

CL.—*A Theory of Colour on the Basis of Molecular Strain. The Effect of Chromophoric Superposition.*

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THE visible colour of substances is due to selective absorption of certain of the electro-magnetic vibrations causing the sensation of white light and the transmission of the remainder. In the present paper an attempt is made to show that selective absorption is due to molecular strain, such strain being imparted to the molecule by the distortion of the normal valency directions produced by any of the following causes :

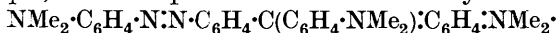
- (a) Formation of a double or triple bond.
- (b) Formation of a cyclic from an open-chain compound.
- (c) Unequal distribution of the masses attached to the atom.

The amount of strain is roughly proportional to the angular displacements of the valency directions of the atoms.

Strain in a molecule can be intensified by loading, the greatest effect being obtained when the load is in close proximity to the centre of strain. The farther the load is from this centre, the less is its effect.

The effect produced when two sources of strain are in close proximity in a molecule is much greater than that produced when they are remote from each other, because in the former case the intervening single linking also assumes a comparatively strained condition, thereby increasing the total rigidity of the molecule. The two strains produce the greatest effect when they originate in the same atom ; they have scarcely any mutual effect, each operating independently of the other, when they are situated at atoms separated by more than one single linking.

The position of the absorption maximum of a dye, the molecule of which contains two different and distantly situated chromophores, is approximately the mean of the positions of the maxima of the two components of the dye, each containing one chromophore. For example, the absorption maximum of the dye



is at  $\lambda$  5570, and those of its components, benzeneazodimethylaniline and malachite-green, are at  $\lambda$  5040 and  $\lambda$  6190 respectively (mean,  $\lambda$  5615). A dye containing several chromophores of the same kind has almost the same absorption maximum as the dye containing only one such chromophore. Hence, in each of these two cases, the effects of the strains, situated in distant positions in the molecule, are independent of each other.

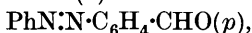
## E X P E R I M E N T A L.

*Azotriphenylmethane Dyes. Series I. Dyes containing One or Two Azo-groups attached to One Benzene Nucleus.*

These dyes were obtained by oxidising the leuco-bases formed by condensing mono- and bis-azobenzaldehydes with dimethylaniline.

*Preparation of Azobenzaldehydes.*—The following mono- and bis-azobenzaldehydes were prepared by diazotising the substance named first in the bracket and coupling the product with the second-named substance. *p*-Aminobenzaldehyde was diazotised as described in D.R.-P. 85233 of 1895, and *m*-aminobenzaldehyde in concentrated hydrochloric acid. The coupling with phenol was done in 10% sodium hydroxide solution. The coupling with aniline or dimethylaniline was done in a mixture of concentrated hydrochloric and glacial acetic acids, which were thereafter gradually neutralised with sodium carbonate.

Monoazobenzaldehydes : (1) Benzeneazobenzaldehyde,



prepared by the method described in Beilstein's "Organische Chemie," Vol. IV, p. 1068. (2) *p*-Hydroxybenzeneazobenzaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenzaldehyde; phenol). (3) *p*-Dimethylaminobenzeneazobenzaldehyde,



(*p*-aminobenzaldehyde; dimethylaniline). (4) *p*-Aminobenzeneazobenzaldehyde,  $(p)\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenzaldehyde; aniline). (5) *p*-Hydroxybenzeneazo-*m*-benzaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(m)$  (*m*-aminobenzaldehyde; phenol).

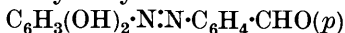
(6) *p*-Dimethylaminobenzeneazo-*m*-benzaldehyde,



(*m*-aminobenzaldehyde; dimethylaniline). (7) *p*-Aminobenzeneazo-*m*-benzaldehyde,  $(p)\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(m)$  (*m*-aminobenzaldehyde; aniline). (8) Benzeneazosalicylaldehyde,

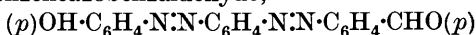


(aniline; salicylaldehyde). This substance is identical with the compound prepared by Borsche (*Ber.*, 1900, **33**, 1325) from benzeneazophenol, chloroform, and sodium hydroxide. (9) *p*-Hydroxybenzeneazosalicylaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_3(\text{OH})(p)\cdot\text{CHO}(m)$  (*p*-aminophenol hydrochloride; salicylaldehyde). (10) *p*-Methoxybenzeneazobenzaldehyde,  $(p)\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$ , prepared by treating (2) with methyl sulphate and 3% sodium hydroxide solution. (11) 2:4-Dihydroxybenzeneazobenzaldehyde,



(*p*-aminobenzaldehyde; resorcinol). (12) 2:3:4-Trihydroxybenzeneazobenzaldehyde,  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenz-

aldehyde; pyrogallol). Bisazobenzaldehydes: (13) *p*-Hydroxybenzeneazobenzeneazobenzaldehyde,



(No. 4, diazotised as described in D.R.-P. 85233; phenol).

