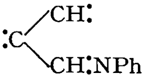
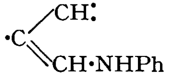
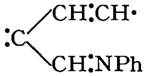
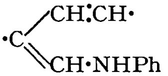
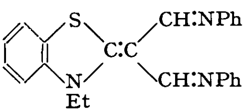
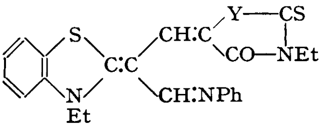
66. *Some Trinuclear Cyanine Dyes. Part IV. The Action of Acid on Dinuclear Intermediate Dyes.*

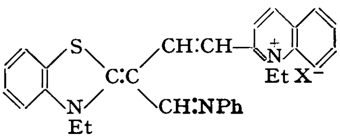
By Frances M. Hamer.

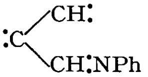
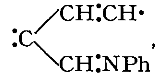
Of seven dinuclear intermediate dyes having the group  $:\mathrm{C}{<}^{\mathrm{CH:}}_{\mathrm{CH:NPh}}$ four gave hydrochlorides * having the group  $\cdot\mathrm{C}{<}^{\mathrm{CH:}}_{\mathrm{CH\cdot NHPh}}$; on more drastic treatment with acid, three gave the corresponding dimethin*mero*cyanine having the chain $:\mathrm{CH\cdot CH}:$. Five dinuclear intermediate dyes having the group  $:\mathrm{C}{<}^{\mathrm{CH:CH\cdot}}_{\mathrm{CH:NPh}}$ gave perchlorate hydroperchlorates having the group  $\cdot\mathrm{C}{<}^{\mathrm{CH:CH\cdot}}_{\mathrm{CH\cdot NHPh}}$; on more drastic treatment with acid, four gave the corresponding trimethincyanines having the chain $:\mathrm{CH\cdot CH:CH}$.

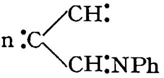
Dinuclear intermediate dyes were obtained by condensing one mol. of a heterocyclic dianil, such as (I), with one mol. of a compound having a reactive methylene group, whereas condensation with two mols. gave the trinuclear dyes themselves (Hamer, Rathbone, and Winton, *J.*, 1947, 1434; 1948, 1872; 1949, 1113). According as the reactive methylene groups were

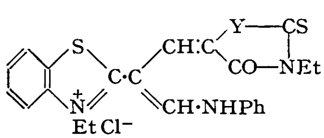

(I.)

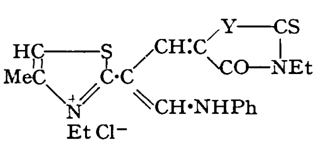

(II.)

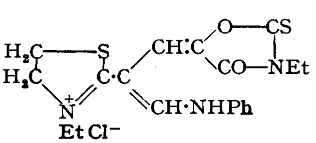

(III.)

cyclic or in the form of external methyl groups, these intermediate compounds, *e.g.*, (II) and (III), fell into two classes, which are characterised, in one of the resonating structures, by the chains  $:\mathrm{C}{<}^{\mathrm{CH:}}_{\mathrm{CH:NPh}}$ and  $:\mathrm{C}{<}^{\mathrm{CH:CH\cdot}}_{\mathrm{CH:NPh}}$, respectively. In recording the absorption maxima of acid and of alkaline solutions of all the intermediate dyes and in determining the pH range of the colour change in nine instances, it was noted that more drastic treatment with acid produced an irreversible colour change (*idem*, *J.*, 1948, 1872; 1949, 1113), which was not further investigated at that time.

The intermediate compound (II; Y = S), and three others, all having the chain  $:\mathrm{C}{<}^{\mathrm{CH:}}_{\mathrm{CH:NPh}}$ (*idem*, *J.*, 1949, 1113), have now been converted into well crystallising hydrochlorides * (IV;


(IV.)


(V.)


(VI.)

