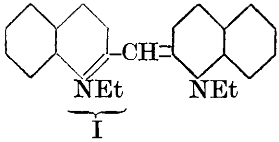
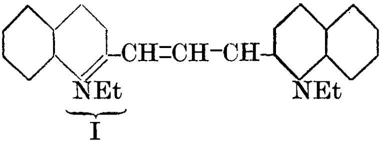
# 35. *Dicarbocyanines. A New Series of Cyanine Dyes.*

By Stanley Beattie, Isidor Morris Heilbron, and Francis Irving.

A study of the absorption spectra of the cyanine dyes reveals that an increase in the length of the polymethine chain effects a movement of the absorption band towards the red end of the spectrum. Thus, whereas 1 : 1′-diethyl-ψ-cyanine iodide (I) has the head of its main absorption band at 520 mμ, 1 : 1′-diethyl-2 : 2′-carbocyanine iodide (II) has its absorption maximum at 607 mμ. Similar results are noted on comparing the absorption spectra of the *iso*cyanines and 2 : 4′-carbocyanines (compare Bloch and Hamer, *Phot. J.*, 1928, **68**, 21). It is therefore to be anticipated, as pointed out by the above authors, that if the heterocyclic nuclei could be linked by a five-carbon chain, whereby " dicarbocyanines " would result, the dyes in this case would show absorption maxima either in the extreme red or in the near infra-red. That this is actually the case is shown in the present paper where details of the preparation and properties of various types of this new class of cyanine dyes are given.

(I.)



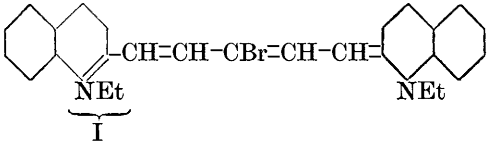


(II.)

It is obvious that the required five-carbon chain giving respectively 2 : 2′-dicarbocyanines and 4 : 4′-dicarbocyanines could theoretically be introduced by the condensation of two molecules of quinaldine or lepidine alkyl halide with either one molecule of malondialdehyde or a suitable acraldehyde derivative such as β-ethoxyacraldehyde acetal. One possible member of this series has indeed been mentioned by König (*Ber.*, 1922, **55**, 3309) without its method of preparation being indicated. Owing, however, to the comparative inaccessibility of the aliphatic initial materials we have, for the present, utilised the more readily obtainable derivatives of bromo- and chloro-malondialdehydes, especially α-bromo(or chloro)-β-anilinoacraldehyde anil, PhN⁚CH·CBr⁚CH·NHPh, which compound results when mucobromic acid, CHO·CBr⁚CBr·$CO_2H$ (Simonis, *Ber.*, 1899, **32**, 2084) is treated with aniline in alcoholic solution (Dieckmann and Platz, *Ber.*, 1904, **37**, 4638).

*Dicarbocyanines.*—By the interaction of quinaldine ethiodide with α-bromo-β-anilinoacraldehyde anil in pyridine solution in presence of excess of piperidine, 11-*bromo*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine iodide* (III) is formed as a blue-green dye. The use of pyridine alone as condensing agent, which proved so successful for the preparation of carbocyanines (Hamer, J., 1927, 2796), did not give satisfactory results in this series.

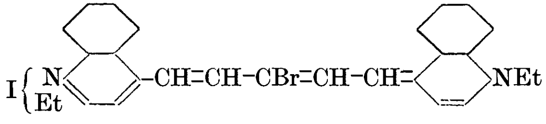
(III.)



The absorption maximum of this compound (700 mμ) is much nearer the red limit of the visible spectrum than that of 1 : 1′-diethyl-2 : 2′-carbocyanine iodide (607 mμ). Like many other members of this group, the dye acts as a powerful photographic sensitiser with maximum action at 755 mμ, this being, as anticipated, considerably nearer the red end of the spectrum than that of the corresponding carbocyanine, which, having a shorter conjugated chain linking the quinoline nuclei, has its sensitising maximum at 640 mμ.

