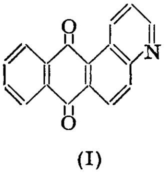
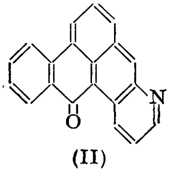
393. *A Synthesis of Cyananthrene.*

By William Bradley and Frank K. Sutcliffe.

Dipyridino(2′ : 3′-3 : 4)(2″ : 3″-12 : 13)*iso*violanthrone (VI) has been synthesised and shown to be identical with cyananthrene, the first colouring matter of the violanthrone series to be discovered.

Prud'homme (*Bull. Soc. chim.*, 1877, **28**, 62) observed that 3-nitroalizarin, when heated with glycerol and sulphuric acid, afforded a blue colouring matter. Graebe (*Annalen*, 1880, **201**, 349) showed it to be a derivative of the "quinone of anthraquinoline" (I).


(I)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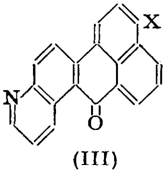
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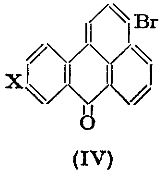
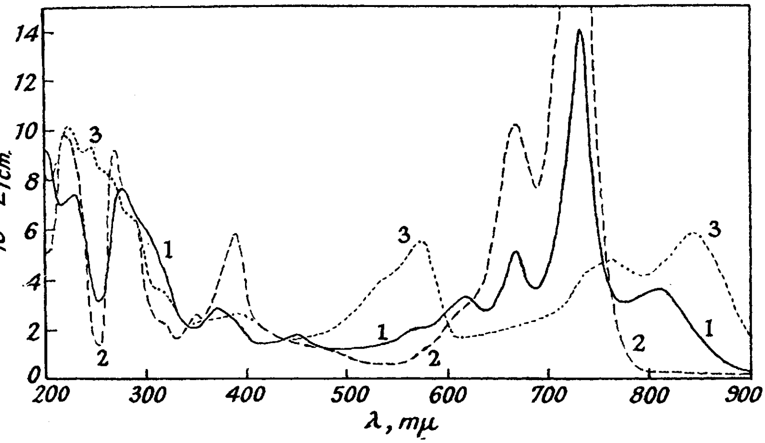

(IV)

Bally (*Ber.*, 1905, **38**, 194) obtained "benzanthronequinoline" by heating 2-aminoanthraquinone with glycerol and sulphuric acid, and showed that the same product could be derived by similar treatment of (I). He believed "benzanthronequinoline" to have the structure (II), but he did not, in fact, obtain evidence for the position of the benzo-ring. The correct formulation (III; X = H) was established by Pandit, Tilak, and Venkataraman (*Proc. Indian Acad. Sci.*, 1950, **32**, 39). Day (*J.*, 1940, 1474) had oriented 3-bromo-

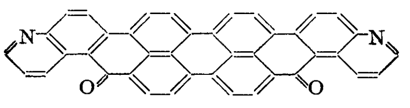
9-nitro*meso*benzanthrone (IV; X = NO_2) and Pandit *et al.* reduced this to the related amine, eliminated the bromine, and formed the resulting 9-amino*meso*benzanthrone into (III; X = H) identical with Bally's " benzanthronequinoline."

Bally (*loc. cit.*; G.P. 172,609) found heating with potassium hydroxide converted "benzanthronequinoline " into a violet-blue quinonoid colouring matter; this he named cyananthrene. According to Houben (" Das Anthracen und die Anthrachinone," G. Thieme Verlag, Leipzig, 1929, p. 782), cyananthrene is a dipyridino-derivative of violanthrone, which itself results in similar circumstances by the alkali fusion of *meso*benzanthrone. Pandit *et al.* adopted the same view, and suggested the formulation (V), based on their proof of the true structure (III; X = H) of " benzanthronequinoline."

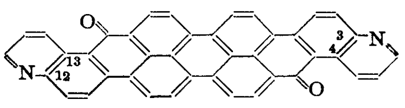


1, *Cyananthrene : Max. at* 220 (*E* = 750), 277 (*E* = 765), 373 (*E* = 290), 450 (*E* = 175), 614 (*E* = 320), 667 (*E* = 445), 737 (*E* = 1400), and 807 mμ (*E* = 360).
2, iso*Violanthrone : Max. at* 220 (*E* = 980), 270 (*E* = 920), 390 (*E* = 508), 668 (*E* = 1030), *and* 732 mμ (*E* = 2470).
3, *Violanthrone : Max. at* 223 (*E* = 1010), 385 (*E* = 260), 573 (*E* = 550), 760 (*E* = 460), *and* 845 mμ (*E* = 580).

