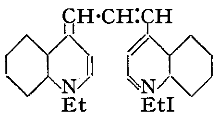
271. *Some Trinuclear Cyanine Dyes. Part I. The Synthesis of Neocyanines.*

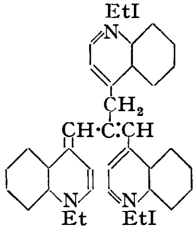
By Frances M. Hamer, Russell J. Rathbone, and Barbara S. Winton.

Neocyanine is a trinuclear cyanine dye, which had been obtained as a by-product by the action of alkali on a lepidinium salt in the presence of iodoform or ethyl orthoformate, and for which three formulæ had been proposed. That which represents it as being both a substituted trimethincyanine and a substituted pentamethincyanine has now been established by synthesis. Analogous dyes having three similar heterocyclic nuclei other than 4-linked quinoline have also been synthesised. The necessary branched-chain intermediates, consisting of *N*-alkyldihydro-derivatives of heterocyclic bases, with a dianilo*iso*propylidene group in the reactive position, were prepared from the corresponding methylene bases or their anilomethyl derivatives, by heating with ethyl*iso*formanilide and zinc chloride. Their condensation with heterocyclic quaternary ammonium salts, having a reactive methyl group, resulted in neocyanines identical with those obtained empirically, when such existed. The absorption maxima of the trinuclear dyes have been compared with those of the related tri- and penta-methincyanines.

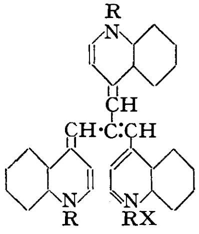
NEOCYANINE, a new sensitiser for the infra-red, was announced by Dundon, Schoen, and Briggs (*J. Opt. Soc. Amer.*, 1926, **12**, 397) as sensitising more powerfully beyond 8000 A. than any dye previously reported. They said it had been isolated by H. T. Clarke as a less soluble by-product in the preparation of 4 : 4'-carbocyanine but did not specify his method. At that time, the normal method for preparing a 4 : 4'-carbocyanine, apart from the synthesis by Mills and Braunholtz which established its constitution (I) (*J.*, 1923, **123**, 2804), consisted in treating a lepidinium salt with alkali in the presence of formaldehyde or chloroform (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661). Only in 1928 did the acceptance of a British patent disclose that neocyanine had been produced in a 4 : 4'-carbocyanine preparation in which iodoform had been used instead (Kodak Ltd., B.P. 292,274/1927); the corresponding American patent did not appear for another three years (Clarke, U.S.P. 1,804,674/1931). Meanwhile one of us (Hamer, *J.*, 1927, 2796), in describing a general method for the preparation of carbocyanines by condensing a quaternary, heterocyclic ammonium salt having a reactive methyl group, with ethyl orthoformate in the presence of pyridine, recorded that the 4 : 4'-carbocyanine was accompanied by a by-product, identical with neocyanine. Soon afterwards, in preparing a neocyanine from each of three lepidinium salts, a modified method gave 36—41% yields. Analyses led to the conclusion that the neocyanine molecule had been formed from three molecules of lepidine alkyl halide, with elimination of hydrogen halide, and that either one or two additional carbon atoms had entered the molecule. Based on the former supposition, the first neocyanine formula (II), showing it as a β-substituted 4 : 4'-carbocyanine (I), was proposed (Hamer, *J.*, 1928, 1472).



(I.)

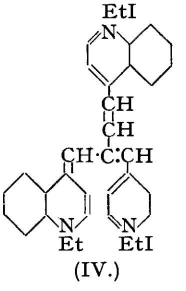


(II.)

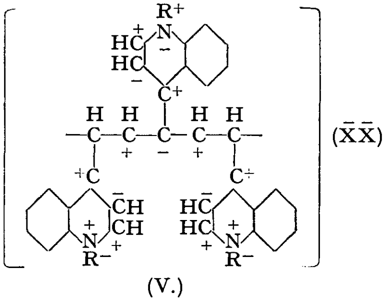


(III.)

To dyes prepared from lepidinium and from quinaldinium salts, with carbon tetrachloride and alkali, Ogata and Tamura assigned formulæ such as (III) (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 475), but Ogata subsequently disclaimed these (*ibid.*, p. 491) and adopted formulæ of type (II) for dyes of the neocyanine class, which he prepared from alkiodides of several heterocyclic bases with orthoformic ester or diphenylformamidine in the presence of various condensing agents (*Proc. Imp. Acad. Tokyo*, 1932, **8**, 503; *ibid.*, 1933, **9**, 602; *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497).



(IV.)



(V.)

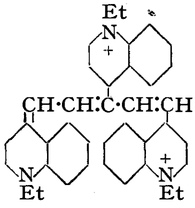
In 1931 Brooker described the neocyanines of the thiazole series and in addition to a formula of type (II) suggested an alternative (IV) with a different carbon chain (B.P. 408,273/1931).

Since alkali would be likely to convert (II) into (III), whereas (IV) had the advantage of explaining the stability of the neocyanines to alkali, formula (IV) was preferred to (II) (Brooker, Hamer, and Mees, *Phot. J.*, 1933, **57**, 258; *J. Opt. Soc. Amer.*, 1933, **23**, 216).

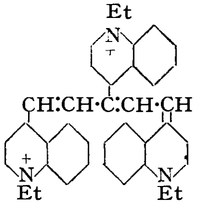
In 1935 W. König, in a theoretical paper on the chemistry of sensitisers, expressed his disbelief in formula (II) and said that he regarded neocyanine as a pentamethincyanine of formula (V). He pointed out that whereas (V) has 4 : 4′-linkings, other analogous substances with 2 : 2′-linkings are also possible, and he gave a general formula for those (*Z. wiss. Phot.*, 1935, **34**, 15).

The essential feature of König's formula was the symmetrical attachment of the three heterocylcic nuclei to an unbranched pentamethin chain, and concurrence with this view of the structure was at once expressed (Hamer, *Chem. and Ind.*, 1935, **13**, 640) on the ground that it accorded with a reasonable manner of formation of the dye; neocyanine could be regarded as arising from the condensation of the methyl group of lepidine ethiodide with two molecules of ethyl orthoformate and the subsequent condensation of the resulting intermediate with two more molecules of lepidine ethiodide.

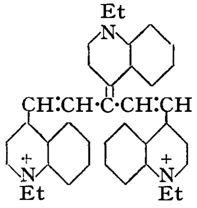
On the modern views a neocyanine kation of this structure would have its two units of positive charge distributed over the three basic groups. It cannot therefore be represented by a single structural formula, but would be regarded as a resonance hybrid of the three canonical structures (VI*a*, *b*, and *c*).