With lepidine ethiodide, 11-*bromo*-1 : 1′-*diethyl*-4 : 4′-*dicarbocyanine iodide* (IV) is formed; with a still longer conjugated chain

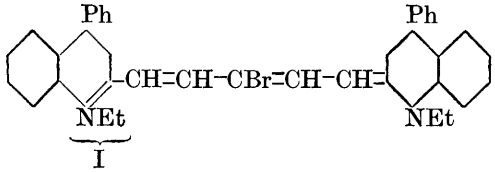
(IV.)



uniting the two nitrogen atoms, the absorption maximum is found at 800 mμ, while the sensitising effect appears at 840 mμ.

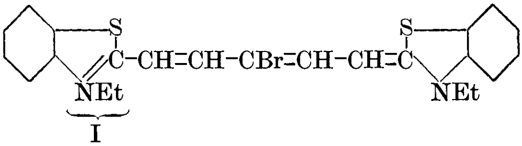
4-Phenylquinaldine and α-bromo-β-anilinoacraldehyde anil hydrobromide yield 11-*bromo*-4 : 4′-*diphenyl*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine iodide* (V) as a green dye with absorption maxima at 730 mμ and 700 mμ respectively. The presence of the 4 : 4′-phenyl groups largely decreases its sensitising action, a further demonstration of the harmful effect of these groups on this property (compare preceding paper).

(V.)



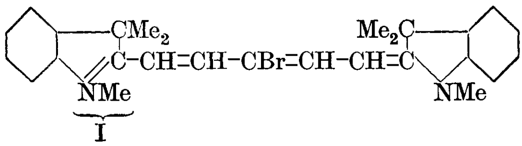
*Thiodicarbocyanines.*—10-*Bromo*-1 : 1′-*diethylthiodicarbocyanine iodide* (VI) has been obtained by condensing 1-methylbenzthiazole ethiodide with α-bromo-β-anilinoacraldehyde anil hydrobromide in acetic anhydride solution in presence of potassium acetate. That the same rule regarding the movement of the absorption maximum with an increase in the length of the polymethine chain holds in the thiocyanine series has already been shown by Bloch and Hamer (*loc. cit.*); and it can now be extended to the new thiodicarbocyanine dye, which has its absorption and sensitising maxima at 645 mμ and 690 mμ respectively as compared with 559 mμ and 580 mμ for 1 : 1′-diethylthiocarbocyanine iodide.

(VI.)



*Indodicarbocyanines.*—When 1 : 2 : 3 : 3-tetramethylindoleninium iodide is condensed with α-bromo-β-anilinoacraldehyde anil, 10-*bromo*-1 : 1′ : 3 : 3 : 3′ : 3′-*hexamethylindodicarbocyanine iodide* (VII) is produced. This reaction proceeds with great readiness and the conditions may be widely varied. The new dye, in striking contrast to the scarlet 1 : 1′ : 3 : 3 : 3′ : 3′-hexamethylindocarbocyanine (Astraphloxine F.F.), is deep blue (maximum absorption 645 mμ), a visible demonstration of the movement of the absorption

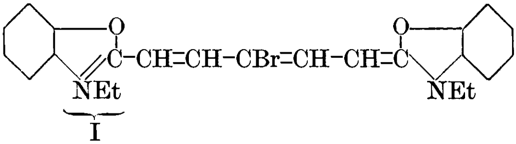
(VII.)



band towards the red end of the spectrum with increasing conjugation.

*Oxadicarbocyanines.*—10 - Bromo - 1 : 1′-diethyloxadicarbocyanine iodide (VIII) has been prepared by a method analogous to that employed for the corresponding thiodicarbocyanine dye. The corresponding *chloro*-derivative, prepared from α-chloro-β-anilinoacraldehyde anil, has its chief absorption maximum at 580 mμ and acts as a fair photographic sensitiser showing its maximum sensitising action at 615 mμ with a less marked maximum at 560 mμ.

(VIII.)



A comparison of the halogenodicarbocyanines with the corresponding carbocyanines shows that the introduction of the further vinyl group causes, for each group, a regular displacement of the main absorption maximum towards the red region of approximately 92 mμ and of the main sensitising maximum of approximately 103 mμ. It has also been noted that whereas replacement of the quinoline nuclei by the other heterocyclic nuclei gives dyes producing brighter and more pleasing shades when applied to fabrics, the former products have vastly superior sensitising values.

