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The Cyclisation of Anthrimides to Carbazoles. III.* The Structure of Indanthrene Gray A

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The anthraquinonyl amino group of the 1, 2′-dianthrimide type, when included in the complex structure of vat dyes, does not cyclise to yield a carbazole structure, with alkali, under the conditions of isoviolanthrone formation; rather, it cleaves to yield an alizarin-type derivative under the conditions of violanthrone formation. The constitution assigned to Indanthrene Gray A (Colour Index No. 60020) has thus been confirmed.

An anthraquinonyl amino group of the 1, 2′-dianthrimide type, when included in the complex structure of such vat dyes as Indanthrene Gray M and Indanthrene Olive T, has been proved to be present as such and not as carbazole (a cyclised structure) during their formation by means of mild treatment with alcoholic alkali.[1] The action of alkali on the 1, 2′-dianthrimide type under conditions of isoviolanthrone and violanthrone fusion needs to be studied further, for 1, 1′-dianthrimide is known to cyclise to a carbazole at 180—230°C.[2]

The Action of Alkali under Conditions of Isoviolanthrone Fusion.—Indanthrene Gray A (Colour Index No. 60020) is manufactured by the condensation of bis (9-bromo-3-benzanthronyl) sulphide (Ib) with two moles of 1-aminoanthraquinone to yield (Ic), and by subsequent fusion with alkali. The dye is assigned the IIIc structure, which contains an isoviolanthrone nucleus and 1, 2′-dianthrimide-type groups.

Isoviolanthrone is formed from bis (3-benzanthronyl) sulphide (Ia) by treatment with isobutanolic alkali at 140°C.[3] Therefore, the assumption of the formation of isoviolanthrone in this case is justified. The dye is obsolete, however, and no manufacturing details are available. The following process was standardised in order to obtain an authentic specimen of the dye. 9-Bromo-3-nitrobenzanthrone, upon being heated with sulphur in trichlorobenzene, gave bis (9-bromo-3-benzanthronyl) disulphide (IIb)[4], which was converted to sulphide (Ib) upon being heated with phenol.[5] The sulphide was condensed with 1-amino-anthraquinone to yield (Ic). The authentic

* Part II: *Indian J. Chem.*, **3**, 273—275 (1965).

1) S. R. Koppikar, K. H. Shah and K. M. Shah, *Indian J. Chem.*, **2**, 361-64 (1964).

2) W. Bradley and C. R. Thitchener, *J. Chem. Soc.*, **1953**, 1085.

3) British Intelligence Objectives Sub-committee, Final Report No. 1363 (Catholic Press India), **35**, (1949).

4) P. Nawiasky, E. Holzapfeb and O. Braunsdorf, D. R. Pat. 443021 (To I. G. Farbenindustrie AKT-GES), March 31, 1927: *Friedlaender*, **15**, 727 (1927).

5) P. Nawiasky, E. Holzappel and O. Braunsdorf, D. R. Pat. 441465 (To I. G. Farbenindustrie AKT-GES), Feb. 17, 1927; *Friedlaender*, **15**, 730 (1927).

dye was obtained by treating (Ic) with isobutanolic potassium hydroxide at 140°C for two hours. It was a dark blue powder which dissolved in concentrated sulphuric acid with a deep olive green colour and dyed cotton from an alkaline dithionite vat a grayish blue. It did not contain sulphur. It was analysed as $C_{62}H_{30}N_2O_6$ and exhibited λ_{max} at 250, 275, 310, 360, 410, 660, 730 mμ in sulphuric acid and two bands at 1675 and 1645 cm^{-1} in its infrared spectrum.

Bradley[6] has recorded the spectral characteristics of violanthrone (λ_{max} at 223, 385, 573, 760, and 845 mμ) and isoviolanthrone (λ_{max} at 220, 270, 390, 668, 732 mμ) in sulphuric acid. The spectra of the dye indicated the presence of an isoviolanthrone nucleus in the dye.

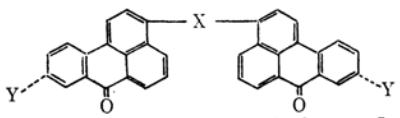
Venkataraman[7] has observed that anthrimides exhibit an λ_{max} in the 360 mμ region and two bands at 1670—1664 and 1665—1630 cm^{-1} in their infrared spectra, and carbazoles, a broad band in the 508 mμ region and one band at 1666 cm^{-1} in their infrared spectra. On this basis the spectrum of the dye indicated the presence of uncyclised anthrimide groups.

