

SULPHUR DYES AND SULPHURISED VAT DYES

Part I. Constitution of Hydron Blue

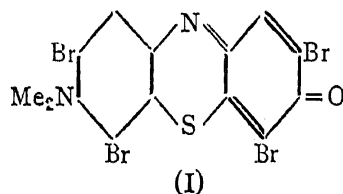
BY K. H. SHAH, B. D. TILAK AND K. VENKATARAMAN, F.A.SC.

(Department of Chemical Technology, University of Bombay)

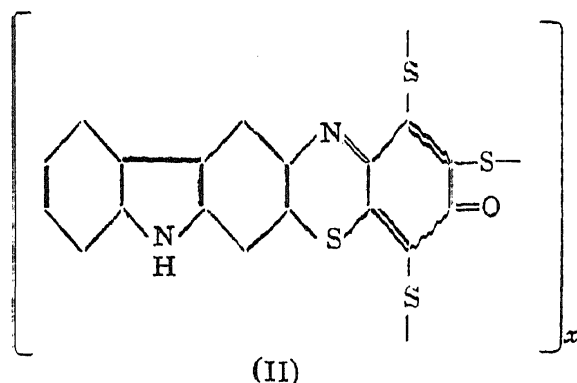
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ATTEMPTS to determine the constitution of the sulphur dyes have so far had only limited success on account of the intrinsic difficulties of the problem: the amorphous and uncrystallisable character of the dyes; their instability and insolubility as a result of which molecular weight determinations have not been made; their variability of composition, and their tendency on treatment with reagents to undergo total decomposition or a breakdown to products which are as difficult to isolate in pure form as the parent dyes themselves.¹ The chemistry of Hydron Blue, which can be regarded as representative of a group of sulphur and sulphurised vat dyes obtained by thionation of indophenols, has now been re-examined. The important dye, Hydron Blue, is prepared by the thionation of carbazole-indophenol which is obtained by the condensation of carbazole and *p*-nitrosophenol. The imports² of the dye into India during 1937-38 were 1,45,433 lbs. of the value of Rs. 3,24,163. An interesting and commercially significant feature of Hydron Blue is the use of carbazole as a starting material, a product which is readily available as a bye-product in the isolation of pure anthracene from crude anthracene. Hydron Blue R and RR are useful for the production of navy and dark blue shades on cotton, especially in piece dyeing, and were marketed as competitors to indigo. The dyeings are carried out from the yellow alkaline hydrosulphite vat. In fastness properties Hydron Blue is superior to the Sulphur Blues, but inferior to anthraquinone vat dyes, the fastness figures for light, washing and chlorine being 6, 4-5 and 3 respectively.

The character of the sulphurised indophenols as thiazine derivatives was indicated by Meyenberg and Levy³ and by Gnehm and Kaufler.⁴ The latter workers found that Immedial Pure Blue, a dye prepared by the thionation of 4-dimethylamino-4'-hydroxydiphenylamine, when heated with potassium bromate and hydrogen bromide gave Tetrabromo-Methylene Violet (I) which was identical with the product obtained from Methylene

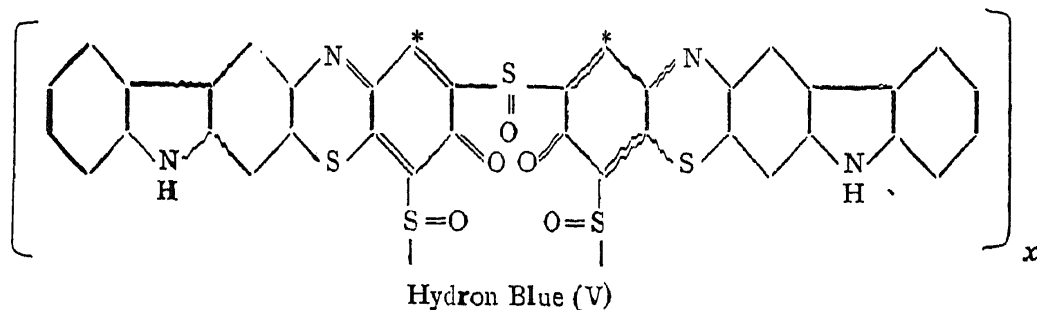
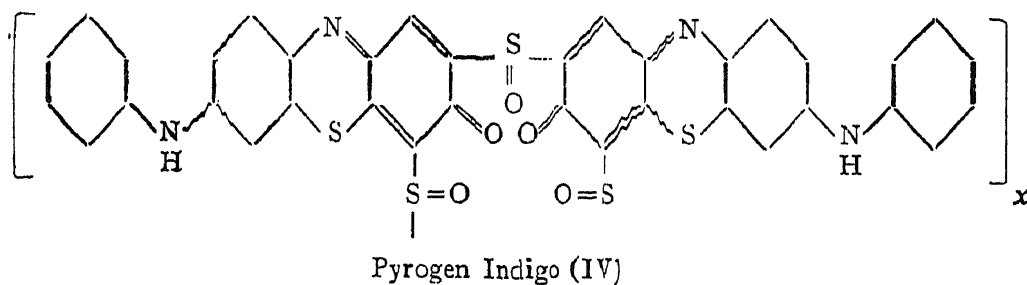
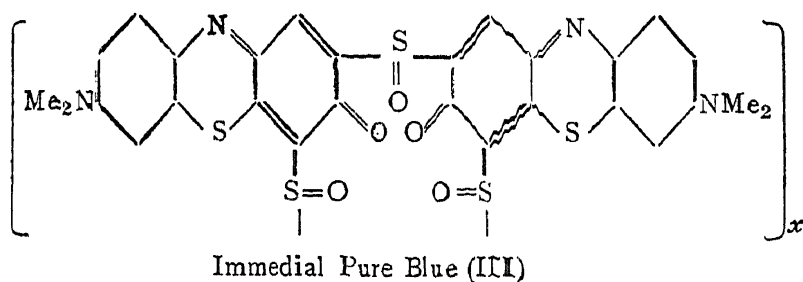