When mucobromic acid is treated with sodium nitrite, the sodium derivative of nitromalondialdehyde is formed, and this on treatment with aniline yields α-nitro-β-anilinoacraldehyde anil (compare Hill and Torrey, *Amer. Chem. J.*, 1899, **22**, 91; Hale and Honan, *J. Amer. Chem. Soc.*, 1919, **41**, 770), from which nitro-dicarbocyanines have been prepared. These react quite differently from either the halogeno-dicarbocyanines or the normal carbocyanines. Thus 11-*nitro*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine iodide* possesses two wide absorption bands with maxima at 490 mμ and 580 mμ and does not sensitise photographic emulsions but possesses slight desensitising properties. Since it is affected by alkalis, however, the latter property is not shown in presence of the developer. The effect of the introduction of a nitro-group into the polymethine chain is thus analogous to that noted by Mills and Hamer (J., 1920, **117**, 1550), who by the action of nitric acid on 1 : 1′-diethyl-2 : 2′-carbocyanine iodide obtained a dinitro-derivative containing both nitro-groups in the polymethine chain. This substance had no sensitising properties but was a strong desensitiser, its action being, however, destroyed by the weak alkali of the developer (Hamer, *Phot. J.*, 1928, **69**, 409).

## EXPERIMENTAL.

*Mucochloric Acid.*—This compound has already been described by Simonis (*loc. cit.*), who, however, gives only scanty details of the preparation. The following method results in a 65% yield of the compound. A mixture of furfuraldehyde (20 g.) and concentrated hydrochloric acid (800 c.c.) contained in a 3 litre flask was treated with finely powdered manganese dioxide (120 g.), added in 20 g. portions so as to maintain a vigorous evolution of chlorine. The first portion of manganese dioxide dissolved without the application of heat being necessary, but during the subsequent additions the flask was gently warmed. After all the manganese dioxide had dissolved, the solution was boiled for 15—20 minutes, a further portion of manganese dioxide (20 g.) being added gradually during this period. The clear solution was allowed to cool, and the mucochloric acid isolated by repeated ether extraction. The crude mucochloric acid separated on removal of the solvent and crystallised from boiling water in colourless plates, m. p. 127°.

The derivatives of the mucochloric and mucobromic acids used in this work were prepared by the methods of Dieckmann and Platz (*loc. cit.*). In the case of α-bromo-β-anilinoacraldehyde, however, we find the melting point to be 164° and not 184° as recorded by these authors.

10-*Bromo*-1 : 1′ : 3 : 3 : 3′ : 3′-*hexamethylindodicarbocyanine Iodide* (VII).—A hot solution of α-bromo-β-anilinoacraldehyde anil (1 g.) and 1 : 2 : 3 : 3-tetramethylindoleninium iodide (1 g.; 1 mol.) in absolute alcohol (15 c.c.) was treated with a solution of the free methylene base prepared from an equal amount of the indoleninium salt in absolute alcohol (10 c.c.). The colour of the solution gradually changed from brown to blue and the reaction was completed by heating under reflux for 1 hour. The dye, which separated on cooling, was repeatedly crystallised from acetone, forming dark green crystals having a metallic reflex. It dissolves in acetone, alcohol, and water, giving intense blue solutions with a faint red fluorescence. The dye may be applied from a neutral bath to natural silk, wool, or tannin-mordanted cotton, brilliant blue shades being obtained (Found : N, 5·0. $C_{27}H_{30}N_2BrI$ requires N, 4·8%).

The dye has also been prepared by the interaction of tetramethylindoleninium iodide with either α-bromo-β-anilinoacraldehyde or mucobromic acid in presence of the calculated amount of potassium acetate necessary to absorb the acid set free during the reaction.

10-*Chloro*-1 : 1′ : 3 : 3 : 3′ : 3′-*hexamethylindodicarbocyanine Iodide.*—This dye was prepared in a similar manner to the corresponding bromo-compound, except that acetic anhydride, in which the reaction is more rapid, was used as solvent. Alternatively a mixture of

1 : 2 : 3 : 3-tetramethylindoleninium iodide (1 g. ; 2 mols.), α-chloro-β-anilinoacraldehyde anil hydrochloride (1 mol.) and anhydrous potassium acetate (2 mols.) in alcohol (20 c.c.) may be heated together under reflux.

The dye separates from alcohol in bright green crystals with a gold reflex, m. p. 240—241° (decomp.). Its solutions resemble those of the bromo-dye, and the dyeings are also similar (Found : N, 5·1. $C_{27}H_{30}N_2ClI$ requires N, 5·1%).

