

237. *Some Trinuclear Cyanine Dyes. Part III. Trinuclear Dimethinmerocyanines and Intermediate Compounds.*

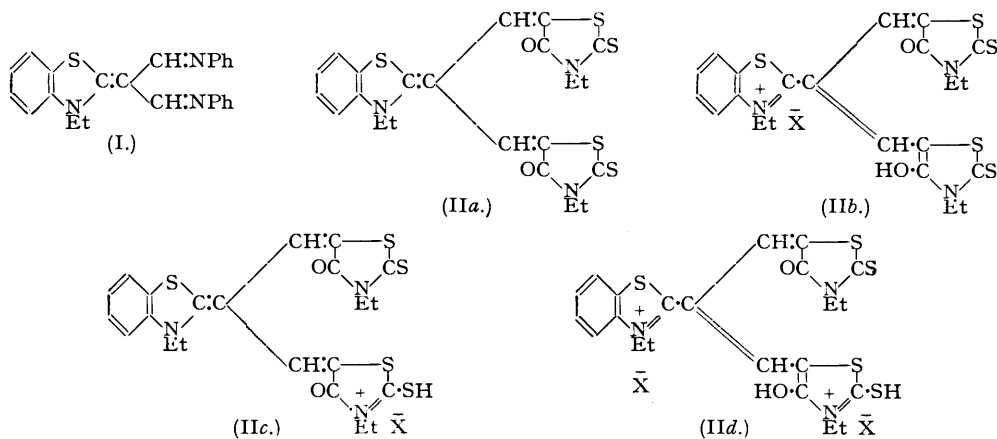
By FRANCES M. HAMER, RUSSELL J. RATHBONE, and BARBARA S. WINTON.

N-Alkyldihydro-derivatives of heterocyclic bases, with a dianiloisopropylidene group in the reactive position, were condensed with two mols. of compounds having a reactive cyclic methylene group, to give *trinuclear dimethinmerocyanines* with the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:} \end{array}$. The dianils were also condensed with one mol., to give intermediate *dinuclear dimethinmerocyanines* having an anilomethyl group. These intermediates yielded (1) *trinuclear dimethinmerocyanines* with two different nuclei terminating the chain, (2) *trinuclear dyes* having the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:CH:} \end{array}$, which were also obtained by an alternative method. Absorption maxima of methyl-alcoholic solutions of the new cyanines were compared with those of simpler ones having chain-systems which build up the complex branched chains.

NEOCYANINES and intermediate dyes were prepared by condensing quaternary, heterocyclic ammonium salts, having a reactive methyl group, with dianilo-compounds, such as (I) (Hamer, Rathbone, and Winton, *J.*, 1947, 1434; 1948, 1872). Such a *neocyanine*, in one of its resonating structures, has the three heterocyclic nuclei attached by the chain $\text{:C} \begin{array}{l} \text{CH:CH:} \\ \text{CH:CH:} \end{array}$.

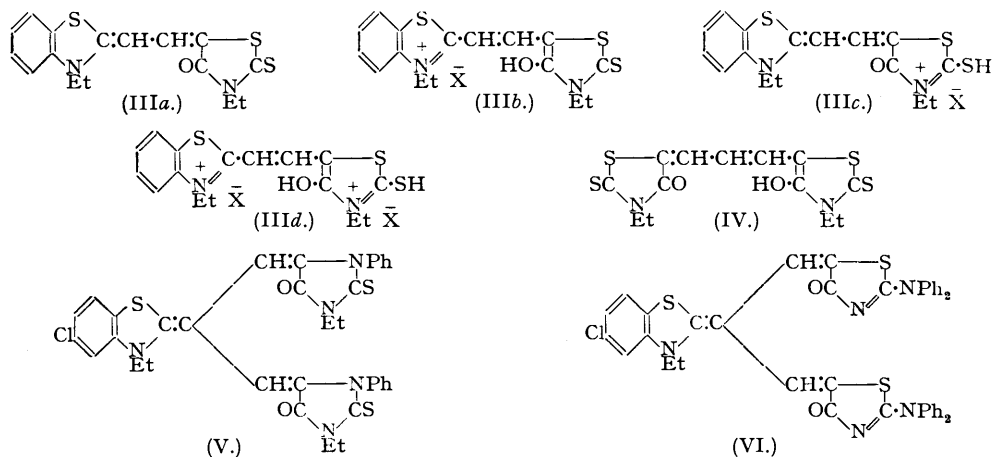
A new type of dye characterised by having three nuclei and the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:} \end{array}$, has now been

prepared by condensing a dianil containing the structure $\text{:C} \begin{matrix} \text{CH:NPh} \\ \text{CH:NPh} \end{matrix}$ with a compound having a reactive cyclic methylene group. For instance, condensation of one molecule of (I) with two of 3-ethylrhodanine gave the dye (IIa). Such a compound may be regarded as derived from the dimethinmerocyanine (IIIa). In theory, addition of acid to (IIa) might give (IIb), (IIc), or



(IIa), etc., which are derived from hypothetical acid forms, (IIIb), (IIIc), and (IIId) of the dimethinmerocyanine. The formulæ (IIb) and (IIc) are also derivable from the trimethin-oxonol (IV).^{*} Other trinuclear dyes of this new type were made. Thus the 5-chloro-derivative of (I) was condensed with two molecules of 3-ethylrhodanine, also with two of 1-phenyl-3-ethyl-2-thiohydantoin to give (V), and with two of 2-diphenylamino-4-keto- Δ^4 -thiazoline (Dixon and Taylor, *J.*, 1912, **101**, 558), to give (VI). Analogues of (I), in which the 3-ethylbenzthiazoline nucleus was replaced by 1-ethyl-1:4-dihydroquinoline, by 4-methyl-3-ethyl- Δ^4 -thiazoline, and by 3-ethylbenzselenazoline, respectively, were condensed with 3-ethylrhodanine to give further compounds of this type; the last two analogues, as also (I) and its analogue having a 3-methylthiazolidine nucleus, were moreover each condensed with two molecules of 4-keto-2-thio-3-ethyltetrahydro-oxazole.

The absorption curves of methyl-alcoholic solutions of the eleven new dyes were plotted. Whereas neocyanines possessed narrow, well-defined curves (Hamer, Rathbone, and Winton,



loc. cit.), in the series with the chain $\text{:C} \begin{matrix} \text{CH} \\ \text{CH} \end{matrix}$ a narrow absorption curve was exceptional, occurring only with dyes having a 4-methyl- Δ^4 -thiazoline nucleus; most of the members had a broad curve, whilst (IIa) itself had a curve with several maxima, such as might normally be attributed to impurities. The principal absorption maximum of each new trinuclear dye was compared

* For the meaning of the term "oxonol," see following paper.

with that of the related dimethinmerocyanine, some of which were prepared for the purpose, but unfortunately only one of the corresponding oxonols was obtainable (Hamer and Winton, succeeding paper). The data are given in Table I. They are discussed together with those of the similar dyes contained in Table III.

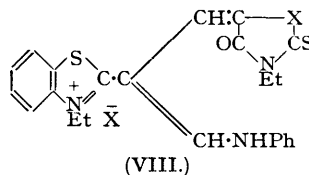
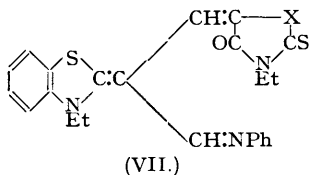
TABLE I.