(14) *p*-Dimethylaminobenzeneazobenzeneazobenzaldehyde,



(No. 4; dimethylaniline). (15) *p*-Hydroxybenzeneazobenzeneazo-*m*-benzaldehyde,  $(p)OH \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot CHO(m)$  (No. 7,

diazotised in concentrated hydrochloric acid; phenol). (16) *p*-Dimethylaminobenzeneazobenzeneazo-*m*-benzaldehyde,



(No. 7; dimethylaniline).

No diazoamino-compound was formed in the preparation of substances 4 and 7.

Substances 2, 11, 12, and 13 were crystallised from glacial acetic acid, and substances 3—8, 10, and 14—16 from alcohol. Substance 9 separated in an amorphous form from acetic acid.

Some properties of the azo-aldehydes are given in Table I.

TABLE I.

*Azobenzaldehydes.*

Azo-aldehyde.	Appearance.	M. p.	N % (theor. % in brackets).
2	Golden-yellow spangles with metallic lustre.	199°	12.5 (12.3)
3	Glistening, red prisms.	170	16.9 (16.6)
4	Yellowish-brown prisms.	158	18.5 (18.7)
5	Orange-yellow prisms.	164—165	12.2 (12.3)
6	Brownish-yellow needles.	116	16.8 (16.6)
7	Yellow prisms.	85—87	18.3 (18.7)
8	Golden-yellow needles.	128	12.1 (12.3)
9	Dark brown powder.	117—120	11.9 (11.6)
10	Bright yellow needles.	130—131	11.4 (11.7)
11	Microscopic, red needles.	Above 300	11.2 (11.6)
12	Microscopic, brown needles.	„	11.1 (10.8)
13	Glistening, brownish-yellow needles.	190	17.3 (16.9)
14	Dark red needles.	142—143	19.2 (19.6)
15	Glistening orange-yellow prisms.	135	16.7 (16.9)
16	„ „ „	128—129	19.8 (19.6)

*General Method of Condensation of Azobenzaldehydes with Dimethylaniline, and Preparation of the Corresponding Azotriphenylmethane Dyes.*—A solution or suspension of the azobenzaldehyde (1 mol.) and dimethylaniline (2 mols.) in ten times their volume of a mixture of equal parts of concentrated hydrochloric and glacial acetic acids was heated under reflux for periods of time varying from 3 to 12 hours, the end of the reaction being shown by the production of a clear solution and the change in colour from dark red to pale yellow.

The solution was poured into water, made alkaline with sodium carbonate, and every trace of dimethylaniline removed by distillation in steam. The white precipitate of the leuco-base was dissolved in dilute hydrochloric acid and reprecipitated from the filtered solution with sodium carbonate. In most cases the leuco-base could not be further purified or crystallised, owing to oxidation, and was therefore directly oxidised to the dye.

The oxidation was carried out by heating a solution of the leuco-base in sufficient 50% acetic acid with slightly more than the theoretical quantity of freshly precipitated and moist manganese dioxide (prepared by quantitative precipitation of potassium permanganate in warm water with alcohol) on the steam-bath for about 1 hour, with frequent stirring. After filtration, the solution of the colouring matter was treated with excess of saturated sodium acetate solution, and the precipitated dye was washed with water, dried, and crystallised from various solvents such as chloroform-ligroin, benzene, acetic acid, alcohol, and acetone, chloroform-ligroin (1 : 2) being the best solvent for the purpose. The substances thus obtained were acetates of the corresponding carbinol bases, and crystallised in glistening prisms or leaflets with a coppery lustre. They are generally sparingly soluble in water or benzene, moderately easily soluble in dilute mineral acids, alcohol, acetone, or acetic acid, very soluble in chloroform or pyridine, and insoluble in ligroin. They dye wool in various shades, from reddish-violet to deep blue.

*Series II. Azotriphenylmethane Dyes containing Two Azo-groups attached to Two Benzene Nuclei.*

Dyes of this series were prepared by tetrazotising *pp'*-diaminotriphenylmethane and its substitution products, coupling the products with dimethylaniline (2 mols.) in the usual manner, and oxidising the leuco-bases thus formed.

1. *pp'*-Diaminotriphenylmethane,  $\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , was obtained by O. Fischer's method (*Annalen*, 1881, **206**, 147).

2. *p*-Hydroxy-*p'p''*-diaminotriphenylmethane,  
 $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ .

—An intimate mixture of *p*-hydroxybenzylideneaniline (1 mol.), aniline hydrochloride (1 mol.), and concentrated hydrochloric acid (5 mols.) was heated in a sealed tube for 6 hours. The product was diluted with water, filtered, and the filtrate rendered alkaline with sodium carbonate solution. The resulting white precipitate, after being washed with water, crystallised from pyridine-alcohol in colourless needles, not melting at 295°. It dissolved very easily in dilute acids to pale yellow solutions, and was found to contain

two amino-groups by titration with *N*/2-sodium nitrite (Found: N, 9.3.  $C_{19}H_{15}ON_2$  requires N, 9.7%).

3. *p*-Dimethylamino-*p*'*p*'-diaminotriphenylmethane,



—*p*-Dimethylaminobenzaldehyde (5 g.), aniline (7 g.), and strong hydrochloric acid (50 c.c.) were boiled under reflux for about 5 hours. The leuco-base was isolated as in the above instance. It crystallised from alcohol in colourless leaflets, m. p. 152°. It was very soluble in dilute acids and was found to contain two amino-groups by the standard method (Found: N, 13.6.  $C_{21}H_{23}N_3$  requires N, 13.2%).

*General Method of Preparation of the Dyes of this Series.*—The diaminotriphenylmethane (1 mol.) in excess of dilute hydrochloric acid was treated with sodium nitrite (2 mols.), and the tetrazo-solution added to dimethylaniline (2 mols.) dissolved in strong hydrochloric or glacial acetic acid. On gradual neutralisation of the acid with sodium carbonate, the azo-dye separated. After being washed and crystallised from alcohol or glacial acetic acid, the leuco-base in hot glacial acetic acid was oxidised to the carbinol by freshly precipitated manganese dioxide in the usual manner. The dyes thus obtained are yellow, but the leuco-bases are brown. They dissolve in concentrated hydrochloric acid with a pink colour, whilst in ordinary solvents the colour is yellow.

*Series III. Azotriphenylmethane Dyes containing Three Azo-groups attached to Three Benzene Nuclei.*

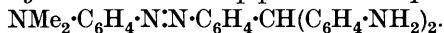
These dyes were obtained by tetrazotising *p*-benzeneazo-*p*'*p*'-diaminotriphenylmethane and its substituted derivatives, and coupling the products with dimethylaniline in the usual way. The leuco-bases thus obtained are unaffected by oxidation. In behaviour they are all similar to simple azo-dyes like benzeneazodimethylaniline. They are all yellow, but dissolve in concentrated hydrochloric acid with a red colour.

1. *p*-Benzeneazo-*p*'*p*'-diaminotriphenylmethane,



—This substance was obtained by heating benzeneazobenzaldehyde (1 mol.) with aniline (2 mols.) and concentrated hydrochloric acid (10 mols.) in a sealed tube at 200° for 6 hours. It crystallises from alcohol in brownish-yellow needles, m. p. 174°, and is very easily soluble in dilute acids (Found: N, 14.5.  $C_{25}H_{22}N_4$  requires N, 14.8%).

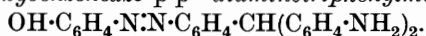
2. *p*-4-Dimethylaminobenzeneazo-*p*'*p*'-diaminotriphenylmethane,



—*p*-Dimethylaminobenzeneazobenzaldehyde (6 g.), 5 g. of aniline,

30 c.c. of strong hydrochloric acid, and 20 c.c. of glacial acetic acid were heated under reflux for about 3 hours until the colour of the solution had changed from dark crimson to pale yellow. The solution was poured into water and made alkaline with sodium carbonate; the precipitate produced, after being filtered off, washed and dried, crystallised from benzene in brownish-yellow needles, m. p. 165° (Found : N, 17.0.  $C_{27}H_{27}N_5$  requires N, 16.6%).

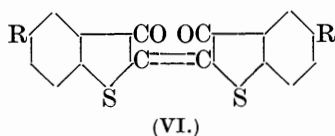
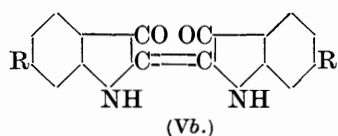
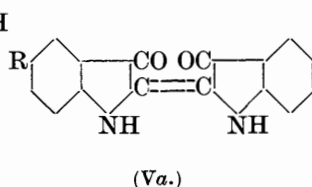
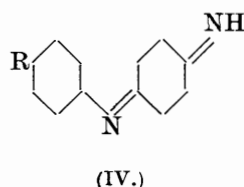
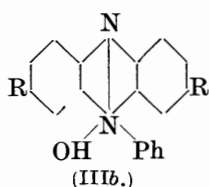
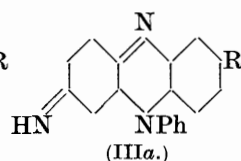
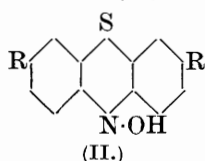
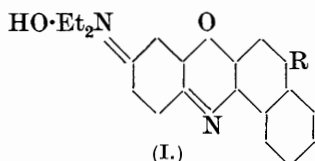
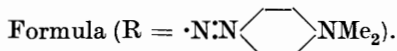
3. *p*-4-Hydroxybenzeneazo-*p*'*p*'-diaminotriphenylmethane,



—This substance was prepared from *p*-hydroxybenzeneazobenzaldehyde (1 mol.) and aniline (2 mols.) in a similar way to the above. It crystallised from alcohol in yellow aggregates, m. p. 162—163° (Found : N, 14.5.  $C_{25}H_{22}ON_4$  requires N, 14.2%).