In the present work cyananthrene was prepared by Bally's method, except that a melt consisting of potassium hydroxide and potassium acetate was advantageous because the reactants remained fluid throughout the operation. It was found that at 240—250° the main product was a black substance; a small amount of an acidic substance was formed at the same time. The black product, purified by dissolution in warm, alkaline sodium dithionite containing pyridine, yielded a portion soluble in 1 : 2 : 4-trichlorobenzene, and this, after further purification by chromatography, exhibited all the reactions of cyananthrene. Analysis showed it to be a dipyridino-derivative of violanthrone or *iso*violanthrone, and its absorption spectrum (see Fig.) in concentrated sulphuric acid showed it to have the *iso*-configuration (VI). The *iso*-structure was confirmed by a synthesis of cyananthrene from 3-bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone (III; X = Br), under conditions which convert 3-bromo*meso*benzanthrone (IV; X = H) into *iso*violanthrone (G.P. 194,252).



(V)



(VI)

As recorded by Brown (*J. Soc. Dyers and Col.*, 1906, **22**, 11) cyananthrene is much less readily reduced by alkaline sodium dithionite solutions than is violanthrone or *iso*violanthrone, a circumstance which probably arises from its larger molecular size.

An attempt was made to prepare (V), the isomer of cyananthrene, from (III; X = Br). 3-Bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone, however, when heated with copper, yielded none of the expected di*meso*benzanthronyl derivative, but only pyridino(3′ : 2′-8 : 9)*meso*benzanthrone or a black, insoluble product, probably a complex pyridinium salt, depending on the reaction conditions.

The 3-bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone employed in these experiments was identical with the monobromo-derivative of pyridino(3′ : 2′-8 : 9)*meso*benzanthrone prepared by bromination of the parent ketone, the constitution of which is thus established.

When heated with potassium hydroxide and manganese dioxide pyridino(3′ : 2′-8 : 9)-*meso*benzanthrone yields a degradation product, $[C_{12}H_8O_4N]_{2n}$. Under similar conditions *meso*benzanthrone and 1 : 8 : 9-naphthanthr-10-one yield hydroxy-derivatives (Bradley and Sutcliffe, *J.*, 1951, 2118).

EXPERIMENTAL

Pyridino(3′ : 2′-8 : 9)meso*benzanthrone*.—Prepared by condensing 2-aminoanthraquinone with glycerol and sulphuric acid, this compound had m. p. 250—252° (Bally, *loc. cit.*, records 251—252°) (Found : C, 85·0; H, 4·0; N, 4·9. Calc. for $C_{20}H_{11}ON$: C, 85·5; H, 3·9; N, 5·0%); yields were generally 20—30%. The compound dissolved in concentrated sulphuric acid with an orange colour and a green fluorescence; light absorption maximum, 503 mμ ($E^{1\%}_{1\,cm.}$ = 480); minimum, 490 mμ ($E^{1\%}_{1\,cm.}$ = 440).

3-*Bromopyridino*(3′ : 2′-8 : 9)meso*benzanthrone*.—(*a*) 3-Bromo-9-nitro*meso*benzanthrone (Day, *loc. cit.*) was reduced to the related amine, as described by Pandit *et al.* (*loc. cit.*).

9-Amino-3-bromo*meso*benzanthrone (3 g.) was dissolved in concentrated sulphuric acid (33 c.c.), and a solution of glycerol (3 g.) in water (10 c.c.) was added slowly, with stirring, below 50°. After 3·5 hours' heating at 140—150°, the product was cooled and added to water (1 l.). The olive-green product was collected, washed, extracted with hot 1% sodium hydroxide solution, then recovered, washed, and dried. Extraction with 300 c.c. of chlorobenzene at the b. p. afforded a solution, from which a solid separated on cooling. Recrystallisation from chlorobenzene gave golden-yellow leaflets, m. p. 297—298° (2·6 g.) (Found : C, 66·5; H, 2·75; N, 4·15; Br, 22·1. $C_{20}H_{10}ONBr$ requires C, 66·7; H, 2·8; N, 3·9; Br, 22·2%). The solution in concentrated sulphuric acid was orange with a weak green fluorescence; light absorption maxima at 444 ($E^{1\%}_{1\,cm.}$ = 325) and 532 mμ ($E^{1\%}_{1\,cm.}$ = 825).

(*b*) Direct bromination of pyridino(3′ : 2′-8 : 9)*meso*benzanthrone, according to G.P. 193,959, afforded a product, m. p. 294—295°, which did not depress the m. p. of the 3-bromo-derivative described in (*a*).