10-*Chloro*-3 : 3 : 3′ : 3′-*tetramethyl*-1 : 1′-*diethylindodicarbocyanine Iodide*.—A solution of 2 : 3 : 3-trimethyl-1-ethylindoleninium iodide (1·0 g.), α-chloro-β-anilinoacraldehyde anil hydrochloride (0·54 g.), and anhydrous potassium acetate (0·31 g.) in acetic anhydride (15 c.c.) was heated under reflux for 1 hour. The dye crystallised from boiling alcohol in fine green needles having a bronze reflex. The corresponding *chloride*, obtained by heating the free trimethylindolenine base with the anil hydrochloride, is similar in appearance but more soluble in water (Found : N, 6·1. $C_{29}H_{34}N_2Cl_2$ requires N, 5·8%).

10-*Nitro*-1 : 1′ : 3 : 3 : 3′ : 3′-*hexamethylindodicarbocyanine Iodide*.—A solution of 1 : 2 : 3 : 3-tetramethylindoleninium iodide (2·25 g.), 1 : 3 : 3-trimethyl-2-methyleneindolenine (1·3 g.), and α-nitro-β-anilinoacraldehyde anil (2 g.) in absolute alcohol (30 c.c.) was heated under reflux for 40 minutes. The *dye*, which separated on cooling, crystallised from acetone in dark brown crystals with a gold reflex. Concentrated solutions of the dye in alcohol or acetone are blue but change to deep red on dilution. This dye gives dull red colours on wool and tannin-mordanted cotton (Found : N, 7·6. $C_{27}H_{30}O_2N_3I$ requires N, 7·6%).

11-*Chloro*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine Iodide*.—A solution of quinaldine ethiodide (2 g.) and α-chloro-β-anilinoacraldehyde anil (0·85 g.) in pyridine (7 c.c.) together with piperidine (0·3 c.c.) was heated under reflux for 1 hour. The *dye* which separated from the deep blue cold solution was crystallised from alcohol, separating in small green crystals having a bronze reflex, m. p. 228—230° (decomp.). The dye is only moderately easily soluble in acetone and alcohol and sparingly soluble in water, giving light blue solutions. It dyes silk and wool somewhat dull greenish-blue shades (Found : N, 5·3. $C_{27}H_{26}N_2ClI$ requires N, 5·2%).

The corresponding 11-*bromo*-1 : 1′-*diethyldicarbocyanine iodide* (III), prepared from quinaldine ethiodide and α-bromo-β-anilinoacraldehyde anil, is similar in all respects (Found : N, 4·7. $C_{27}H_{26}N_2BrI$ requires N, 4·8%).

11-*Nitro*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine Iodide*.—A solution of quinaldine ethiodide (1·0 g.) and α-nitro-β-anilinoacraldehyde anil

(0·44 g.) in pyridine (5 c.c.) was gently boiled in presence of piperidine (0·2 c.c.) for 1 hour. The *dye* which separated from the cold solution was crystallised from acetone, forming dark brown crystals sparingly soluble in alcohol and water, giving blue solutions which became bluish-red on dilution. It gives dull red shades on silk, wool, and tannin-mordanted cotton (Found : N, 7·6. $C_{27}H_{26}O_2N_3I$ requires N, 7·6%).

10-*Chloro*-1 : 1′-*diethyloxadicarbocyanine Iodide*.—This compound is difficult to prepare and the following method is the only one from which satisfactory results have been obtained. 1-Methylbenzoxazole ethiodide (1 g.) was added during 5 minutes, with constant stirring, to a boiling solution of α-chloro-β-anilinoacraldehyde anil (0·44 g.) and anhydrous potassium acetate (0·17 g.) in acetic anhydride (10 c.c.) contained in a small open beaker. Heating was then discontinued and the *oxadicarbocyanine iodide*, which separated on cooling from the dark red solution, was crystallised from acetone, forming greyish-green crystals, m. p. 214—215° (decomp.). The salt is sparingly soluble in water, more soluble in alcohol and acetone, giving bluish-red solutions with an intense red fluorescence. It gives brilliant reddish-purple shades on natural silk, wool and tannin-mordanted cotton (Found : N, 5·3. $C_{23}H_{22}O_2N_2ClI$ requires N, 5·4%).