Y = S), (V; Y = NPh or S), and (VI), possessing, in one of the resonating structures, the chain  $\cdot\mathrm{C}{<}^{\mathrm{CH:}}_{\mathrm{CH\cdot NHPh}}$ The absorption maxima of methyl-alcoholic solutions of these hydrochlorides are the same as those already recorded for acidified solutions of the bases (*loc. cit.*, 1949). Nor is there anything fresh to record regarding sensitising action, since it is known that dye

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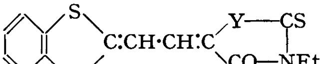
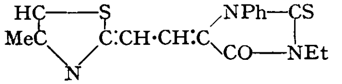
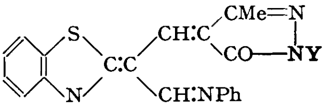
* The compounds are termed hydrochlorides because they are formed by addition of hydrochloric acid, although in the particular resonating structure formulated both nitrogen atoms are in fact quaternary. The same applies to the hydroperchlorates.

bases and their hydrochlorides appear to reach an equilibrium depending on the pH of the photographic emulsion. Attempts to acetylate two of the hydrochlorides were unsuccessful.

A dye now obtained from the first intermediate compound (II; Y = S), by more drastic treatment with hydrochloric acid, has been identified as the known dimethin*mero*cyanine (VII; Y = S) (Hamer and Winton, *J.*, 1949, 1126). Similarly, such more drastic treatment of the second intermediate compound yielded the dimethin*mero*cyanine (VIII), which is here described. In the third instance, more drastic treatment with acid still gave the hydrochloride (V; Y = S), and not the corresponding dimethin*mero*cyanine; in the fourth, the hydrochloride (VI) was destroyed but the related dimethin*mero*cyanine was not obtained. On the other hand the 5-chloro-derivative of the intermediate compound (II; Y = NPh) did not give the 5-chloro-derivative of the hydrochloride (IV; Y = NPh) but readily yielded the 5-chloro-derivative of the dimethin*mero*cyanine (VII; Y = NPh). The observed lower melting point and mixed melting point of a specimen now prepared by the synthetic method, as compared with that prepared from the anilomethyl compound, has been confirmed but is not explained.

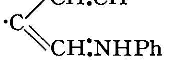

(VII.)

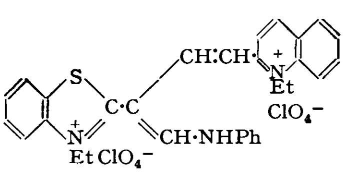

(VIII.)

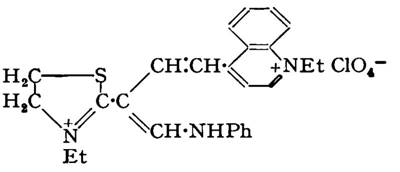

(IX.)

The hydrolysis which occurs with three of five of the above dinuclear intermediate dyes is of an unusual type, consisting in replacement by a hydrogen atom of the group ·CH:NPh, which is attached to the dimethin chain of the parent substances.

Two new anilomethyl compounds were made, namely (IX; Y = Ph) and its *p*-sulpho-derivative (IX; Y = *p*-$C_6H_4\cdot SO_3H$), but neither gave a hydrochloride, presumably, like the 5-chloro-derivative of (II; Y = NPh) which also failed to give one, because of their electro-negative character. The first of the new anilomethyl compounds was so unstable to acid that the absorption maximum of its acidified methyl-alcoholic solution could not be determined, but neither it nor its *p*-sulpho-derivative underwent a smooth conversion into the corresponding dimethin*mero*cyanine. The bathochromic shift, 940 A., on passing from (IX; Y = Ph) to the parent dimethin*mero*cyanine lies outside the range, —30 to 705 A., previously recorded for 14 such compounds (Hamer, Rathbone, and Winton, *J.*, 1949, 1113), as does that of (IX; Y = *p*-$C_6H_4\cdot SO_3H$), where it is 1015 A. for alkaline and 1795 A. for acid methyl-alcoholic solutions. With (IX; Y = *p*-$C_6H_4\cdot SO_3H$) itself, the hypsochromic shift on passing from base to acid salt is 120 A., which again lies outside the earlier range of 220—875 A. (*loc. cit.*).