Dyes with chain: :C(CH) ₂ : 4-q Etrhod Etrhod	Abs. max. (A.).	Dimethinmerocyanines; chain: :CH·CH:	Abs. max. (A.).	Oxonol in alkali; chain: :CH·CH·CH	Abs. max. (A.).	Bathochromic shifts : Dimethinmerocyanine to :C(CH) ₂ : to oxonol
4-q Etrhod Etrhod	5875	4-q Etrhod	6140 †	Etrhod Etrhod	6100 †	-265 225
Etrhod bzth (IIa) Etrhod	5600 etc.	Etrhod bzth	5300 †	Etrhod Etrhod	6100 †	300 500
tetraH-ox bzth tetraH-ox	5120	tetraH-ox bzth	5030 †	tetraH-ox tetraH-ox	—	90 —
Etrhod Clbzth Etrhod	5080	Etrhod Clbzth	5220 †	Etrhod Etrhod	6100 †	-140 1020
thiohyd Clbzth (V) thiohyd	5180	thiohyd Clbzth	5095 *	thiohyd thiohyd	—	85 —
Δ ² -thiaz Clbzth (VI) Δ ² -thiaz	4955	Δ ² -thiaz Clbzth	4925 *	Δ ² -thiaz Δ ² -thiaz	—	30 —
Etrhod Me-th Etrhod	5720	Etrhod Me-th	5390 *	Etrhod Etrhod	6100 †	330 380
tetraH-ox Me-th tetraH-ox	5350	tetraH-ox Me-th	5165 *	tetraH-ox tetraH-ox	—	185 —
Etrhod bzSe Etrhod	5300	Etrhod bzSe	5260 *	Etrhod Etrhod	6100 †	40 800
tetraH-ox bzSe tetraH-ox	5000	tetraH-ox bzSe	4990 *	tetraH-ox tetraH-ox	—	10 —
tetraH-ox thiazoline tetraH-ox	4455 (5030)	tetraH-ox thiazoline	5075	tetraH-ox tetraH-ox	—	-620 —

* Private communication from Dr. L. G. S. Brooker and Mr. F. L. White.

† Hamer and Winton, succeeding paper.

By using comparatively mild conditions, the reaction could be stopped when the dianilo-intermediate had condensed with only one molecular equivalent of the compound having a



reactive cyclic methylene group. For instance, (I) with 3-ethylrhodanine gave (VII; X = S) and with 4-keto-2-thio-3-ethyltetrahydro-oxazole gave (VII; X = O); (I) was also condensed

with one molecule of 3-carboxymethylrhodanine, and the 5-chloro-derivative of (I) with one molecule of 1-phenyl-3-ethyl-2-thiohydantoin or with one of 2-diphenylamino-4-keto- Δ^2 -thiazoline. Analogues of (I) having a 4-methyl-3-ethyl- Δ^2 -thiazoline or a 3-ethylbenzselazoline nucleus were each condensed with one molecule of 3-ethylrhodanine, 4-keto-2-thio-3-ethyltetrahydro-oxazole, or 1-phenyl-3-ethyl-2-thiohydantoin; the analogue having a 3-ethylthiazolidine nucleus was similarly condensed with 3-ethylrhodanine, 4-keto-2-thio-3-ethyltetra-

TABLE

Anilomethyl Compounds. $\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ \\ \text{CH}_2\text{NPh} \end{array}$	Abs. max. Alkali.	(A.). Acid.	Hypso- chromic shifts, alkali to acid.	Dimethin <i>merocyanines</i> ; chain : $\begin{array}{c} \text{CH} \\ \\ \text{CH} \end{array}$	Abs. max. (A.).	Anilo- ethylidene compounds. $\begin{array}{c} \text{CH} \\ \\ \text{CH} \\ \\ \text{NPh} \end{array}$
$\begin{array}{c} \text{Etrhod} \\ \text{bzth} \\ \backslash \text{anMe} \end{array}$ (VII; X = S)	5230	4400	830	$\begin{array}{c} \text{Etrhod} \\ \text{bzth} \end{array}$	5300 *	$\begin{array}{c} \text{bzth} \\ \backslash \text{anMe} \end{array}$
$\begin{array}{c} \text{tetraH-ox} \\ \text{bzth} \\ \backslash \text{anMe} \end{array}$ (VII; X = O)	4975	4100	875	$\begin{array}{c} \text{tetraH-ox} \\ \text{bzth} \end{array}$	5030 *	„
$\begin{array}{c} \text{rhod}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{bzth} \\ \backslash \text{anMe} \end{array}$	5055	4395	660	$\begin{array}{c} \text{rhod}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{bzth} \end{array}$	5025 *	„
$\begin{array}{c} \text{thiohyd} \\ \text{Clbzth} \\ \backslash \text{anMe} \end{array}$	5110	4300	810	$\begin{array}{c} \text{thiohyd} \\ \text{Clbzth} \end{array}$	5095 *	$\begin{array}{c} \text{Clbzth} \\ \backslash \text{anMe} \end{array}$
$\begin{array}{c} \Delta^2\text{-thiaz} \\ \text{Clbzth} \\ \backslash \text{anMe} \end{array}$	4835	4250	585	$\begin{array}{c} \Delta^2\text{-thiaz} \\ \text{Clbzth} \end{array}$	4925 •	„
$\begin{array}{c} \text{Etrhod} \\ \text{Me-th} \\ \backslash \text{anMe} \end{array}$	4685	4465	220	$\begin{array}{c} \text{Etrhod} \\ \text{Me-th} \end{array}$	5390 *	$\begin{array}{c} \text{Me-th} \\ \backslash \text{anMe} \end{array}$
$\begin{array}{c} \text{tetraH-ox} \\ \text{Me-th} \\ \backslash \text{anMe} \end{array}$	4510	4150	360	$\begin{array}{c} \text{tetraH-ox} \\ \text{Me-th} \end{array}$	5165 *	„
$\begin{array}{c} \text{thiohyd} \\ \text{Me-th} \\ \backslash \text{anMe} \end{array}$	4860	4470	390	$\begin{array}{c} \text{thiohyd} \\ \text{Me-th} \end{array}$	5290 *	„
$\begin{array}{c} \text{Etrhod} \\ \text{bzSe} \\ \backslash \text{anMe} \end{array}$	5100	4400	700	$\begin{array}{c} \text{Etrhod} \\ \text{bzSe} \end{array}$	5260 *	$\begin{array}{c} \text{bzSe} \\ \backslash \text{anMe} \end{array}$
$\begin{array}{c} \text{tetraH-ox} \\ \text{bzSe} \\ \backslash \text{anMe} \end{array}$	4850	4105	745	$\begin{array}{c} \text{tetraH-ox} \\ \text{bzSe} \end{array}$	4990 *	„
$\begin{array}{c} \text{thiohyd} \\ \text{bzSe} \\ \backslash \text{anMe} \end{array}$	5055	4290	765	$\begin{array}{c} \text{thiohyd} \\ \text{bzSe} \end{array}$	5140 *	„
$\begin{array}{c} \text{Etrhod} \\ \text{thiazoline} \\ \backslash \text{anMe} \end{array}$	4825	4410	415	$\begin{array}{c} \text{Etrhod} \\ \text{thiazoline} \end{array}$	4825	$\begin{array}{c} \text{thiazoline} \\ \backslash \text{anMe} \end{array}$
$\begin{array}{c} \text{tetraH-ox} \\ \text{thiazoline} \\ \backslash \text{anMe} \end{array}$	4370	4110	260	$\begin{array}{c} \text{tetraH-ox} \\ \text{thiazoline} \end{array}$	4575	„
$\begin{array}{c} \Delta^2\text{-thiaz} \\ \text{thiazoline} \\ \backslash \text{anMe} \end{array}$	4380	3990	390	$\begin{array}{c} \Delta^2\text{-thiaz} \\ \text{thiazoline} \end{array}$	4600	„

* Private communication from Dr. L. G. S. Brooker and Mr. F. L. White.