*Series IV. Dyes containing Different Kinds of Chromophores.*

For the preparation of the following dyes of the mixed type, all the diazotisations or tetrazotisations were carried out in cold strong sulphuric acid solution with the theoretical quantities of sodium nitrite. The sulphuric acid solutions were then diluted with ice-water and coupled with the required quantities of dimethylaniline in the usual manner :



(1) Azo-oxazine dye : *Nile-blue-2-azodimethylaniline* (formula I), from diazotised Nile-blue A; dark violet, microscopic needles from chloroform-benzene (N found, 15.4; theo., 14.9%).

(2) Azo-thiazine dye : *Lauth's violet-2 : 7-bisazodimethylaniline*

(II), from tetrazotised Lauth's violet; brownish-yellow powder from pyridine (N found, 19.7; theo., 19.2%).

(3) Azo-safranine dyes: (a) *Safranine-2-azodimethylaniline* (IIIa), from diazotised phenosafranine hydrochloride; dark violet needles from alcohol (N found, 20.4; theo., 20.1%). (b) *Safranine-2:7-bisazodimethylaniline* (IIIb), from tetrazotised phenosafranine hydrochloride; brownish-yellow needles from alcohol (N found, 19.3; theo., 19.7%).

(4) Azo-indamine dye: *Indamine-3-azodimethylaniline* (IV), from diazotised phenylene-blue; violet, microscopic needles from chloroform (N found, 21.5; theo., 21.3%).

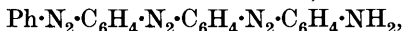
(5) Azo-indigoid dyes: (a) *Indigotin-5-azodimethylaniline* (Va), from diazotised 5-aminoindigotin; violet needles with silky lustre from pyridine (N found, 17.3; theo., 17.1%). (b) *Indigotin-4:4'-bisazodimethylaniline* (Vb), from tetrazotised 4:4'-diaminoindigotin (*Monatsh.*, 1905, **62**, 1262); brownish-yellow, microscopic needles from acetic acid (N found, 19.3; theo., 19.2%).

(6) Azo-thioindigoid dye: "*Thioindigo*"-5:5'-*bisazodimethylaniline* (VI), from tetrazotised 5:5'-diaminothioindigo (D.R.-P. 240805); light brown, amorphous powder (N found, 14.5; theo., 14.2%).

#### *Series V. Reduplication of the Same Chromophore.*

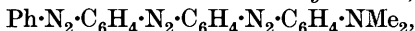
A. *The Azo-group.*—1. *Benzeneazobenzeneazobenzeneazophenol*,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . Benzeneazobenzeneazoaniline (*Ber.*, 1888, **21**, 2145) (1 mol.) was diazotised in cold concentrated hydrochloric acid solution, and the product coupled with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual manner. The final product crystallised from glacial acetic acid in bright yellow prisms, m. p. 248° (Found: N, 20.4.  $\text{C}_{24}\text{H}_{18}\text{ON}_6$  requires N, 20.7%).

#### 2. *Benzeneazobenzeneazobenzeneazoaniline*,



was obtained by coupling diazotised benzeneazobenzeneazoaniline (1 mol.) with aniline (1 mol.) dissolved in the minimum quantity of strong hydrochloric acid and, after thorough stirring, adding an excess of sodium acetate. The product crystallised from alcohol in yellow leaflets, m. p. 194°. No diazoamino-compound was formed (Found: N, 24.4.  $\text{C}_{24}\text{H}_{19}\text{N}_7$  requires N, 24.2%).

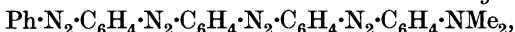
#### 3. *Benzeneazobenzeneazobenzeneazodimethylaniline*,



was prepared in a similar way to the above by using dimethylaniline in place of aniline. It crystallised from alcohol in orange leaflets, m. p. 218° (Found: N, 22.8.  $\text{C}_{26}\text{H}_{23}\text{N}_7$  requires N, 22.6%).