Of dinuclear intermediate dyes characterised by the chain  $:C\begin{smallmatrix}\diagup CH:CH\cdot \\ \diagdown CH:NPh\end{smallmatrix}$, it was hoped to prepare hydrochlorides, characterised by the chain  $\cdot C\begin{smallmatrix}\diagup CH:CH\cdot \\ \diagdown CH:NHPh\end{smallmatrix}$ in one resonating form. Therefore (III; X = Cl), as also the corresponding chloride having a benzthiazolium in place of a 2-quinolinium nucleus, were prepared, earlier compounds of this type having been confined to iodides and perchlorates (*idem*, *J.*, 1948, 1872). Hydrochlorides did not separate but the perchlorate hydroperchlorate * (X) could be precipitated and, similarly, its analogue having a benzthiazolium in place of a 2-quinolinium nucleus. From dinuclear intermediate dye iodides, which have already been described (*loc. cit.*), three other such hydroperchlorates were prepared, namely (XI), its analogue having a benzthiazolium in place of a 4-quinolinium nucleus, and (XII).


(X.)


(XI.)

From the chloride (III; X = Cl), more drastic treatment with hydrochloric acid, followed

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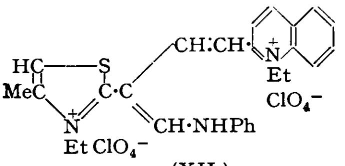
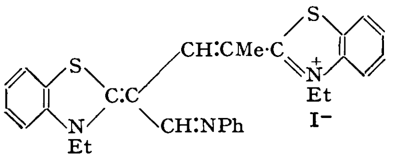
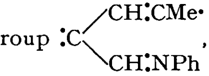
* See footnote, p. 294.

by potassium perchlorate, yielded a dye perchlorate, which was identified as the unsubstituted parent trimethincyanine. Three dinuclear intermediate dye iodides similarly underwent conversion into the corresponding unsubstituted trimethincyanine perchlorates. Thus in this series also, acid under the more drastic conditions replaces by a hydrogen atom the group •CH:NPh, which here is attached to the trimethin chain.


(XII.)


(XIII.)

A dinuclear intermediate compound (XIII), characterised by the group  $:C{<}\begin{matrix}CH:CMe\cdot\\CH:NPh\end{matrix}$, was prepared by condensing (I) with 2-ethylbenzthiazole ethiodide; it was unstable to light.

EXPERIMENTAL.

*[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine Hydrochloride* (IV; Y = S).—On treating [5-(3-ethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine (II; Y = S) (1·46 g.) with concentrated hydrochloric acid (2 c.c.), the red solid became orange. Alcohol (10 c.c.) was added and the mixture heated and then cooled. The washed crystals (1·54 g.) were recrystallised from a mixture of water (35 c.c.), alcohol (35 c.c.), and hydrochloric acid (3·5 c.c.), and the yield was 81%. After a second recrystallisation from a mixture of water (55 c.c. per g.), methyl alcohol (55 c.c. per g.), and hydrochloric acid (5 c.c. per g.), the yield was 66% (Found, on a sample dried in a vacuum at 60—80°: Cl, 7·25. $C_{23}H_{22}ON_3ClS_3$ requires Cl, 7·25%). The orange crystals darkened from 180° and had m. p. 189° (decomp.). An attempt to acetylate this dye by boiling acetic anhydride was unsuccessful.

*[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)]dimethin*mero*cyanine* (VII; Y = S).—A mixture of [5-(3-ethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine (II; Y = S) (1 g.) with alcohol (16 c.c.) and concentrated hydrochloric acid (4 c.c.) was boiled for 2 hours. The resultant washed dye (82%), after recrystallisation from benzene (430 c.c. per g.), gave a 54% yield, and after a second recrystallisation from pyridine (40 c.c. per g.), a 42% yield [Found, in a sample dried in a vacuum at 80—100° (which method of drying was used also in other analyses unless otherwise stated): S, 27·3. Calc. for $C_{16}H_{16}ON_2S_3$: S, 27·6%]. Samples of this substance, of a synthetic specimen (Hamer and Winton, *J.*, 1949, 1126), and of their mixture melted simultaneously at 265° (decomp.), with previous darkening.