(VI*a*.)



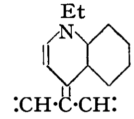
(VI*b*.)

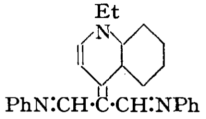


(VI*c*.)

These formulæ, in particular (VI*c*), suggest the possibility of a rational synthesis of neocyanine from a suitable intermediate containing the grouping (VII), and the dianilo-compound (VIII) seemed most likely to fulfil this purpose. We have succeeded in preparing a number of dianils of this type and have found that with their aid the synthesis of the corresponding neocyanines can in fact be readily accomplished.

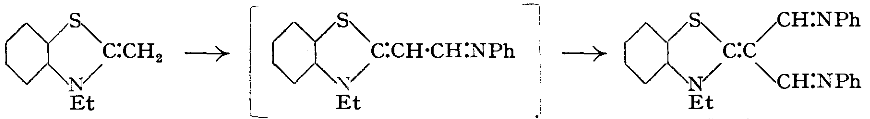
(VII.)





(VIII.)

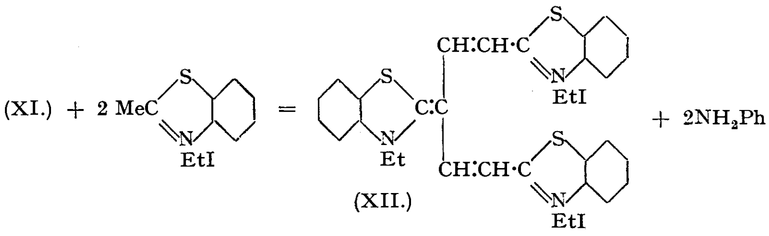
The synthesis was first carried out in the benzthiazole series, with the aid of ethyl*iso*formanilide which, as Knott has recently shown (*J.*, 1946, 120), condenses even more readily than diphenylformamidine (I.C.I. Ltd., Piggott, and Rodd, B.P. 344,409/1929) with pyridinium salts having a reactive methyl group. As a starting point we employed, instead of a quaternary salt, the methylene base 3-ethyl-2-methylenebenzthiazoline (IX) (Hamer, Rathbone, and Winton, this vol., p. 954). Heated with ethyl*iso*formanilide in the presence of zinc chloride, this yielded a zinc chloride complex of the base (XI), from which the *base* itself could be isolated by appropriate treatment with alkali.



(IX.) (X.) (XI.)

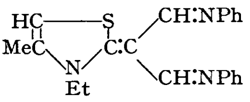
The presumed intermediate (X) had already been described by Brooker and White, who obtained it by the action of alkali on 2-β-anilinovinylbenzthiazole ethiodide (U.S.P. 2,298,732/1942), and we found that it also could be condensed with ethyl*iso*formanilide to yield (XI). It is safe to assume that the methin group attached to the ring is attacked, rather than the more remote methin group, since the former is in the well-known reactive position. We should have liked to have obtained direct proof of this assumption and therefore prepared the α- and β-methyl derivatives of (X) (Hamer, Rathbone, and Winton, *loc. cit.*), hoping to be able to condense the β-methyl derivative with ethyl*iso*formanilide, but the attempt, as also that with the α-methyl derivative, was unsuccessful.

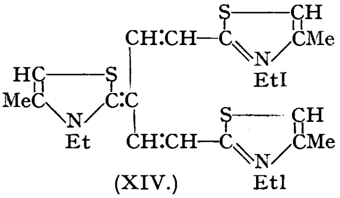
The final stage in the synthesis was readily effected. The dianilo-base (XI), heated for a few minutes with 2-methylbenzthiazole ethiodide, either in pyridine solution or with sodium acetate and acetic anhydride, gave in excellent yield a neocyanine (XII), identical with that obtained by Ogata's method (*Proc. Imp. Acad. Tokyo*, **1933**, **9**, 602; *Bull. Inst. Phys. Chem. Res. Japan*, **1934**, **13**, 497) from a 2-methylbenzthiazolium salt and ethyl orthoformate.


(XII.)

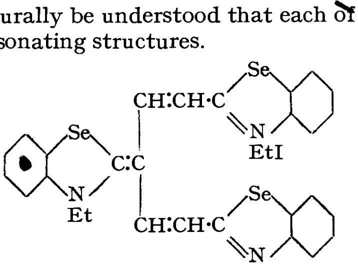
In the thiazole series we prepared the *dianilo-base* (XIII) from 4-methyl-3-ethyl-2-anilo-ethylidene-Δ^4-thiazoline, condensed it with 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate in pyridine, and isolated the dye as iodide (XIV), which was identical with that obtained by the empirical method from the same quaternary salt with ethyl orthoformate and pyridine (B.P. 408,273/1931).

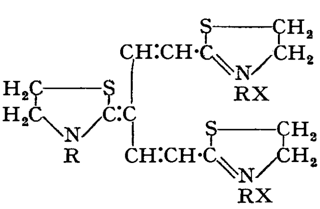
Neocyanine itself was synthesised in a similar manner. The necessary *dianil* (VIII) was prepared by condensation of the methylene base from lepidine etho-*p*-toluenesulphonate with ethyl*iso*formanilide and this, heated with lepidine ethiodide, acetic anhydride and sodium acetate, gave in 20% yield a product identical with the neocyanine obtained from lepidine ethiodide and ethyl orthoformate in the presence of pyridine (Hamer, *J.*, 1927, 2796; cf. *idem, J.*, 1928, 1472). The synthesis of neocyanines in this manner may be taken as proof of the correctness of the structure now assigned to them.


(XIII.)


(XIV.)

In addition to the three dianilo-bases, (VIII), (XI), and (XIII), the following representatives of this class have been prepared : 5-*chloro*-3-*ethyl*-2-*dianilo*iso*propylidenebenzthiazoline*, 3-*ethyl*-2-*dianilo*iso*propylidene*-6 : 7-*benzbenzthiazoline*, 3-*ethyl*-2-*dianilo*iso*propylidenebenzselenazoline*, 3-*methyl*-2-*dianilo*iso*propylidenethiazolidine*, 3-*ethyl*-2-*dianilo*iso*propylidenethiazolidine*, 1-*ethyl*-2-*dianilo*iso*propylidene*-1 : 2-*dihydroquinoline*, 3-*ethyl*-2-*dianilo*iso*propylidenebenzoxazoline*. From the dianils, new neocyanines were prepared, namely the *dichloride* corresponding with the di-iodide (XII), *analogues* of (XII) having, respectively, three 6 : 7-benzbenzthiazole and three 5-chlorobenzthiazole nuclei, its *selena*-analogue (XV), and two Δ^2-*thiazoline* analogues (XVI). It will naturally be understood that each of these formulæ is to be taken as the representative of a set of resonating structures.