3-Bromopyridino*meso*benzanthrone was recovered unchanged after being heated with copper in 2-methylnaphthalene, phenol, or *m*-cresol at the b. p.s of these solvents. Heated and stirred with activated copper bronze (3 g.; Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4225) in quinoline (10 c.c.) for 5 hours, 3-bromopyridino*meso*benzanthrone (3 g.) afforded a suspension and this was filtered. The residue was extracted with boiling *o*-dichlorobenzene (100 c.c.), and the filtered solution was added to the quinoline filtrate. On cooling, 2·2 g. of yellowish-brown crystals separated, which, recrystallised from *o*-dichlorobenzene, had m. p. 250° alone or mixed with authentic pyridino(3′ : 2′-8 : 9)*meso*benzanthrone.

At 320—330°, and in the absence of an added solvent, copper and 3-bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone afforded only a black powder, m. p. above 360°.

Dipyridino(2′ : 3′-3 : 4)(2″ : 3″-12 : 13)iso*violanthrone*.—(a) *Action of potassium hydroxide on pyridino*(3′ : 2′-8 : 9)meso*benzanthrone*. Pyridino(3′ : 2′-8 : 9)*meso*benzanthrone (20 g.) was added portionwise, with stirring, to potassium hydroxide (200 g.) and potassium acetate (20 g.) at 240—250°. The addition complete, the mixture was kept at this temperature for an hour, then added, while still molten, to water (2 l.). The resulting suspension was stirred and aërated for an hour at 90—100°, then filtered, and the black, insoluble portion was extracted with 4% aqueous sodium hydroxide (2 l.) at 90—100°. After repetition of the alkali-extraction twice, nothing more dissolved.

The black product (16 g.), extracted with acetone, afforded 0·1 g. of unchanged pyridino*meso*benzanthrone. The undissolved residue was continuously extracted with a mixture of 1 : 2 : 4-trichlorobenzene (300 c.c.) and phenol (30 g.) until the extracts, initially blue-black, were only pale blue. A portion (A) (12 g.) remained undissolved. The cooled extracts afforded 4 g. of a violet-black product (B), and an additional 0·5 g. of the same material was obtained by concentrating the mother-liquors. The remaining solution, chromatographed on alumina, gave mainly pyridino*meso*benzanthrone.

A portion (0·25 g.) of (B) was dissolved in trichlorobenzene (250 c.c.) and was passed through a 200 × 25-mm. column of alumina (B.D.H. for chromatographic analysis) at 160—170°. The chromatogram was developed by means of nearly boiling trichlorobenzene (500 c.c.), and then with 1 l. of trichlorobenzene–phenol (10 : 1). A black product remained at the top of the column, and a dark blue, homogeneous band formed immediately below; a pale yellow band passed through the column. The blue band was eluted by means of hot trichlorobenzene–phenol (1 : 1); the eluate, concentrated to half-bulk and then cooled, afforded a solid, and this was crystallised from trichlorobenzene, giving 0·03 g. of a violet-black powder (Found: N, 4·8. $C_{40}H_{18}O_2N_2$ requires N, 5·0%). It formed a greenish-blue solution in concentrated sulphuric acid light absorption maxima at 277 ($E^{1\%}_{1\,\text{cm.}} = 765$), 667 ($E^{1\%}_{1\,\text{cm.}} = 445$), and 737 mμ ($E^{1\%}_{1\,\text{cm.}} = 1400$).

When chromatography was omitted in the purification of (B), the product showed the same light absorption maxima, but the *E* values were smaller.

The solubility of *dipyridino*(2′ : 3′-3 : 4)(2″ : 3″-12 : 13)iso*violanthrone* in boiling 1 : 2 : 4-trichlorobenzene is approximately 0·1%. The solution is blue with a red fluorescence, which in concentrated solutions is so intense as almost to mask the blue colour; the fluorescence is inhibited by small amounts of phenol or cresols. The *iso*violanthrone derivative dissolved sparingly in hot alkaline aqueous sodium dithionite with a deep greenish-blue colour; dissolution was greatly facilitated when the medium contained 5—10% (by volume) of pyridine.

The insoluble material (A) was a mixture. Extraction with a solution of sodium dithionite (10 g.) and sodium hydroxide (15 g.) in water (850 c.c.) and pyridine (150 c.c.) afforded a deep greenish-blue solution. This was filtered in an inert atmosphere, the filtrate was aërated, and the precipitate collected, washed, and dried (4·2 g.). A portion of this (0·258) g. was extracted with boiling trichlorobenzene–phenol (1 : 1) until no more dissolved. The extract, cooled and then mixed with benzene, afforded a precipitate consisting of impure dipyridino*iso*violanthrone (0·02 g.). The insoluble material was a black powder (0·216 g.), which was only slightly soluble in boiling phenol. It gave a bluish-green solution in concentrated sulphuric acid, but the absorption spectrum (maxima at 613, 680, and 747 mμ) differed from that of the dipyridino*iso*violanthrone. It dissolved with a bluish-green colour in a solution of sodium hydroxide and sodium dithionite in aqueous pyridine.