*[5-(3-Ethyl-1-phenyl-2-thiohydantoin)] [2-(3-ethyl-4-methyl-Δ^4-thiazoline)]-β-anilomethyldimethin*mero*cyanine Hydrochloride* (V; Y = NPh).—A suspension of [5-(3-ethyl-1-phenyl-2-thiohydantoin)][2-(3-ethyl-4-methyl-Δ^4-thiazoline)]-β-anilomethyldimethin*mero*cyanine (1 g.) in alcohol (4 c.c.) was treated with concentrated hydrochloric acid (2 c.c.), and the mixture cooled. Dissolution, followed by crystallisation, occurred. The washed crystals (1·09 g.) were twice recrystallised from methyl alcohol (10 c.c. per g.), with hydrochloric acid (5 drops per g.) and water (5 c.c. per g.), after which the yield was 61% (Found: Cl, 7·0. $C_{26}H_{27}ON_4ClS_2$ requires Cl, 6·95%). The yellow crystals had m. p. 165° (decomp.), with darkening from 135°.

*[5-(3-Ethyl-1-phenyl-2-thiohydantoin)][2-(3-ethyl-4-methyl-Δ^4-thiazoline)]dimethin*mero*cyanine* (VIII).—After the original filtrate from the preceding preparation had been heated for 15 minutes, precipitation with aqueous ammonia gave a 4% yield of this dimethin*mero*cyanine (1% after recrystallisation). In another experiment, the reaction mixture was boiled for 10 minutes and the resultant dye (1·35 g., 86%) recrystallised from methyl alcohol (500 c.c.), giving a 59% yield (Found: S, 17·45. $C_{19}H_{21}ON_3S_2$ requires S, 17·3%). The red crystals had m. p. 240° (decomp.), with previous shrinking and darkening. A specimen synthesised as follows melted simultaneously, as did their mixture.

A mixture of 3-ethyl-1-phenyl-2-thiohydantoin (1·10 g., 1 mol.), 2-β-acetanilidovinyl-4-methylthiazole ethiodide (1 mol.), triethylamine (2 mols.), and absolute alcohol (20 c.c.) was boiled for 15 minutes. After recrystallisation of the washed product (1·63 g.) from methyl alcohol (600 c.c.), the yield was 69% (Found: S, 17·4%). The absorption maximum previously quoted (*J.*, 1949, 1113) was provided by Dr. L. G. S. Brooker and Mr. F. L. White.

*[2-(3-Ethyl-4-methyl-Δ^4-thiazoline)] [5-(3-ethylrhodanine)]-α-anilomethyldimethin*mero*cyanine Hydrochloride* (V; Y = S).—A suspension of [2-(3-ethyl-4-methyl-Δ^4-thiazoline)][5-(3-ethylrhodanine)]-α-anilomethyldimethin*mero*cyanine (0·83 g., 1 mol.) in cold alcohol (20 c.c.) was treated with concentrated hydrochloric acid (2 c.c., 10 mols.). From the resultant orange solution dye began to crystallise. Water (20 c.c.) was added and the washed *hydrochloride* (0·82 g.) was recrystallised from methyl alcohol (40 c.c.) and obtained in 72% yield (Found, on a sample dried in a vacuum at 60—80°: Cl, 7·85. $C_{20}H_{22}ON_3ClS_3$ requires Cl, 7·85%). The orange crystals had m p. 268° (decomp.). Attempted acetylation with acetic anhydride was unsuccessful.

For the above preparation I thank Dr. R. J. Rathbone.

When the original reaction mixture was boiled for 30 minutes, the *hydrochloride* was obtained as before, in undiminished yield.

*[5-(3-Ethyl-4-keto-2-thio-oxazolidine)][2-(3-ethylthiazolidine)]-β-anilomethyldimethin*mero*cyanine Hydrochloride* (VI).—A suspension of [5-(3-ethyl-4-keto-2-thio-oxazolidine)][2-(3-ethylthiazolidine)]-β-anilomethyldimethin*mero*cyanine (1 g.) in hot alcohol (10 c.c.), on treatment with hot concentrated hydrochloric acid solution (2 c.c.), gave a solution which deposited a 91% yield of *hydrochloride.* After recrystallisation from methyl alcohol (10 c.c.), containing concentrated hydrochloric acid (4 drops), the yield was 63% (Found : Cl, 8·3. $C_{19}H_{22}O_2N_3ClS_2$ requires Cl, 8·35%). The deep yellow crystals melted at 192—202° (decomp.), the exact point depending on the rate of heating.

The effect of boiling the original solution was to destroy the hydrochloride but the dimethin*mero*cyanine (Hamer and Winton, *J.*, 1949, 1126) was not isolated.