An unambiguous synthesis of the structure IIIc was carried out by condensing 2, 11-diamino isoviolanthrone with 1-chloroanthraquinone in naphthalene in the presence of copper oxide. The product exhibited chemical and spectral properties identical with those of the above product. The compound IIIc was cyclised with aluminium chloride in nitrobenzene. Crystallisation from nitrobenzene gave blue black needles which dissolved in concentrated sulphuric acid with a bluish green colour and which had no affinity for cotton from an alkaline dithionite vat. It exhibited λ_{max} at 270, 310, 380, 410, 500, 665, and 735 mμ and a band at 1670 cm^{-1} in the infrared spectrum and so can be assigned the structure IV.

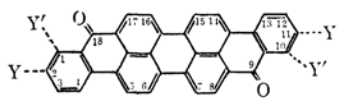
The Action of Alkali under Conditions of Violanthrone Fusion.—Fierz-David[8] has suggested the structure V for the product obtained by the alkali fusion of 9-(1-anthraquinonyl amino) benzanthrone (VIc). The structure assumes the formation of a carbazole ring and a violanthrone nucleus. Fierz-David assumes cyclisation to take place at the 2, 13-positions of the violanthrone nucleus. However, 1, 2′-dianthrimide cyclises at 1′, 2-positions with titanium tetrachloride.[9] Therefore, the cyclisation probably takes place at 4, 11-positions, as in VII.

Bradley[2] has observed that the action of fused alkali on 1, 2′-dianthrimide yields alizarin as the main product. 1, 2′-Dianthrimide type structures, unlike 1, 1′-dianthrimide, do not cyclise under the conditions of alkali fusion to yield carbazole, but they cleave to yield alizarin-type derivatives. Therefore, confirmation is essential for the structure V.

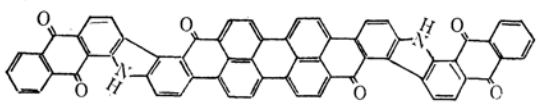
The fusion of VIc with potassium hydroxide at 220°C gave a violet substance which did not contain nitrogen; it was analysed as $C_{34}H_{16}O_6$, and its infrared spectra indicated the presence of the



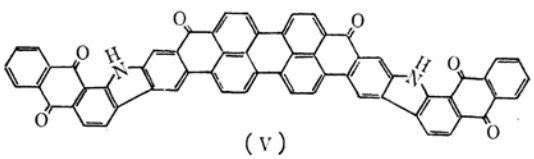
(I) X=-S- ; (II) X=-S-S-



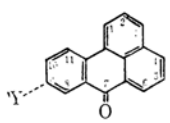
(III)



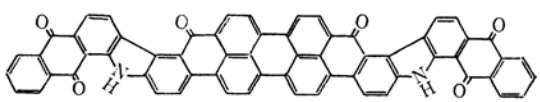
(IV)



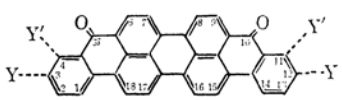
(V)



(VI)



(VII)



(VIII)

a, Y=H
b, Y=Br
c, Y=1-anthraquinonyl amino
Y′=H if present
d, Y=Y′=-OH

6) W. Bradley and F. K. Sutcliffe, *J. Chem. Soc.*, **1952**, 2118.
7) K. Venkataraman, *J. Indian Chem. Soc.*, **1961**, 205.
8) H. Fierz-David, *Friedlaender*, **16**, 1159 (1927).
9) H. J. Lecher, M. Scalera and W. S. Forster, U. S. Pat. 2416931 (To American Cyanamide Co.); *Chem. Abstr.*, **41**, 5151-i (1947).

hydroxyl group. It showed λ_{max} in sulphuric acid at 385, 500, 580, 630, 765, 845 mμ, indicating the presence of a violanthrone nucleus, and gave a tetrachloroacetoxy derivative. This substance can be assigned the structure VIIId. It dyed cotton a greenish violet from an alkaline dithionite vat and dissolved in concentrated sulphuric acid with a greenish blue colour.

Similarly, the fusion of Ic with caustic potash at 220°C gave a product which did not contain nitrogen. It was analysed for $C_{34}H_{16}O_6$ and gave a tetrachloroacetoxy derivative. It exhibited λ_{max} in sulphuric acid at 380, 490, 635, 670 and 740 mμ, showing the presence of isoviolanthrone, and its infrared spectrum indicated the presence of a hydroxyl group. It dissolved in concentrated sulphuric acid with a bluish green colour and dyed cotton from an alkaline dithionite vat a greenish violet. It can be assigned the structure IIId.