Blue by similar treatment. Many years later Weinberg⁵ suggested the constitution (II) for Hydron Blue without giving any analytical or other



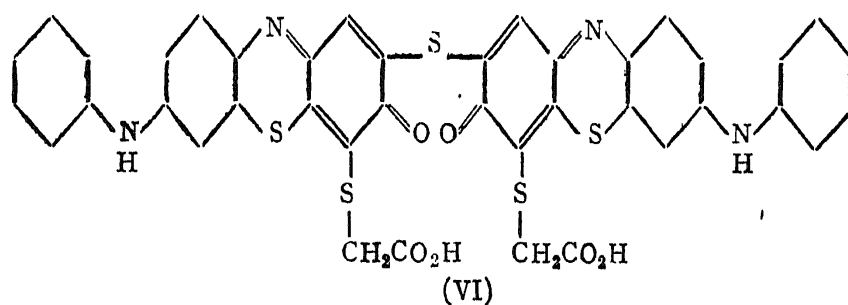
evidence.

The main contribution to the chemistry of sulphur dyes and sulphurised vat dyes is due to Fierz-David and his collaborators^{6,7} who have collected valuable data regarding the type of linkages and ring systems occurring in sulphur dyes, especially in the blue and green series. Fierz-David formulated a scheme for the purification of these dyes, the impurities being removed by exhaustive extraction successively with dilute hydrochloric acid, dilute ammonia, water, alcohol and ether. Several blue and green dyes obtained by the sulphurisation of indophenols from diphenylamine (Pyrogen Indigo), dimethylaniline (Immedial Pure Blue), carbazole (Hydron Blue), 1-phenylaminonaphthalene-8-sulphonic acid (Pyrogen Green), etc., were thus purified.



In spite of the inevitable limitations of this method of purification, and although important data, such as the molecular weight, could not be determined, Fierz-David was able to suggest structures for these dyes (*e.g.*, Immedial Pure Blue; Pyrogen Indigo; Hydron Blue) which explain most of their known properties. The thiazine units in these dyes were estimated by sulphonating the dyes with a mixture of concentrated sulphuric acid and chlorosulphonic acid to make them water-soluble, and then titrating them with titanous chloride.⁷ The possibility of decomposition of the dyes during the acid treatment and the recorded results of the titrations indicated the limited value of the method.

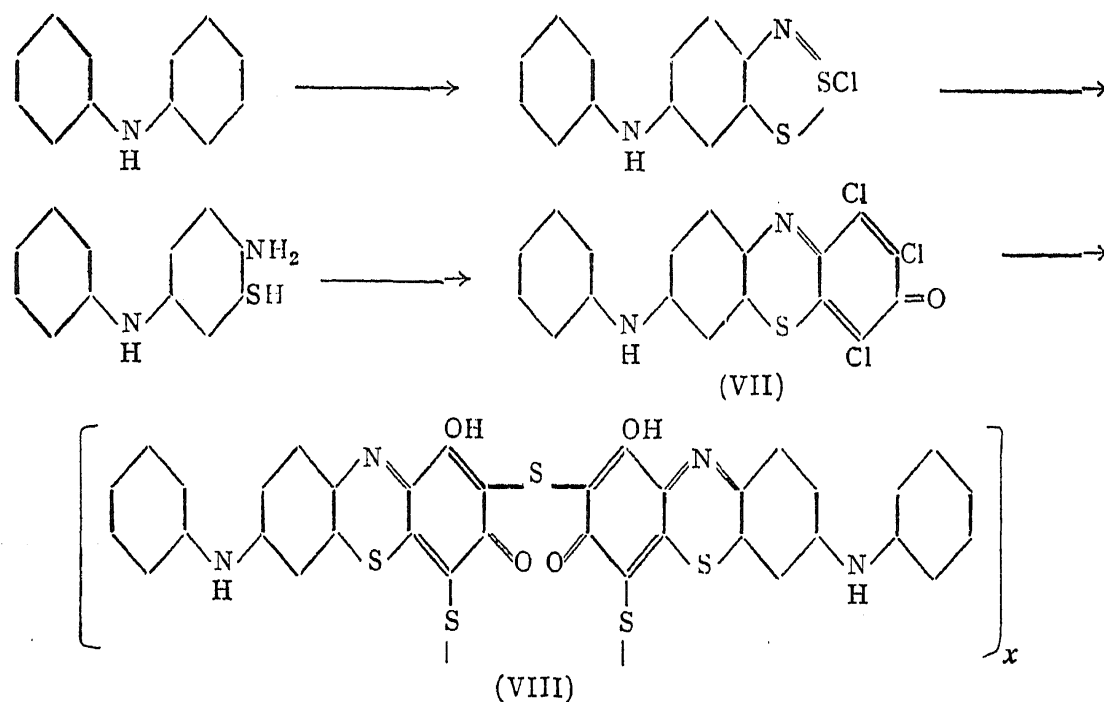
The solubility of the Immedial Pure Blue type of dye in aqueous sodium sulphide is attributed by Fierz-David⁷ to the reduction of the quinonimine groups and to the fission of the disulphoxide groups to the thiols. The yellow solution obtained by alkaline reduction gave on air-oxidation a blue solution which was stable in the cold for a very long time. This behaviour distinguishes these sulphur dyes from the sulphurised vat dyes which are soluble as leuco-derivatives only in the presence of alkaline hydrosulphite and are precipitated in the quinonoid form by air-oxidation. In the case of sulphur dyes mild oxidation by air causes the re-formation of the quinonimine groups, but the thiol groups formed in the reduction remain unaffected under these conditions and impart alkali solubility to the dye. On boiling or acidification re-oxidation of the thiols to the insoluble disulphides occurs, resulting in the precipitation of the dye from the blue solution. The leuco-compounds from Pyrogen Indigo and Hydron Blue were condensed with chloracetic acid to form alkali-soluble derivatives which, however, were very unstable to air-oxidation. By carefully working in absence of air Bernasconi and Fierz-David⁶ successfully isolated and purified the derivative from Pyrogen Indigo, for which the structure (VI) has been assigned on