† Hamer and Winton, succeeding paper.

hydro-oxazole, and 2-diphenylamino-4-keto- Δ^2 -thiazoline. The conditions for success in the above condensations varied greatly according to the nature of the reactants. Although boiling pyridine was usually the medium, sometimes this was too drastic and a temperature of 50—70° was desirable. In other instances still milder conditions were necessary, comprising condensation in boiling, or even in ice-cold, absolute alcohol.

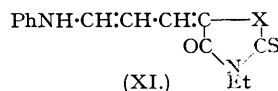
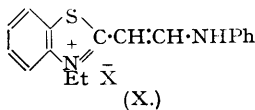
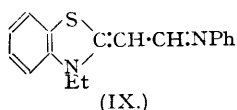
In Table II the absorption maxima of basified methyl-alcoholic solutions of intermediate

II.

Abs. max. Base.	(A.) Salt.	Batho- chromic shifts, base to salt.	Anilino- allylidene compounds; chain: :CH·CH:CH·NHPH	Abs. max. (A.).	Bathochromic shifts (A.).			
					AniloMe base to dimethin- mero- cyanine.	Bases. Anilo- ethyl- idene to AniloMe.	Salts. Anilo- ethyl- idene to AniloMe.	AniloMe salt to anilino- allylidene compound.
3935 ‡	4175 ‡	240	Etrhod anMe	4775 (alk.) †	70	1295	225	375
"	"	"	tetraH-ox anMe	4460 †	55	1040	-75	360
"	"	"	rhod·CH ₂ ·CO ₂ H anMe	4800 (acid) †	-30	1120	220	405
4075 ‡	4205 ‡	130	thiohyd anMe	4650 †	-15	1035	95	350
"	"	"	Δ^2 -thiaz anMe	4680 (acid) †	90	760	45	430
4090 ‡	4030 ‡	-60	Etrhod anMe	4775 (alk.) †	705	595	435	310
"	"	"	tetraH-ox anMe	4460 †	655	420	120	310
"	"	"	thiohyd anMe	4650 †	430	770	440	180
3940 ‡	4235 ‡	295	Etrhod anMe	4775 (alk.) †	160	1160	165	375
"	"	"	tetraH-ox anMe	4460 †	140	910	-130	355
"	"	"	thiohyd anMe	4650 †	85	1115	55	360
3585 ‡	3660 ‡	75	Etrhod anMe	4775 (alk.) †	0	1240	750	365
"	"	"	tetraH-ox anMe	4460 †	205	785	450	350
"	"	"	Δ^2 -thiaz anMe	4680 (acid) †	220	795	330	690

‡ See Hamer, Rathbone, and Winton, *J.*, 1947, 954, for data about 3-ethyl-2-aniloethylidenebenzthiazoline, 5-chloro-3-ethyl-2-aniloethylidenebenzthiazoline, 4-methyl-3-ethyl-2-aniloethylidene- Δ^4 -thiazoline, 3-ethyl-2-aniloethylidenebenzselenazoline, 3-ethyl-2-aniloethylidenethiazolidine, and corresponding salts.

dyes, characterised by the chain $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:NPh} \end{matrix}$, were compared on the one hand with those of methyl-alcoholic solutions of parent dimethinmerocyanines having the chain $\text{:CH}\cdot\text{CH:}$, and on the other with alkaline methyl-alcoholic solutions containing parent bases with the chain $\text{:CH}\cdot\text{CH:NPh}$. Thus (VII; X = S) was correlated with (IIIa) and with (IX). Further, the absorption maxima of acidified methyl-alcoholic solutions of intermediate dyes containing salts such as (VIII) were compared with acidified solutions containing quaternary salts, such as (X), and also with heterocyclic anilinoallylidene compounds such as (XI; X = S). Whereas on passing from five parent aniloethylidene bases to the corresponding salts there was only one hypsochromic shift, of 60 Å., and four bathochromic, varying from 75 to 295 Å., yet on passing



from dinuclear anilomethyl bases (such as VII) to acid salts (such as VIII), all fourteen shifts were hypsochromic, varying from 220 to 875 Å. With the somewhat similar anilomethyl compounds of Part II (*J.*, 1948, 1872), ten out of twelve showed a hypsochromic shift on passing from base to salt. On passing from each of the present new anilomethyl bases to the related dimethinmerocyanine, there were two hypsochromic shifts, of 15 Å. and 30 Å., one case of no change, and eleven bathochromic shifts, which varied from 55 to 705 Å. On passing from mononuclear aniloethylidene bases (*e.g.*, IX) to the corresponding dinuclear anilomethyl bases (*e.g.*, VII), the shifts were all bathochromic, varying in the fourteen instances from 420 to 1295 Å.; so also with the similar substances of Part II, all twelve shifts were bathochromic (*loc. cit.*). On passing from the mononuclear β -anilino vinyl salts (*e.g.*, X) to the corresponding acidified dinuclear intermediate compounds (*e.g.*, VIII), ten of the twelve shifts of absorption maximum were bathochromic, varying from 45 to 750 Å., and the other two were hypsochromic, of 75 Å. and 130 Å. It seemed logical to compare the mononuclear heterocyclic compounds having the chain $\text{:CH}\cdot\text{CH:CH}\cdot\text{NHPH}$, *e.g.*, (XI), with the acidified dinuclear anilomethyl compounds, *e.g.*, (VIII), having the chain $\text{-CH}\cdot\text{C:CH}\cdot\text{NHPH}$, and here, with fourteen pairs, the absorption maximum of the mononuclear compound always lay at a longer wave-length than that of its dinuclear derivative, the amounts varying from 180 to 690 Å.

TABLE III.

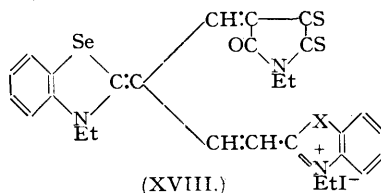
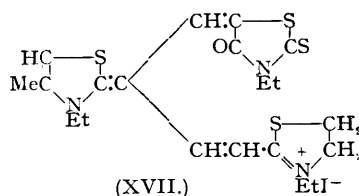
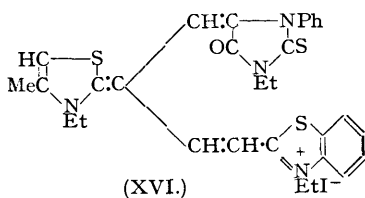
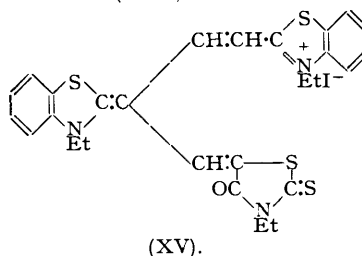
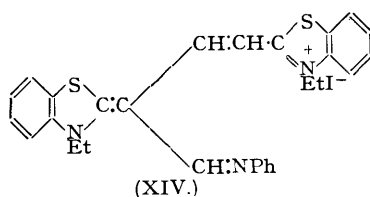
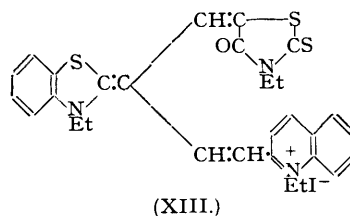
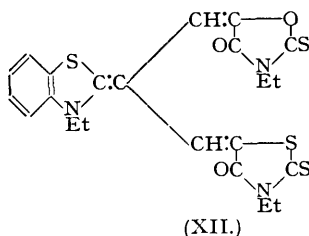
Dyes with chain :	Abs. max. (Å.).	Dimethinmerocyanines : chain : $\text{:CH}\cdot\text{CH:}$	Abs. max. (Å.).	Bathochromic shifts (Å.). Dimethinmerocyanine to $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:} \end{matrix}$
bzth $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox (XII)} \end{matrix}$	5475	bzth $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox} \end{matrix}$	5300	175
Me-th $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox} \end{matrix}$	5545	Me-th $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox} \end{matrix}$	5390 *	155
bzSe $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox} \end{matrix}$	5190	bzSe $\begin{matrix} \text{Etrhod} \\ \text{tetraH-ox} \end{matrix}$	5260 *	-70
			4990 *	200

* Private communication from Dr. L. G. S. Brooker and Mr. F. L. White.