When the temperature of the alkali fusion was 220—230°, about 30% of the pyridino*meso*benzanthrone was recovered unchanged. When the fusion was conducted with water (40 g.) instead of potassium acetate the result was similar, but the melt became more viscous and difficult to stir.

(b) *Action of alcoholic potassium hydroxide on 3-bromopyridino*(3′ : 2′-8 : 9)meso*benzanthrone.* 3-Bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone (4 g.) was added at 125° to a solution of potassium hydroxide (20 g.) in alcohol (15 c.c.) containing water (2 c.c.). After an hour's heating under reflux, the dark product was cooled and mixed with water (250 c.c.), and the precipitated solid was collected. The filtrate was green; a very small amount of a gelatinous precipitate was slowly formed, leaving a colourless supernatant solution. The solid was extracted with hot 1% aqueous sodium hydroxide (3 × 300 c.c.). The initial extracts were purple, the last was colourless; acidification of the combined extracts gave only a minute amount of material. The residue (3·5 g.) was extracted exhaustively with hot chlorobenzene; unchanged 3-bromopyridino(3′ : 2′-8 : 9)*meso*benzanthrone (2 g.) dissolved. The insoluble fraction (1·3 g.) dissolved in concentrated sulphuric acid with a dull violet colour; it was very sparingly soluble in alkaline sodium dithionite solution. It dissolved readily in a solution of sodium dithionite (1·5 g.) and sodium hydroxide (2 g.) in water (85 c.c.) containing pyridine (15 c.c.). Filtered in an inert atmosphere and then aërated, the deep greenish-blue solution afforded a dark precipitate. This dissolved almost completely in boiling cresol (mixed isomers; 100 c.c.); the filtered solution, concentrated and then mixed with 1 : 2 : 4-trichlorobenzene, gave a black powder (0·5 g.). This gave a dull greenish-blue solution in concentrated sulphuric acid. A portion (0·2 g.) in hot trichlorobenzene (200 c.c.) was chromatographed on alumina (B.D.H. for chromatographic analysis; 50 g.) at 160—170°, and the chromatogram was developed with trichlorobenzene and then with trichlorobenzene–cresol (10 : 1). A blue band formed at the top of the column, and a yellow band passed through. The blue band was eluted by cresol at 100°, and the extract so obtained was concentrated and then mixed with toluene. A violet-black powder separated, and this, washed with toluene and dried, showed all the properties of dipyridino*iso*violanthrone prepared as in (a).

(c) Pyridino(3′ : 2′-8 : 9)*meso*benzanthrone (7·75 g.) was recovered almost unchanged after being heated (10 g.) for 12 hours at 88—90° with a solution of potassium hydroxide (50 g.) in ethanol (200 c.c.).

Oxidation of Pyridino(3′ : 2′-8 : 9)meso*benzanthrone.*—An intimate mixture of pyridino*meso*benzanthrone (10 g.) and manganese dioxide (10 g.) was added during 10 minutes to potassium hydroxide (50 g.) and potassium acetate (5 g.) at 220—230°. The mixture rapidly became deep purple in colour and pasty. After 1·75 hours it was added to water (1 l.), and the black precipitate was collected. Repeated extraction with hot 2% sodium hydroxide solution (800, 500, and 500 c.c.) dissolved 4·6 g. of material (C). The residue was suspended in water and treated with sulphur dioxide. The undissolved material dissolved in a solution of sodium dithionite (20 g.) and sodium hydroxide (20 g.) in water (950 c.c.) containing pyridine (50 c.c.), and the solution, filtered in an inert atmosphere and then aërated, yielded a solid (4·6 g.). Extracted with nitrobenzene, this yielded a small soluble portion and a residue (3·6 g.), which consisted mainly of dipyridino*iso*violanthrone.

The *substance* (C) [Found : C, 62·2; H, 3·4; N, 6·2. $(C_{12}H_8O_4N)_{2n}$ requires C, 62·6; H, 3·5; N, 6·1%] was insoluble in aqueous acids or sodium carbonate. It was unaffected by hot acetic anhydride, alone or with boroacetic anhydride. It formed a sodium salt, but this did not react with acetyl chloride in xylene. Its solution in aqueous sodium hydroxide remained unaltered after being shaken in the cold for several hours with methyl sulphate. It dissolved in concentrated sulphuric acid with an orange-brown colour and a green fluorescence; light absorption maxima at 481 ($E^{1\%}_{1\,\text{cm.}} = 1{\cdot}2$) and 455 mμ ($E^{1\%}_{1\,\text{cm.}} = 1{\cdot}08$).

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THE CLOTHWORKERS RESEARCH LABORATORY,
UNIVERSITY OF LEEDS.

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