*[5-(3-Ethyl-1-phenyl-2-thiohydantoin)][2-(5-chloro-3-ethylbenzthiazoline)]dimethin*mero*cyanine.*—In an attempt to prepare its hydrochloride, [5-(3-ethyl-1-phenyl-2-thiohydantoin)][2-(5-chloro-3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine (1 g.) was suspended in alcohol (4 c.c.), and concentrated hydrochloric acid was stirred in, with ice-cooling, but the resultant deep-red solution deposited tar.

In an experiment where the reaction mixture was boiled for 20 minutes, an 81% yield of the *dimethin*mero*cyanine* crystallised; after recrystallisation from pyridine (8 c.c. per g.), the yield was 60% (Found : Cl, 8·0; S, 14·55. $C_{22}H_{20}ON_3ClS_2$ requires Cl, 8·05; S, 14·5%). The vermilion crystals had m. p. at about 230° (decomp.), with previous darkening and shrinking. A sample synthesised as below had an identical absorption curve and photographic sensitising properties but melted at about 220° (decomp.), whilst the mixture melted at about 208° (decomp.).

A mixture of 3-ethyl-1-phenyl-2-thiohydantoin (2·20 g., 1 mol.), 2-β-acetanilidovinyl-5-chlorobenzthiazole ethiodide (1 mol.), triethylamine (2 mols.), and absolute alcohol (50 c.c.) was boiled and stirred for 5 minutes. The washed product (3·53 g.), after recrystallisation from benzene (50 c.c.), resulted in 65% yield and, after a second recrystallisation from benzene and light petroleum (b. p. 60—80°; 80 c.c. of each), in 55% yield (Found : Cl, 8·1; S, 14·4%). The absorption maximum previously quoted (*J.*, 1949, 1113) was provided by Dr. L. G. S. Brooker and Mr. F. L. White.

*[4-(3-Methyl-1-phenyl-5-pyrazolone)][2-(3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine* (IX; Y = Ph).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (1·92 g., 1 mol.) and 3-methyl-1-phenyl-5-pyrazolone (1 mol.) in pyridine (20 c.c.) were heated together at 50—60° for 10 minutes. The substance precipitated in 78% yield by absolute ether (100 c.c.) was recrystallised from pyridine (5 c.c. per g.) and obtained in 53% yield (Found : S, 7·0. $C_{28}H_{24}ON_4S$ requires S, 6·9%). The reddish-orange dye had m. p. 205° (decomp.). The absorption maximum of its methyl-alcoholic solution containing ammonia was at 3930 A. One containing sulphuric acid (1 g. in 100 c.c.) was orange but faded to yellow before the absorption measurements could be made. The substance was photographically inert.

*[4-(3-Methyl-1-phenyl-5-pyrazolone)][2-(3-ethylbenzthiazoline)]dimethin*mero*cyanine.*—3-Methyl-1-phenyl-5-pyrazolone (0·87 g., 1 mol.), 2-β-acetanilidovinylbenzthiazole ethiodide (1 mol.), triethylamine (1·1 mols.), and absolute alcohol (15 c.c.) were boiled and stirred together for 5 minutes. The washed product (96% yield) was recrystallised from benzene and light petroleum (b. p. 60—80°; 100 c.c. of each per g.), leaving a very little thiacarbocyanine undissolved, and giving an 89% yield. After a second such recrystallisation, the yield was 81% (Found : S, 9·2. $C_{21}H_{19}ON_3S$ requires S, 8·85%). The red crystals had m. p. about 204° (decomp.), with previous darkening and softening. The absorption maximum of a methyl-alcoholic solution was at 4870 A. The sensitising maximum lay at 5200 A.

*[4-(3-Methyl-1-*p*-sulphophenyl-5-pyrazolone)][2-(3-ethylbenzthiazoline)]-β-anilomethyldimethin*mero*cyanine* (IX; Y = p-C_6H_4·SO_3H).—3-Methyl-1-*p*-sulphophenyl-5-pyrazolone (1·27 g., 1 mol.), which had been rendered anhydrous in a vacuum at 100° (cf. Möllenhof, *Ber.*, 1892, **25**, 1941) was heated at 50—60° for 10 minutes with 2-dianilo*iso*propylidene-3-ethylbenzthiazoline (1 mol.) and pyridine (10 c.c.). The product precipitated by absolute ether (100 c.c.) was washed with ether, ground with water (15 c.c.), and further thoroughly washed with water (Found : S, 11·55. $C_{28}H_{24}O_4N_2S_2$ requires S, 11·8%). The vermilion crystals had m. p. at about 240° (decomp.) with darkening from about 180°. Their methyl-alcoholic solution containing ammonia had its absorption maximum at 3875 A. and one containing sulphuric acid had the maximum at 3755 A. Towards a gelatino bromide photographic plate the dye was inert but it sensitised a gelatino chloride plate weakly to 5300 A.