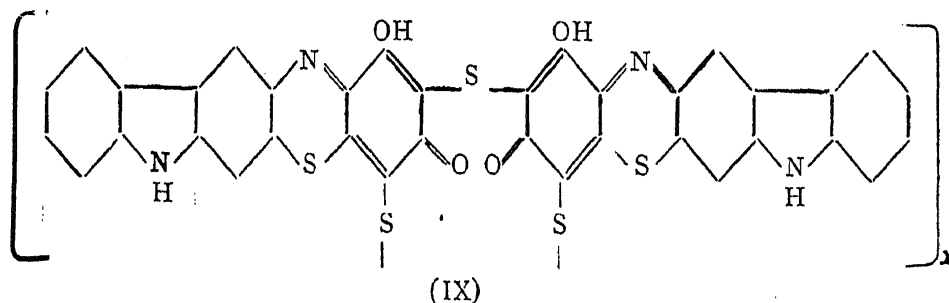
the basis of elementary analysis. The formation of the thioglycollic acid derivatives was considered as a further proof of disulphide or disulphoxide linkages in the molecule of Pyrogen Indigo and its analogues. Considering the possibility of the phenolic hydroxyls in the leuco-derivatives also (or in fact in preference to the thiol groups) reacting with chloracetic acid,

and the instability of the derivatives as being due to the ready fission of O-carboxymethyl ($-\text{OCH}_2\text{CO}_2\text{H}$) on account of the great tendency for the re-formation of thiazones by air-oxidation, it is necessary to interpret the results of Bernasconi and Fierz-David⁶ with caution.

The problem of the constitution of sulphurised indophenol dyes was then approached from the synthetic angle. Employing the Herz synthesis,⁸ Fierz-David⁷ synthesised (VIII), which was very similar to Pyrogen Indigo by the following scheme:



On similar grounds synthetic equivalent of Hydron Blue was formulated as (IX):

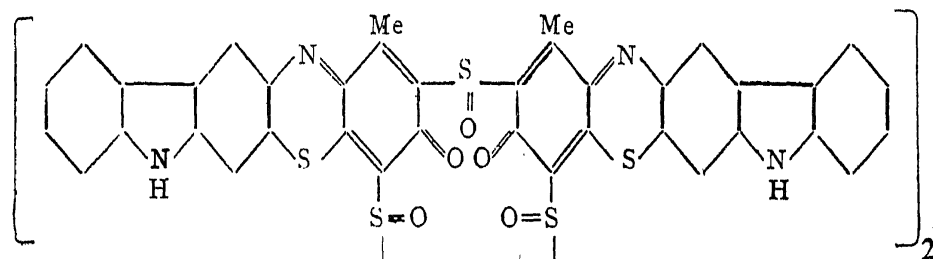


Employing trichlorotoluquinone and dichloro-*p*-xyloquinone in place of chloranil, Fierz-David⁷ observed that the product in the first case had poor tinctorial power, while the latter did not behave as a sulphide or sulphurised vat dye. This proved that at least one of the important sulphur containing groups must be in the *o*-position to the thiazine ring. On the basis of these results and elementary analysis the structures (VIII) and (IX) were suggested for synthetic Pyrogen Indigo and Hydron Blue, and (IV) and (V) respectively for the purified commercial dyes.