The new intermediate compounds with the chain $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:NPh} \end{matrix}$ made it possible to arrive at dyes having the chain $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:} \end{matrix}$ but differing from those in the earlier part of this paper in that the nuclei terminating the trimethin chain are dissimilar instead of similar. Theoretically each of these new dyes may be reached by either of two routes. We prepared three such dyes. The

first was obtained by condensing (VII; X = O) with 3-ethylrhodanine and is represented by (XII). In the other two the 3-ethylbenzthiazoline nucleus of (XII) was replaced by the 4-methyl-3-ethyl- Δ^4 -thiazoline nucleus and the 3-ethylbenzselenzoline nucleus, respectively, but each was prepared by condensing the analogue of (VII; X = S) with 4-keto-2-thio-3-ethyltetrahydro-oxazole.

The absorption maxima of methyl-alcoholic solutions of these new dyes are correlated in Table III with those of the related dimethinmerocyanines. Whereas each dye having the chain $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:} \end{matrix}$ in Table I was comparable with one dimethinmerocyanine, each in Table III was comparable with two such parent dyes. Summarising the two tables together, the shift of absorption maximum in passing from dimethinmerocyanine to trinuclear dye was bathochromic in thirteen out of seventeen instances, the values varying from 10 to 445 Å., whilst the four hypsochromic values varied from 70 to 620 Å. The absorption maximum of an alkaline solution of the oxonol (IV) was correlated with those of solutions of five trinuclear dyes having the chain $\text{:C} \begin{matrix} \text{CH:} \\ \text{CH:} \end{matrix}$. It always lay at a longer wave-length, the values of the differences varying from 225 to 1020 Å.



By condensing the new type of intermediate dye with a quaternary salt having a reactive methyl group, yet another new kind of dye, characterised by possessing the chain $\text{:C} \begin{matrix} \text{CH:CH} \\ \text{CH:} \end{matrix}$, was obtained. Thus (XIII) was prepared by condensation of (VII; X = S) with quinaldine, ethiodide. Dyes of this new group are also obtainable by a second route, according to which the intermediate dyes of Part II (*J.*, 1948, 1872) are condensed with compounds having a reactive cyclic methylene group. Thus condensation of (XIV) (*loc. cit.*) with 3-ethylrhodanine gave

TABLE IV.

Dye with chain : $\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XIII)	Abs. max. (A.)	Trimethin- cyanines : $\begin{array}{c} \text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ ^{2q} / bzth	Abs. max. (A.)	Dimethin- <i>mero-</i> cyanines : $\begin{array}{c} \text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ bzth \ Etrhod	Abs. max. (A.)	Tetramethin- <i>merocyanines</i> : $\begin{array}{c} \text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ ^{2-q} / Etrhod	Abs. max. (A.)	Bathochromic shifts (A.)
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ ^{2q} / Etrhod	6080	5600 ¶	5300	6575	480	780	-495	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XV)	5750	5570 †	"	5950	180	450	-200	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ Me-th \ Etrhod	5750	5470 §	5390 *	"	280	360	-200	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ Me-th \ Etrhod	5945	5660	"	5700	285	555	—	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XVII)	5360	4995 §	"	5700	365	-30	-340	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XVI)	5765	5470 §	5290 *	5650	295	475	115	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XVIII; X = S)	5800	5620 †	5260 *	5950	180	540	-150	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ bzSe \ Etrhod	5930	5810 †	"	5590	120	670	—	
$\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{C} \\ \\ \text{CH} \end{array}$ (XVIII; X = Se)	5820	5700 †	"	5590	120	560	230	

* Private communication from Dr. L. G. S. Brooker and Mr. F. L. White.

§ Hamer, Rathbone, and Winton, *J.*, 1948, 1872.

¶ Hamer and Winton, succeeding paper.

† Beilenson, Fisher, and Hamer, *ibid.*, 1937, 4, 163, 138.‡ 5780 A. is given by Brooker and Sprague (*J. Amer. Chem. Soc.*, 1941, 63, 3203).

(XV). Two more dyes of this type were prepared by condensing an analogue of (VII; X = S), having a 4-methyl-3-ethyl- Δ^4 -thiazoline in place of the benzthiazoline nucleus, with 2-methylbenzthiazole ethiodide and with its 6:7-benz-derivative, respectively; a third (XVI) was also obtained by this type of reaction. (XVII), however, was obtained by reaction of the appropriate intermediate of the other type (*loc. cit.*) with 3-ethylrhodanine. An analogue of (VII; X = S), having the 3-ethylbenzselenzoline in place of the 3-ethylbenzthiazoline nucleus, was condensed with 2-methylbenzthiazole ethiodide to give (XVIII; X = S), with 2-methyl-6:7-benzbenzthiazole ethiodide to give the 6:7 benz-derivative of (XVIII; X = S), and with 2-methylbenzselenzole ethiodide to give (XVIII; X = Se).

The absorption maximum of each new dye having the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:CH} \end{array}$ may be compared with that of a trimethincyanine, of a dimethinmerocyanine, and of a tetramethinmerocyanine. It appears from Table IV that with all nine pairs there was a bathochromic shift on passing from trimethincyanine to trinuclear dye, these shifts varying from 120 to 480 Å. With eight out of nine pairs, there was a bathochromic shift on passing from dimethinmerocyanine to trinuclear dye, the values of the shifts varying from 360 to 780 Å., and there was one hypsochromic shift of 30 Å. On passing from tetramethinmerocyanine to trinuclear dye, there were, however, out of seven pairs, only two bathochromic shifts, of 115 Å. and 230 Å., the other five being hypsochromic, varying from 150 to 495 Å.

Photographic tests were carried out on gelatino-bromide plates except where otherwise stated. Some of the anilomethyl intermediate dyes sensitised strongly but the trinuclear dyes with the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:} \end{array}$ sensitised only weakly and sometimes desensitised, whilst those with the chain $\text{:C} \begin{array}{l} \text{CH:} \\ \text{CH:CH} \end{array}$ were mostly characterised by possessing only desensitising properties.

Nomenclature.—In the experimental section of the paper, the nomenclature is that explained in Part I (*J.*, 1947, 1434), the shorter methin chain being taken as the fundamental one, as is done there and in Part II (*J.*, 1948, 1872). All the new dyes of the present paper are therefore named as dimethinmerocyanines, the nomenclature of which is explained elsewhere (Hamer and Winton, succeeding paper).