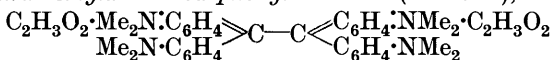
4. *Benzeneazobenzeneazobenzeneazobenzeneazophenol*,

was obtained by diazotising benzeneazobenzeneazobenzeneazoaniline (1 mol.) in cold strong sulphuric acid solution and coupling the product with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual way. It crystallised from nitrobenzene in brownish-yellow prisms, not melting at  $290^\circ$  (Found : N, 22.3.  $\text{C}_{30}\text{H}_{22}\text{ON}_8$  requires N, 22.9%).

5. *Benzeneazobenzeneazobenzeneazobenzeneazodimethylaniline*,

was prepared by adding diazotised benzeneazobenzeneazoaniline (1 mol.) to dimethylaniline (1 mol.), dissolved in concentrated hydrochloric acid, and, after thorough stirring, adding an excess of sodium acetate. It crystallised from pyridine in orange-yellow prisms, not melting at  $290^\circ$  (Found : N, 23.2.  $\text{C}_{32}\text{H}_{27}\text{N}_9$  requires N, 23.4%).

B. *The Diphenylmethane Group*.—1. *Bistetramethyldiaminodiphenylmethane*,  $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ . A mixture of 10 g. of glyoxal, 22 g. of dimethylaniline, and 50 c.c. of fuming hydrochloric acid was heated in a sealed tube at  $180^\circ$  for 8 hours. The product was diluted with water, rendered alkaline with sodium carbonate, and distilled in steam until no more dimethylaniline passed over. The residue, which solidified on cooling, was ground up, washed with water, and its solution in dilute hydrochloric acid was decolorised by boiling with animal charcoal and sulphurous acid. The filtered solution on treatment with dilute sodium hydroxide gave a white precipitate of the leuco-base, which was filtered off, washed, and dried on a porous plate; it crystallised from ether in colourless needles, m. p.  $96\text{--}98^\circ$ , which became brownish-violet on exposure to air (Found : N, 11.4.  $\text{C}_{34}\text{H}_{42}\text{N}_4$  requires N, 11.1%).

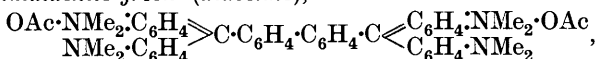
2. *Bistetramethyldiaminodiphenylcarbinol (diacetate)*,

The above leuco-base was dissolved in sufficient 50% acetic acid, slightly more than the calculated quantity of freshly precipitated manganese dioxide added, and the mixture thoroughly stirred. The solution, dark green at first, on warming on the steam-bath became brilliant violet-blue. After heating for about an hour, it was filtered, cooled, and treated with an excess of saturated sodium acetate solution. The precipitated colouring matter was filtered off, washed, and dried; it crystallised from chloroform–ligroin in dark violet-blue needles with a coppery lustre which dissolved in organic solvents and dilute acids with a violet-blue colour (Found : N, 9.3.  $\text{C}_{38}\text{H}_{46}\text{O}_4\text{N}_4$  requires N, 9.0%).



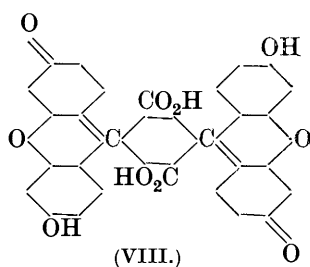
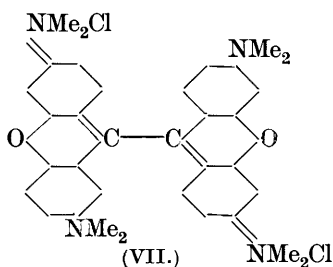
C. *The Triphenylmethane Group*.—1. *leuco-Dimalachite-green*,  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ . *p*-Bromoleucomalachite-green [m. p.  $128^\circ$ , obtained from *p*-bromobenzaldehyde (1 mol.) and dimethylaniline (2 mols.), concentrated hydrochloric acid at  $200^\circ$  being used as the condensing agent] was intimately mixed with an equal weight of very fine copper bronze, and the mixture heated at  $210$ — $220^\circ$  in an atmosphere of hydrogen. In 1 hour, a reaction took place which was indicated by the loss of metallic lustre of the bronze powder. After heating for about 4 hours, the melt was dissolved in dilute hydrochloric acid, the solution filtered, the filtrate decolorised with animal charcoal and sulphur dioxide, and the leuco-base precipitated with dilute sodium hydroxide. It could not be crystallised and was a white powder, m. p.  $135$ — $138^\circ$ , which readily became green on exposure to air (Found: N, 8.2.  $\text{C}_{46}\text{H}_{50}\text{N}_4$  requires N, 8.5%).

2. *Dimalachite-green (diacetate)*,



prepared by oxidising the above leuco-base with manganese dioxide, could not be crystallised and was obtained as a brilliant green powder which dissolved in organic solvents and dilute acids with a deep green colour (Found: N, 7.6.  $\text{C}_{50}\text{H}_{54}\text{O}_4\text{N}_4$  requires N, 7.2%).