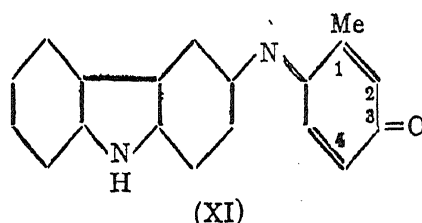
Bernasconi and Fierz-David⁶ have formulated the synthetic analogue (VIII) of Pyrogen Indigo as a hydroxylated derivative containing one hydroxyl group per benzothiazine unit and the sulphur links as sulphide and disulphide links as against sulphoxide and disulphoxide linkages in the commercial dyes without giving any evidence barring elementary analysis. Shibata and Nishi⁶ have also supported the phenolic structure for synthetic Hydron Blue on the basis of elementary analysis. Fierz-David^{7, 10} however has sometimes assumed the complete identity of the synthetic dyes with the commercial analogues prepared by a thionation process, and on other occasions he has merely marked the positions in question with asterisks.¹⁰ In one case⁷ he has formulated a carbon-carbon linkage between pairs of dibenzothiazine units in a black dye obtained by intense thionation of a sulphur dye prepared from *p*-anisidine. Considering that no proof as regards the presence of the hydroxyl groups in (VIII) and (IX) is available, and secondly the very close resemblance in the elementary analysis of the purified commercial dyes and their synthetic analogues^{6, 9} (the molecular formulæ of V and IX differ only in the latter having one oxygen atom less), there appears to be no reason for differentiating between the commercial and synthetic dyes. In support of this view may be cited the observation of Bernasconi and Fierz-David⁶ that the two are very similar and give similar absorption spectra.

The constitution (V) for Hydron Blue can be valid only if x stands for 2, or if polymerisation has taken place by a carbon-carbon linkage at the position marked *. The latter possibility is unlikely on the assumption that Hydron Blue (V) and Immedial Pure Blue (III) are similarly constituted, since the latter on bromination gave (I).⁴ We have now desulphurised Hydron Blue by treatment with Raney nickel in morpholine solution and obtained a product, which is identical with the reduction product from carbazole-indophenol, thus providing further and more definite proof of the absence of carbon-carbon linkages between the thionated carbazole indophenol units.

If Hydron Blue was a dimer ($x = 2$ in V), a compound such as (X) should be similar to Hydron Blue in its dyeing and other properties. Carba-

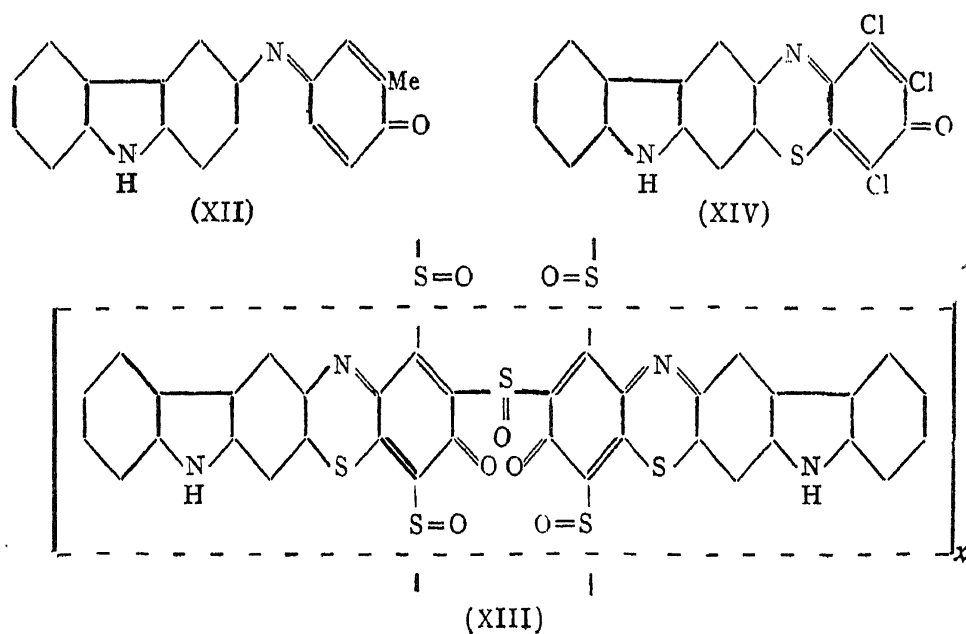


zole was condensed with nitroso-*m*-cresol, and the indophenol (XI) was thionated when a dye presumably of the structure (X) was obtained. This



product, however, gave a weak greyish blue shade, indicating the importance of polymerisation through the positions occupied by the methyl groups for the dyeing property associated with Hydron Blue. Fierz-David⁷ had also observed the poor tinctorial power of the dye from methyldichloro-thiazone obtained by the condensation of mercaptoaminocarbazole and trichloro-toluquinone, but since the methyldichloro-thiazone can have three alternative structures, sulphurisation can take place in three different ways. When, however, (XI) is thionated, cyclisation to the thiazine must take place in the 5-position, and further sulphurisation can only proceed through the 2 and 4 positions leading to (X) or a similar structure. The poor dyeing property of (X) thus provides definite proof that x must be more than two in structure (V) and that the 1-position must be involved in the polymerisation. If the structure (IX) for synthetic Hydron Blue were correct, (IX) and (X) should have similar dyeing properties, while in actual fact (X) had poor tinctorial power. This indicates that synthetic Hydron Blue is not a phenolic derivative such as (IX), as suggested by Fierz-David,⁶ but is essentially identical with the commercial dye.

