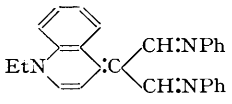
375. *Some Trinuclear Cyanine Dyes. Part II. Neocyanines with Dissimilar Nuclei.*

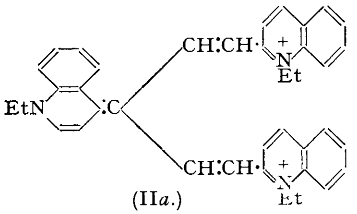
By Frances M. Hamer, Russell J. Rathbone, and Barbara S. Winton.

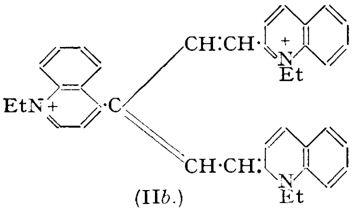
N-Alkyldihydro-derivatives of heterocyclic bases, with a dianilo*iso*propylidene group in the reactive position, were condensed with two mols. of heterocyclic quaternary ammonium salts, having a reactive methyl group, to give *neocyanines* with two similar nuclei and one dissimilar, the two similar nuclei being at the ends of the pentamethin chain. The dianils were also condensed with one mol. of quaternary salts, to give intermediate *dyes* having two nuclei and one anilomethyl group; these gave rise to *isomerides* of the above neocyanines, having the two similar nuclei at the ends of a trimethin chain, and also to *neocyanines* with three dissimilar nuclei. Absorption maxima of methyl-alcoholic solutions of the new dyes were compared with those of such related simpler dyes as have chain-systems which build up the complex chains of the neocyanines and intermediates.

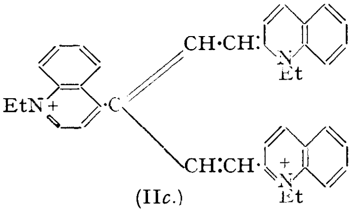
Neocyanine was the name given to a by-product obtained in the preparation of 4 : 4′-trimethincyanine. Its trinuclear nature had been known for nineteen years (Hamer, *J.*, **1928**, 1472) and its possible constitution for twelve (König, *Z. wiss. Phot.*, **1935**, **34**, 15), before our synthesis of it from the dianilo-base (I) established that it has two 4-linked quinoline nuclei connected by an unbranched pentamethin chain, with a third such nucleus attached in the *meso*-position (Hamer, Rathbone, and Winton, *J.*, 1947, 1434). We also synthesised other neocyanines containing three similar heterocyclic nuclei; two of these were identical with dyes which had previously been obtained empirically, whilst five were new. For this work nine dianilo-compounds besides (I) were themselves synthesised.

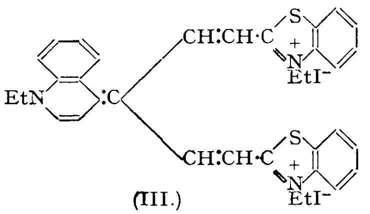
The present paper shows the synthetic method to have enormously greater scope than the empirical one. Thus one molecule of a dianilo-compound such as (I) may be condensed with two molecules of any quaternary, heterocyclic ammonium salt, having a reactive methyl group, and if the nucleus of the salt differs from that of the dianilo-compound, neocyanines having two similar nuclei and one dissimilar will result. For instance, by condensing (I) with quinaldine ethiodide, we prepared a *dye* of which the kation may be represented by the three resonating structures (II*a*), (II*b*), and (II*c*). The use of 2-methylbenzthiazole ethiodide or 2-methyl-Δ^2-thiazoline ethiodide instead of quinaldine ethiodide led to the *neocyanines* represented, respectively, by formulæ (III) and (IV), to give for each substance only one out of each group of three canonical structures. An *isomeride* of (III), having a 1 : 2- instead of a 1 : 4-dihydroquinoline nucleus, was prepared by condensing the 1 : 2-isomeride of (I) with 2-methylbenzthiazole ethiodide. By condensing a dianilo-compound having a benzthiazoline nucleus with lepidine ethiodide we prepared (V); with quinaldine ethiodide this dianil gave an *analogue* of (II), in which a benzthiazole nucleus took the place of the 4-linked quinoline; with 2-methylbenzoxazole ethiodide and 2-methylbenzselenazole ethiodide, respectively, it gave *dyes* represented by (VI; Y = S, R = Et, X = I, Z = O or Se). By condensing a dianil having a 6 : 7-benzbenzthiazoline nucleus with 2-methyl-6 : 7-benzbenzoxazole ethiodide we obtained (VII). From a dianil having a benzselenazoline nucleus and quinaldine etho-*p*-toluenesulphonate we prepared an *analogue* of (II), with a benzselenazole in place of the 4-linked quinoline nucleus; this dianil on reacting with 2-methylbenzoxazole ethiodide and 2-methylbenzthiazole ethiodide, respectively, gave (VI; Y = Se, R = Et, X = I, Z = O or S); it was also condensed with 2-methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate and with 1 : 3 : 3-trimethylindolenine methiodide, the latter yielding (VI; Y = Se, R = Me, X = ClO_4, Z = CMe_2), accompanied by an unsymmetrical *trimethincyanine* as by-product. Further *neocyanines* were prepared by condensing a dianil having a 4-methyl-Δ^4-thiazoline nucleus with

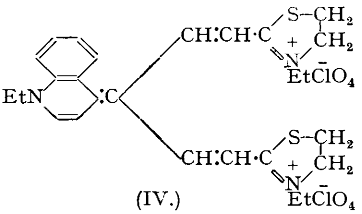

(I.)


(II*a*.)

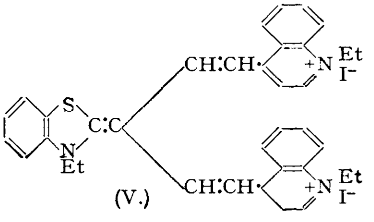

(II*b*.)


(II*c*.)

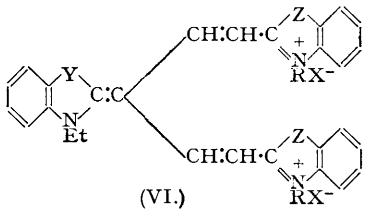

(III.)


(IV.)

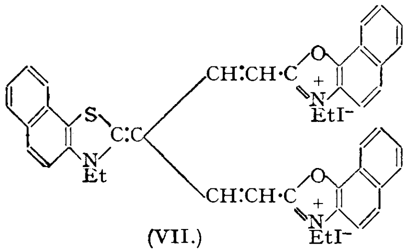
2-methylbenzthiazole ethiodide and with 2-methylbenzselenazole ethiodide, and by condensing a dianil having a thiazolidine nucleus with lepidine ethiodide and with 2-methylbenzthiazole ethiodide.



(V.)



(VI.)



(VII.)

The absorption curves of methyl-alcoholic solutions of the neocyanines were plotted and their maxima are recorded in Table I. Like neocyanines having three similar nuclei, these also had narrow, well-defined curves, with sometimes an inflexion on the side of shorter wave-length. We have here, as also in the first paper of the series, compared each absorption maximum with those of the corresponding tri- and penta-methincyanines. Whereas in Part I both parent dyes were symmetrical, here only the pentamethincyanine is symmetrical whilst the trimethincyanine is unsymmetrical. The abbreviations used in the table are obvious if taken in conjunction with the text. To each maximum that has been previously recorded, a bibliographic reference is given, and all those with no reference belong to compounds described here. Six of the parent *trimethincyanines* were prepared for the purpose of this comparison. With nineteen of the twenty neocyanines, as for the seven already described (Hamer, Rathbone, and Winton, *loc. cit.*), the absorption maximum lay between those of the corresponding unsubstituted tri- and penta-methincyanines. For these nineteen the bathochromic shifts on passing from trimethincyanine to neocyanine varied from 20 to 1675 A., whilst the anomalous hypsochromic shift on passing from the trimethincyanine to the neocyanine (IV) was 495 A. In all nineteen instances, there was a bathochromic shift on passing from neocyanine to pentamethincyanine, the amounts varying from 180 to 900 A. Many other comparisons may also be made from this table.

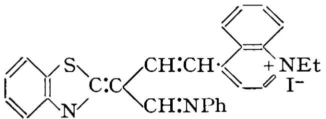
For preparing neocyanines with three similar nuclei (*idem, ibid.*) or the above neocyanines with two similar nuclei and one dissimilar, our usual procedure was to heat a mixture of dianil and quaternary salt with pyridine, which often gave a result as good as did the alternative of heating with sodium acetate in acetic anhydride. In instances where it gave an unsatisfactory product, we resorted to the latter method, which proved more drastic. When a dianil, such as that having a benzthiazoline nucleus, was mixed with a quaternary salt, *e.g.*, lepidine ethiodide, a purple colour appeared directly the pyridine was added, although heat was necessary to develop the bluer colour of the neocyanine (V). These observations led to the discovery that such reactions can be stopped when one molecule of dianil has reacted with only one molecule of quaternary salt. With the reactants specified, the resultant product is a *dye*, which may be represented by two canonical resonating structures (VIII*a*) and (VIII*b*). In the presence of acid there are three ways in which two positive charges can be distributed between the three basic groups and these may be represented by formulæ (IX*a*), (IX*b*), and (IX*c*). By causing 3-ethyl-2-dianilo*iso*propylidenebenzthiazoline to react with other quaternary salts we prepared *dyes* analogous to (VIII) but having the 4-linked quinoline nucleus replaced by a 2-linked quinoline, a benzthiazole, a benzselenazole, a substituted indolenine, and a Δ^2-thiazoline nucleus, respectively. Other such *dyes* were prepared by reaction of a dianil having a 4-methyl-Δ^4-thiazoline nucleus with lepidine ethiodide, quinaldine ethiodide and 2-methyl-Δ^2-thiazoline ethiodide, and by reaction of a dianil having a thiazolidine nucleus with the alkiodide of lepidine

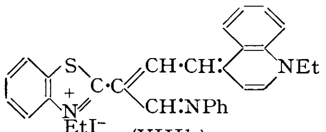
TABLE I.

