gave *2-amino*-1 : 9-*pyrazoloanthrone* (3·5 g.), which crystallised from nitrobenzene as brown needles with a green fluorescence (Found: C, 71·3; H, 4·0; N, 17·4. $C_{14}H_9ON_3$ requires C, 71·5; H, 3·9; N, 17·9%). It formed a potassium salt, but an attempt to bring this into reaction with 3-bromo*meso*benzanthrone was unsuccessful.

*3-Nitro*meso*benzanthrone-4-carboxylic Acid.*—A solution of nitric acid (*d* 1·5; 1 ml.) in nitrobenzene (5 ml.) was added during 1 hr. to a suspension of *meso*benzanthrone-4-carboxylic acid (2 g.) in nitrobenzene (20 ml.) heated on a boiling-water bath. Heating was continued for 1 hr. longer, then the resulting solution was cooled. Benzene was then added and the solid which was precipitated was collected [1·7 g.; m. p. 310° (decomp.)] and purified by dissolution in aqueous sodium hydroxide and reprecipitation from the filtered solution. *3-Nitro*meso*benzanthrone-4-carboxylic acid* crystallised from nitrobenzene as yellow plates (Found: C, 67·7; H, 3·1; N, 4·4. $C_{18}H_9O_5N$ requires C, 67·7; H, 2·8; N, 4·4%).

Methyl ester. By the Schotten–Baumann method the acid gave the *methyl ester* as golden-yellow plates (from dioxan), m. p. 245° (Found: C, 68·7; H, 3·5; N, 4·0. $C_{19}H_{11}O_5N$ requires C, 68·5; H, 3·3; N, 4·2%).

No condensation product could be isolated from the acid or the methyl ester with α-amino-anthraquinone or the potassium salt of 1 : 9-pyrazoloanthrone.

Reduction. 3-Nitro*meso*benzanthrone-4-carboxylic acid (5 g.), sodium sulphide crystals (5 g.), water (20 ml.), and methanol (80 ml.) were stirred under reflux for 4 hr. The resulting solution was filtered, the filtrate was acidified, and the precipitate purified from nitrobenzene as brown crystals, m. p. 278°, which appeared to be identical with the lactam, m. p. 278°, of 3-amino*meso*benzanthrone-4-carboxylic acid obtained [8] by the action of acids on 4-methyl-3-nitro*meso*benzanthrone.

*3-Bromo*meso*benzanthrone-4-carboxylic Acid.*—*meso*Benzanthrone-4-carboxylic acid (1·5 g.) was stirred at 40° for 3 hr. with a solution of bromine (0·3 ml.) and a trace of iodine in chlorosulphonic acid (5 ml.). Sulphuric acid was then added and the resulting solution poured into water. The precipitate which formed was collected, washed, and then dissolved in dilute sodium hydroxide. Acidification of the filtered solution gave 3-bromo*meso*benzanthrone-4-carboxylic acid which crystallised from dioxan as greenish-yellow needles, m. p. 305° (Found: C, 59·5; H, 3·0; Br, 22·1. $C_{18}H_9O_3Br,0{\cdot}5H_2O$ requires C, 59·6; H, 2·8; Br, 22·1%), which did not react when heated with the potassium salt of 1 : 9-pyrazoloanthrone.

Ethyl 1 : 9-Pyrazoloanthrone-2-carboxylate.—1 : 9-Pyrazoloanthrone-2-carboxylic acid (5 g.; prepared from 1-chloroanthraquinone-2-carboxylic acid according to G.P. 515,680) was refluxed for 2 hr. with thionyl chloride (15 ml.) in trichlorobenzene (50 ml.). On being cooled the *chloride* crystallised and this was collected, added to dry ethanol, and refluxed for 2 hr. The resulting solution was cooled and the *ethyl 1 : 9-pyrazoloanthrone-2-carboxylate* which separated crystallised from dioxan as yellow needles, m. p. 220° (Found: C, 69·6; H, 4·4; N, 9·9. $C_{17}H_{12}O_3N_2$ requires C, 69·8; H, 4·1; N, 9·6%).

Potassium 1 : 9-pyrazoloanthrone-2-carboxylate did not react with 3-bromo*meso*benzanthrone in refluxing nitrobenzene during 24 hr.

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[8] G.P. 482,560.