D. *The Pyronine Group*.—*Dipyronine G* (formula VII). Glyoxal (1 mol.), dimethyl-*m*-aminophenol (4 mols.), and strong hydrochloric acid (10 mols.) were heated together on the steam-bath for about 12 hours under reflux in a current of carbon dioxide. The product was diluted with water, and the leuco-base precipitated with sodium carbonate. As it could not be purified in this state, being very easily oxidised in the air, it was repeatedly dissolved in dilute hydrochloric acid and reprecipitated with sodium carbonate before being converted into the dye. This conversion was done by dissolving the leuco-base in cold strong sulphuric acid and adding



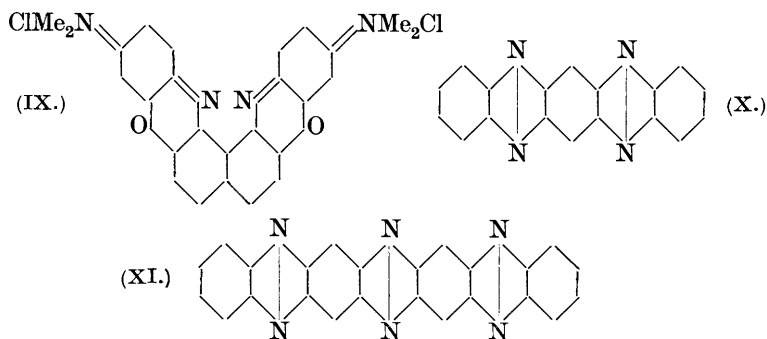
slightly more than the calculated quantity of sodium nitrite, with vigorous stirring. The solution became dark red and small steel-

s s\*

blue needles began to separate. After 1 hour, the solution was poured into ice-water, and the dye precipitated by adding a concentrated solution of sodium chloride. It came down in fine steel-blue needles with a golden iridescence, and was filtered off, washed with a little water, and dried. Its solutions in water and in organic solvents have a brilliant pink colour (Found : N, 9.6.  $C_{34}H_{36}O_2N_4Cl_2$  requires N, 9.3%).

E. *The Phthalein Group.*—*Difluorescein* (VIII) was obtained by condensing pyromellitic acid with resorcinol (4 mols.) according to the method (J., 1906, **89**, 1787) by which the corresponding compound was prepared from mellitic acid. It is a dark yellow, amorphous substance, not melting at  $300^\circ$  (Found : C, 69.5; H, 3.4.  $C_{34}H_{18}O_{10}$  requires C, 69.6; H, 3.0%).

F. *The Oxazine Group.*—*Di-Meldola's blue* (IX). *p*-Nitrosodimethylaniline hydrochloride ( $4\frac{1}{2}$  mols.) and 2 : 7-dihydroxynaphthalene (1 mol.) were heated together in alcoholic solution under reflux for 24 hours. The black crystalline colouring matter that had separated was filtered off, washed with alcohol and water, and dried. It was a black, crystalline powder, dissolving in organic solvents with a dark green colour (Found : N, 11.6.  $C_{26}H_{22}O_2N_4Cl_2$  requires N, 11.3%).



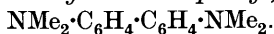
G. *The Azine Group.*—1. *Phenazineazine* (X) was obtained by condensing 2 : 3-diaminophenazine (Ber., 1889, **22**, 356) with *o*-benzoquinone in concentrated sulphuric acid solution. It crystallises from nitrobenzene, and also sublimes on careful heating, in bright yellow needles which do not melt at  $290^\circ$  (Found : N, 19.7.  $C_{18}H_{10}N_4$  requires N, 19.8%).

2. *Phenazineazineazine* (XI) was obtained by condensing 2 : 3-diaminophenazine with 2 : 3-dihydroxyphenazine (Ber., *loc. cit.*) in cold strong sulphuric acid solution containing 30% of sulphur trioxide. It crystallises from nitrobenzene in microscopic yellow

needles which do not melt at 290° (Found : N, 21.6.  $C_{24}H_{12}N_6$  requires N, 21.8%).

*Series VI.*

*A. Malachite-green with a Bridge Linking between Two Benzene Nuclei.*—1. 3 : 3'-Tetramethyldiaminodiphenyl,