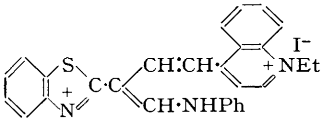
Neocyanine.	Abs. max. (A.)	Trimethin-cyanine.	Abs. max. (A.)	Penta-methin-cyanine.	Abs. max. (A.)	Bathochromic shifts. Tri-methin- to neo-cyanine.	Neo- to penta-methin-cyanine.
/2-q 4-q< (II) \2-q	6725	4-q/2-q	6560 †	/2-q \2-q	7080 *	165	355
/bzth 4-q< (III) \bzth	6320	4-q/bzth	6300 †	/bzth \bzth	6500 *	20	180
/thiazoline 4-q< (IV) \thiazoline	5270	4-q/thiazoline	5765	/thiazoline \thiazoline	5450 ‡	−495	180
/bzth 2-q< \bzth	6180	2-q/bzth	5600 †	/bzth \bzth	6500 *	580	320
/4-q bzth (V) \4-q	7200	/4-q bzth	6300 †	/4-q \4-q	8100 *	900	900
/2-q bzth \2-q	6365	/2-q bzth	5600 †	/2-q \2-q	7080 *	765	715
/thiazoline bzth \thiazoline	5045	/thiazoline bzth	5020	/thiazoline \thiazoline	5450 ‡	25	405
/bzox (VI; Y = S, Z = bzth O, R = Et, \bzox X = I)	5400	/bzox bzth	5200 †	/bzox \bzox	5800 *	200	400
/bzbzox bzbzth \bzbzox	5700	/bzbzox bzbzth	5500 †	/bzbzox \bzbzox	6080 *	200	380
/bzSe (VI; Y = S, Z = bzth Se, R = Et, \bzSe X = I)	6155	/bzSe bzth	5620 †	/bzSe \bzSe	6600 *	535	445
/2-q bzSe \2-q	6435	/2-q bzSe	5820 †	/2-q \2-q	7080 *	615	645
/bzox (VI; Y = Se, bzSe Z = O, R = \bzox Et, X = I)	5465	/bzox bzSe	5270 †	/bzox \bzox	5800 *	195	335
/bzth (VI; Y = Se, Z = bzSe S, R = Et, \bzth X = I)	6085	/bzth bzSe	5620 †	/bzth \bzth	6500 *	465	415
/bzbzth bzSe \bzbzth	6405	/bzbzth bzSe	5810 †	/bzbzth \bzbzth	6870 *	595	465
/ind (VI; Y = Se, Z = bzSe CMe$_2$, R = Me, \ind X = ClO$_4$)	6115	/ind bzSe	5500	/ind \ind	6360 *	615	245
/bzth Me-th \bzth	6075	/bzth Me-th	5470	/bzth \bzth	6500 *	605	425
/thiazoline Me-th \thiazoline	5050	/thiazoline Me-th	4995	/thiazoline \thiazoline	5450 ‡	55	400
/bzSe Me-th \bzSe	6205	/bzSe Me-th	5510	/bzSe \bzSe	6600 *	695	395
/4-q thiazoline \4-q	7440	/4-q thiazoline	5765	/4-q \4-q	8100 *	1675	660
/bzth thiazoline \bzth	6070	/bzth thiazoline	5020	/bzth \bzth	6500 *	1050	430

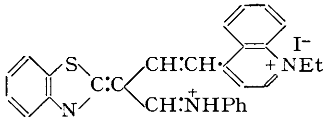
* Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.
† Beilenson, Fisher, and Hamer, *ibid.*, 1937, *A*, **163**, 138.
‡ Hamer, Rathbone, and Winton, *loc. cit.*

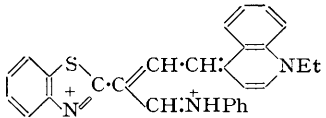
to give (X), of 2-methylbenzthiazole, to give (XI), of a substituted indolenine, and of 2-methyl-Δ^2-thiazoline. In preparing these intermediate *dyes*, temperature was an important controlling factor but their ease of formation varied greatly.

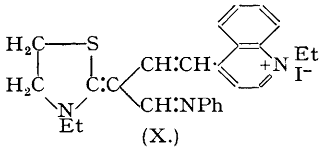

(VIII*a*.)

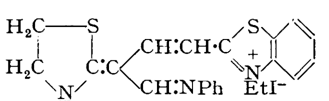

(VIII*b*.)


(IX*a*.)


(IX*b*.) I⁻

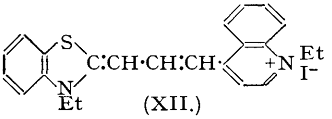

(IX*c*.) I⁻

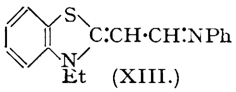

(X.)


(XI.)

With these intermediate dyes changes of pH produced some striking colour changes. For instance, the blue alcoholic solution of (VIII) became flame-coloured on acidification. For five of the compounds, the pH range of the colour change was determined, but it was concluded that they would be unsatisfactory as indicators because more drastic treatment with acid produced an irreversible change.

Alkaline methyl-alcoholic solutions of the anilomethyl compounds, as also such acidified solutions, had broader absorption curves than had the neocyanines. It seemed worth comparing the absorption maximum of each new anilomethyl compound with those of the related trimethincyanine, aniloethylidene compound, and anilobutenylidene compound : thus (VIII) would be compared with (XII), (XIII), and (XIV). In addition to this comparison, the absorption maxima of acidified solutions of the twelve *anilomethyl* compounds, represented for


(XII.)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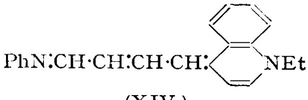
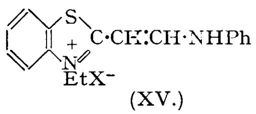
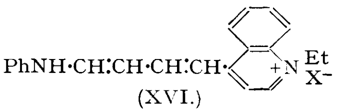

(XIV.)


(XV.)

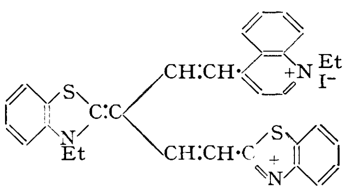

(XVI.)

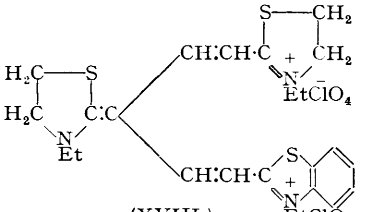
instance by (IX), were compared with acidified methyl-alcoholic solutions of aniloethylidene compounds, such as (XIII), which would contain the corresponding β-anilinovinyl salts, such as (XV) ; they were also compared with acidified solutions of anilobutenylidene compounds, such as (XIV), which would contain the corresponding β-anilinobutadienyl salts, such as (XVI). These comparisons are contained in Table II.

It there appears that on passing from a dinuclear anilomethyl dye, *e.g.*, (VIII), to the corresponding trimethincyanine, *e.g.*, (XII), there was in nine cases a bathochromic shift, varying from 55 to 1080 A., and in three cases a hypsochromic one, varying from 45 to 80 A. : in each of these three the thiazoline nucleus is involved. On passing from three aniloethylidene compounds to the corresponding acid salts, *e.g.*, from (XIII) to (XV), there were two bathochromic shifts and one hypsochromic ; on passing from six anilobutenylidene compounds to the corresponding acid salts, *e.g.*, from (XIV) to (XVI), there was in every instance a bathochromic shift varying from 295 to 715 A. ; with the new anilomethyl dyes, however, *e.g.*, (VIII), the shift on passing from alkaline to acid solution was hypsochromic in ten instances, its amount varying from 110 to 1030 A., and bathochromic, of 95 A. and 450 A., in two. On passing from a mononuclear aniloethylidene base, *e.g.*, (XIII), to a dinuclear anilomethyl compound, *e.g.*, (VIII), the shift was always bathochromic, varying in the twelve instances from 80 to 2225 A.; on passing from the mononuclear β-anilinovinyl salt, *e.g.*, (XV), to the corresponding acidified dinuclear intermediate dye, *e.g.*, (IX), there were again twelve bathochromic shifts, varying from 60 to 1290 A. On passing from a mononuclear anilobutenylidene base, *e.g.*, (XIV), to a dinuclear anilomethyl compound, *e.g.*, (VIII), the shift was bathochromic in ten cases, varying from 80 to 1005 A., and hypsochromic in two, of 30 and 35 A.; on passing from the mononuclear β-anilinobutadienyl salt, *e.g.*, (XVI), to the corresponding acidified dinuclear intermediate dye, *e.g.* (IX), all the shifts were hypsochromic, varying from 230 to 710 A.

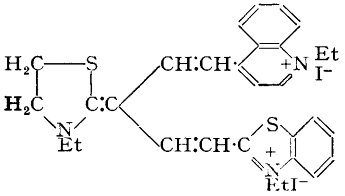
Through the new type of dye (VIII, etc.) it is possible to arrive at neocyanines of various kinds. In the first place there is afforded an alternative route to neocyanines of the type already described, which have two similar nuclei and one dissimilar, the two similar nuclei being connected by a pentamethin chain. Thus dyes having a Δ^2-thiazoline nucleus at each end of such a chain, and either a benzthiazole or a 4-methylthiazole nucleus in the *meso*-position, were obtained by this route; the absorption data relating to these two dyes have been included in Table I.

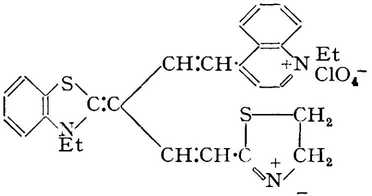
Secondly, the new intermediate dyes provide a means of preparing neocyanines, again with two similar nuclei and one dissimilar, but differing from those already described in that the two similar nuclei are connected by a trimethin chain. Thus (XVII), which is the isomeride of (III), was prepared by condensing (VIII) with 2-methylbenzthiazole ethiodide, whilst an *analogue* having a 2-linked instead of a 4-linked quinolinium nucleus was similarly prepared from the corresponding analogue of (VIII). An analogue of (VIII), having a benzthiazolium in place of the 4-linked quinolinium nucleus, was condensed with 2-methylbenzselenazole ethiodide to give an *analogue* of (XVII) having a benzselenazole in place of the 4-linked quinoline nucleus; an analogue of (VIII) having a Δ^2-thiazolinium in place of the 4-linked quinolinium nucleus, was condensed with 2-methylbenzthiazole ethiodide to give an *analogue* of (XVII), having a thiazolinium in place of the 4-linked quinolinium nucleus. (XVIII) was prepared through the condensation product of (XI) and 2-methyl-Δ^2-thiazoline ethiodide; an *analogue* of (XVIII) having a 4-linked quinolinium in place of the benzthiazolium nucleus was prepared from (X), through condensation with 2-methyl-Δ^2-thiazoline ethiodide.