*[4-(3-Methyl-1-*p*-sulphophenyl-5-pyrazolone)][2-(3-ethylbenzthiazoline)]dimethin*mero*cyanine.*—To a mixture of anhydrous 3-methyl-1-*p*-sulphophenyl-5-pyrazolone (1·27 g., 1 mol.) and 2-β-acetanilidovinylbenzthiazole ethiodide (1 mol.) in absolute alcohol (25 c.c.) was added triethylamine (2·2 mols.), and the whole was boiled and stirred for 5 minutes. The solvent was removed under a vacuum and the residual red tar dissolved in hot water (15 c.c.) and treated with acetic acid. To remove a trace of thiacarbocyanine from the washed dye (77% yield), it was ground with 8½% ammonia solution (10 c.c.); the filtered solution was evaporated to remove excess of ammonia, diluted with water, and acidified with acetic acid. After cooling, filtering off, and washing, the yield was 64% (Found : S, 14·85. $C_{21}H_{19}O_4N_3S_2$ requires S, 14·55%). The purplish solid remained unmelted at 290°. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4890 A. and that of one containing sulphuric acid was at 5550 A., with a secondary maximum at 4350 A. The sensitising maximum was at 5900 A.

[2-(1-Ethylquinoline)][2-(3-ethylbenzthiazole)]-γ-anilomethyltrimethincyanine Chloride (III; X = Cl).—A mixture of 2-dianilo*iso*propylidene-3-ethylbenzthiazoline (3·83 g., 1 mol.), quinaldine ethochloride (1 mol.), and pyridine (20 c.c.) was heated at 60—70° for 20 minutes. Recrystallisation of the washed dye (3·27 g.) from ethyl alcohol (30 c.c.) gave a 50% yield and, after a second recrystallisation, 36% (Found : Cl, 7·1. $C_{30}H_{28}N_3ClS$ requires Cl, 7·1%). The dark purplish crystals had m. p. at about 175° (decomp.).

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)]-γ-*anilomethyltrimethincyanine Perchlorate Hydroperchlorate* (X).—On treatment of the deep-purple suspension of the preceding chloride (0·20 g.) in absolute alcohol (1 c.c.) with concentrated hydrochloric acid (0·2 c.c.), an orange solution resulted. Addition of a solution of sodium perchlorate (0·20 g.) in water (2 c.c.) precipitated the *hydroperchlorate* in 86% yield. It was recrystallised by dissolving it in boiling methyl alcohol and adding 60% perchloric acid (1 drop per c.c. of methyl alcohol), giving a 49% yield. After a second such recrystallisation the yield was 38%. This and subsequent compounds were dried for microanalysis at 56°/0·4 mm. unless otherwise stated (Found: N, 6·4. $C_{30}H_{29}O_8N_3Cl_2S$ requires N, 6·35%). The orange crystals had m. p. 264° (decomp.), with previous darkening and shrinking.

[2-(1-*Ethylquinoline*)][2-(3-*ethylbenzthiazole*)]*trimethincyanine Perchlorate.*—The dye chloride (0·50 g.) was boiled for 30 minutes with hydrochloric acid (2 N.; 5 c.c.), and the hot solution treated with one of sodium perchlorate (1 g.) in water (5 c.c.), and then with aqueous ammonia. After two digestions with water to remove neocyanine, the residue amounted to a 49% yield. On recrystallisation from methyl alcohol (250 c.c. per g.), the yield dropped to 23%, and on a second recrystallisation to 8% (Found: Cl, 7·65. $C_{23}H_{23}O_4N_2ClS$ requires Cl, 7·75%). The dark blue crystals had m. p. 272° (decomp.). Their alcoholic solution was identical in colour with one of the corresponding dye iodide (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138).