EXPERIMENTAL.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)][β -methin-5'-(3'-ethylrhodanine)]dimethinmerocyanine (IIa).—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (I) (0.38 g.; 1 mol.), 3-ethylrhodanine (0.48 g.; 3 mols.), anhydrous sodium acetate (0.49 g.; 6 mols.), and acetic anhydride (5 c.c.) were heated together at 140–150° for 10 minutes. Absolute ether (20 c.c.) precipitated a solid from the reaction mixture. After washing with ether and with water (0.41 g. left), this was recrystallised from pyridine and obtained in 64% yield. It was dried in a vacuum at 60–80° and analysed by the method of Carius, which conditions were used throughout this work unless otherwise stated (Found: S, 31.1. $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}_3\text{S}_5$ requires S, 30.85%). The green and gold crystals had m. p. 229°, with previous shrinking. The broad absorption band had maxima at 5090, 5225, 5350, and 5600 Å. The compound was a photographic desensitiser.

When the condensing agent was hot pyridine, the product was liable to consist of a mixture of (IIa) with [5-(3-ethylrhodanine)][2-(3-ethylbenzthiazoline)] β -anilomethyldimethinmerocyanine (VII; X = S).

In a second method of preparation, (VII; X = S) (0.45 g.; 1 mol.), 3-ethylrhodanine (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (10 c.c.) were stirred together at 140–150° for 5 minutes. The dye was precipitated with absolute ether, washed (0.45 g. obtained), and recrystallised from pyridine, resulting in 70% yield (Found: S, 30.8%).

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzthiazoline)][β -methin-5'-(4'-keto-2'-thio-3'-ethyltetrahydro-oxazole)]dimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (1.03 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2 mols.), anhydrous sodium acetate (8 mols.), and acetic anhydride (13 c.c.) were heated together at 140–150° for 2 minutes. After cooling, filtering off, and washing with water, the residue (0.55 g.) was recrystallised from pyridine (5 c.c.) and gave a 37% yield (Found: S, 19.75. $\text{C}_{22}\text{H}_{21}\text{O}_4\text{N}_3\text{S}_3$ requires S, 19.75%). The dark red crystals darkened from 210° and had m. p. 228° (decomp.). The broad absorption curve had its maximum at 5120 Å. The dye sensitised weakly to 6200 Å., with the maximum at 5600 Å., and depressed the normal blue speed.

[5-(3-Ethylrhodanine)][2-(5-chloro-3-ethylbenzthiazoline)][β -methin-5'-(3'-ethylrhodanine)]dimethinmerocyanine.—5-Chloro-3-ethyl-2-dianiloisopropylidenebenzthiazoline (2.60 g.; 1 mol.), 3-ethylrhodanine (3 mols.), and pyridine (25 c.c.) were stirred together at 130–135° for 5 minutes. The liquid was treated with water and cooled and some dye was filtered off (0.68 g.). To obtain more, the filtrate was extracted with ether and the extract concentrated and treated with water (1.22 g. obtained). The total product (1.90 g.) was freed from a brown impurity by Soxhlet extraction with ether and the residue (1.04 g.), after recrystallisation from pyridine (10 c.c. per g.), gave a 23% yield (Found: Cl, 6.75. $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_3\text{ClS}_5$ requires Cl, 6.4%). The bronze powder had m. p. 128–130° (decomp.), with previous shrinking. The broad absorption curve had its maximum at 5880 Å. Weak sensitising was from 5500 to 5900 Å., with strong decrease of blue sensitivity.

[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(5-chloro-3-ethylbenzthiazoline)][β -methin-5'-(1'-phenyl-3'-ethyl-2'-thiohydantoin)]dimethinmerocyanine (V).—The reaction mixture from 5-chloro-3-ethyl-2-dianilo-

isopropylidenebenzthiazoline (3.12 g.; 1 mol.), 1-phenyl-3-ethyl-2-thiohydantoin (3 mols.), anhydrous sodium acetate (6 mols.), and acetic anhydride (20 c.c.), after 10 minutes at 140—150°, was treated with ether (120 c.c.), and sodium acetate was filtered off. The ether was distilled off from the filtrate, and the residual liquid treated with water. The resultant sticky product was recrystallised from methyl alcohol (300 c.c.) (2.85 g. obtained). After boiling out with, and recrystallising from, methyl alcohol (8 c.c., 300 c.c.), the yield was 13% (Found: Cl, 5.45. $C_{34}H_{30}O_2N_5ClS_3$ requires Cl, 5.3%). The dark green crystals had m. p. 174° (decomp.). The broad absorption curve had its maximum at 5180 Å. The dye decreased the normal photographic sensitivity, whilst conferring extra sensitivity up to 6700 Å., with the maximum effect at 6150 Å.

[5-(2-Diphenylamino-4-keto- Δ^2 -thiazoline)][2-(5-chloro-3-ethylbenzthiazoline)][β -methin-5'-(2'-diphenylamino-4'-keto- Δ^2 -thiazoline)]dimethinmerocyanine (VI).—This was similarly prepared, 2-diphenylamino-4-keto- Δ^2 -thiazoline being used instead of the thiohydantoin. Ether precipitated the product; after water-washing the yield was 78% and after recrystallisation from pyridine (3 c.c. per g.) 44% (Found: Cl, 4.7. $C_{42}H_{30}O_2N_5ClS_3$ requires Cl, 4.6%). The terra-cotta powder had m. p. 193—194° (decomp.). The broad absorption curve had its maximum at 4955 Å., sloping down to a shoulder at 4700 Å. There was no photographic sensitisation but slight depression of blue sensitivity.

In an attempt to use pyridine as condensing agent, the product was unsatisfactory, unchanged reagents being recovered.

[5-(3-Ethylrhodanine)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][β -methin-5'-(3'-ethylrhodanine)]dimethinmerocyanine.—4-Methyl-3-ethyl-2-dianiloisopropylidene- Δ^4 -thiazoline (1.39 g.; 1 mol.), 3-ethylrhodanine (3 mols.), and pyridine (10 c.c.) were heated together at 130° for 3 minutes, and the reaction mixture was poured into water (150 c.c.). The resultant tar was induced to solidify by treatment with spirit and was crystallised from pyridine (10 c.c.), being obtained in 57% yield (Found: S, 33.35. $C_{19}H_{21}O_2N_3S_2$ requires S, 33.15%). The greyish blue crystals had m. p. 223° (decomp.). The narrow absorption curve had its maximum at 5720 Å. and an inflexion at 5220 Å. The substance considerably reduced the normal sensitivity of a photographic plate, whilst sensitising weakly to 6600 Å. with the maximum at 6450 Å.

With sodium acetate in acetic anhydride as condensing agent, in place of pyridine, the yield was substantially the same (54%).