The corresponding bromo-dye (VIII) requires for its preparation a larger proportion of acetic anhydride. The separation of the dye, which is similar in all respects to the chloro-analogue, was assisted by the addition of alcohol at the end of the reaction.

10-*Chloro*-1 : 1′-*diethylthiodicarbocyanine Iodide*.—1-Methylbenzthiazole ethiodide (1 g.) was added gradually with stirring to a boiling solution of α-chloro-β-anilinoacraldehyde anil (0·5 g.) and anhydrous potassium acetate (0·18 g.) in acetic anhydride (10 c.c.). The solution attained a deep blue colour and was allowed to cool immediately the addition of the benzthiazole salt had been completed. The dye crystallised from acetone in bluish-green crystals having a bronze reflex, m. p. 233—234° (decomp.). The *thiodicarbocyanine iodide* is sparingly soluble in water, moderately easily soluble in alcohol and acetone, the deep blue solutions showing a slight red fluorescence. From neutral baths, it may be applied to wool, natural silk, and tannin-mordanted cotton, brilliant blue shades being obtained (Found : N, 5·1. $C_{23}H_{22}N_2ClIS_2$ requires N, 5·1%).

The corresponding 10-*bromo*-1 : 1′-*diethylthiodicarbocyanine iodide* is similar in all respects. At normal concentrations the salt has only a slight sensitising effect, but this increases at very high dilutions (Found : N, 4·8. $C_{23}H_{22}N_2BrIS_2$ requires N, 4·7%).

11-*Chloro*-4 : 4′-*diphenyl*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine Iodide.*—4-Phenylquinaldine ethiodide (3·75 g.) was added slowly to a solution of α-chloro-β-anilinoacraldehyde anil (1·3 g.) and anhydrous potassium acetate (0·48 g.) in boiling acetic anhydride. The solution, which immediately became bright green, was gently refluxed for 1½ hours; the *dye* then began to separate. Purification was effected by repeated extraction with boiling acetone, in which the salt is sparingly soluble, green crystals with a golden reflex being obtained. Owing to the sparing solubility of this product in water, its use as a dye is difficult, but good green shades can be obtained on natural silk (Found: N, 4·2. $C_{39}H_{34}N_2ClI$ requires N, 4·0%).

11-*Bromo*-4 : 4′-*diphenyl*-1 : 1′-*diethyl*-2 : 2′-*dicarbocyanine Iodide* (V).—A solution of 4-phenylquinaldine ethiodide (3·0 g.) and α-bromo-β-anilinoacraldehyde anil hydrobromide (1·7 g.) in hot pyridine (20 c.c.) was treated with piperidine (0·9 c.c.) and heated for 3 hours on a boiling water-bath. The pyridine was removed under reduced pressure, and the residue dissolved in boiling absolute alcohol, from which the pure *salt* separated on cooling in fine green needles, sparingly soluble in alcohol or acetone to bright green solutions which became blue-green on dilution with water (Found: N, 3·9. $C_{39}H_{34}N_2BrI$ requires N, 3·8%).

11-*Chloro*-1 : 1′-*diethyl*-4 : 4′-*dicarbocyanine Iodide.*—A solution of α-chloro-β-anilinoacraldehyde anil (0·9 g.) and anhydrous potassium acetate (0·5 g.) in the minimum quantity of hot acetic anhydride contained in a small beaker was treated with lepidine ethiodide (2·0 g.), added during 5 minutes. The solution rapidly acquired a brownish-green colour, and the product separated without further heating being required. After being washed with ether, the *salt* was crystallised from alcohol, dark green plates with a golden reflex separating from the bright green solution. In preparing this compound it is necessary to follow precisely the above method, otherwise brown decomposition products result (Found: N, 5·1. $C_{27}H_{26}N_2ClI$ requires N, 5·2%).

11-*Bromo*-1 : 1′-*diethyl*-4 : 4′-*dicarbocyanine Iodide* (IV).—A solution of lepidine ethiodide (2 g.) and α-bromo-β-anilinoacraldehyde anil hydrobromide (1·45 g.) in warm dry pyridine (15 c.c.) was treated with piperidine (1·5 c.c.). A deep bluish-red colour was immediately formed, changing to deep purple after 2 minutes' boiling. The pure product commenced to separate at this stage in small green plates having a brilliant golden reflex. The *salt* is sparingly soluble in alcohol and acetone, giving deep green solutions

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