[*Bis*-2-(3-*ethylbenzthiazole*)]-α-*anilomethyltrimethincyanine Chloride.*—A mixture of 2-dianilo*iso*propylidene-3-ethylbenzthiazoline (3·83 g., 1 mol.), 2-methylbenzthiazole ethochloride (1 mol.), and pyridine (20 c.c.) was heated at 60—70° for 5 minutes. The tar obtained by precipitation with absolute ether (160 c.c.) was washed with ether and treated with hot water (36% yield). It was dissolved in hot absolute alcohol (6 c.c.) and treated with ethyl acetate (15 c.c.), giving a 24% yield. After a second such recrystallisation, the yield was 18% (Found: Cl, 7·0. $C_{28}H_{26}N_3ClS_2$ requires Cl, 7·05%). The dark bronze substance had m. p. at about 174° (decomp.), with previous darkening.

[*Bis*-2-(3-*ethylbenzthiazole*)]-α-*anilomethyltrimethincyanine Perchlorate Hydroperchlorate.*—On treatment of a suspension of the preceding chloride (0·20 g.) in ethyl alcohol (1 c.c.) with concentrated hydrochloric acid (0·2 c.c.), dissolution occurred. A solution of sodium perchlorate (0·20 g.) in water (2 c.c.) precipitated the *hydroperchlorate* in 94% yield. Dissolution in hot methyl alcohol (30 c.c.) with subsequent addition of 60% perchloric acid (1 drop per c.c.) gave a 64% yield (Found: N, 6·4. $C_{28}H_{27}O_8N_3Cl_2S_2$ requires N, 6·3%). The maroon crystals had m. p. 254° (decomp.), with previous darkening.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]-γ-*anilomethyltrimethincyanine Perchlorate Hydroperchlorate* (XI).—When the bluish-purple suspension of [4-(1-ethylquinoline)][2-(3-ethyl-Δ^2-thiazoline)]-γ-anilomethyltrimethincyanine iodide (0·2 g.) in alcohol (1 c.c.) was treated with concentrated hydrochloric acid (0·2 c.c.), the colour reddened. The solution obtained on heating was treated with one of sodium perchlorate (0·2 g.) in hot water (2 c.c.). The washed *hydroperchlorate* (79% yield) was recrystallised by dissolving it in hot methyl alcohol (60 c.c.) and adding 60% perchloric acid (1 drop per c.c.), giving a 53% yield (Found: N, 6·65. $C_{26}H_{29}O_8N_3Cl_2S$ requires N, 6·85%). The crimson crystals had m. p. 228° (decomp.).

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]*trimethincyanine Perchlorate.*—The clear red solution obtained by heating [4-(1-ethylquinoline)][2-(3-ethyl-Δ^2-thiazoline)]-γ-anilomethyltrimethincyanine iodide (1·00 g.) with dilute hydrochloric acid (20 c.c.; 2N.) became very pale when boiled for 1 minute. The solution was treated hot with one of sodium perchlorate (2 g.) in water (5 c.c.). Addition of aqueous ammonia precipitated a tar, which stiffened on cooling; after decantation of the liquid, it was washed with cold water. Whilst still wet, it was boiled with methyl alcohol (4 c.c.), and hot filtration left a crystalline residue (0·25 g., 33%). Recrystallisation from methyl alcohol (120 c.c. per g.) gave a 12% yield and, a second recrystallisation, 4% (Found: N, 6·6. $C_{19}H_{23}O_4N_2ClS$ requires N, 6·8%). The dark violet crystals had no definite m. p.; shrinking began at about 212° and progressive decomposition became violent at about 245—253°. The colours of alcoholic solutions of this *perchlorate* and the corresponding iodide (Hamer, Rathbone, and Winton, *J.*, 1948, 1872) were identical.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)]-α-*anilomethyltrimethincyanine Perchlorate Hydroperchlorate.*—[2-(3-Ethyl-Δ^2-thiazoline)][2-(3-ethylbenzthiazole)]-α-anilomethyltrimethincyanine iodide was suspended in alcohol, heated with concentrated hydrochloric acid, and then treated with aqueous sodium perchlorate solution. The washed *hydroperchlorate* (0·12 g., 44%) was recrystallised by means of methyl alcohol (37 c.c.), with later addition of 60% perchloric acid (37 drops), giving a 33% yield (Found: N, 6·65. $C_{24}H_{27}O_8N_3Cl_2S_2$ requires N, 6·75%). The bright reddish-orange crystals had m. p. 253° (decomp.), with previous darkening and shrinking.