(XV.)


(XVI.)

The absorption curves of methyl-alcoholic solutions of the trinuclear dyes were plotted. They were well-defined and rather narrow, with sometimes an inflexion on the short wave-length side. Since the neocyanines might be regarded as combining the structural characters of the tri- and penta-methincyanines, we give in the following table the wave-lengths of the absorption maxima of seven neocyanines and for comparison those of the corresponding tri- and penta-methincyanines. Certain abbreviations, obvious in conjunction with the text, have been used. Each previously recorded absorption maximum is marked with a bibliographic reference, the unmarked ones being those of compounds described in the present paper. Some of the parent cyanines were prepared for the sake of this comparison. With each of the seven neocyanines, the absorption maximum lies between that of the unsubstituted trimethincyanine and pentamethincyanine, as recorded already for one such dye (Hamer, *Chem. and Ind.*, 1935, **13**, 640). The bathochromic shifts on passing from trimethincyanine to neocyanine vary from 375 to 710 A. and those on passing from neocyanine to pentamethincyanine vary from 350 to 520 A. Other comparisons may also be made. For instance, replacement of the three 4-linked quinoline nuclei of neocyanine by three benzthiazole nuclei caused a hypsochromic shift of 1735 A. Replacement of three benzthiazole nuclei by three methylthiazole nuclei caused a hypsochromic shift of 140 A., whilst their replacement by three 5-chlorobenzthiazole, three 6 : 7-benzbenzthiazole, or three benzselenazole nuclei caused bathochromic shifts of 90,335, and 185 A., respectively.

The new dyes comprised photographic sensitisers and desensitisers.

Neocyanine.	Abs. max., A.	Trimethin-cyanine.	Abs. max., A.	Pentamethin-cyanine.	Abs. max., A.	Bathochromic shifts : trimethin- to neo-cyanine.	Bathochromic shifts : neo- to pentamethin-cyanine.
4-q 4-q (VI) 4-q	7750 *	4-q 4-q (I)	7040 †	4-q 4-q	8100 †	710	350
bzth bzth (XII) bzth	6015	bzth bzth	5570 †	bzth bzth	6500 †	445	485
bzbzth bzbzth bzbzth	6350	bzbzth bzbzth	5930 †	bzbzth bzbzth	6870 †	420	520
Clbzth Clbzth Clbzth	6105	Clbzth Clbzth	5625 ‡	Clbzth Clbzth	6560	480	455
bzSe bzSe (XV) bzSe	6200	bzSe bzSe	5700 †	bzSe bzSe	6600 †	500	400
Me–th Me–th (XIV) Me–th	5875	Me–th Me–th	5520 §	Me–th Me–th	6370	375	495
thiazoline thiazoline thiazoline (XVI; R = Et, X = ClO_4)	5060	thiazoline thiazoline	4435 ‖	thiazoline thiazoline	5450	625	390

* Hamer, *Chem. and Ind.*, 1935, **13**, 640.
† Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.
‡ Hamer, Rathbone, and Winton, this vol., p. 954.
§ Cf. Fisher and Hamer, *J.*, 1930, 2502.
‖ Brooker, *J. Amer. Chem. Soc.*, 1936, **58**, 662.

Nomenclature.—Some years ago we first adopted the practice of publishing the systematic names for the cyanines in addition to other names (Fisher and Hamer, *J.*, 1937, 907) or, as the structures became more complex, exclusively (Beilenson and Hamer, J., 1942, 98). Thus whilst (I) may be described as 1 : 1′-diethyl-4 : 4′-carbocyanine iodide (Mills and Braunholtz, *J.*, 1923, **123**, 2804), its systematic name is [bis-4-(1-ethylquinoline)]trimethincyanine iodide. This nomenclature presupposes only a knowledge of the fundamental structure of a cyanine dye; each ring is denoted by its usual description and numbering, and the positions of linking are indicated. In extending the systematic nomenclature to the present trinuclear cyanines, it is apparent that neocyanine itself might be named either as a substituted trimethincyanine or as a substituted pentamethincyanine. In introducing one fresh convention, that a trinuclear dye is named as a derivative of that parent cyanine having the shorter chain, of course we do not intend to imply that it actually is a derivative of that cyanine rather than of the one having the longer chain. A second parenthesis is introduced to comprise the third nucleus and here the numbers which indicate the position of linking and the positions of substituents are each followed by a dash, whilst the Greek letters show the positions of attachment of the chain linking the third nucleus. Thus neocyanine is called [bis-4-(1-ethylquinoline)][αβ′-dimethin-4′-(1′-ethylquinoline)]trimethincyanine di-iodide.

EXPERIMENTAL.

3-*Ethyl-2-dianilo*iso*propylidenebenzthiazoline* (XI).—3-Ethyl-2-methylenebenzthiazoline (33·17 g.; 1 mol.), zinc chloride powder (76·5 g.; 3 mols.), and ethyl*iso*formanilide (277 c.c.; 10 mols.) were heated together at 175—180° for 2½ hours, with mechanical stirring. Acetone (700 c.c.) was added, and the mixture heated until all lumps had gone. After cooling, the zinc chloride complex was filtered off and washed with acetone. It was ground with, and stirred into, water (750 c.c.). It was filtered off, washed with methyl alcohol, boiled out twice with that solvent (1000 c.c., 200 c.c.), and washed twice with hot methyl alcohol (50 c.c. × 2).

For converting the complex (54·2 g.) into base, it was ground with water (10 c.c. per g.) and with 40% sodium hydroxide solution (20 c.c. per g.) and the suspension was shaken with acetone (100 c.c. per g.). The acetone extract was filtered and the aqueous residue was further extracted twice with acetone (10 c.c. per g. × 2). The extracts were dried over stick sodium hydroxide for a period of days, then filtered, and the acetone was distilled off under a vacuum (in six lots) and the concentrate (volume about 15 c.c. × 6) cooled. The *base* crystallised and was filtered off and washed with methyl alcohol until the washings were no longer brown. The yield was 28% (19·76 g.). In recrystallising from methyl alcohol (110 c.c. per g.), the time of heating was kept to a minimum and the yield was 21% (15·36 g.). (After drying in a vacuum desiccator, it was analysed by the method of Carius, which method was used throughout this work for sulphur and halogen determinations.) (Found: S, 7·9. Found, after a second recrystallisation: S, 8·2. $C_{24}H_{21}N_3S$ requires S, 8·35%). The yellow crystals had m. p. 127°, becoming orange at about 110°. The broad absorption curve had its maximum at 4020 A. and an inflexion at 3500 A. The base was photographically inert.