In order to establish other sites of polymerisation, the indophenol (XII), from nitroso-*o*-cresol and carbazole, was thionated. The resulting product



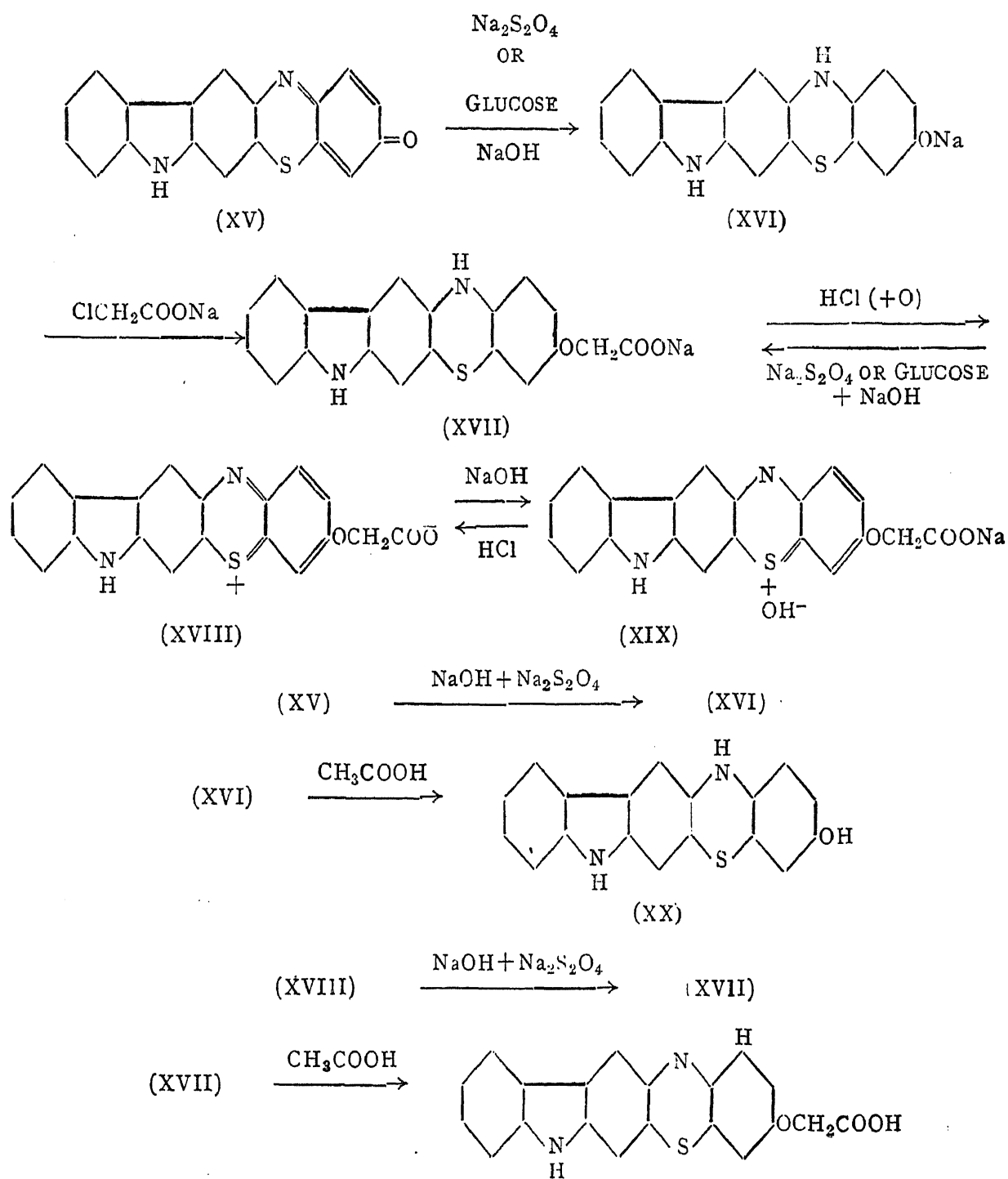
gave a weak grey shade, indicating that polymerisation through at least one of the positions *ortho* to the carbonyl group in the thiazones is fundamental to the dyeing property of Hydron Blue.

Taking all these facts into consideration, the constitution (XIII) is now proposed for Hydron Blue. This differs from the structure (V) suggested by Fierz-David with regard to the manner in which the thiazine from carbazole-indophenol polymerises to give Hydron Blue. Fierz-David suggested polymerisation through disulphoxide linkages, but it has been pointed out earlier that such a structure does not allow polymerisation beyond the tetrameric stage ($x = 2$ in V), and does not take into account polymerisation at the 1:1' positions. The constitution now suggested postulates polymerisation through sulphoxide linkages. Other analogous sulphurised indophenols such as Immedial Pure Blue and Pyrogen Indigo can also be similarly constituted as units polymerising through sulphoxide groups.