When the original dye iodide (0·2 g.) was boiled with dilute hydrochloric acid (5 c.c.; 2N.) for 5 minutes, decomposition occurred; lessening the time of heating did not yield a clean product.

[2-(1-*Ethylquinoline*)][2-(3-*ethyl*-4-*methylthiazole*)]-γ-*anilomethyltrimethincyanine Perchlorate Hydroperchlorate* (XII).—From [2-(1-ethylquinoline)][2-(3-ethyl-4-methylthiazole)]-γ-anilomethyltrimethincyanine iodide in alcohol with hydrochloric acid, followed by sodium perchlorate, a 69% yield (0 21 g.) of washed *hydroperchlorate* was obtained. Recrystallisation by use of methyl alcohol (35 c.c.), followed by 60% perchloric acid (35 drops), gave a 46% yield (Found: N, 6·95. $C_{27}H_{29}O_8N_3Cl_2S$ requires N, 6·7%). The purple crystals had m. p. 264° (decomp.).

[2-(1-*Ethylquinoline*)][2-(3-*ethyl*-4-*methylthiazole*)]*trimethincyanine Perchlorate.*—Dilute hydrochloric acid (12 c.c.; 2N.) was added to [2-(1-ethylquinoline)][2-(3-ethyl-4-methylthiazole)]-γ-anilomethyltrimethincyanine iodide (0·5 g.). The resultant red solid dissolved when the mixture was heated; the solution was boiled for 5 minutes and then treated with a hot solution of sodium perchlorate (1 g.) in water (5 c.c.). Addition of aqueous ammonia precipitated the *dye*, which was filtered off when cold and well washed with water (84% yield). After recrystallisation from methyl alcohol (250 c.c. per g.), the yield was 39% (Found : C, 56·7; H, 5·5; Cl, 8·5. $C_{20}H_{23}O_4N_2ClS$ requires C, 56·8; H, 5·5; Cl, 8·4%). The dark green crystals had m. p. 263° (decomp.). Their alcoholic solution was identical in colour with that of the corresponding dye iodide (Hamer, Rathbone, and Winton, *J.*, 1948, 1872).

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-4-*methylthiazole*)]*trimethincyanine Perchlorate.*—By boiling [4-(1-ethylquinoline)][2-(3-ethyl-4-methylthiazole)]-γ-anilomethyltrimethincyanine iodide with dilute hydrochloric acid and treating the solution with sodium perchlorate and ammonia, a 95% yield of dye *perchlorate* resulted. Recrystallisation from methyl alcohol (120 c.c. per g.) gave a 56% yield, which dropped to 35% after a further recrystallisation (Found : C., 8·15. $C_{20}H_{23}O_4N_2ClS$ requires Cl, 8·4%). The dark blue crystals had m. p. 233° (decomp.). Their alcoholic solution was identical in colour with one of the corresponding dye iodide (*loc. cit.*).

[*Bis*-2-(3-*ethylbenzthiazole*)]-α-*anilomethyl*-γ-*methyltrimethincyanine Iodide* (XIII).—A mixture of 2-dianilo*iso*propylidene-3-ethylbenzthiazoline (1·9 g., 1 mol.), 2-ethylbenzthiazole ethiodide (1 mol.), and pyridine (10 c.c.) was heated at 60—65° for 5 minutes. A tar precipitated by absolute ether (70 c.c.) was, after being washed with ether, converted into a solid by treatment with water (80 c.c.). After dissolution of the product (2·60 g.) in 50% aqueous methyl alcohol (30 c.c.) and treatment with water (50 c.c.), the yield was 58% and, after a second such purification, 43% (Found, on a sample dried in a vacuum at 80—100° : I, 20·65. $C_{29}H_{28}N_3IS_2$ requires I, 20·85%). The maroon substance underwent violent decomposition at 194—196°, with darkening from 130°. Absorption curves were difficult to obtain. A freshly prepared methyl-alcoholic solution containing pyridine had the maximum at 5420 A., but one containing sulphuric acid faded too quickly for the maximum in the visible region to be recorded.

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