In the second method of preparation, 3-ethyl-2-aniloethylidenebenzthiazoline (X) (47 g.; 1 mol.), zinc chloride (94 g.; 4·1 mols.), and ethyl*iso*formanilide (250 g.; 10 mols.) were heated together at 160—185° for 1 hour. After partial cooling, acetone (1000 c.c.) was added; refluxing was applied, in order to break up a hard lump. When cold, the solid was filtered off, washed with acetone, and ground with water (107 g. obtained). It was thrice boiled out with methyl alcohol (2350 c.c. × 3) (8·01 g., 0·09 g., and 0·16 g., respectively, crystallised from the filtrates). When a test portion of the solid from the first boiling out was heated with a 2-methylbenzthiazolium salt in pyridine, it gave a red colour, whilst a test portion of the second or third, when similarly treated, gave a blue. The boiling out with methyl alcohol halved the weight of zinc chloride complex. It was converted into free base as before and gave a 17% yield (11 g.), and after recrystallisation from methyl alcohol 10% (6·46 g.). Its m. p. was the same as that of the sample prepared by the first method, and that of the mixture was identical.

5-*Chloro-3-ethyl-2-dianilo*iso*propylidenebenzthiazoline*.—5-Chloro-3-ethyl-2-methylenebenzthiazoline (24 g.; 1 mol.), zinc chloride (47 g.; 3 mols.), and ethyl*iso*formanilide (170 g.; 10 mols.) were heated together at 190°, with mechanical stirring, for 1½ hours. After partial cooling, acetone (1000 c.c.) was added and the solid was filtered off, ground with water (28 g. left), and boiled out with methyl alcohol (500 c.c. × 4). The filtrates varied from purple to pale pink, but a negligible amount of solid (total, 0·1 g.) separated from them. The yellow zinc chloride complex (24·12 g.) was ground with 40% sodium hydroxide solution (400 c.c.) and water (200 c.c.) and extracted with acetone (5000 c.c.). The extract was dried with stick sodium hydroxide, the solvent distilled off under a vacuum, and the concentrate cooled, giving a 16% yield of crude *base* (7·83 g.). A sample was recrystallised from pyridine (5 c.c. per g.; yield 12%) (Found, after drying in a vacuum at 60—80°, which method of drying was employed throughout this work except where otherwise stated: Cl, 8·7. $C_{24}H_{20}N_3ClS$ requires Cl, 8·5%). The yellow crystals had m. p. 182—184°. The absorption curve had its maximum at 4100 A. and tailed off very gradually on the short wave-length side. Towards a gelatino-chloride photographic emulsion the substance exerted slight sensitisation as far as 4700 A.

3-*Ethyl-2-dianilo*iso*propylidene-6 : 7-benzbenzthiazoline*.—To 3-ethyl-2-methylene-6 : 7-benzbenzthiazoline (11·43 g.) was added ethyl*iso*formanilide; zinc chloride powder was stirred in, and the mixture heated. It was stirred by hand, in order to break up the lumps of zinc chloride, until the oil-bath temperature reached 80°. Mechanical stirring was then applied and the temperature was raised to 175—180° and held there for an hour. After cooling, the hard reaction product was treated with acetone (250 c.c.), being heated and stirred at intervals for a few hours in order to break up the lumps. The solid was filtered off, washed with acetone, ground with water, and then boiled out four times with methyl alcohol (450 c.c. × 4). The residual complex (9·52 g.) was ground with water (10 c.c. per g.), added to acetone (100 c.c. per g.), and shaken with 40% sodium hydroxide solution (20 c.c. per g.) until all solid had disappeared. The acetone layer was filtered, and the aqueous part further twice extracted with acetone (200 c.c., 100 c.c.). The extracts were dried over stick sodium hydroxide for 2 days. The filtrate was then concentrated under a vacuum until almost all the acetone had been removed and only a little aqueous liquid was left. The solid which separated on cooling was filtered off and obtained, after washing with acetone, in 21% yield (4·49 g.). It was recrystallised from methyl alcohol (4000 c.c.), the time of heating being reduced to the very minimum. The yield was 9% (1·86 g.) but in a recrystallisation where boiling with mechanical stirring went on for 7 minutes the yield was only half that (Found: S, 7·2. $C_{28}H_{23}N_3S$ requires S, 7·4%). The dull yellow crystals melted at about 173° with previous darkening and shrinking. The absorption maximum was at 3890 A. and the *base* did not sensitise a gelatino-chloride photographic emulsion.

3-*Ethyl-2-dianilo*iso*propylidenebenzselenazoline*.—3-Ethyl-2-aniloethylidenebenzselenazoline (20 g.; 1 mol.), ethyl*iso*formanilide (44 g.; 5 mols.), and zinc chloride (18 g.; 2·2 mols.) were heated together at 160—170° for 30 minutes. The product was treated with water, and the solid was next thoroughly ground and washed with acetone and boiled out with methyl alcohol (1400 c.c.). The zinc chloride complex (11·5 g.) was converted into base, by grinding to a paste with water and shaking with 40% sodium hydroxide solution (100 c.c.) and acetone (500 c.c.). The filtered acetone extract was dried with stick sodium hydroxide, then concentrated considerably. The *base* was filtered off, washed with spirit, and obtained in 14% yield (3·8 g.). On recrystallisation from methyl alcohol (80 c.c. per g.), the yield fell to 7% (Found : N, 9·9. $C_{24}H_{21}N_3Se$ requires N, 9·75%). The bright yellow crystals had m. p. 140° (decomp.). The absorption curve had a maximum at 4070 A. and an inflexion at 3550 A. The substance did not sensitise a gelatino-chloride photographic emulsion.

In a second method of preparation, 3-ethyl-2-methylenebenzselenazoline (22·4 g.; 1 mol.), ethyl*iso*formanilide (75 c.c.; 5 mols.) and zinc chloride (41 g.; 3 mols.) were heated together at 150—170° for 2 hours. The washed product was boiled out with methyl alcohol (1000 c.c.), leaving a residue of zinc chloride complex (5·62 g.). The yield of crude base was 10%, falling to 7% on recrystallisation from methyl alcohol. M. p. and mixed m. p. showed its identity with the sample prepared by the first method. A by-product (5·25 g.) which separated from the methyl-alcoholic extract of crude zinc chloride complex was identified as follows as a zinc chloride complex of 3-ethyl-2-aniloethylidenebenzselenazoline. It was treated with 40% sodium hydroxide solution (40 c.c.) and acetone (100 c.c.); on pouring the concentrated acetone extract into water, a base (4·11 g.) resulted, and after recrystallisation from light petroleum (b. p. 80—100°), consisted of a 20% yield (2·83 g.) of what was proved to be 3-ethyl-2-aniloethylidenebenzselenazoline, by comparison with a genuine specimen.