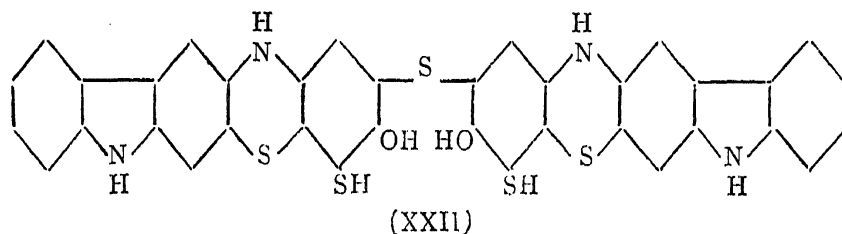
It is well known that when chlorinated intermediates are thionated the halogen is generally replaced by sulphur; under suitable conditions of thionation each chlorine atom can be replaced by a thiol group, so that this provides a useful method for locating the position of the latter. It is therefore likely that when the trichlorothiazone (XIV), obtained by Herz synthesis, is thionated all the halogen atoms are replaced by sulphur linkages leading to (XIII), as this is the only structure possible which will agree with the sulphur content of Hydron Blue. The preparation of the 1:3:6:8-tetra-bromo-derivative (I) from Immedial Pure Blue suggests substitution in the 1:3-positions by sulphur linkages, which are split off and replaced by bromine during bromination of the dye. The apparent anomaly of the absence of a bromine atom in the 4-position in (I) in place of a sulphur linkage in the parent dye, may be due to the lability of bromine in this position. In this connection it may be mentioned that Fierz-David⁷ found that trichlorothiazones of the type of (XIV) could not be isolated in an analytically pure condition due to the lability of one of the chlorine atoms, probably that substituted in the 4-position.

Frank¹¹ has prepared a thioglycollic acid from Immedial Indone, which on oxidation gave a blue dye; the thioglycollic acid linkage remaining unaffected during this oxidation. The instability of the thioglycollic acid derivatives such as (VI) to air-oxidation noted by Fierz-David⁷ cannot thus be readily explained. The formation of these derivatives from Hydron Blue and other analogous dyes represented by the structure (XIII) is due to the reaction of chloracetic acid with the phenolic hydroxyls of the leuco-compounds, giving glycollic instead of thioglycollic acid derivatives as

suggested by Fierz-David. When these derivatives are exposed to air the thiazones are readily re-formed with fission of the carboxymethyl groups; the great instability of these derivatives to air-oxidation is thus accounted for. As an experimental proof of the formation of the diglycollic acid derivative from the unit (XIII) of Hydron Blue by the interaction of the phenolic groups of the leuco-compound with chloracetic acid, the glycollic acid from the leuco-derivative (XVI) of the simple thiazone (XV) was prepared. Condensation of the leuco-compound (XVI) with sodium chloracetate under weakly alkaline conditions, followed by acidification, gave a blue precipitate of the glycollic acid derivative (XVIII). As this product (XVIII)



is slowly oxidised by air under acid conditions to the parent thiazone (XV), it was worked up in an atmosphere of carbon dioxide. The glycollic acid dissolves in aqueous sodium hydroxide giving a violet blue solution from which the glycollic acid can be reprecipitated by acidification. On reduction with glucose and alkali, (XVIII) gave a pale grey vat (XVII) from which it can be regenerated by air oxidation or acidification. On the other hand, the vat (XVII), obtained by treatment of (XVIII) with alkaline hydrosulphite, when acidified gave the acid vat (XXI) as a yellowish olive precipitate. The thiazone (XV) also behaved similarly giving an olive acid vat (XX) on acidification of the alkaline hydrosulphite vat, and giving the parent thiazone (XV) on acidification of the alkaline glucose vat. The deep blue colour of the glycollic acid and of its solution in aqueous alkali can be accounted for by constituting the glycollic acid as (XVIII) and (XIX) under acid and alkaline conditions. It may be mentioned that the blue glycollic acid obtained by Frank¹¹ from Immedial Indone, referred to earlier, has been assigned a constitution similar to (XVIII). While the thiazone (XV) dyes a bright reddish blue shade on cotton from an alkaline hydrosulphite vat which is fast to soaping, the glycollic acid (XVIII) is non-substantive. The latter (XVIII) is further distinguished from the thiazone (XV) by the fact that it dyes a purple shade on wool when dyed as an acid dye. The formation of the glycollic acid (XVIII) from the thiazone (XV) provides experimental evidence for the suggestion that in Hydron Blue also similar derivatives are formed, and not the thioglycollic acid derivatives as proposed by Fierz-David.⁶ If thiols are formed during the reduction of Hydron Blue (V) to the leuco-derivative, reaction of the latter with chloroacetic acid should yield a tetra-acetic acid derivative, corresponding to the two thiol and the two phenolic groups in (XXII) as against the di-acetic acid deriva-



tive (VI) obtained by Fierz-David⁶ in the case of the analogous dye, Pyrogen Indigo. It appears, therefore, that the chloroacetic acid reaction product of Fierz-David is a diglycollic acid derivative of the type (XVIII).