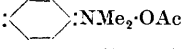
3 : 3'-Dinitrodiphenyl (*Ber.*, 1901, **34**, 2177) was reduced with tin and hydrochloric acid in the usual way, the tin precipitated with hydrogen sulphide, and the filtered solution evaporated to dryness. The hydrochloride of 3 : 3'-diaminodiphenyl, thus obtained in long, colourless, silky needles, was dissolved (10 g.) in 150 c.c. of water, and 60 g. of methyl sulphate were added, about 5 g. at a time with vigorous shaking, during an hour, the solution being neutralised from time to time with 10% sodium hydroxide solution; methylation was complete when excess of sodium hydroxide failed to precipitate any amino-compound. The yellow crystalline chromate of the quaternary base precipitated from this solution by a strong aqueous solution of chromic acid was filtered off, washed with water, and treated in aqueous suspension with sulphur dioxide. The dark green solution thus obtained was boiled to drive off the excess of sulphur dioxide and rendered strongly alkaline with ammonia, the precipitated chromium hydroxide washed with water, and the filtrate and washings were evaporated to dryness. The residue was extracted with absolute alcohol, and the extract, after being distilled on the steam-bath until no more alcohol came over, was heated at 250° in a vacuum for  $\frac{1}{2}$  hour; only a small, pale yellow distillate, however, was obtained. The distillate and the residue were dissolved in hot dilute hydrochloric acid and the solution was decolorised with animal charcoal. From the filtered solution dilute aqueous sodium hydroxide precipitated a solid, which crystallised from alcohol in clusters of colourless needles, m. p. 126—128°, easily soluble in dilute mineral acids (Found : N, 11.5.  $C_{16}H_{20}N_2$  requires N, 11.8%).

2. *The leuco-base, 3 : 6-tetramethyldiamino-9-phenylfluorene (XII).*

A solution of 3 : 3'-tetramethyldiaminodiphenyl (1 mol.) and benzal chloride (1 mol.) in dry carbon disulphide was heated under reflux with powdered anhydrous aluminium chloride (2 mols. plus 10% excess) for about 6 hours. The carbon disulphide was distilled off, the dark brown aluminium compound decomposed with water, and the white residue filtered, washed, and extracted with very dilute acetic acid (in which 3 : 3'-tetramethyldiaminodiphenyl is insoluble). The extract was rendered alkaline with sodium carbonate, and the precipitated leuco-base filtered off and washed with

TABLE II.

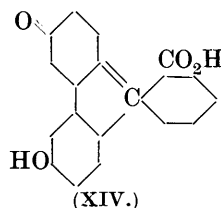
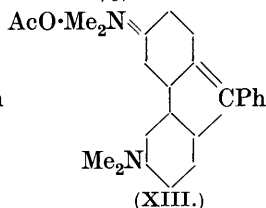
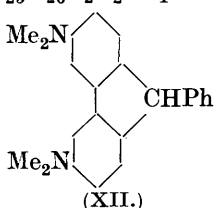
*Absorption Maxima of Azotriphenylmethane Dyes.*

The dye whose symbolical formula is in the first column was prepared from the aldehyde, the reference number of which is in the second column.  $\alpha$  denotes the absorption maximum of the dye in alcoholic solution containing 1 mol. of HCl, and in the last column are its found and theoretical (in brackets) percentages of nitrogen. A = C<sub>6</sub>H<sub>5</sub>·N:N· or ·C<sub>6</sub>H<sub>4</sub>·N:N·, B = C<sub>6</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>4</sub>, etc., C = methane carbon atom, and R and R' respectively =  and .

Formula.	Aldehyde.	$\alpha$ .	N %.
B·C:RR' (malachite-green).	—	6190	—
A·B (azobenzene).	—	4310	—
A·R (butter-yellow).	—	5040	—
A·B·C:RR'.	I, 1	5720	11·5 (11·2)
(4)HO·B·A·C:RR'.	I, 2	5560	11·3 (11·0)
(4)HO·B·C:RR'.	—	5960	(J., 1917, <b>111</b> , 815)
(4)HO·B·A·A·C:RR'.	I, 13	5580	14·1 (13·7)
(2:4)(HO) <sub>2</sub> B·C:RR'.	—	6010	(J., <i>ibid.</i> )
(2:4)(HO) <sub>2</sub> B·A·C:RR'.	I, 11	5650	11·0 (10·7)
(2:3:4)(HO) <sub>3</sub> B·C:RR'.	—	6120	(J., <i>ibid.</i> )
(2:3:4)(HO) <sub>3</sub> B·A·C:RR'.	I, 12	5670	10·8 (10·4)
R·C:RR' (crystal-violet).	—	5990	—
R·A·C:RR'.	I, 3	5570	13·4 (13·0)
R·A·A·C:RR'.	I, 14	5580	15·8 (15·3)
(3)HO·B·C:RR' (patent blue).	—	6010	7·1 (6·9)
(4)HO·B·(1)A·(3)C:RR'.	I, 5	5650	11·8 (11·0)
(4)HO·B·A·(1)A·(3)C:RR'.	I, 15	5780	14·0 (13·7)
(2)HO·B·(1)C:RR'.	—	5990	7·2 (6·9)
$\text{HO} \begin{matrix} \text{A(4)} \\ \text{(2)} \end{matrix} > \text{B} \cdot (1) \text{C} : \text{RR}'$ .	I, 8	5570	11·9 (11·8)
(4)MeO·B·C:RR'.	—	6050	(Ber., 1881, <b>14</b> , 2523)
(4)MeO·B·A·C:RR'.	I, 10	5610	10·9 (10·7)
(1)HO·A(4) $\text{HO} \begin{matrix} \text{A(4)} \\ \text{(2)} \end{matrix} > \text{B} \cdot (1) \text{C} : \text{RR}'$ .	I, 9	5650	11·1 (10·7)

water. It could not be crystallised and melted at 92—94° (Found: N, 8·7. C<sub>23</sub>H<sub>24</sub>N<sub>2</sub> requires N, 8·5%).