It is noteworthy that we were unable to prepare the dianilo-base by the action of ethyl*iso*formanilide and zinc chloride on the zinc chloride complex of 3-ethyl-2-aniloethylidenebenzselenazoline, which tallies with the fact that it could not be thus prepared from the hydrochloride either, *i.e.*, from 2-β-anilinovinylbenzselenazole ethochloride.

4-*Methyl*-3-*ethyl*-2-*dianilo*iso*propylidene*-Δ^4-*thiazoline* (XIII).—4-Methyl-3-ethyl-2-aniloethylidene-Δ^4-thiazoline (48·8 g.; 1 mol.), ethyl*iso*formanilide (152 g.; 5 mols.), and zinc chloride (80 g.; 3 mols.) were heated together at 150—170° for 2 hours. The crude zinc chloride complex was washed with acetone, treated with water, and boiled out with methyl alcohol (3200 c.c.) (64·8 g. left). It was then shaken vigorously at room temperature with 40% sodium hydroxide solution (560 c.c.) and acetone (3200 c.c.). The acetone extract was concentrated to small bulk and the base precipitated by addition of ice-water (31·6 g. obtained). On recrystallisation from light petroleum (b. p. 80—100°; 35 c.c. per g.), a 35% yield (23·9 g.) of golden-yellow crystals was obtained (Found : S, 9·05. $C_{21}H_{21}N_3S$ requires S, 9·25%). M. p. 111° (decomp.). The absorption maximum was at 3475 A. The *base* was inert towards a gelatino-chloride photographic emulsion.

3-*Methyl*-2-*dianilo*iso*propylidenethiazolidine*.—3-Methyl-2-aniloethylidenethiazolidine (10·20 g.; 1 mol.), ethyl*iso*formanilide (70 c.c.; 10 mols.), and zinc chloride (19·13 g.; 3 mols.) were heated together at 175—180° for 1½ hours. The warm viscous mass was treated with acetone (150 c.c.). The solid was filtered off, treated with water (300 c.c.), and boiled out four times with methyl alcohol (125 c.c. × 4) (12·85 g. of zinc chloride complex left).

In order to liberate the free base, the zinc chloride complex (8 g.) was ground with acetone (120 c.c.), and the mixture cooled with ice and stirred mechanically. An ice-cold solution of sodium (2 g.) in absolute alcohol (120 c.c.) was run in, and stirring with cooling was applied for 10 minutes; when the sodium ethoxide solution was first added, the liquid became bright yellow. The solid, which apparently consisted of zinc oxide and sodium zincate, was filtered off and washed with acetone (16 c.c.). On pouring the filtrate and washings into ice-cold water (500 c.c.), the *base* was precipitated as a yellow solid, being obtained in 36% yield (3·33 g.). Rapid recrystallisation from methyl alcohol (25 c.c. per g.) gave a 30% yield, but when boiling and mechanical stirring were applied for 5 minutes, decomposition took place, so that the yield was only 4% (Found : S, 9·95. $C_{19}H_{19}N_3S$ requires S, 10·0%). Recrystallisation from light petroleum (b. p. 80—100°) was less precarious and gave an 18% yield. The lemon-yellow crystals had m. p. 127°. The absorption maximum was at 3720 A. The base was photographically inert.

3-*Ethyl*-2-*dianilo*iso*propylidenethiazolidine*.—The zinc chloride complex (66 g.) was prepared similarly from 3-ethyl-2-aniloethylidenethiazolidine (90·6 g.) and was converted (in 20 g. lots) into the free *base*, of which the yield was 33% (43 g.). After recrystallisation from light petroleum (b. p. 80—100°; 120 c.c. per g.), the yield was 22% (Found, after drying in a vacuum at 50° : S, 9·6. $C_{20}H_{21}N_3S$ requires S, 9·55%). The bright yellow crystals had m. p. 104°. The absorption maximum of the broad curve was at 3530 A. The base was photographically inert in a gelatino-chloride emulsion.

1-*Ethyl*-4-*dianilo*iso*propylidene*-1 : 4-*dihydroquinoline* (VIII).—1-Ethyl-4-methylene-1 : 4-dihydroquinoline (10·44 g.; 1 mol.) was treated with ethyl*iso*formanilide (90·5 c.c.; 10 mols.) and zinc chloride powder (25 g.; 3 mols.) and the mixture was heated in an oil-bath and stirred by hand until the temperature reached 80° and the large lumps had been broken up. Mechanical stirring was then applied and the mixture was heated at 175—185° for 1¼ hours. Whilst still warm, the reaction mixture was treated with acetone (150 c.c.), whereupon hardening occurred. After intermittent heating, the dark syrupy liquid was poured off and the hard residue heated with another equal amount of acetone, and finally with yet another, which left no residue. All the dark mixtures were filtered after cooling and the residual solid was further washed with acetone, and with water (600 c.c.). The solid was boiled out thrice with methyl alcohol (400 c.c. × 3). The first filtrate was almost black, the second dark brown, the third amber, and the residual solid (12·74 g.) a clean, bright orange.

In order to obtain the base, the zinc chloride complex (2 g.) was ground with acetone (30 c.c.), and the suspension cooled with ice and treated with an ice-cold solution of sodium (0·45 g.) in absolute alcohol (30 c.c.). The solid was crushed until orange streaks were no longer visible : the liquid became dark yellow. The grey residue was filtered off and washed with a cooled alcohol–acetone mixture : the filtrates were poured into ice-cold water (60 c.c.). Before the bright yellow solid could be filtered off it had become brown. It was washed with ice-cold water and dried in the air and finally in a vacuum desiccator. The yield of base was 34% (1·24 g.). 1 G. was twice extracted with hot light petroleum (b. p. 40—60°; 20 c.c. × 2), each extract being filtered into a tube cooled with ice. The yield of recrystallised product was only 3% (Found, after drying in a vacuum desiccator : N, 11·0. $C_{26}H_{23}N_2$

requires N, 11·15%). When heated, the light brown powder began to shrink at 90°; decomposition was gradual and the substance was quite black by 154° but without any definite m. p. The absorption maximum was at 4785 A., with another maximum at 4020. The *base* sensitised a gelatino-chloride photographic emulsion weakly up to 5400 A., with the maximum at 4950.