(XVII.)


(XVIII.)

Thirdly, through the new intermediate dyes there can be obtained neocyanines in which all three nuclei are different. (XIX) was prepared by condensing (X) with 2-methylbenzthiazole ethiodide; (XX), which has the same three nuclei differently arranged, was derived by condensing lepidine ethiodide with an analogue of (VIII), having a thiazoline in place of a lepidine nucleus. A *dye* having a 2-linked quinoline, a 4-linked quinoline, and a benzthiazole nucleus, the first and second being at the ends of the pentamethin chain, and the third in the *meso*-position, was prepared, first from (VIII) with quinaldine ethiodide and, secondly, from the analogue of (VIII), having a 2-linked instead of a 4-linked quinolinium nucleus, with lepidine ethiodide. A *dye* having a benzselenazole, a 2-linked quinoline, and a benzthiazole nucleus, the first and second being at the ends of the pentamethin chain, and the third in the *meso*-position, was prepared, first from 2-methylbenzselenazole ethiodide and the analogue of (VIII), having a


(XIX.)


(XX.)

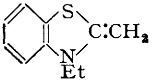
TABLE

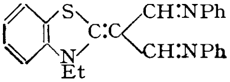
Anilomethyl compounds. /CH:CH: :C< \CH:NPh	Abs. max. (A.) Alkali.	 Acid.	Hypsochromic shifts, alkali → acid	Trimethin-cyanines. :CH·CH:CH·.	Abs. max. (A.)	Anilo-ethylidene compounds. :CH·CH:NPh.	Abs. max. (A.) Base.	 Acid salt.
/4-q bzth (VIII) \anMe	6030	5000 (IX)	1030	/4-q bzth (XII)	6300 ‡	bzth (XIII) \anMe	3935 §	4175 § (XV)
/2-q bzth \anMe	5150	4750	400	/2-q bzth	5600 ‡	,,	,,	,,
/bzth bzth \anMe	5515	4695	820	/bzth bzth	5570 ‡	,,	,,	,,
/bzSe bzth \anMe	4780	4670	110	/bzSe bzth	5620 ‡	,,	,,	,,
/ind bzth \anMe	4350	4800	−450	/ind bzth	5430	,,	,,	,,
/thiazoline bzth \anMe	(4005) 4905	4235	670	/thiazoline bzth	5020	,,	,,	,,
/4-q Me-th \anMe	5720	5010	710	/4-q Me-th	6295	Me-th \anMe	4090 §	4030 §
/2-q Me-th \anMe	5060	4815	245	/2-q Me-th	5900	,,	,,	,,
/thiazoline Me-th \anMe	4170	4265	−95	/thiazoline Me-th	4995	,,	,,	,,
/4-q thiazoline (X) \anMe	5810	4950	860	/4-q thiazoline	5765	thiazoline \anMe	3585 §	3660 §
/bzth thiazoline (XI) \anMe	5100	4725	375	/bzth thiazoline	5020	,,	,,	,,
/thiazoline thiazoline \anMe	4500	4370	130	/thiazoline thiazoline	4435 *	,,	,,	,,

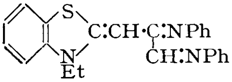
* Brooker, *J. Amer. Chem. Soc.*, 1936, **58**, 662.
† Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.
‡ Beilenson, Fisher, and Hamer, *ibid.*, 1937, *A*, **163**, 138.
§ Hamer, Rathbone, and Winton, *J.*, 1947, 954, for data about 3-ethyl-2-aniloethylidenebenzthiazoline, 4-methyl-3-ethyl-2-aniloethylidene-Δ^4-thiazoline, 3-ethyl-2-aniloethylidenethiazolidine, and corresponding salts.

2-linked instead of a 4-linked quinoline nucleus and, secondly, from quinaldine ethiodide and the analogue of (VIII), having a benzselenazole instead of a 4-linked quinoline nucleus.

In the first paper of this series (*J.*, 1947, **1434**), we felt justified in assuming that when a base such as (XXI) is condensed with ethyl*iso*formanilide, the two anilomethyl groups successively replace the reactive hydrogen atoms of the methylene group to give the dianil, in this case (XXII), the alternative (XXIII) seeming so improbable that the idea could be dismissed. Structures such as (XXIII) are now definitely disproved by two facts : first, that when a dianil


(XXI.)


(XXII.)


(XXIII.)

is caused to react with one molecular proportion of a heterocyclic quaternary ammonium salt, having a reactive methyl group, only one intermediate dye has ever been obtained, whereas formula (XXIII) for the dianil could lead to two ; secondly, that when neocyanines having three different nuclei have been synthesised, the order of introduction of the second and the third

II.

Batho-chromic shifts, base → salt.	Anilo-butenylidene compounds. CH:CH·CH:CH:NPh	Abs. max. (A.) Base.	Abs. max. (A.) Salt.	Batho-chromic shifts, base → salt.	Bathochromic shifts. AniloMe Base → tri-methin-cyanine.	Bases : Anilo-ethyl-idene → AniloMe.	Salts : Anilo-ethyl-idene → AniloMe.	Bases : Anilo-butenyl-idene → AniloMe.	Salts : Anilo-butenyl-idene → AniloMe.
240	<4-q anMe (XIV)	5355 ‖	5660 ‖ (XVI)	305	270	2095	825	675	−660
,,	<2-q anMe	4980 ‖	5275 ‖	295	450	1215	575	170	−525
,,	<bzth anMe	4510 ‖	5120 ‖	610	55	1580	520	1005	−425
,,	<bzSe anMe	4505 ‖	5220 ‖	715	840	845	495	275	−550
,,	<ind anMe	4385 ‖	5090 ‖	705	1080	415	625	−35	−290
,,	<thiazoline anMe	4200 ‖	4600 ‖	400	115	970	60	705	−365
−60	<4-q anMe	5355 ‖	5660 ‖	305	575	1630	980	365	−650
,,	<2-q anMe	4980 ‖	5275 ‖	295	840	970	785	80	−460
,,	<thiazoline anMe	4200 ‖	4600 ‖	400	825	80	235	−30	−335
75	<4-q anMe	5355 ‖	5660 ‖	305	−45	2225	1290	455	−710
,,	<bzth anMe	4510 ‖	5120 ‖	610	−80	1515	1065	590	−395
,,	<thiazoline anMe	4200 ‖	4600 ‖	400	−65	915	710	300	−230

‖ Hamer, *J.*, in the press, for data about 4 (and 2)-(4′-anilino-buta-1′ : 3′-dienyl)quinoline ethoperchlorate, 2-(4′-anilino-buta-1′ : 3′-dienyl)benzthiazole (and benzselenazole) ethoperchlorate, 2-(4′-anilino-buta-1′ : 3′-dienyl)-3 : 3-dimethylindolenine methoperchlorate, 2-(4′-anilino-buta-1′ : 3′-dienyl)-Δ^2-thiazoline ethiodide, and corresponding bases.

nucleus has been immaterial, which can only be explained by the dianil having the symmetrical structure (XXII).

Clearly, our new synthetic methods afford the possibility of preparing countless new dyes. Thus taking three nuclei, A, B, and C, eighteen different dyes are theoretically possible, *viz.*, three having three similar nuclei, indicated as

$$A{<}^{A}_{A},\quad B{<}^{B}_{B},\quad \text{and}\quad C{<}^{C}_{C};$$

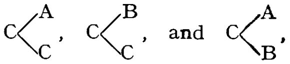
twelve having two similar nuclei and one dissimilar, indicated as

$$A{<}^{A}_{B},\ A{<}^{B}_{B},\ A{<}^{A}_{C},\ A{<}^{C}_{C},\ B{<}^{A}_{B},\ B{<}^{A}_{A},\ B{<}^{B}_{C},\ B{<}^{C}_{C},\ C{<}^{A}_{C},\ C{<}^{A}_{A},\ C{<}^{B}_{C},\ \text{and}\ C{<}^{B}_{B};$$

and lastly three having three dissimilar nuclei, indicated as

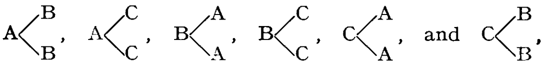
$$A{<}^{B}_{C},\quad B{<}^{A}_{C},\quad \text{and}\quad C{<}^{A}_{B}.$$

The preparation of a whole such set of eighteen dyes seemed attractive. In choosing three suitable nuclei, we decided on Δ^2-thiazoline (A), benzthiazole (B), and 4-linked quinoline (C), because the first nucleus tends to push the absorption maximum towards the most refrangible, and the last towards the least refrangible region, whilst the benzthiazole nucleus has an intermediate effect. Evidence has been adduced to show that, of these three nuclei, the Δ^2-thiazoline is the least basic and the 4-linked quinoline the most (Brooker, Sklar, Cressman, Keyes, Smith, Sprague, Van Larc, Van Zandt, White, and Williams, *J. Amer. Chem. Soc.*, **1945**, **67**, 1875). The first three dyes have already been described in the first paper of this series (*loc. cit.*), and twelve others are described here. The three



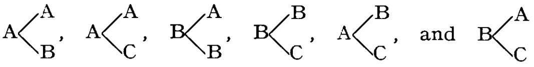
$\mathrm{C}\langle^{\mathrm{A}}_{\mathrm{C}}$, $\mathrm{C}\langle^{\mathrm{B}}_{\mathrm{C}}$, and $\mathrm{C}\langle^{\mathrm{A}}_{\mathrm{B}}$,

are missing, owing to the difficulty of preparing a pure anilomethyl intermediate dye from (I). The absorption data for



$\mathrm{A}\langle^{\mathrm{B}}_{\mathrm{B}}$, $\mathrm{A}\langle^{\mathrm{C}}_{\mathrm{C}}$, $\mathrm{B}\langle^{\mathrm{A}}_{\mathrm{A}}$, $\mathrm{B}\langle^{\mathrm{C}}_{\mathrm{C}}$, $\mathrm{C}\langle^{\mathrm{A}}_{\mathrm{A}}$, and $\mathrm{C}\langle^{\mathrm{B}}_{\mathrm{B}}$,

are given in Table I, whilst those for



$\mathrm{A}\langle^{\mathrm{A}}_{\mathrm{B}}$, $\mathrm{A}\langle^{\mathrm{A}}_{\mathrm{C}}$, $\mathrm{B}\langle^{\mathrm{A}}_{\mathrm{B}}$, $\mathrm{B}\langle^{\mathrm{B}}_{\mathrm{C}}$, $\mathrm{A}\langle^{\mathrm{B}}_{\mathrm{C}}$, and $\mathrm{B}\langle^{\mathrm{A}}_{\mathrm{C}}$

are given, together with others, in Table III.