The solubility of Hydron Blue and analogous dyes after air-oxidation of the leuco derivatives of these dyes, which was explained by Fierz-David on the basis of disulphide or disulphoxide linkages, cannot be readily accounted for if the structure such as (XIII) is postulated for these dyes. In view of

the ready oxidation of thiols in alkaline solution by air, the stability of the sodium thiophenolates noted by Fierz-David⁷ is indeed surprising. When Hydron Blue is reduced by sodium sulphide it gives a green vat from which cotton can be dyed to give a dull blue shade. It appears in Hydron Blue (XIII), the quinoneimine groups are progressively reduced, the final stage of reduction being the pale yellow vat obtained by treatment with alkaline hydrosulphite. The green vat obtained on treatment with sodium sulphide and the blue solution obtained after air-oxidation may represent intermediate stages in oxidation in which only part of the quinoneimine groups in the polymeric structure (XIII) are regenerated, while others remain reduced as phenolic groups giving alkali-solubility. The sulphurised vat dyes such as Hydron Blue are distinguished from the sulphide dyes such as Immedial Pure Blue and Pyrogen Indigo by their greater fastness, insolubility or sparing solubility in sodium sulphide and by their being dyed from an alkaline hydrosulphite vat. Since all these dyes are now regarded as possessing the same structural pattern as represented by (XIII), the differences in solubility in sodium sulphide may be due to the decreased solubility on account of the presence of carbazole units in Hydron Blue as against *p*-dimethylamino and *p*-phenylamino groups which are present in Immedial Pure Blue and Pyrogen Indigo respectively.

EXPERIMENTAL

Preparation of carbazole-indophenols.—Carbazole (10 g.) was dissolved in concentrated sulphuric acid (250 c.c.) and cooled to -13° . A solution of *p*-nitrosophenol (7.5 g.) in concentrated sulphuric acid (75 c.c.) was also cooled to -13° , and then added rapidly to the above solution under vigorous stirring when the temperature rose to -4 to -5° . The solution was further worked up under cooling till the temperature was again -13° (5–10 minutes) and was then poured over ice. The indophenol which separated was washed, dried in vacuum (15 g.), and then purified by dissolving in acetone and reprecipitation with water when it separated as a finely divided precipitate. (Found: N, 10.0. $C_{18}H_{12}ON_2$ requires N, 10.2%.) Carbazole-indophenol gave a light brown suspension in aqueous sodium sulphide and a colourless colloidal alkaline hydrosulphite vat. It is non-substantive to cotton.

Indophenols (XII) and (XI) from carbazole *p*-nitroso-*o*-cresol and *p*-nitroso-*m*-cresol were similarly prepared. (Found: for XI N, 10.2, and for XII N, 10.0. $C_{19}H_{14}ON_2$ requires N, 10.0%.)

Thionation of carbazole-indophenols.—Hydron Blue R was prepared by heating carbazole-indophenol (3.6 g.), fused sodium sulphide (3.4 g.),

sulphur (4.32 g.), and butanol (25 c.c.) under reflux with mechanical agitation for 48 hours. After distilling the solvent, the melt was diluted with sodium chloride solution and the excess of sulphur was removed from the crude dye by extraction with aqueous sodium sulphide (yield, 5 g.). Thionation of the indophenols (XI) and (XII) was similarly carried out to give the corresponding dyes.

The thionated dyes were purified according to Fierz-David⁷ by washing with water and then extracting successively with alcohol, ether and carbon disulphide in a soxhlet. The nitrogen content of the purified Hydron Blue is in agreement with the constitution (XIII). (Found: N, 7.2. $C_{36}H_{16}O_5N_4S_5$ requires N, 7.5%), but the analysis of the purified dyes from (XI) and (XII) could not be related to any definite structure.

The dyeing properties of the purified dyes were then compared. Hydron Blue R had good substantivity to cotton, practically all the dye being exhausted at the end of the dyeing (3% shade), and very little bleeding was observed in soaping. Thionated *m*-cresol indophenol (XI) was less substantive than Hydron Blue and dyed a pale blue shade, which bled considerably in soaping. The purified thionated dye from (XII) had little or no dyeing property, but the crude product gave a brownish black shade inferior in tinctorial power as compared to Hydron Blue. The dyeings were again not fast to soaping. Hydron Blue R also dyes a deep blue shade on cotton from sodium sulphide vat.

Raney nickel reduction of carbazole-indophenol.—Pure carbazole-indophenol (2 g.), Raney nickel (20 g.) and morpholine (50 c.c.) were refluxed under stirring for 8 hours. The blue solution turned yellow on reduction. The reaction mixture was filtered and the nickel residue was washed twice with hot morpholine. The total morpholine extracts were poured into a mixture of ice and hydrochloric acid. The precipitate obtained was filtered and washed till free from hydrochloric acid, dried (1.5 g.), and finally purified by dissolving in acetone and precipitating by water. The reduced bluish violet product was collected and dried in vacuum, m.p. 220–2°. (Found: N, 10.0. $C_{18}H_6ON_2$ requires N, 10.1%.) The parent carbazole-indophenol does not possess a sharp m.p.