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][β -methin-5'-(4'-keto-2'-thio-3'-ethyltetrahydro-oxazole)]dimethinmerocyanine.—4-Methyl-3-ethyl-2-dianiloisopropylidene- Δ^4 -thiazoline (1.39 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (3 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (20 c.c.) were heated at 145—150° for 7 minutes, and the mixture poured into water. The tarry product was caused to solidify by means of spirit and was crystallised from methyl alcohol (60 c.c.), being obtained in 28% yield (Found: S, 21.35. $C_{16}H_{21}O_4N_3S_2$ requires S, 21.3%). The dark purple crystals had m. p. 189° (decomp.). The narrow absorption curve had its maximum at 5350 Å. and an inflexion at 5000 Å. The compound sensitised very weakly to 5700 Å., the maximum being at 5400 Å., and it considerably decreased the normal sensitivity.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzselenaazoline)][β -methin-5'-(3'-ethylrhodanine)]dimethinmerocyanine.—This was similarly prepared from 3-ethyl-2-dianiloisopropylidenebenzselenaazoline, 3-ethylrhodanine, and sodium acetate in acetic anhydride, precipitated by ether, ground with water, and washed with spirit (88% yield). It was recrystallised from a mixture of ethyl alcohol and pyridine (16 c.c. of each per g.) and obtained in 75% yield. In this and other instances, nitrogen was determined by the method of Dumas (Found: N, 7.55. $C_{22}H_{21}O_2N_3S_4Se$ requires N, 7.4%). The dark green and gold crystals had m. p. 206° (decomp.). The broad absorption curve had its maximum at 5300 Å. and an inflexion at 5700 Å. To a photographic plate the dye imparted a trace of sensitisation, with the maximum about 5850 Å., and decreased the normal blue sensitivity.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzselenaazoline)][β -methin-5'-(4'-keto-2'-thio-3'-ethyltetrahydro-oxazole)]dimethinmerocyanine.—3-Ethylrhodanine in the preceding preparation was replaced by 4-keto-2-thio-3-ethyltetrahydro-oxazole and heating at 145—150° was for 15 minutes. After ether-precipitation and water-washing the product (61% yield) was boiled out with methyl alcohol (10 c.c. per g.) and recrystallised from a mixture of methyl alcohol and pyridine (15 c.c. of each per g.), giving a 48% yield (Found: N, 7.95. $C_{22}H_{21}O_4N_3S_2Se$ requires N, 7.85%). The scarlet crystals had m. p. 231° (decomp.). The broad absorption curve had its principal maximum at 5000 Å., a slightly weaker one at 5150 Å., and a shoulder at 5300 Å. The dye reduced the normal sensitivity of a plate but caused extra-sensitivity to 6200 Å. with the maximum at 5550 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-methylthiazolidine)][β -methin-5'-(4'-keto-2'-thio-3'-ethyltetrahydro-oxazole)]dimethinmerocyanine.—3-Methyl-2-dianiloisopropylidene-thiazolidine (1.61 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2.2 mols.), anhydrous sodium acetate (6 mols.), and acetic anhydride (8 c.c.) were heated together at 130—140° for 5 minutes. The solid was filtered off, washed (45% yield), and recrystallised from pyridine (5 c.c. per g.), resulting in 27% yield (Found: S, 22.3. $C_{17}H_{19}O_4N_3S_2$ requires S, 22.6%). The reddish-orange solid had m. p. about 229° with previous darkening and shrinking. Of two absorption maxima at 4455 and 5030 Å., the former was the stronger. The substance strongly sensitised a gelatino-chloride photographic plate, with the maximum at 4500 Å., sensitisation extending to 5700 Å. for moderate exposures.

[4-(1-Ethylidihydroquinoline)][5-(3-ethylrhodanine)][α -methin-5'-(3'-ethylrhodanine)]dimethinmerocyanine.—A mixture of crude 1-ethyl-4-dianiloisopropylidene-1:4-dihydroquinoline (1.89 g.; 1 mol.), 3-ethylrhodanine (3 mols.), anhydrous sodium acetate (8 mols.), and acetic anhydride (20 c.c.) was stirred at 140—150° for 2 minutes. The solid was filtered off, washed (24% yield), and recrystallised from pyridine and water (22 c.c. of each per g.), leaving a 21% yield (Found: S, 25.1. $C_{24}H_{23}O_2N_3S_4$ requires S, 25.0%). The dark blue crystals had m. p. about 285° (decomp.). The absorption maximum was at 5875 Å. The compound did not sensitise and decreased the normal blue sensitivity of the plate.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)]- β -anilomethyl dimethinmerocyanine (VII; X = S).—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (2 g.; 1 mol.), 3-ethylrhodanine (0.84 g.; 1 mol.), and pyridine (10 c.c.) were stirred together at 50—60° for 10 minutes. The solid precipitated by absolute ether (50 c.c.) (89% yield) was thrice boiled out with methyl alcohol (3 × 20 c.c.), leaving an 84% yield

(Found: S, 21.25. $C_{22}H_{21}ON_3S_3$ requires S, 21.3%). On recrystallisation from pyridine (9 c.c. per g.), the yield dropped to 60% (Found: S, 21.45%). The red crystals began to blacken at about 175°, were quite black and shrunken by 185°, and had m. p. about 195° (decomp.). A methyl-alcoholic solution was red at pH 6.0 and yellow at pH 5.3. One containing ammonia had its absorption maximum at 5230 Å. and one containing sulphuric acid at 4400 Å. The dye strongly sensitised a gelatino-chloride plate; the maximum was at 5750 Å. and sensitisation extended to 6400 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzthiazoline)]-β-anilomethylidimethinmerocyanine (VII; X = O).—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (3.83 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2 mols.), and pyridine (20 c.c.) were stirred together at 50–63° for 30 minutes. The product precipitated by ether (200 c.c.) amounted to a 72% yield and, after boiling out with methyl alcohol (25 c.c.), a 71% yield remained (Found: S, 14.55. $C_{33}H_{31}O_2N_3S_2$ requires S, 14.75%). The red solid began to darken at about 195° and had m. p. at about 208° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4975 Å., and of one containing sulphuric acid at 4100 Å. The substance sensitised a gelatino-chloride plate to 5400 Å. with the maximum at 4800 Å.

[5-(Pyridinium 3-carboxymethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethylidimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (1.56 g.; 1 mol.), 3-carboxymethylrhodanine (1 mol.), and pyridine (20 c.c.) were heated together at 60–70° for 10 minutes, and the product precipitated with absolute ether. After being washed with water and with ether (1.87 g. left), it was boiled out with methyl alcohol (4 × 25 c.c.), and the residue was recrystallised from methyl alcohol (700 c.c.) (0.92 g. obtained), and again from methyl alcohol (500 c.c. per g.), giving a 22% yield (Found: S, 17.05. $C_{29}H_{19}O_3N_3S_3$ requires S, 17.15%). The flame-coloured crystals had m. p. 174° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 5055 Å. with a secondary maximum at 4405 Å.; one containing pyridine had maxima at 4325 Å. and 5030 Å., the former being the principal one. One containing sulphuric acid had its maximum at 4395 Å. The substance sensitised a gelatino-chloride plate strongly to 6300 Å. with the maximum at 5750 Å.

[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(5-chloro-3-ethylbenzthiazoline)]-β-anilomethylidimethinmerocyanine.—5-Chloro-3-ethyl-2-dianiloisopropylidenebenzthiazoline (1.56 g.; 1 mol.), 1-phenyl-3-ethyl-2-thiohydantoin (3 mols.), and pyridine (15 c.c.) were heated together at 130–135° for 5 minutes. The product (2.81 g.), precipitated by water, was boiled out twice with methyl alcohol (40 c.c., 500 c.c.). The residue (1.35 g.) was taken up in hot acetic acid (3 c.c.) and precipitated by ether in 52% yield (Found: Cl, 6.25. $C_{39}H_{35}ON_4ClS_2$ requires Cl, 6.5%). The brick-red powder had m. p. 242–243° (decomp.), with shrinking from 137°. A methyl-alcoholic solution containing ammonia had the absorption maximum at 5110 Å. and one containing sulphuric acid at 4300 Å. The compound sensitised a gelatino-chloride emulsion to 6000 Å. with the maximum at 5500 Å.