The ten neocyanines of Table III differ from those of Table I in having two different nuclei attached to that in the *meso*-position. Whereas the absorption maximum of each neocyanine of Table I was compared with that of an unsymmetrical trimethincyanine and a symmetrical pentamethincyanine, each neocyanine of Table II is compared with two trimethincyanines, of which at least one is unsymmetrical, and with an unsymmetrical pentamethincyanine. Some of the parent pentamethincyanines required for the comparisons in Table III, as also the anilobutenylidene compounds required for those in Table II, are not described in the literature and were therefore prepared (Hamer, *J.*, in the press). Of the twenty shifts on passing from trimethincyanine to neocyanine, nineteen were bathochromic, varying from 10 to 1615 A., and one hypsochromic, of 310 A. Of the ten shifts on passing from neocyanine to pentamethincyanine, all were bathochromic, varying from 425 to 875 A.

Unless otherwise stated, the absorption maxima recorded are those of methyl-alcoholic solutions, and the photographic tests were carried out with gelatino-bromide plates. In view of the fact that the first neocyanine was described as the best infra-red sensitiser of its time (Dundon, Schoen, and Briggs, *J. Opt. Soc. Amer.*, 1926, **12**, 397), it may seem surprising that some of the new neocyanines confer little or no extra-sensitivity, whilst decreasing the normal blue sensitivity of the photographic plate. A partial explanation is the fact that meanwhile standards of comparison of infra-red sensitisers have been raised, by the discovery of the pentamethincyanines (I.C.I. Ltd., Piggott, and Rodd, B.P. 355,693/1930), heptamethincyanines (Fisher and Hamer, *J.*, 1933, 189), etc. Our anilomethyl intermediate dyes comprise photographic sensitisers.

Nomenclature.—In the experimental section of this paper, the nomenclature used is that explained in Part I (*loc. cit.*). The shorter methin chain is taken as the fundamental one, the α, β, γ . . . running from the system named first to that named second. The side chain has α', β', γ' . . . with α' attached to the system named third.

EXPERIMENTAL.

[2-(1-*Ethylquinoline*)][4-(1-*ethylquinoline*)][$\gamma\beta'$-*dimethin*-2'-(1'-*ethylquinoline*)]*trimethincyanine Diiodide* (II.)—Crude 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (I) (0·75 g.; 1 mol.), quinaldine ethiodide (1·20 g.; 2 mols.), anhydrous sodium acetate (1·31 g.; 8 mols.), and acetic anhydride (8 c.c.) were heated together in a glycerol-bath at 135—140° for 10 minutes. After cooling with ice, the solid was filtered off, washed with acetic anhydride and then with ether, ground with water (15 c.c.), and washed thrice with methyl alcohol. The crude dye (0·48 g.; 31% yield) was recrystallised from methyl alcohol (90 c.c. per g.) and thus obtained in 24% yield. A specimen was dried in a vacuum at 60—80° and analysed by the method of Carius, which methods of drying and analysis were used throughout this work (Found : I, 32·35. $C_{38}H_{37}N_3I_2$ requires I, 32·15%). The greenish-gold crystals gave off solvent from about 120°; shrinking began at about 190°, m. p. 264° (decomp.). The absorption curve had its maximum at 6725 A. and an inflexion at 6200 A. Towards a photographic emulsion the *dye* showed desensitising but no sensitising action.

TABLE III.

Neocyanines.	Abs. max. (A.)	Trimethin-cyanines.	Abs. max. (A.)	Penta-methin-cyanines.	Abs. max. (A.)	Bathochromic shifts. Tri-methin- to neo-cyanine.	Bathochromic shifts. Neo- to penta-methin-cyanine.
/bzth bzth< (XVII) \4-q	6480	bzth/bzth	5570 *	/bzth \4-q	7250 ‡	910	770
		bzth\4-q	6300 ‡			180	
/bzth bzth< \2-q	6110	bzth/bzth	5570 *	/bzth \2-q	6760 ‡	540	650
		bzth\2-q	5600 ‡			510	
/bzth bzth< \bzSe	6100	bzth/bzth	5570 *	/bzth \bzSe	6590 ‡	530	490
		bzth\bzSe	5620 ‡			480	
/bzth bzth< \thiazoline	5580	bzth/bzth	5570 *	/bzth \thiazoline	6005 §	10	425
		bzth\thiazoline	5020			560	
/4-q bzth< \2-q	6730	bzth/4-q	6300 ‡	/4-q \2-q	7605 §	430	875
		bzth\2-q	5600 ‡			1130	
/4-q bzth< \thiazoline (XX)	5990	bzth/4-q	6300 ‡	/4-q \thiazoline	6705 §	−310	715
		bzth\thiazoline	5020			970	
/2-q bzth< \bzSe	6260	bzth/2-q	5600 ‡	/2-q \bzSe	6750 ‡	660	490
		bzth\bzSe	5620 ‡			640	
/thiazoline thiazoline \4-q	6050	thiazoline/thiazoline	4435 †	/thiazoline \4-q	6705 §	1615	655
		thiazoline\4-q	5765			285	
/thiazoline thiazoline (XVIII) \bzth	5580	thiazoline/thiazoline	4435 †	/thiazoline \bzth	6005 §	1145	425
		thiazoline\bzth	5020			560	
/4-q thiazoline (XIX) \bzth	6555	thiazoline/4-q	5765	/4-q \bzth	7250 ‡	790	695
		thiazoline\bzth	5020			1535	

* Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.
† Brooker, *J. Amer. Chem. Soc.*, 1936, **58**, 662.
‡ Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138.
§ Hamer, *J.*, in the press.

[4-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*αβ'-dimethin-2'-*(3'-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (III.)—Crude 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (I) (0·38 g.; 1 mol.), 2-methylbenzthiazole ethiodide (0·62 g.; 2 mols.), and pyridine (2 c.c.) were heated together at 115—122° for 5 minutes. The *dye* was filtered off and washed with pyridine and with ether; yield 59% (0·48 g.). After recrystallisation from methyl alcohol (115 c.c. per g.), the yield was 31% (Found: I, 31·65. $C_{34}H_{33}N_3I_2S_2$ requires I, 31·7%). The green crystals had m. p. 281° (decomp.), and desensitised, without sensitising, a photographic emulsion. The absorption curve had its maximum at 6320 A.

When heating for 10 minutes at 135—140° with sodium acetate and acetic anhydride took the place of condensation by means of pyridine, the yields of crude and recrystallised dye were 56% and 42%, respectively.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide*.—Crude 1-ethyl-2-dianilo*iso*propylidene-1 : 2-dihydroquinoline (0·69 g.) was condensed with 2-methylbenzthiazole ethiodide in pyridine. The washed dye (0·47 g.) was recrystallised from methyl alcohol (45 c.c.; 32% yield), ground with water (5 c.c.; 28% yield), and again recrystallised from methyl alcohol (30 c.c.; 19% yield) (Found : I, 31·5. $C_{34}H_{33}N_3I_2Se$ requires I, 31·7%). The dark green crystals had m. p. 255° (decomp.). The absorption maximum was at 6180 A. The *substance* showed slight desensitisation.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)][*αβ′-dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate* (IV).—The reaction mixture from the heating of crude 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (I) (0·75 g.) with 2-methyl-Δ^2-thiazoline ethiodide, anhydrous sodium acetate, and acetic anhydride, was treated with absolute ether. The solid was filtered off, washed with ether, and treated with cold water (20 c.c.); this was decanted off from the resultant red tar, which was further washed with water (20 c.c.). On treating its solution in hot methyl alcohol (12 c.c.) with one of sodium perchlorate (1·47 g.; 6 mols.) in water (12 c.c.), the dye *perchlorate* crystallised (38% yield); after recrystallisation from methyl alcohol, the yield was 12% and after a second recrystallisation (230 c.c. per g.) 6% (Found : Cl, 11·1. $C_{26}H_{33}O_8N_3Cl_2S_2$ requires Cl, 10·9%). The dark blue crystals melted at about 260° (decomp.). Their absorption maximum was at 5270 A. The substance slightly depressed the sensitivity of a photographic emulsion.

[4-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-4′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide* (V).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (0·77 g.; 1 mol.), lepidine ethiodide (1·20 g.; 2 mols.), anhydrous sodium acetate (0·66 g.; 4 mols.), and acetic anhydride (4 c.c.) were heated together at 140—150° for 5 minutes. Precipitation with absolute ether (20 c.c.) was effected and the solid was washed with ether. On grinding with water (5 c.c.), it became tarry, but heating the tar with methyl alcohol (10 c.c.) caused it to crystallise. The yield of washed dye was 67% (1·07 g.). By boiling out with, and recrystallising from, methyl alcohol (5 c.c., 25 c.c.), it was obtained in 46% yield (Found : I, 32·15. $C_{36}H_{35}N_3I_2S$ requires I, 31·9%). The coppery crystals had m. p. 221° (decomp.). The absorption maximum was at 7200 A. The *dye* gave no photographic sensitation but desensitised strongly.

Attempts to prepare this dye by use of pyridine gave a product of lower iodine content, which was recognised as its mixture with the anilomethyl intermediate. Further heating of the mixed dyes with lepidine ethiodide, sodium acetate, and acetic anhydride yielded (V).

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-2′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide*.—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (0·77 g.) and quinaldine ethiodide were heated together in pyridine (4 c.c.). The dye was precipitated with absolute ether (20 c.c.) and heated with methyl alcohol (10 c.c.). The yield was 33%. It was boiled out with, and recrystallised from, methyl alcohol (9 c.c. per g., 85 c.c. per g.) and thus obtained in 23% yield (Found : I, 32·0. $C_{36}H_{35}N_3I_2S$ requires I, 31·9%). The green crystals had m. p. about 249° (decomp.) but depending on the rate of heating. The absorption maximum was at 6365 A. with an inflexion to the curve at about 5870 A. The *dye* sensitised weakly from 6600 to 6900 A.