Raney nickel reduction of Hydron Blue R.—Hydron Blue R, purified according to Fierz-David,⁷ (1 g.), Raney nickel (10 g.) and morpholine (50 c.c.) were refluxed for 8 hours. The reduction product was found to be free from sulphur and was isolated as above (yield, 0.4 g.). After purification from acetone, it melted at 218–220°; undepressed when mixed with the reduction product from carbazole-indophenol (Found: N, 10.1%).

Preparation of the thiazone (XV).—The thiazone was prepared according to Kulikov.¹² A solution of carbazole-indophenol (1 g.) in acetic acid (8 c.c. of 80%) and alcohol (500 c.c.) was treated with 0.05 N sodium thio-sulphate solution till the violet colour disappeared. The solution was filtered and the leuco-indophenol thiosulphate obtained was oxidised by the addition of a solution of sodium acetate (1.5 g.) and ferric chloride (18 c.c. of 50%). After leaving the mixture overnight the precipitate of the thiazone (XV) separated. The thiazone is sparingly soluble in aqueous sodium hydroxide, and gives a pale yellow vat in alkaline hydrosulphite from which cotton is dyed a bright blue shade. On acidification of the alkaline hydrosulphite vat with acetic acid an olive precipitate of the acid vat (XX) separated. The thiazone is not reduced in alkaline glucose solution at room temperature, but on warming it gives a vat from which the thiazone could be regenerated by acidification with acetic acid.

Preparation of the glycollic acid (XVIII).—The above thiazone (0.62 g.), glucose (2.17 g.) and 5% sodium hydroxide solution (30 c.c.) were boiled together till the thiazone was reduced. The volume was then made to 120 c.c. with water and the solution was heated to boil. A solution of chloracetic acid (1.86 g.) in 5% sodium hydroxide (16 c.c.) was then added and the solution was heated on water-bath for an hour. The unconverted thiazone was removed by filtration and the filtrate was cooled to 0–5°, acidified with 5% hydrochloric acid (Congo Red) and then transferred to a 250 c.c. stoppered measuring cylinder. The air in the cylinder was displaced by carbon dioxide and the precipitated glycollic acid allowed to settle at 5–10°. The supernatant pale greenish yellow solution was decanted off, the glycollic acid was shaken with water and again allowed to settle after covering with carbon dioxide. The glycollic acid was further washed thrice in a similar manner and then filtered under a current of carbon dioxide and washed with water. It was dissolved in cold 5% sodium hydroxide solution (50 c.c.) when a greenish blue solution was obtained. After filtration the alkaline solution was acidified with dilute hydrochloric acid and the blue precipitate of the glycollic acid (XVIII) was cooled to 10°, filtered under carbon dioxide, washed till neutral and finally dried over phosphorous pentoxide in vacuum. The dry blue powder of the glycollic acid decomposed above 230°. The glycollic acid (XVIII) gives a purple solution in aqueous sodium bicarbonate and a violet blue solution in aqueous sodium hydroxide from which it can be recovered as a blue precipitate on acidification. On warming with alkaline glucose solution, it gave a pale grey vat from which the acid can be recovered by acidification with acetic acid. Alkaline hydrosulphite reduces the acid (XVIII) to a pale grey vat in the cold

and acidification of the reduced solution gives a yellowish olive precipitate of the acid vat, presumably of the reduced glycollic acid (XXI). When wool is dyed first from a weak sodium bicarbonate and then an acetic solution of the glycollic acid (XVIII), a purple shade is obtained. The glycollic acid did not possess affinity to cotton as a vat dye.

SUMMARY

The constitution (V) proposed by Fierz-David for Hydron Blue, in which polymerisation of the thiazine from carbazole-indophenol through disulphoxide linkages is postulated, does not take into account the necessity of polymerisation through the positions marked by asterisks in (V) to account for the dyeing property of Hydron Blue. The fact that polymerisation of thionated carbazole-indophenol units does not proceed through carbon-carbon linkages has been proved by the identity of the reduction products from carbazole-indophenol and from Hydron Blue, obtained by treatment with Raney nickel. The formation of the glycollic acid (XVIII) from the thiazone (XV) indicates the possibility of reaction between the phenolic groups in leuco-Hydron Blue and chloracetic acid. If disulphoxide linkages were present in Hydron Blue (V) and its analogues, such as Pyrogen Indigo (IV), the condensation of their leuco-derivatives with chloracetic acid should have given tetra-acetic acid derivatives corresponding to the two thiol and the two phenolic groups in their leuco-compounds (*e.g.*, XXII). Fierz-David, however, obtained a diacetic acid derivative from Pyrogen Indigo. Taking these facts into consideration, the constitution (XIII) is now proposed for Hydron Blue, in which polymerisation of thionated carbazole-indophenol units through sulphoxide linkages is postulated. Other analogous sulphurised indophenols can also be similarly constituted. The new constitution for sulphurised indophenol dyes readily accounts for the formation of a diacetic acid derivative from Pyrogen Indigo on the basis of the reaction between chloracetic acid and the phenolic groups in leuco-Pyrogen Indigo as in the case of the simple thiazone (XV).

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