1-*Ethyl*-2-*dianilo*iso*propylidene*-1 : 2-*dihydroquinoline*.—1-Ethyl-2-methylene-1 : 2-dihydroquinoline (10·14 g.) was heated with ethyl*iso*formanilide and zinc chloride as in the previous preparation. The warm product was treated with acetone (120 c.c.) and left to stand, with occasional warming. The suspension was poured off from the hard residue, which was similarly treated with a second portion of acetone (120 c.c.) and later with a third (120 c.c.). After cooling, the extracts were filtered, giving a black, treacly filtrate. The residual product was washed with acetone, ground with water (400 c.c.), and thrice boiled out with methyl alcohol (750 c.c. × 3). The residue of zinc chloride complex was a dull orange (7·31 g. obtained).

Its conversion into *base* was carried out as in the preceding preparation. The yield of washed, dried base was 7% (0·82 g. from two 2 g. lots of complex). It was a dirty yellow when first precipitated but finally a dark green. On recrystallising as quickly as possible from light petroleum (b. p. 80—100°; 60 c.c. per g.), the yield dropped to 1% (Found, after drying in a vacuum desiccator : N, 10·85. $C_{26}H_{23}N_2$ requires N, 11·15%). The light brown powder had no definite m. p.; shrinking began at about 95° and considerable decomposition had occurred by 105°. The broad absorption curve had its maximum at 4100 A. On a gelatino-chloride emulsion the base conferred traces of sensitivity up to 5200 A.

3-*Ethyl*-2-*dianilo*iso*propylidenebenzoxazoline*.—3-Ethyl-2-aniloethylidenebenzoxazoline (106 g.; 1 mol.), ethyl*iso*formanilide (300 c.c.; 5 mols.) and zinc chloride (168 g.; 3 mols.) were heated together at 150—160° for 1 hour. The reaction mixture was heated with acetone, and the solid boiled out with methyl alcohol (1600 c.c.). The resultant zinc chloride complex (45 g.) was warmed and shaken with 20% sodium hydroxide solution (7·5 c.c. per g.) and acetone (65 c.c. per g.). After concentration, the acetone extract was precipitated with aqueous ammonium chloride solution, and the crude base recrystallised from methyl alcohol (100 c.c. per g.) (18 g. obtained). As a sample left some ash on heating, the base was purified by suspending it in spirit (20 c.c. per g.) and acidifying with concentrated hydrochloric acid (4 c.c. per g.). The filtered solution was treated with ammonia and the precipitated *base* was obtained in 6% yield (8·6 g.). On recrystallisation from methyl alcohol (700 c.c.), the yield dropped to 4% (5·3 g.) and on a second recrystallisation (from 450 c.c.) to 3% (Found : N, 11·6. $C_{24}H_{21}ON_3$ requires N, 11·45%). The bright yellow crystals had m. p. 210° (decomp.). The absorption maximum was at 3755 A. The compound was photographically inert.

[*Bis*-2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (XII).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (XI) (0·19 g.; 1 mol.) was ground with 2-methylbenzthiazole ethiodide (0·31 g.; 2 mols.) and the mixture heated with pyridine (2 c.c.) at 130—140° for 5 minutes. A blue colour rapidly developed and solid crystallised. It was filtered off when cold and washed with pyridine and with ether, being obtained in 90% yield (0·36 g.). After recrystallisation from methyl alcohol (100 c.c. per g.) it was obtained in 74% yield (0·28 g.) (Found : I, 31·55. $C_{32}H_{31}N_3I_2S_3$ requires I, 31·45%). The dark green crystals had m. p. 243° (decomp.). The absorption maximum was at 6015 A. with an inflexion to the curve at 5550. The *dye* caused weak photographic sensitisation, extending to 7000, with its maximum at 6450 A.

In a preparation in which the pyridine was replaced by anhydrous sodium acetate (0·33 g.; 8 mols.) and acetic anhydride (2 c.c.), the yield of crude product, after washing with acetic anhydride, ether, and water, was 65%, and after recrystallisation from methyl alcohol it was 55%.

Ogata (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497; cf. *idem*, *Proc. Imp. Acad. Tokyo*, 1933, **9**, 602) heated together 2-methylbenzthiazole ethiodide, orthoformic ester, and succinic acid at 170°, and claimed a 15% yield of thiacarbocyanine and a 1% yield of more soluble neocyanine, with no indication that a troublesome purification is necessary. In repeating the preparation, our best result was obtained by heating together 2-methylbenzthiazole etho-*p*-toluenesulphonate (3 g.; 3 mols.), succinic acid (2·72 g.; 8 mols.), and ethyl orthoformate (3 c.c.; 3·2 mols.) at 180—190° for 10 minutes. After cooling, the liquid was poured off, and the residual tar washed with absolute ether (25 c.c.). It was then heated with a solution of crystalline sodium carbonate (6·6 g.; 8 mols.) in water (10 c.c.), so as to remove any succinic acid. To convert the dyes into iodides, potassium iodide (3 g.) was added and the green solid was filtered off. In addition to a dye giving a pink and one giving a blue solution, other matter was present. After two washings with water (10 c.c. × 2), the residue (1·18 g.) was thrice boiled out with methyl alcohol (10 c.c. × 3). The blue dyes from the first two fractions were put together (0·33 + 0·13 g.), but the bluish-pink dye (0·10 g.) from the third was rejected. The residue was recrystallised from absolute alcohol (50 c.c.) and gave the pink thiacarbocyanine (0·20 g.). On precipitating the combined methyl-alcoholic filtrates with absolute ether (150 c.c.), a further yield of the blue dye was obtained (0·06 g., making the total 0·52 g.). The dye giving a blue solution was twice boiled out with absolute alcohol (50 c.c. per g. × 2), and was then recrystallised from methyl alcohol (50 c.c. per g.), in which the neocyanine was considerably more soluble than in absolute alcohol. The final yield of purified thiacarbocyanine was 17% (0·15 g.) and of purified *neocyanine* 9% (0·09 g.) (Found : I, 31·9. $C_{32}H_{31}N_3I_2S_3$ requires I, 31·45%). Ogata correlated his nitrogen determination with the formula $C_{31}H_{31}N_3I_2S_3$ and gave m. p. 256° (decomp.). The present specimen was found to have the same m. p., mixed m. p., and absorption as the synthetic one.