[2-(3-*Ethylbenzoxazole*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-2′-(3′-*ethylbenzoxazole*)]*trimethincyanine Di-iodide* (VI; Y = S, Z = O, R = Et, X = I).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (0·77 g.), 2-methylbenzoxazole ethiodide, and pyridine (4 c.c.) were heated together at 130—135° for 2 minutes and the *product* was precipitated with ether (30 c.c.). By heating with methyl alcohol (4 c.c.) it was obtained crystalline in 56% yield (0·87 g.). It was boiled out with, and recrystallised from, methyl alcohol (5 c.c., 25 c.c.), resulting in 31% yield. After a second recrystallisation (42 c.c. per g.), the yield was 23% (Found : I, 32·6. $C_{32}H_{31}O_2N_3IS$ requires I, 32·75%). The bronze crystals had m. p. 236° (decomp.) and sensitised weakly from 5600 to 6000 A., whilst depressing the normal blue sensitivity of the plate. The absorption curve had its maximum at 5400 A. with an inflexion at 5000 A.

[2-(3-*Ethyl*-6 : 7-*benzbenzoxazole*)][2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)][*γβ′-dimethin*-2′-(3′-*ethyl*-6′ : 7′-*benzbenzthiazole*)]*trimethincyanine Di-iodide* (VII).—3-Ethyl-2-dianilo*iso*propylidene-6 : 7-benzbenzthiazoline (0·58 g.) and 2-methyl-6 : 7-benzbenzoxazole ethiodide were similarly heated in pyridine. The *product* which separated (1·04 g.) was boiled out with methyl alcohol (10 c.c.), and the residue then boiled out twice more with methyl alcohol (25 c.c. × 2, giving 0·05 g.) and once with pyridine (15 c.c., giving 0·01 g.). The undissolved residue (0·55 g.) was added to what had crystallised (0·06 g.), making a 49% yield (Found : I, 27·3. $C_{44}H_{37}O_2N_3I_2S$ requires I, 27·45%). The purple crystals had m. p. at about 238° (decomp.). The absorption maximum was at 5700 A. There was weak sensitisation to 6700 A. with decrease of the normal blue speed of the plate.

[2-(3-*Ethylbenzthiazole*)][2-(3-*ethylbenzselenazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide* (VI; Y = S, Z = Se, R = Et, X = I).—This was similarly prepared from 3-ethyl-2-dianilo*iso*propylidenebenzthiazoline and 2-methylbenzselenazole ethiodide, with heating for 5 minutes (83% yield). After recrystallisation from methyl alcohol (440 c.c. per g.), the yield was 48% (Found : I, 28·05. $C_{32}H_{31}N_3I_2SSe_2$ requires I, 28·15%). The dark green crystals had m. p. about 235° (decomp.), with previous softening, but dependent upon the rate of heating. The absorption maximum was at 6155 A. with a secondary maximum at 5580 A. The *dye* showed no sensitising but only desensitising properties.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzselenazole*)][*γβ′-dimethin*-2′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide*.—3-Ethyl-2-dianilo*iso*propylidenebenzselenazoline (1·72 g.; 1 mol.), quinaldine etho-*p*-toluenesulphonate (3·42 g.; 2·5 mols.), anhydrous sodium acetate (1·32 g.; 4 mols.), and acetic anhydride (30 c.c.) were heated together at 145—150° for 5 minutes. The hot reaction mixture was treated with a solution of potassium iodide (5·6 g.; 8 mols.) in water (200 c.c.). The crude dye (0·7 g.) was twice boiled out with methyl alcohol (10 c.c. × 2) and the residue then recrystallised from it (75 c.c.), giving an 8% yield (Found : I, 30·25. $C_{36}H_{35}N_3I_2Se$ requires I, 30·15%). The green and gold crystals had m. p. 235° (decomp.). The absorption curve had its maximum at 6435 A. The *dye* desensitised and did not sensitise.

[2-(3-*Ethylbenzoxazole*)][2-(3-*ethylbenzselenazole*)][*γβ′-dimethin*-2′-(3′-*ethylbenzoxazole*)]*trimethincyanine Di-iodide* (VI; Y = Se, Z = O, R = Et, X = I).—Prepared by heating together 3-ethyl-2-dianilo*iso*propylidenebenzselenazoline (1·72 g.), 2-methylbenzoxazole ethiodide, and pyridine, this *dye* was precipitated by absolute ether and treated with water, being obtained in 57% yield. It was boiled out with absolute alcohol (10 c.c.) and fractionally crystallised from methyl alcohol (10 c.c., 35 c.c.). The solid (0·16 g.) from the second fraction gave an orange spirit solution and was rejected. That from the first (0·48 g.) and a second crop from it (0·54 g.) were combined, making a 31% yield) (Found : I, 31·0. $C_{32}H_{31}O_2N_3I_2Se$ requires I, 30·85%). The dark red crystals had m. p. 215° (decomp.). The absorption maximum was at 5465 A. with an inflexion to the curve at about 5150 A. The substance sensitised weakly from 5400 to 6100 A. with the maximum at 5850 A. It depressed the normal blue sensitivity.

[2-(3-*Ethylbenzthiazole*)][2-(3-*ethylbenzselenazole*)][*γβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (VI; Y = Se, Z = S, R = Et, X = I).—Prepared by heating together 3-ethyl-2-dianilo*iso*propylidenebenzselenazoline, 2-methylbenzthiazole ethiodide, and pyridine, some *dye* crystallised on cooling and more was precipitated by absolute ether (total yield 86%). Recrystallisation from methyl alcohol (80 c.c. per g.) gave a 66% yield (Found : I, 29·85. $C_{32}H_{31}N_3I_2S_2Se$ requires I, 29·7%). The dark green crystals had m. p. 235° (decomp.). The absorption maximum was at 6085 A. with a slight inflexion to the curve at about 6600 A. The dye imparted no extra photographic sensitivity but caused some depression of the normal blue sensitivity.

[2-(3-*Ethyl*-6 : 7-*benzbenzthiazole*)][2-(3-*ethylbenzselenazole*)][*γβ′-dimethin*-2′-(3′-*ethyl*-6′ : 7′-*benzbenzthiazole*)]*trimethincyanine Di-iodide.*—3-Ethyl-2-dianilo*iso*propylidenebenzselenazoline (0·86 g.), 2-methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate, and pyridine were heated together and the reaction mixture treated hot with an aqueous potassium iodide solution. The washed dye iodide (1·7 g.) was boiled out with methyl alcohol (25 c.c.) and the residual solid (1·4 g.) fractionally crystallised from methyl alcohol (50 c.c., 155 c.c.). The second fraction (0·58 g.) consisted of bronze crystals giving a pure blue solution. The first fraction (0·5 g.) was given a second crystallisation from methyl alcohol (25 c.c.; 0·2 g. obtained). The total yield (0·78 g.) was 41% (Found : I, 26·4. $C_{40}H_{35}N_3I_2S_2Se$ requires I, 26·6%. The *dye*, m. p. 193° (decomp.), did not sensitise but depressed the blue sensitivity. The absorption maximum was at 6405 A. and the curve had a faint inflexion in the more refrangible region.

[2-(1 : 3 : 3-*Trimethylindolenine*)][2-(3-*ethylbenzselenazole*)][*γβ′-dimethin*-2′-(1′ : 3′ : 3′-*trimethylindolenine*)]*trimethincyanine Diperchlorate* (VI; Y = Se, Z = CMe₂, R = Me, X = ClO₄).—3-Ethyl-2-dianilo*iso*propylidenebenzselenazoline (1·08 g.; 1 mol.) and 2 : 3 : 3-trimethylindolenine methiodide (1·51 g.; 2 mols.) did not condense in pyridine. After they had been boiled with acetic anhydride (20 c.c.) and anhydrous sodium acetate (2·44 g.; 8 mols.) for 3 minutes, the mixture was poured into a hot solution of sodium perchlorate (2·8 g.; 8 mols.) in water (100 c.c.). The dye perchlorate (73% yield, 1·45 g.) was fractionally recrystallised from absolute ethyl alcohol (8 c.c. × 2) and methyl alcohol (8 c.c., 23 c.c., 65 c.c.). The third fraction (0·1 g.) was discarded. The fourth and fifth amounted to a 24% yield (0·48 g.) of dark bluish-green crystals, m. p. 252° (decomp.) (Found : Cl, 9·1. $C_{36}H_{39}O_8N_3Cl_2Se$ requires Cl, 8·95%). The absorption maximum was at 6115 A. with a secondary maximum at 5720 A. The *dye* did not sensitise but considerably depressed blue sensitivity. It was accompanied by more soluble, dark purple crystals (0·39 g.), obtained from the first two fractions (Found : Cl, 7·2. $C_{23}H_{25}O_4N_2ClSe$ requires Cl, 7·0%). By the analysis, and by m. p. and mixed m.p., this by-product was identified as the *carbocyanine*, which was synthesised for comparison, and is described at the end of the paper (p. 1887).

[2-(4-*Methyl*-3-*ethylthiazole*)][2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide.*—When 4-methyl-3-ethyl-2-dianilo*iso*propylidene-Δ^4-thiazoline (0·7 g.), 2-methylbenzthiazole ethiodide, and pyridine were heated together, dye crystallised (86% yield). After boiling out with, and recrystallising from, methyl alcohol (15 c.c. per g., 280 c.c. per g.), it was obtained in 57% yield (Found : I, 32·8. $C_{29}H_{31}N_3I_2S_3$ requires I, 32·9%). The green and gold crystals had m. p. 247° (decomp.). Their methyl-alcoholic solution was blue by transmitted and purple by reflected light. The absorption maximum was at 6075 A., and the curve had an inflexion at 5600 A. The *dye* sensitised weakly from 5700 to 6900 A., with the maximum at 6500 A., and depressed blue sensitivity.