[5-(2-Diphenylamino-4-keto-Δ²-thiazoline)][2-(5-chloro-3-ethylbenzthiazoline)]-β-anilomethylidimethinmerocyanine.—This was prepared by heating 5-chloro-3-ethyl-2-dianiloisopropylidenebenzthiazoline (1.03 g.; 1 mol.), 2-diphenylamino-4-keto-Δ²-thiazoline (3 mols.) and pyridine (10 c.c.) in a steam-bath for 9 hours. The precipitate obtained by ether was thrice boiled out with methyl alcohol (15 c.c., 2 × 25 c.c.) and, by recrystallising from pyridine (10 c.c.), obtained in 47% yield (Found: Cl, 6.3. $C_{33}H_{25}ON_4ClS_2$ requires Cl, 6.0%). The bright yellow powder had m. p. 247–248° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4835 Å. and one containing sulphuric acid at 4250 Å. The substance sensitised a chloride plate to 5900 Å. with the maximum at 5200 Å.

[2-(4-Methyl-3-ethyl-Δ⁴-thiazoline)][5-(3-ethylrhodanine)]-α-anilomethylidimethinmerocyanine.—4-Methyl-3-ethyl-2-dianiloisopropylidene-Δ⁴-thiazoline (0.69 g.; 1 mol.), 3-ethylrhodanine (1.5 mols.), and absolute ethyl alcohol (7 c.c.) were boiled and stirred together for 2 minutes. After cooling, the dye was filtered off and washed (73% yield). On recrystallising from a mixture of ethyl alcohol (5 c.c.) and pyridine (2 c.c.), the yield was 65% (Found: S, 23.35. $C_{26}H_{21}ON_3S_3$ requires S, 23.15%). The crimson crystals had m. p. 182° (decomp.). A methyl-alcoholic solution was orange red at pH 7.8 and bright yellow at pH 6.8; one containing ammonia had its principal maximum at 4685 Å., with a weaker one at 4830 Å., and one containing sulphuric acid had the maximum at 4465 Å. The compound sensitised a chloride plate to 6400 Å. with the maximum at 5850 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(4-methyl-3-ethyl-Δ⁴-thiazoline)]-β-anilomethylidimethinmerocyanine.—4-Methyl-3-ethyl-2-dianiloisopropylidene-Δ⁴-thiazoline (1.74 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2.2 mols.), and pyridine (10 c.c.) were stirred together at 130° for 5 minutes and the resultant solution was poured into water. After decanting off the liquid, the residue was boiled out with ethyl alcohol (10 c.c.) and recrystallised from methyl alcohol (40 c.c.), giving a 47% yield (Found: S, 16.2. $C_{30}H_{21}O_2N_3S_3$ requires S, 16.05%). The bright orange crystals had m. p. 155° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4510 Å. and one containing sulphuric acid at 4150 Å. The compound sensitised a chloride plate weakly up to 5700 Å., the maximum lying at 5200 Å.; the normal blue sensitivity was decreased.

[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(4-methyl-3-ethyl-Δ⁴-thiazoline)]-β-anilomethylidimethinmerocyanine.—4-Methyl-3-ethyl-2-dianiloisopropylidene-Δ⁴-thiazoline (3.47 g.; 1 mol.), 1-phenyl-3-ethyl-2-thiohydantoin (1.5 mols.), and ethyl alcohol (20 c.c.) were boiled together with stirring for 3 minutes. The dye was filtered off and boiled out twice with methyl alcohol (2 × 75 c.c.), the residue amounting to a 92% yield (Found: S, 13.3. $C_{28}H_{24}ON_4S_3$ requires S, 13.5%). A preparation similarly carried out in boiling pyridine for 4 minutes was poured into water and the crude dye was boiled out with methyl alcohol (30 c.c.) and recrystallised from pyridine (15 c.c.), giving a 68% yield (Found: S, 13.35%). The maroon and gold crystals had m. p. 222° (decomp.). Their methyl-alcoholic solution was orange red at pH 8.4 and bright yellow at pH 6.8. One containing ammonia had its absorption maximum at 4860 Å., and one containing sulphuric acid at 4470 Å. The dye sensitised a chloride emulsion very weakly with the maximum at 4850 Å., sensitisation extending to 5200 Å.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethylidimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidenebenzthiazoline (0.86 g.; 1 mol.), 3-ethylrhodanine (3 mols.), and pyridine (5 c.c.) were heated together at 120° for 3 minutes. The precipitate (0.91 g.) obtained with ether was recrystallised from a mixture of pyridine (10 c.c.) and methyl alcohol (10 c.c.) and resulted in 80% yield (Found:

N, 8.55. $C_{23}H_{21}ON_3S_2Se$ requires N, 8.45%). The lustrous vermilion crystals had m. p. 197° (decomp.). A methyl-alcoholic solution was pink at pH 4.6 and bright yellow at pH 3.9. One containing ammonia had its absorption maximum at 5100 Å., and one containing sulphuric acid at 4400 Å., with an inflexion to the curve at 4540 Å. The compound sensitised a washed chloride plate fairly strongly, the maximum lying at 5700 Å. and sensitisation extending to 6300 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzselena-zoline)]-β-anilomethyl-dimethinmerocyanine.—This was similarly prepared but with 4-keto-2-thio-3-ethyltetrahydro-oxazole in place of 3-ethylrhodanine and heating was for 5 minutes. The product (62% yield) precipitated by ether was recrystallised from a mixture of ethyl alcohol and pyridine (13 c.c. of each per g.) and gave a 47% yield (Found : N, 8.9. $C_{23}H_{21}O_2N_3S_2Se$ requires N, 8.7%). The bright orange crystals had m. p. 161° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4850 Å. and one containing sulphuric acid at 4105 Å. The dye sensitised a chloride plate to 5900 Å., with the maximum at 5400 Å.

[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(3-ethylbenzselena-zoline)]-β-anilomethyl-dimethinmerocyanine.—This was similarly prepared but with 1-phenyl-3-ethyl-2-thiohydantoin (2.64 g.; 3 mols.) as the compound with reactive methylene, and was precipitated by water. The product was boiled out with methyl alcohol (30 c.c.) and the residue crystallised from pyridine (20 c.c.), giving a 32% yield (Found : N, 10.2. $C_{29}H_{25}ON_4S_2Se$ requires N, 10.05%). The brick-red crystals had a gold reflex and melted at 236° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 5055 Å., and one containing sulphuric acid at 4290 Å. The substance sensitised a chloride plate strongly, the maximum lying at 5600 Å. and sensitisation extending to 6150 Å.

[2-(3-Ethylthiazolidine)][5-(3-ethylrhodanine)]-α-anilomethyl-dimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidene-thiazolidine (0.84 g.; 1 mol.) and 3-ethylrhodanine (1 mol.) were suspended in ethyl alcohol (30 c.c.) at 0° and kept thus for 15 minutes, with thorough stirring. The solid was filtered off, washed (0.88 g. left), and recrystallised from a mixture of ethyl alcohol and pyridine (10 c.c. of each), being obtained in 66% yield (Found : S, 23.65. $C_{19}H_{21}ON_3S_3$ requires S, 23.85%). The orange crystals had m. p. 172° (decomp.). A methyl-alcoholic solution containing pyridine had its absorption maximum at 4825 Å., and one containing sulphuric acid at 4410 Å. The substance sensitised a chloride plate strongly from 4600 to 5800 Å., with the maximum at 5350 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylthiazolidine)]-β-anilomethyl-dimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidene-thiazolidine (1.68 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (1 mol.), and alcohol (40 c.c.) were mixed and kept at 0° for 1 hour. After water-washing, the product (1.4 g.) was recrystallised from a mixture of ethyl alcohol (10 c.c.) and pyridine (5 c.c.), giving a 60% yield (Found : S, 16.75. $C_{19}H_{21}O_2N_3S_2$ requires S, 16.55%). The orange crystals had m. p. 139° (decomp.). A methyl-alcoholic solution containing pyridine had a broad absorption curve with its maximum at 4370 Å., whilst one containing sulphuric acid had a curve with a sharp peak at 4110 Å. On a chloride plate the substance conferred slight extra-sensitivity extending to 4500 Å.