[*Bis*-2-(3-*ethylbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethylbenzthiazole*)]*trimethincyanine Dichloride*.—The preceding di-iodide (0·88 g.) was converted into the *dichloride* by boiling its solution in spirit (176 c.c.) with freshly precipitated silver chloride and taking the filtered solution down to dryness. The dichloride (0·52 g.; 76% yield) was given two recrystallisations from ethyl alcohol (3 c.c. per g.) and ethyl acetate (18 c.c. per g.) and thus obtained in 49% yield (Found : Cl, 10·6; S, 14·4. $C_{32}H_{31}N_3Cl_2S_3,C_2H_5OH$ requires Cl, 10·4; S, 14·35%). Its green crystals melted at about 200° (decomp.). It was insoluble in anhydrous ether or in ethyl acetate but readily soluble in methyl or ethyl alcohol and in water.

[*Bis*-2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)][*αβ′-dimethin*-2′-(3′-*ethyl*-6′ : 7′-*benzbenzthiazole*)]*trimethincyanine Di-iodide*.—3-Ethyl-2-dianilo*iso*propylidene-6 : 7-benzbenzthiazoline (0·87 g.; 1 mol.) and 2-methyl-6 : 7-

benzbenzthiazole ethiodide (1·42 g.; 2 mols.) were ground together, treated with pyridine (16 c.c.), and heated with mechanical stirring at 130—140° for 10 minutes. The washed solid was recrystallised from methyl alcohol (600 c.c.) and gave a 56% yield (1·07 g.). A second recrystallisation from spirit (630 c.c. per g.) gave a 36% yield. Filtration of the recrystallised *dye* was extraordinarily slow (Found : I, 26·2. $C_{44}H_{37}N_3I_2S_3$ requires I, 26·5%). The dark bronze substance had m. p. 216° (decomp.). The absorption maximum was at 6350 A. with an inflexion to the curve at 5900 A. The dye did not sensitise but caused some depression of the normal sensitivity of the plate.

[*Bis*-2-(5-*chloro*-3-*ethylbenzthiazole*)][*αβ′*-*dimethin*-2′-(5′-*chloro*-3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide*.—5-Chloro-3-ethyl-2-dianilo*iso*propylidenebenzthiazoline (1·56 g.; 1 mol.), 5-chloro-2-methylbenzthiazole ethiodide (2·55 g.; 2 mols.), anhydrous sodium acetate (1·23 g.; 4 mols.), and acetic anhydride (10 c.c.) were heated together at 150° for 10 minutes. The washed *dye* (2·93 g.; 86% yield) was recrystallised from methyl alcohol (320 c.c. per g.), after which the yield was 51% (Found : 3 Cl + 2I, 39·35. $C_{32}H_{28}N_3Cl_3I_2S_3$ requires 3Cl + 2I, 39·55%). The green crystals had m. p. 240° (decomp.). The absorption maximum was at 6105 A. with an inflexion to the curve at 5700 A. The compound did not sensitise and strongly depressed the blue sensitivity of a photographic emulsion. A pure product was not obtained in earlier experiments where the condensing agent was pyridine.

[*Bis*-2-(3-*ethylbenzselenazole*)][*αβ′*-*dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide* (XV).—3-Ethyl-2-dianilo*iso*propylidenebenzselenazoline (0·66 g.; 1 mol.), 2-methylbenzselenazole ethiodide (1·06 g.; 2 mols.), and pyridine (6 c.c.) were heated and stirred together at 135—140° for 5 minutes. On recrystallising the washed *dye* (0·93 g. obtained; 65% yield) from methyl alcohol (195 c.c. per g.), the yield was 56% (0·80 g.) (Found : I, 26·85. $C_{32}H_{31}N_3I_2Se_3$ requires I, 26·75%). The dull green crystals had m. p. 226° (decomp.). The absorption maximum was at 6200 A., with an inflexion to the curve at about 5740 A. The compound had a strong desensitising effect on a photographic plate.

[*Bis*-2-(4-*methyl*-3-*ethylthiazole*)][*αβ′*-*dimethin*-2′-(4′-*methyl*-3′-*ethylthiazole*)]*trimethincyanine Di-iodide* (XIV).—4-Methyl-3-ethyl-2-dianilo*iso*propylidene-Δ^4-thiazoline (XIII) (0·69 g.; 1 mol.), 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate (1·25 g.; 2 mols.), and pyridine (5 c.c.) were heated together at 130° for 40 minutes. The pyridine was removed under reduced pressure, and the residue dissolved in hot spirit and poured into a hot aqueous solution of potassium iodide (2·2 g.; 8 mols.). The dye (1·04 g.; 74% yield) was recrystallised from absolute alcohol (20 c.c.) and thus obtained in 59% yield (0·82 g.) as dark blue crystals (Found : I, 36·25. Calc. for $C_{23}H_{31}N_3I_2S_3$: I, 36·3%); it had m. p. 206° (decomp.), which was also the m. p. of the mixture of this synthetic specimen with that of the one prepared by the empirical method given below. The substance had a narrow absorption curve with its maximum at 5875 A. It sensitised to 7100 A., the maximum lying at 6300. In these respects it was identical with the sample prepared by the following method.

By the empirical method, 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate (31 g.), ethyl orthoformate, and pyridine were boiled together for 5 hours (Kodak Ltd. and Brooker, B.P. 408,273/1931). The product (6·23 g.) obtained by concentration in a vacuum, followed by precipitation with potassium iodide, was boiled out four times with methyl alcohol (15 c.c. × 3, 25 c.c.). The fraction which crystallised from the first two extracts was combined with a second crop which resulted on concentration of the first three filtrates (total 5·2 g.). This was given a second fractional crystallisation from absolute alcohol (20 c.c., 25 c.c.) and methyl alcohol (15 c.c.) but this time there was no residue and the neocyanine crystallised in 18% yield (3·97 g.) (Found : I, 36·2%). In the first fractional crystallisation, the less soluble residue (0·46 g.) was combined with the dye which crystallised from the last two extracts (0·47 g.) and was recrystallised from methyl alcohol (100 c.c.), being obtained in 3% yield (0·6 g.) (Found : I, 30·3. Calc. for $C_{15}H_{21}N_2IS_2$: I, 30·2%). This is bis-2-(4-methyl-3-ethylthiazole)trimethincyanine iodide, identical with that prepared by Fisher and Hamer (*J.*, 1930, 2502).

[*Bis*-2-(3-*methyl*-Δ^2-*thiazoline*)][*αβ′*-*dimethin*-2′-(3′-*methyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Di-iodide* (XVI; R = Me, X = I). 3-Methyl-2-dianilo*iso*propylidenethiazolidine (0·64 g.; 1 mol.), 2-methyl-Δ^2-thiazoline methiodide (1·07 g.; 2·2 mols.), and pyridine (8 c.c.) were heated together at 130—140° for 2 minutes. The washed *dye* (0·83 g.; 67% yield) was recrystallised from methyl alcohol (25 c.c.). The yield was 53% (0·65 g.) and after a second recrystallisation from methyl alcohol (40 c.c. per g.) it was 42% (Found : I, 40·95. $C_{17}H_{25}N_3I_2S_3$ requires I, 40·85%). When the purplish-red crystals were heated they began to shrink at about 115° and had largely melted and decomposed by 125° but there was no definite m. p. The absorption maximum was at 5065 A. The dye sensitised a gelatino-bromide photographic emulsion up to 5900 A.