3. *The dye (acetate) (XIII).* The above leuco-base was oxidised in 50% acetic acid solution with freshly precipitated manganese dioxide in the usual manner. It was obtained from chloroform-ligroin as a dark green, crystalline powder, which formed dark green solutions in organic solvents and dilute acids (Found: N, 7·5. C<sub>25</sub>H<sub>26</sub>O<sub>2</sub>N<sub>2</sub> requires N, 7·2%).



B. *Phenolphthalein with a Bridge across two Benzene Nuclei (XIV).*  
—A mixture of 9 g. of 3:3'-dihydroxydiphenyl (Ber., 1894, **27**,

2107), 7.5 g. of phthalic anhydride, and 15 g. of anhydrous aluminium chloride was heated at 200° for 5 hours. The product was powdered, extracted with boiling water, the residue dissolved in hot aqueous sodium carbonate, the solution filtered, and the filtrate acidified; the dye was thus obtained in pale purple flocks. It crystallised from glacial acetic acid (animal charcoal) in colourless needles, not melting at 285°. It dissolved in alkalis with a bluish-red colour (Found: C, 75.7; H, 4.0.  $C_{20}H_{12}O_4$  requires C, 75.9; H, 3.7%).

TABLE III.

*Absorption Maxima of Azotriphenylmethane Dyes (Series II and III).*

These dyes were prepared by tetrazotising the amines referred to in the second column, coupling the products with dimethylaniline (2 mols.) and oxidising the final products. *a* is now the absorption maximum of the dye in conc. HCl.

Formula.	Amine.	<i>a</i> .	N %.
B·C(OH):(A·R) <sub>2</sub> .	II, 1	5050	15.5 (15.1)
(4)OH·B·C(OH):(A·R) <sub>2</sub> .	II, 2	5140	15.1 (14.7)
R·C(OH):(A·R) <sub>2</sub> .	II, 3	5160	16.1 (16.4)
B·A·CH:(A·R) <sub>2</sub> .	III, 1	5070	17.8 (17.4)
(4)OH·B·A·CH:(A·R) <sub>2</sub> .	III, 3	5070	17.5 (17.0)
R·A·CH:(A·R) <sub>2</sub> .	III, 2	5070	18.2 (18.3)

TABLE IV.

*Absorption Maxima of Azo-dyes of the Mixed Type (Series IV).*

Name or reference.	Absorption maxima (λ).	Name or reference.	Absorption maxima (λ).
Nile-blue A.....	6040	Indigotin .....	6050
IV, 1 .....	5820	5-Aminoindigotin .....	5890
Lauth's-violet .....	5970	IV, 5a .....	5720
IV, 2 .....	5050	4 : 4'-Diaminoindigotin...	5940
Phenylene-blue .....	6600	IV, 5b .....	5010
IV, 4 .....	5980	"Thioindigo" .....	5240
Phenosafranine .....	5250	5 : 5'-Diaminothioindigo	5230, 5920
IV, 3a .....	5790	IV, 6 .....	4990
IV, 3b .....	5130		

*Absorption Maxima of Dyes with Reduplicated Chromophores (Series V).*

Benzeneazophenol .....	4330	Malachite-green .....	6190
Benzeneazobenzeneazo-phenol .....	4350	V, C 2 .....	6220
V, A 1 .....	4360	Pyronine .....	5380 (6670)
V, A 4 .....	4360	V, D .....	5380 (6680)
Benzeneazodimethyl-aniline .....	5040	Meldola's blue .....	6060
Benzeneazobenzeneazo-dimethylaniline .....	5090	V, F .....	7020
V, A 3 .....	5130	Phenazine .....	4290
V, A 5 .....	5140	V, G 1 .....	4310
Michler's hydrol .....	6080	V, G 2 .....	4320
V, B 2 .....	5990	Fluorescein .....	4940
		V, E .....	4950
		VI, A 3 .....	6210
		Phenolphthalein .....	5540
		VI, B .....	5550

My best thanks are due to Professor J. F. Thorpe, F.R.S., for the kind interest he has taken in this work, to Professor A. Fowler, F.R.S., for permission to use his quartz spectrograph, and to the Chemical Society for a grant which has defrayed part of the expense of this research.

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