An authentic specimen of VII was obtained as follows: 3, 12-Diamino violanthrone was condensed with 1-chloroanthraquinone. The product exhibited two bands at 1675 and 1650 cm^{-1} in its infrared spectrum and λ_{max} at 315, 365, 385, 405, 570, 765 and 845 mμ. It dyed cotton a grayish blue and dissolved in concentrated sulphuric acid with a dark bluish green colour: it was analysed as $C_{62}H_{30}N_2O_6$(VIIIc). Treatment with aluminium chloride gave a product exhibiting a band at 1660 cm^{-1} in the infrared spectrum and λ_{max} in sulphuric acid at 310, 395, 405, 510, 570, 765 and 840 mμ. It gave a greenish blue colour in concentrated sulphuric acid and had no dyeing property. This shows that the cyclisation has taken place as in VII.

Experimental

Bis(9-bromo-3-benzanthronyl) Sulphide (Ib).—9-Bromo-3-nitrobenzanthrone (5 g.) was stirred under reflux with sulphur (15 g.) in trichlorobenzene (120 g.) for three hours. The trichlorobenzene was then steam-distilled, and the product IIb was collected. Crystallisation from *o*-dichlorobenzene gave yellow plates, m. p. 320° (3 g.). The above product (3 g.) was then stirred with phenol (15 g.) for 8 hr. at 180°C. The yellow product (2 g.) obtained after dilution with alcohol (30 ml.) was crystallised from *o*-dichlorobenzene in the form of yellow needles, m. p. above 300°C.

Found: S, 4.5. Calcd. for $C_{34}H_{16}Br_2O_2S$: S, 4.9%.

Bis- 9, 9'-di(1-anthraquinonylamino) - 3 - benzanthronyl Sulphide (Ic).—Ib (1.7 g.), 1-aminoanthraquinone (1.2 g.), anhydrous sodium carbonate (0.60 g.), and a trace of copper oxide were stirred under reflux in naphthalene (12 g.) for 24 hr. The product (2.5 g.) was collected after the naphthalene had been removed by steam distillation and the copper oxide had been removed by washing it with dilute hydrochloric acid. Crystallisation from nitrobenzene gave deep brown needles.

Found: N, 3.4; S, 3.3. Calcd. for $C_{62}H_{32}N_2O_6S$: N, 3.0; S, 3.4%.

Indanthrene Gray A.—One gram of Ic was added to a mixture of caustic potash (2 g.) in isobutanol (4 g.) at 70°C and the mixture was then stirred at 140°C for 2 hr. After dilution with water and air oxidation, a blue black residue was collected. Crystallisation from nitrobenzene gave blue black needles. They dissolved in concentrated sulphuric acid with a deep olive green colour and dyed cotton from an alkaline dithionite vat a grayish blue. λ_{max} in concentrated sulfuric acid: 250, 275, 310, 360, 410, 660, 730 mμ. IR: 1675 and 1645 cm^{-1}.

Found: C, 82.7; H, 3.0; N, 2.7. Calcd. for $C_{62}H_{30}N_2O_6$: C, 82.9; H, 3.3; N, 3.1%.

2,11-Bis(1-anthraquinonylamino)isoviolanthrone (IIIc).—2, 11-Diamino isoviolanthrone (2 g.), 1-chloroanthraquinone (2 g.), anhydrous sodium carbonate (0.8 g.) and traces of copper oxide were stirred under reflux in naphthalene (25 g.) for 48 hr. The product, collected after steam distillation, was washed free of copper. It crystallised from nitrobenzene in the form of blue-black needles. It showed spectral properties and colour reactions identical to those of the above product.

Found: C, 82.5; H, 3.5; N, 3.4. Calcd. for $C_{62}H_{30}N_2O_6$: C, 82.9; H, 3.3; N, 3.1%.

The Cyclisation of IIIc.—One gram of IIIc was stirred with anhydrous aluminum chloride (4 g.) and nitrobenzene (25 ml.) at 140°C for six hours. The resulting mixture was steam-distilled to remove the nitrobenzene. The product gave blue-black needles on crystallisation from nitrobenzene. It dissolved in concentrated sulphuric acid with a bluish green colour and had no affinity for cotton from an alkaline dithionite vat. λ_{max} in concentrated sulphuric acid at 270, 310, 380, 410, 500, 665 and 735 mμ. IR.; 1670 cm^{-1}.