[*Bis*-2-(3-*ethyl*-Δ^2-*thiazoline*)][*αβ′*-*dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate* (XVI; R = Et, X = ClO_4).—3-Ethyl-2-dianilo*iso*propylidenethiazolidine (1·02 g.; 1 mol.), 2-methyl-Δ^2-thiazoline ethiodide, and pyridine were heated together at 130—140° for 5 minutes. The gum, precipitated by absolute ether, was dissolved in hot spirit (30 c.c.) and treated with a hot solution of sodium perchlorate (1·68 g.; 4 mols.) in water (30 c.c.). The crude *perchlorate* (1·59 g.) was boiled out with and recrystallised from methyl alcohol (15 c.c., 225 c.c.), the product being obtained in 51% yield (0·93 g.) (Found : Cl, 11·7. $C_{20}H_{31}O_8N_3Cl_2S_3$ requires Cl, 11·65%). The brick-red crystals had m. p. 230° (decomp.). The absorption maximum was at 5060 A. In a gelatino-bromide photographic emulsion the compound produced extra-sensitivity up to 5700 A.

[*Bis*-4-(1-*ethylquinoline*)][*αβ′*-*dimethin*-4′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide*.—Crude 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (VIII) (0·75 g.; 1 mol.), lepidine ethiodide (1·20 g.; 2 mols.), and anhydrous sodium acetate (1·31 g.; 8 mols.) were ground together, treated with acetic anhydride (8 c.c.), and heated at 135—140° for 10 minutes. Brassy crystals of dye began to separate when the temperature reached 110°. The solid was filtered off, washed with acetic anhydride and with ether, ground with water (10 c.c.), washed with methyl alcohol, and boiled out with it three times (20 c.c. × 3). The first fraction was rejected but the dye which crystallised from the second and third (0·01 g.) was put with the undissolved residue (0·41 g.) making a 27% yield (0·42 g.). On recrystallisation from methyl alcohol (1000 c.c. per g.) the yield was 20% (0·32 g.) (Found : I, 32·3. Calc. for $C_{38}H_{37}N_3I_2$: I, 32·15%). When samples of the original neocyanine ethiodide (Hamer, *J.*, 1928, 1472), of the present synthetic dye, and of their mixture were heated, all melted simultaneously at 280° (decomp.).

We failed to isolate the dye when heating with pyridine took the place of heating with sodium acetate and acetic anhydride, but in another experiment 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (0·19 g.; 1 mol.) and excess of lepidine ethiodide (0·45 g.; 3 mols.) were ground together, treated with ice-cold pyridine (2 c.c.), and left in the cold for six days, with occasional stirring. The crystals were filtered off and well washed; the residue (0·12 g.) was twice boiled out with methyl alcohol (15 c.c., 25 c.c.), and the product which crystallised (0·01 g.) added to what remained (0·02 g.), making up a 7% yield. After recrystallisation from methyl alcohol (30 c.c.), the yield of the characteristic brassy crystals was 2% (0·01 g.).

Bis-2-(5-chloro-3-ethylbenzthiazole)pentamethincyanine Iodide.—5-Chloro-2-methylbenzthiazole ethiodide (1·97 g.; 2 mols.) and β-anilinoacraldehyde anil hydrochloride (0·75 g.; 1 mol.) in boiling absolute alcohol (20 c.c.) were treated with a solution of sodium (0·14 g.; 2 atoms) in absolute alcohol (5 c.c.). The mixture was boiled and stirred for 3 minutes, during which time the solids dissolved and a green dye separated. After three recrystallisations of the washed *dye* (1·35 g.; 80% yield) from methyl alcohol (2600 c.c., 3900 c.c., and 5000 c.c. per g.) the yield was 38% (Found: 2Cl + I, 33·55. $C_{23}H_{21}N_2Cl_2IS_2$ requires 2Cl + I, 33·7%). The bluish-green crystals had m. p. 298° (decomp.). The absorption maximum was at 6560 A. The dye sensitised a gelatino-bromide photographic emulsion from 6500—7400 A., with a maximum at 7000 A. This preparation was carried out by Dr. V. P. Pittman, whom we thank.

Bis-2-(4-methyl-3-ethylthiazole)pentamethincyanine Iodide.—2 : 4-Dimethylthiazole etho-*p*-toluenesulphonate (12·52 g.; 2 mols.), β-ethoxyacraldehyde diethyl acetal (3·84 g.; 1·1 mols.), and triethylamine (5·6 c.c.; 2 mols.) in pyridine (40 c.c.) were boiled and stirred together for 7 minutes. Ether precipitated a sticky solid which was dissolved in hot spirit and treated with a solution of potassium iodide (13 g.; 4 mols.) in hot water. The crude *dye* (2·3 g.) was boiled out with and recrystallised from absolute ethyl alcohol (15 c.c., 100 c.c.), being obtained in 21% yield (1·92 g.) (Found: I, 28·3. $C_{17}H_{23}N_2IS_2$ requires I, 28·45%). The steely bluish-green crystals had m. p. 214° (decomp.). The absorption curve had its maximum at 6370 A. and an inflexion at 6050 A. It sensitised from 6500—6900 A. with the maximum at 6800 A.

Bis-2-(3-ethyl-Δ^2-thiazoline)pentamethincyanine Iodide.—A mixture of 2-methyl-Δ^2-thiazoline ethiodide (3·98 g.; 2 mols.), β-anilinoacraldehyde anil hydrochloride (2 g.; 1 mol.), anhydrous potassium carbonate (5·36 g.; 5 mols.; 180-mesh), and ethyl alcohol (10 c.c.) was boiled for 4 minutes. The washed solid (1·71 g.) was recrystallised from methyl alcohol (10 c.c.) and obtained in 27% yield (0·88 g.). After a second recrystallisation from methyl alcohol (10 c.c.), the yield was 24% (0·77 g.) (Found: I, 30·2. $C_{15}H_{23}N_2IS_2$ requires I, 30·05%). The steely crystals had m. p. 231° (decomp.). The absorption maximum was at 5450 A. The *dye* sensitised a gelatino-bromide photographic emulsion, the maximum lying at 5700 A.

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