[2-(4-*Methyl*-3-*ethylthiazole*)][2-(3-*ethylbenzselenazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide.*—This was similarly prepared by use of 2-methylbenzselenazole ethiodide. The crude product (77% yield), after recrystallisation from methyl alcohol (240 c.c. per g.), was obtained in 61% yield (Found : I, 29·3. $C_{29}H_{31}N_3I_2SSe_2$ requires I, 29·35%), as emerald-green crystals with a golden reflex. They melted at 230° (decomp.). The absorption maximum was at 6205 A. with an inflexion to the curve at 5750 A. The *substance* sensitised weakly from 6300 to 6800 A., with the maximum at 6700 A., and depressed blue sensitivity.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)][*γβ′-dimethin*-4′-(1′-*ethylquinoline*)]*trimethincyanine di-iodide* was prepared by heating together 3-ethyl-2-dianilo*iso*propylidenethiazolidine (1·12 g.; 1 mol.), lepidine ethiodide, anhydrous sodium acetate (4 mols.), and acetic anhydride at 130—140° for 2 minutes. It crystallised and was washed, then was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 550 c.c.), being obtained in 37% yield (Found : I, 34·0. $C_{32}H_{35}N_3I_2S$ requires I, 33·95%). The golden crystals melted at 272° (decomp.). Their absorption maximum was at 7440 A. The compound fogged a photographic plate and decreased its sensitivity.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide.*—This was prepared by heating together 3-ethyl-2-dianilo*iso*propylidenethiazolidine (1·12 g.), 2-methylbenzthiazole ethiodide, and pyridine. It crystallised on cooling and the washed product was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 1070 c.c.) and gave a 79% yield (Found : I, 33·35. $C_{28}H_{31}N_3I_2S_3$ requires I, 33·45%). The green and gold crystals had m. p. 237° (decomp.). The absorption maximum was at 6070 A. The *dye* decreased the normal blue sensitivity of a photographic emulsion, while conferring weak sensitisation from 5500 to 6800 A.

[4-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)]-*γ-anilomethyltrimethincyanine Iodide* (VIII).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (3·07 g.; 1 mol.), lepidine ethiodide (2·40 g.; 1 mol.), and pyridine

(16 c.c.) were heated together for 10 minutes at 60—70°. The *dye* was precipitated with absolute ether (160 c.c.), well washed with water, and washed with ether in a Soxhlet apparatus (4·17 g. left; 88% yield). On recrystallisation from methyl alcohol (100 c.c. per g.) it resulted in 71% yield (Found : I, 21·45. $C_{30}H_{28}N_3IS$ requires I, 21·55%). The dark green powder had m.p. 218—219° (decomp.). The methyl-alcoholic solution was orange-red at pH 8·0 and violet-blue at pH 9·4. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 6030 A. and of one containing sulphuric acid at 5000 A., this curve showing an inflexion at 4710 A. The substance was a photographic desensitiser.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)]-*γ-anilomethyltrimethincyanine iodide* was similarly prepared, with quinaldine ethiodide in place of lepidine ethiodide (67% yield after Soxhlet extraction). After recrystallising from methyl alcohol (35 c.c. per g.), grinding with water, and again recrystallising, the yield was 32% (Found : I, 21·65. $C_{30}H_{28}N_3IS$ requires I, 21·55%). The m. p. of the extremely dark maroon crystals was dependent on the rate of heating and was about 210° (decomp.). A methyl-alcoholic solution was crimson at pH 8·6 and bright yellow at pH 7·4. One containing ammonia had its absorption maximum at 5150 A., whilst one containing sulphuric acid had a narrower curve, with its maximum at 4750 A. There was weak sensitisation, with the maximum at 6000 A., and strong blue depression.

The preparation could be effected in boilding absolute alcohol for 1 minute, instead of in pyridine at 60—70° for 10 minutes.

[*Bis*-2-(3-*ethylbenzthiazole*)]-*α-anilomethyltrimethincyanine Iodide*.—This preparation was carried out as for (VIII) but with 2-methylbenzthiazole ethiodide instead of lepidine ethiodide. After Soxhlet extraction, the undissolved residue (94% yield) was recrystallised from methyl alcohol (23 c.c. per g.), ground with water and again thus recrystallised (30 c.c. per g.), giving a 41% yield (Found : I, 21·4; S, 10·55. $C_{28}H_{26}N_3IS_2$ requires I, 21·3; S, 10·75%). The dark maroon powder had an indefinite m. p., at about 210° (decomp. from 180°). A methyl-alcoholic solution was red at pH 7·8 and lemon-yellow at pH 6·8. One containing ammonia faded rapidly in the light but one containing pyridine had its absorption maximum at 5515 A. and one containing sulphuric acid at 4695 A. There was no sensitisation, but depression of the normal blue sensitivity by the *dye*.

[2-(3-*Ethylbenzthiazole*)][2-(3-*ethylbenzselenazole*)]-*α-anilomethyltrimethincyanine Iodide*.—A mixture of 3-ethyl-2-dianilo*iso*propylidenebenzthiazoline (1·92 g.), 2-methylbenzselenazole ethiodide, and pyridine was heated at 50—60° for 10 minutes. The liquid was treated with absolute ether (100 c.c.), and the sticky solid was filtered off, ground with benzene (50 c.c.), and twice extracted with hot water (500 c.c. × 2). The residual *dye* (2·44 g.; 76% yield) was first recrystallised from pyridine and water (24 c.c. of each; 58% yield), next boiled out with, and recrystallised from, methyl alcohol (10 c.c., 110 c.c.), and finally twice more recrystallised from methyl alcohol (65 c.c. per g.), giving a 24% yield (Found : I, 19·5. $C_{28}H_{26}N_3ISSe$ requires I, 19·75%). The maroon solid had m. p. about 198—204° (decomp.). A methyl-alcoholic solution containing ammonia had its maximum at 4780 A.; one containing sulphuric acid had the maximum at 4670 A. with a secondary one at 5455 A. There was very weak sensitisation up to 5700 A.

[2-(1 : 3 : 3-*Trimethylindolenine*)][2-(3-*ethylbenzthiazole*)]-*γ-anilomethyltrimethincyanine Perchlorate*.—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (1·54 g.; 1 mol.) and 2 : 3 : 3-trimethylindolenine methiodide (1·22 g.; 1 mol.), mixed with pyridine (20 c.c.), were kept at room temperature for 4½ hours. The tar precipitated by anhydrous ether (100 c.c.) was taken up in methyl alcohol (20 c.c.) and added to a hot solution of sodium perchlorate (1·23 g.; 5 mols.) in water (50 c.c.). The solid was filtered off, washed, and again dissolved in methyl alcohol and treated with sodium perchlorate solution. The *product* (1·88 g.) was fractionally recrystallised from spirit (5 c.c., 7 c.c., 10 c.c. × 2, 15 c.c.). The crystals from the three intermediate fractions (0·69 g.), together with a second crop (0·12 g.) obtained by concentration of the filtrates, amounted to a 36% yield (0·81 g.). This was again fractionated with spirit (5 c.c., 10 c.c.×2), the first two fractions giving a 19% yield (0·43 g.) (Found : Cl, 6·55. $C_{30}H_{30}O_4N_3ClS$ requires Cl, 6·3%). The dark bronze powder melted at about 123—128° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4350 A. and of one containing sulphuric acid at 4800 A., with an inflexion to the curve at 5400 A. There was very weak sensitisation from 5300 to 5900 A., with slight depression of the normal sensitivity.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)]-*γ-anilomethyltrimethincyanine Iodide*.—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (0·77 g.; 1 mol.) and 2-methyl-Δ^2-thiazoline ethiodide (0·62 g.; 1·2 mols.) were stirred together in ice-cold pyridine (4 c.c.). After 6 hours in ice, the red solution was treated with ice-cold water (32 c.c.). The resultant red oil solidified and was washed (88% yield, 0·97 g.). The yield was 66% after one recrystallisation from absolute ethyl alcohol (15 c.c.) and 56% after a second (Found : S, 11·5. $C_{24}H_{26}N_3IS_2$ requires S, 11·7%). The bright red crystals began to shrink at about 80° and to darken at about 100°; there was considerable decomposition from 125° to 130° but no definite m. p. A methyl-alcoholic solution containing pyridine had absorption maxima at 4005 and 4905 A. One containing sulphuric acid had the maximum at 4235 A. The *dye* weakly sensitised a gelatino-chloride photographic emulsion to 5000 A., the maximum lying at 4500 A.

[4-(1-*Ethylquinoline*)][2-(4-*methyl*-3-*ethylthiazole*)]-*γ-anilomethyltrimethincyanine Iodide*.—4-Methyl-3-ethyl-2-dianilo*iso*propylidene-Δ^4-thiazoline (1·16 g.; 1 mol.), lepidine ethiodide (1·0 g.; 1 mol.), and pyridine (15 c.c.) were heated together at 100° for 4 minutes. The dye was precipitated with ether, washed with water, recrystallised from methyl alcohol (50 c.c.), and obtained in 57% yield (Found : I, 23·1. $C_{27}H_{28}N_3IS$ requires I, 22·95%). The dark green crystals had m. p. 211° (decomp.). A methyl-alcoholic solution was purple at pH 10·1 and reddish-orange at pH 8·7. One containing ammonia had its absorption maximum at 5720 A., with an inflexion to the curve at 5410 A., and one containing sulphuric acid had its maximum at 5010 A. The *substance* sensitised weakly to 5500 A., with slight depression of the normal sensitivity.

[2-(1-*Ethylquinoline*)][2-(4-*methyl*-3-*ethylthiazole*)]-*γ-anilomethyltrimethincyanine Iodide*.—This was similarly prepared from the dianilo-compound (1·16 g.) with quinaldine etho-*p*-toluenesulphonate, instead of lepidine ethiodide, and the crude dye was precipitated with ether. The resultant sticky solid was dissolved in hot spirit and converted into dye iodide by treatment with aqueous potassium iodide solution. The *iodide* was recrystallised from methyl alcohol (15 c.c.; 0·64 g. obtained), and then again (10 c.c.), a little neocyanine being left undissolved, and the yield was 28% (Found: I, 23·1. $C_{27}H_{28}N_3IS$ requires I, 22·95%). The purple crystals had m. p. 217° (decomp.). A methyl-alcoholic solution was brick-red at pH 9·2 and orange-yellow at pH 8·0. One containing ammonia had its absorption maximum at 5060 A., and one containing sulphuric acid at 4815 A. On a gelatino-chloride photographic emulsion the dye conferred sensitivity extending to 5900 with the maximum at 5250 A.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(4-*methyl*-3-*ethylthiazole*)]-γ-*anilomethyltrimethincyanine Iodide*.—This was similarly prepared from the dianilo-compound (3·48 g.) with 2-methyl-Δ^2-thiazoline ethiodide, heating being continued for 7 minutes. Ether precipitated a sticky solid, which hardened on treatment with cold water. It was recrystallised from absolute alcohol (25 c.c.) and thus obtained in 45% yield (Found: I, 25·0. $C_{21}H_{26}N_3IS_2$ requires I, 24·8%). The orange *dye* had m. p. 163° (decomp.). A methyl-alcoholic solution containing pyridine had its absorption maximum at 4170 A., and one containing sulphuric acid at 4265 A. In a chlorobromide emulsion there was very weak sensitisation with the maximum at 5300 A.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]-γ-*anilomethyltrimethincyanine Iodide* (X).—3-Ethyl-2-dianilo*iso*propylidenethiazolidine (4·48 g.; 1 mol.), lepidine ethiodide (4·4 g.; 1·1 mols.), and absolute ethyl alcohol (160 c.c.) were mixed together at 0° and kept thus for an hour. The product was filtered off, ground with ether and with water (6·5 g. left), and recrystallised from methyl alchool (120 c.c.), this resulting in an 81% yield (Found: I, 23·4. $C_{26}H_{28}N_3IS$ requires I, 23·45%). The dark green crystals had m. p. 133° (decomp.). A methyl-alcoholic solution containing pyridine had its absorption maximum at 5810 A., whilst one containing sulphuric acid had the maximum at 4950 A. The *dye* conferred very weak extra-sensitivity, extending to 6300 A., and depressed the blue speed.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)]-α-*anilomethyltrimethincyanine Iodide* (XI.).—This was similarly prepared from the thiazolidine (1·12 g.) with 2-methylbenzthiazole ethiodide in pyridine. After 20 minutes at 0° the dye was filtered off, ground with ether and with water (1·42 g. left), and recrystallised from methyl alcohol (16 c.c.), being obtained in 68% yield (Found: I, 23·05. $C_{24}H_{26}N_3IS_2$ requires I, 23·2%). The crystals were brick-red with a golden reflex and had m. p. 110° (decomp.). The absorption maximum of their methyl-alcoholic solution containing pyridine was at 5100 A., whilst that of one containing sulphuric acid was at 4725 A. The *dye* was photographically inert.