Found: N, 2.9. Calcd. for $C_{62}H_{26}N_2O_6$: N, 3.1%.

3, 4, 11, 12-Tetrahydroxy Violanthrone (VIIId).—9-(1-Anthraquinonyl amino) benzanthrone (1 g.) was added to molten caustic potash (8 g.) at 220°C, and then the mixture was stirred for 30 min. at the same temperature. The product was collected after dilution with water and aerial oxidation for one hour. Repeated crystallisations from nitrobenzene gave bluish-violet needles (0.35 g.). The product dissolved in concentrated sulphuric acid with a blue colour and dyed cotton from an alkaline dithionite vat a greenish violet. λ_{max} in sulphuric acid at 385, 500, 580, 630, 765, and 845 mμ, and IR: 3350 cm^{-1}.

Found: C, 78.6; H, 4.0. Calcd. for $C_{34}H_{16}O_6$: C, 78.5; H, 3.1%.

The Chloroacetoxy Derivative of VIIId. — The above compound (1 g.) and chloroacetyl chloride (6 ml.) were stirred under reflux for 8 hr. The resulting product (1.2 g.) was collected after dilution with water. Crystallisation from nitrobenzene gave brownish-black needles which dissolved in concentrated sulphuric acid with a greenish blue colour and which dyed cotton from an alkaline dithionite vat a greenish violet.

Found: Cl, 17.6. Calcd. for $C_{42}H_{20}Cl_4O_{10}$: Cl, 17.2%.

1, 2, 10, 11-Tetrahydroxy Isoviolanthrone (IIId).—One gram of Ic was added to molten caustic potash at 220°C and the mixture was stirred for 30 min. The residue was collected after dilution with water and air oxidation. Crystallisation from nitrobenzene gave

blue-black needles (0.30 g.). They dissolved in concentrated sulphuric acid with a bluish green colour and dyed cotton from alkaline dithionite vat a greenish violet. The product did not contain nitrogen; λ_{max} in sulphuric acid at 380, 490, 635, 670 and 740 mμ, and IR: 3350 cm^{-1}.

Found: C, 78.2; H, 3.8. Calcd. for $C_{34}H_{16}O_6$: C, 78.5; H, 3.1%.

The Chloroacetoxy Derivative of IIId.—The above product, IIId (1 g.), was refluxed with chloroacetyl chloride (6 ml.) for 8 hr. The resulting product (1.1 g.) was collected after dilution with water. It crystallized from nitrobenzene in brownish-blue needles which dissolved in sulphuric acid with a greenish blue colour and which dyed cotton from an alkaline dithionite vat a greenish violet.

Found: Cl, 16.8%. Calcd. for $C_{42}H_{20}Cl_4O_{10}$: Cl, 17.2%.

3, 12 - Bis(1 - anthraquinonylamino)violanthrone (VIIIc).—3, 12-Diaminoviolanthrone (2 g.), 1-chloroanthraquinone (2 g.), anhydrous sodium carbonate (0.80 g.), and a trace of copper oxide were stirred under reflux in naphthalene for 48 hr. The product was collected after steam distillation.

It crystallised from nitrobenzene in the form of grayish blue needles which dissolved in concentrated sulphuric acid with a greenish blue colour. It dyed cotton from an alkaline dithionite vat a grayish blue. λ_{max} in sulphuric acid: 315, 365, 385, 405, 570, 765, and 845 mμ. IR: 1675, 1650 cm^{-1}.

Found: C, 82.6; H, 3.2; N, 2.8. Calcd. for $C_{62}H_{30}N_2O_6$: C, 82.9; H, 3.3; N, 3.1%.

The Cyclisation of VIIIc.—The substance VIIIc (2 g.) and anhydrous aluminum chloride (8 g.) and nitrobenzene (40 ml.) were stirred at 140°C for 6 hr. The product obtained after steam distillation gave a blue-black powder from nitrobenzene. It dissolved in concentrated sulphuric acid with a greensish blue colour and had no dyeing property. λ_{max} in sulphuric acid at 310, 395, 405, 510, 570, 765 and 845 mμ IR: 1660 cm^{-1}.

Found: N, 2.8. Calcd. for $C_{62}H_{26}N_2O_6$: N, 3.1%.