[*Bis*-2-(3-*methyl*-Δ^2-*thiazoline*)]-α-*anilomethyltrimethincyanine Perchlorate*.—This was similarly prepared from 3-methyl-2-dianilo*iso*propylidenethiazolidine (1·60 g.) and 2-methyl-Δ^2-thiazoline methiodide in pyridine. After an hour in ice, precipitation was carried out with ice-cold water. After being washed with water, the solid was extracted with ether (1·61 g. left, 69% yield). The dye iodide was taken up in hot absolute alcohol (20 c.c.) and treated with a hot solution of sodium perchlorate (1·23 g.; 2 mols.) in water (20 c.c.). The yield of washed dye *perchlorate* was 57% (1·27 g.); after recrystallisation from methyl alcohol (100 c.c.) it was 31% and after a second recrystallisation 21% (Found: Cl, 8·15. $C_{18}H_{22}O_4N_3ClS_2$ requires Cl, 8·0%). The orange crystals had m. p. 148° (decomp.) with previous darkening and shrinking. The absorption maximum of their methyl-alcoholic solution containing pyridine was at 4500 A. One containing sulphuric acid had its maximum at 4370 A. The dye sensitised a chloride emulsion weakly to 5000 A., with the maximum at 4400 A.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)][$\gamma\beta'$-*dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate*.—[2-(3-Ethyl-Δ^2-thiazoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (2·60 g.; 1 mol.), 2-methyl-Δ^2-thiazoline ethiodide (2·45 g.; 2 mols.), anhydrous sodium acetate (3·15 g.; 8 mols.), and acetic anhydride (40 c.c.) were heated together at 140—150° for 5 minutes. After cooling, the dye iodide was filtered off, washed (44% yield, 1·49 g.), and recrystallised from methyl alcohol (10 c.c.). The iodide (32% yield; 1 mol.) was dissolved in hot methyl alcohol (6 c.c. per g.) and treated with a hot solution of sodium perchlorate (5 mols.) in water (2 c.c. per c.c. of MeOH). The dye *perchlorate* crystallised (30% yield) and, after recrystallisation from methyl alcohol (110 c.c. per g.), was obtained in 18% yield (Found: Cl, 11·05. $C_{24}H_{31}O_8N_3Cl_2S_3$ requires Cl, 10·8%). The puce powder had m. p. 244° (decomp.). The absorption maximum was at 5045 A. with an inflexion to the curve at 4690 A. The substance slightly depressed the photographic blue speed and sensitised weakly to 5900 A. with the maximum at 5300 A.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(4-*methyl*-3-*ethylthiazole*][$\gamma\beta'$-*dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate*.—[2-(3-Ethyl-Δ^2-thiazoline)][2-(4-methyl-3-ethylthiazole)]-γ-anilomethyltrimethincyanine iodide (1·28 g.; 1 mol.), 2-methyl-Δ^2-thiazoline ethiodide (1·5 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (20 c.c.) were heated together at 140—150° for 5 minutes. After precipitation with absolute ether, the product was treated with water. The residue, dissolved in hot spirit, was treated with hot aqueous sodium perchlorate solution and the washed dye *perchlorate*, after recrystallisation from methyl alcohol (30 c.c.), was obtained in 55% yield (0·85 g.) (Found: Cl, 11·3. $C_{21}H_{31}O_8N_3Cl_2S_3$ requires Cl, 11·45%). The maroon crystals had m. p. 220° (decomp.). The absorption maximum was at 5050 A. The sensitising maximum was at 5300 A., sensitisation extending to 5800 A.

[4-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][$\gamma\beta'$-*dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (XVII).—[4-(1-Ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (VIII) (1·18 g.; 1 mol.), 2-methylbenzthiazole ethiodide (3 mols.), anhydrous sodium acetate (6 mols.), and acetic anhydride (15 c.c.) were heated together at 140—150° for 8 minutes. The product precipitated by absolute ether (40 c.c.) was washed with ether, ground with water, and boiled out six times with methyl alcohol (13 c.c. × 6), the first two fractions of solid being rejected, whilst the last four (0·55 g.; 34% yield) were given a second recrystallisation from methyl alcohol (70 c.c. per g.), resulting in a 19% yield (Found: I, 31·5. $C_{34}H_{33}N_3I_2S_2$ requires I, 31·7%). The bronze *dye* had m. p. 210—212° (decomp.), with previous shrinking, and was a desensitiser. Its absorption maximum was at 6480 A.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][$\gamma\beta'$-*dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide*.—This was similarly prepared but from [2-(1-ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (1·18 g.; 1 mol.), 2-methylbenzthiazole ethiodide (1 mol.), sodium acetate (4 mols.), and acetic anhydride (8 c.c.) at 140—150° for 2 minutes. The reaction mixture was cooled and filtered, and the solid ground with water (8 c.c.) (1·37 g. obtained). After recrystallisation from methyl alcohol (50 c.c.), the yield was 59% (Found : I, 31·6. $C_{34}H_{33}N_3I_2S_2$ requires I, 31·7%). The bronze crystals had m. p. 228° (decomp.). The absorption maximum was at 6110 A. with an inflexion to the curve at 5700 A. The *dye* desensitised and did not sensitise.

[*Bis*-2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide*.—This was similarly prepared by heating together [bis-2-(3-ethylbenzthiazole)]-α-anilomethyltrimethincyanine iodide (0·60 g.), 2-methylbenzselenazole ethiodide, sodium acetate, and acetic anhydride. The dye was filtered off, washed with ether and with water (4 c.c.) (78% yield, 0·67 g. obtained), and boiled out with, and recrystallised from, methyl alcohol (7 c.c., 100 c.c.), giving a 48% yield (Found : I, 29·8. $C_{32}H_{31}N_3I_2S_2Se$ requires I, 29·7%). The decomposition point of the dark green *dye* lay at about 234° but depended on the rate of heating. The absorption maximum was at 6100 A. with an inflexion to the curve at 5650 A. There was no sensitisation but strong desensitisation.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide*.—This was similarly prepared by 10 minutes' heating of [2-(3-ethyl-Δ^2-thiazoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (1·65 g.), 2-methylbenzthiazole ethiodide, sodium acetate, and acetic anhydride. After being washed with ether and with water, the residue (1·39 g.) was recrystallised from methyl alcohol (5 c.c. per g.) and gave a 47% yield (Found : I, 33·55. $C_{28}H_{31}N_3I_2S_3$ requires I, 33·45%). The gold and green crystals had m. p. 211° (decomp.). The absorption maximum was at 5580 A. and the curve had two inflexions on the side of shorter wave-length, one at 5230 and the other at 5355 A. There was weak sensitisation to 6300 A. with the maximum at 5900 A. and depression of blue sensitivity by the *dye*.

[*Bis*-2-(3-*ethyl*-Δ^2-*thiazoline*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Diperchlorate* (XVIII).—[2-(3-Ethyl-Δ^2-thiazoline)][2-(3-ethylbenzthiazole)]-α-anilomethyltrimethincyanine iodide (XI) (1·82 g.; 1 mol.), 2-methyl-Δ^2-thiazoline ethiodide (1·71 g.; 2 mols.), and pyridine (15 c.c.) were heated together at 120° for 3 minutes. Addition of absolute ether precipitated a sticky solid, which was dissolved in hot spirit and treated with a hot aqueous solution of sodium perchlorate (1·9 g.; 4 mols.). The washed *dye* (1·54 g.) was freed from a residue by recrystallisation from methyl alcohol (300 c.c.), and obtained in 49% yield as green crystals with a gold reflex, m. p. 235° (decomp.) (Found : Cl, 10·85. $C_{24}H_{31}O_8N_3Cl_2S_3$ requires Cl, 10·8%). The absorption maximum was at 5580 A., with an inflexion to the curve at 5250 A. It conferred extra-sensitivity to 6200 A. whilst depressing the blue speed.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)][*γβ′-dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate*.—[4-(1-Ethylquinoline)][2-(3-ethyl-Δ^2-thiazoline)]-γ-anilomethyltrimethincyanine iodide (X), 2-methyl-Δ^2-thiazoline ethiodide, anhydrous sodium acetate, and acetic anhydride were boiled together for 5 minutes. The *dye* was precipitated by ether and treated with water. The tar was dissolved in hot spirit and treated with a hot solution of sodium perchlorate in water. The washed solid (1·07 g.; 49% yield) was recrystallised from methyl alcohol (250 c.c.) and thus obtained in 37% yield (Found : Cl, 10·8. $C_{26}H_{33}O_8N_3Cl_2S_2$ requires Cl, 10·9%). The dark green crystals had m. p. 190° (decomp.). The absorption maximum of the unusually broad curve was at 6050 A. with two inflexions on the side of shorter wave-length, one at 5375 A. and one at 5700 A. The dye sensitised very weakly to 6600 A. with a maximum at 6200 A., whilst depressing the blue sensitivity.

(4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)][*γβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (XIX).—The intermediate dye (1·35 g.) used in the preceding preparation, 2-methylbenzthiazole ethiodide, and pyridine were boiled together for 2 minutes. The washed solid (0·86 g.) was recrystallised from methyl alcohol (275 c.c.) and thus obtained in 35% yield (Found : I, 33·55. $C_{30}H_{33}N_3I_2S_2$ requires I, 33·7%). The golden crystals had m. p. 242° (decomp.). The absorption maximum was at 6555 A., with an inflexion to the curve at 6150 A. The *dye* showed photographic desensitising power.

[4-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate* (XX).—[2-(3-Ethyl-Δ^2-thiazoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (2·36 g.; 1 mol.), lepidine ethiodide (3 mols.), and anhydrous sodium acetate (4 mols.) were ground together and acetic anhydride (24 c.c.) was added. After 70 hours at room temperature, the liquid was filtered off, and the residue, dissolved in hot methyl alcohol (40 c.c.), was added to a hot solution of sodium perchlorate (2·68 g.; 5 mols.) in water (60 c.c.). The washed solid (1·24 g.) was given a second treatment with sodium perchlorate, whereupon the yield was 34% (1·03 g.). It was extracted with hot methyl alcohol (25 c.c.), from which the *dye* crystallised (0·34 g.), and more was obtained (0·27 g.) by further treatment with sodium perchlorate, making a 20% yield (Found : Cl, 10·15. $C_{30}H_{33}O_8N_3Cl_2S_2$ requires Cl, 10·15%). The bronze crystals melted between 145° and 155° (decomp.). The absorption maximum was at 5990 A. Very weak sensitisation extended to 7000 A., with depression of the normal blue sensitivity.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-4′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide*.—[4-(1-Ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (VIII) (1·18 g.), quinaldine ethiodide, anhydrous sodium acetate, and acetic anhydride were heated together at 140—150° for 10 minutes. Dye crystallised and more was precipitated by ether. After ether- and water-washing, the product (1·39 g.) was boiled out with, and recrystallised from, methyl alcohol (25 c.c., 140 c.c.), and the yield was 38% (Found : I, 31·75. $C_{36}H_{35}N_3I_2S$ requires I, 31·9%. The brownish-bronze crystalline powder had m. p. 253° (decomp.). The absorption maximum was at 6730 A. with an inflexion to the curve at about 6200 A. The *compound* caused weak photographic sensitisation and strong desensitisation.

It was similarly prepared by use of [2-(1-ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide and lepidine ethiodide, the yield of recrystallised product being 46% (Found : I, 31·9%).

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)][*γβ′-dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide*.—[(2-(1-Ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine iodide (1·13 g.), 2-methylbenzselenazole ethiodide, anhydrous sodium acetate, and acetic anhydride were heated together at 73—80° for 10 minutes. The solid was filtered off, washed with ether, and washed with water until the washings came through blue. The residual dye (1·30 g.; 80% yield) was boiled out with, and recrystallised from, methyl alcohol (5 c.c., 70 c.c.) (44% yield). After a second recrystallisation (104 c.c. per g.), the yield was 28% (Found: I, 30·25. $C_{34}H_{33}N_3I_2SSe$ requires I, 29·9%). The green crystals melted at about 234° (decomp.). The absorption maximum was at 6260 A. with an inflexion to the curve at 5700 A. The *dye* had desensitising power.

When pyridine was used as condensing agent the yields of crude and once recrystallised dye were 61% and 32%, respectively. An alternative preparation from [2-(3-ethylbenzthiazole)][2-(3-ethylbenzselenazole)]-α-anilomethyltrimethincyanine iodide and quinaldine ethiodide in pyridine gave only a 19% yield of crude dye.

Parent Carbocyanines.—[4-(1-*Ethylquinoline*)][2-(4-*methyl*-3-*ethylthiazole*)]*trimethincyanine iodide.* 4-Methyl-2-β-acetanilidovinylthiazole ethiodide (2·07 g.; 1 mol.), lepidine ethiodide (1·5 g.; 1 mol.), triethylamine (1·5 c.c.; 2·2 mols.), and absolute alcohol (45 c.c.) were mixed, and kept in ice for 7 days. The washed *dye* (1·96 g.) was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 50 c.c.), giving a 72% yield (Found: I, 28·3. $C_{20}H_{23}N_2IS$ requires I, 28·2%). The dark blue crystals had m. p. 253° (decomp.), with shrinking from 186°, and sensitised from 5900 to 7100 A. with the maximum at 6750 A. The absorption maximum was at 6295 A.

[2-(1-*Ethylquinoline*)][2-(4-*methyl*-3-*ethylthiazole*)]*trimethincyanine iodide* was similarly prepared, except that quinaldine ethiodide (1·5 g.) replaced lepidine ethiodide. The washed dye (1·3 g.) was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 65 c.c.), giving a 32% yield (Found: I, 28·15. $C_{20}H_{23}N_2IS$ requires I, 28·2%). The green and gold crystals had m. p. 260° (decomp.). The principal absorption maximum was at 5900 A. with a secondary one at 5580 A. Sensitisation extended to 6900 A., with maxima at 5250, 5650, and 6200 A.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(4-*methyl*-3-*ethylthiazole*)]*trimethincyanine iodide* was similarly prepared but from 2-methyl-Δ^2-thiazoline ethiodide (1·29 g.). After recrystallisation of the washed dye (0·68 g.) from methyl alcohol (4 c.c.), the yield was 10% (Found: I, 31·15. $C_{14}H_{21}N_2IS_2$ requires I, 31·1%). The maroon crystals had m. p. 213° (decomp.). The absorption maximum was at 4995 A. Sensitisation extended to 5600 with the maximum at 5250 A.

[2-(4-*Methyl*-3-*ethylthiazole*)][2-(3-*ethylbenzthiazole*)]*trimethincyanine iodide* was similarly prepared but from 2-methylbenzthiazole ethiodide (1·53 g.). Recrystallisation of the washed dye (2·25 g.) from methyl alcohol (160 c.c.) gave a 75% yield (Found: I, 27·85. $C_{18}H_{21}N_2IS_2$ requires I, 27·8%). The dark purple crystals had m. p. 252° (decomp.) and sensitised to 6400 A. with maxima at 5220 and 5700 A. The absorption maximum was at 5470 A.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)]*trimethincyanine iodide.* 2-β-Acetanilidovinyl-Δ^2-thiazoline ethiodide (4·02 g.; 1 mol.), 2-methylbenzthiazole ethiodide (1 mol.), triethylamine (1 mol.), and absolute alcohol (50 c.c.) were mixed, and kept in ice for 7 days. The washed solid (2·85 g.) was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 40 c.c.), and gave a 32% yield. After two more recrystallisations (21 c.c. per g.), the yield was 22% (Found: I, 28·65. $C_{17}H_{21}N_2IS_2$ requires I, 28·55%). The orange-red *dye* had m. p. 237° (decomp.). The absorption maximum was at 5020 A. and the sensitising maximum at 5300 A., sensitisation extending to 5700 A.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]*trimethincyanine iodide* was similarly prepared but with lepidine ethiodide (2·99 g.) replacing 2-methylbenzthiazole ethiodide, and with excess of triethylamine (2·2 mols.). Recrystallisation of the washed dye (3·9 g.) from methyl alcohol (100 c.c.) gave a 72% yield (Found: I, 29·1. $C_{19}H_{23}N_2IS$ requires I, 28·15%). The dark violet iridescent crystals had m. p. 228° (decomp.) and sensitised from 5000 to 6400 A. with the maximum at 6050 A. and a minimum at 5000 A. The absorption maximum was at 5765 A.

[2-(4-*Methyl*-3-*ethylthiazole*)][2-(3-*ethylbenzselenazole*)]*trimethincyanine iodide.* 2-β-Acetanilidovinylbenzselenazole ethiodide (4·97 g.; 1 mol.), 2 : 4-dimethylthiazole ethiodide (1 mol.), anhydrous potassium carbonate (180-mesh; 1·2 mols.), and absolute alcohol (20 c.c.) were mixed, and kept in ice for some days. The washed solid (4·24 g.) was boiled out with, and recrystallised from, methyl alcohol (50 c.c., 200 c.c.) and gave a 39% yield (Found: I, 25·1. $C_{18}H_{21}N_2ISSe$ requires I, 25·2%). The dark violet-blue *dye* had m. p. 257° (decomp.) and sensitised uniformly from 5000 to 6000 A., sensitisation extending to 6400 A. The absorption maximum was at 5510 A.

[2-(1 : 3 : 3-*Trimethylindolenine*)][2-(3-*ethylbenzthiazole*)]*trimethincyanine iodide.* 2-β-Acetanilidovinylbenzthiazole ethiodide (2·5 g.; 1 mol.), 2 : 3 : 3-trimethylindolenine methiodide (1 mol.), anhydrous sodium acetate (0·5 g.), and acetic anhydride (15 c.c.) were boiled together for 15 minutes (I.C.I. Ltd., Piggott, and Rodd, B.P. 354,898/1930). The washed solid (1·58 g.) was boiled out with methyl alcohol (10 c.c.), which extract gave a 40% yield of dark steel-blue crystals, m. p. at about 185—188° with shrinking from 158° (Found: I, 26·15. $C_{23}H_{25}N_2IS$ requires I, 26·0%). The *dye* had its absorption maximum at 5430 A. and sensitised to 6400 A. with maxima at 5400 and 5950 A.

[2-(1 : 3 : 3-*Trimethylindolenine*)][2-(3-*ethylbenzselenazole*)]*trimethincyanine perchlorate.* 3-Ethyl-2-aniloethylidenebenzselenazoline (1·64 g.; 1 mol.), 2 : 3 : 3-trimethylindolenine methiodide (1 mol.), anhydrous sodium acetate (8 mols.), and acetic anhydride (30 c.c.) were boiled together for 3 minutes. The reaction mixture was treated hot with a solution of sodium perchlorate (4 mols.) in water (150 c.c.). The resultant dye *perchlorate* (2·9 g.), after recrystallisation from methyl alcohol (75 c.c.), was obtained in 82% yield (Found: Cl, 7·05. $C_{23}H_{25}O_4N_2ClSe$ requires Cl, 7·0%). The bluish-grey, metallic-looking crystals had m. p. 170° (decomp.) and depressed blue sensitivity but gave extra-sensitisation to beyond 6100 A., with the maximum at 5750 A. The narrow absorption curve had its maximum at 5500 A.

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