[2-(3-Ethylthiazolidine)][5-(2-diphenylamino-4-keto-Δ²-thiazoline)]-α-anilomethyl-dimethinmerocyanine.—3-Ethyl-2-dianiloisopropylidene-thiazolidine (1.68 g.; 1 mol.), 2-diphenylamino-4-keto-Δ²-thiazoline (1 mol.), and ethyl alcohol (40 c.c.) were boiled and stirred together for 5 minutes. The washed product (2.03 g.) was recrystallised from a mixture of ethyl alcohol (10 c.c.) and pyridine (18 c.c.) and obtained in 74% yield (Found : S, 12.45. $C_{29}H_{26}ON_4S_2$ requires S, 12.55%). The deep yellow crystals had m. p. 209° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4380 Å. and one containing sulphuric acid at 3990 Å. The compound strongly sensitised a chloride plate, the maximum lying at 5000 Å. and sensitisation extending to 5500 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzthiazoline)][β-methin-5'-(3'-ethylrhodanine)]-dimethinmerocyanine (XII).—[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzthiazoline)]-β-anilomethyl-dimethinmerocyanine (VII; X = O) (0.87 g.; 1 mol.), 3-ethylrhodanine (1 mol.), anhydrous sodium acetate (4 mols.), and acetic anhydride (8 c.c.) were stirred together at 130–140° for 6 minutes. After cooling, the solids were filtered off and washed successively with acetic anhydride, ether, and water. The residue (0.76 g.) was dissolved in hot pyridine (15 c.c.) and precipitated with absolute ether (55 c.c.), giving a 58% yield (Found : S, 25.55. $C_{22}H_{21}O_3N_3S_4$ requires S, 25.5%). The maroon solid had no definite m. p. but melting and decomposition took place from 215° to 270°. The absorption maximum was at 5475 Å. The substance decreased the normal sensitivity of a plate whilst sensitising weakly from 5600 to 6000 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(4-methyl-3-ethyl-Δ⁴-thiazoline)][β-methin-5'-(3'-ethylrhodanine)]-dimethinmerocyanine.—This was prepared by heating together [2-(4-methyl-3-ethyl-Δ⁴-thiazoline)][5-(3-ethylrhodanine)]-α-anilomethyl-dimethinmerocyanine (1.04 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (25 c.c.) at 145–150° for 7 minutes. The reaction mixture was poured into water. After decantation of the cooled liquid, crystallisation of the residue was effected by stirring with spirit; it was recrystallised from methyl alcohol (70 c.c.) and obtained in 65% yield (Found : S, 27.6. $C_{16}H_{19}O_3N_3S_4$ requires S, 27.4%). The purple crystals had m. p. 215° (decomp.). The narrow absorption curve had its maximum at 5545 Å. The compound strongly sensitised a gelatin-chloride plate, sensitisation extending to 6500 Å. and the maximum lying at 5500 Å.

[5-(4-Keto-2-thio-3-ethyltetrahydro-oxazole)][2-(3-ethylbenzselena-zoline)][β-methin-5'-(3'-ethylrhodanine)]-dimethinmerocyanine.—[5-(3-Ethylrhodanine)][2-(3-ethylbenzselena-zoline)]-β-anilomethyl-dimethinmerocyanine (1.00 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (30 c.c.) were heated together at 150° for 15 minutes, and the reaction mixture poured into water. The resultant solid was washed with ether and recrystallised from methyl alcohol (100 c.c.), being obtained in 56% yield (Found : N, 7.6. $C_{22}H_{21}O_3N_3S_3Se$ requires N, 7.65%). The dark purple crystals had m. p. 135° (decomp.). The broad absorption curve had its maximum at 5190 Å. The substance sensitised a chloride plate to 6200 Å. with maxima at 4900 Å. and 5750 Å.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)][β'-dimethin-2'-(1'-ethylquinolinium iodide)]-dimethinmerocyanine (XIII).—[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazoline)]-β-anilomethyl-dimethinmerocyanine

cyanine (VII; X = S) (0.45 g.; 1 mol.), quinaldine ethiodide (1 mol.), anhydrous sodium acetate (4 mols.), and acetic anhydride (20 c.c.) were stirred together at 140—150° for 5 minutes. The solid was filtered off, washed with ether, and ground with water (15 c.c.). The residue (0.41 g.) was recrystallised from methyl alcohol (225 c.c.) and gave a 47% yield (Found: I, 19.2. $C_{29}H_{26}ON_3IS_3$ requires I, 19.3%). The dark bronze crystals had m. p. 244° (decomp.). The absorption maximum was at 6080 Å. The substance considerably desensitised a photographic plate and did not confer extra-sensitivity.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzthiazole)][$\beta\beta'$ -dimethin-2'-(3'-ethylbenzthiazolium iodide)]dimethinmerocyanine (XV).—Bis-2-(3-ethylbenzthiazole)- α -anilomethyltrimethincyanine iodide (XIV) (1.20 g.; 1 mol.), 3-ethylrhodanine (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (20 c.c.) were heated together at 140—150° for 10 minutes. The washed product (0.98 g.) was boiled out with, and recrystallised from, methyl alcohol (27 c.c., 150 c.c.), giving a 38% yield (Found: I, 18.85. $C_{27}H_{26}ON_3IS_4$ requires I, 19.15%). The bronze powder had m. p. 227° (decomp.). The absorption maximum was at 5750 Å. The compound showed photographic desensitising power and did not sensitise.

[5-(3-Ethylrhodanine)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][$\beta\beta'$ -dimethin-2'-(3'-ethylbenzthiazolium iodide)]dimethinmerocyanine.—[5-(3-Ethylrhodanine)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)]- β -anilomethyl-dimethinmerocyanine (0.83 g.; 1 mol.), 2-methylbenzthiazole ethiodide (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (25 c.c.) were stirred together at 145—150° for three minutes. Ether-precipitation was carried out and the solid washed with warm water and boiled out with methyl alcohol (20 c.c.). On recrystallising the residue from acetic acid (200 c.c.), the yield was 76% (Found: I, 20.4. $C_{23}H_{26}ON_3IS_4$ requires I, 20.2%). The emerald-green crystals had m. p. 240° (decomp.). The absorption curve had its maximum at 5750 Å. and an inflexion at 5300 Å. The dye did not sensitise and decreased the normal blue sensitivity of the plate.

[5-(3-Ethylrhodanine)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][$\beta\beta'$ -dimethin-2'-(3'-ethyl-6':7'-benzbenzthiazolium iodide)]dimethinmerocyanine.—This was similarly prepared but from 2-methyl-6':7'-benzbenzthiazole ethiodide instead of from 2-methylbenzthiazole ethiodide. After being washed with hot water, the residue (1.37 g.) was recrystallised from methyl alcohol (535 c.c.) and gave a 76% yield (Found: I, 18.9. $C_{28}H_{28}ON_3IS_4$ requires I, 18.75%). The brilliant green crystals had m. p. 260° (decomp.). The narrow absorption curve had its maximum at 5945 Å. and an inflexion at 5500 Å. The dye decreased the normal blue sensitivity of a plate without conferring extra-sensitivity.

[5-(3-Ethylrhodanine)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][$\beta\beta'$ -dimethin-2'-(3'-ethyl- Δ^2 -thiazolinium iodide)]dimethinmerocyanine (XVII).—[2-(3-Ethyl- Δ^2 -thiazoline)][2-(4-methyl-3-ethylthiazole)]- γ -anilomethyltrimethincyanine iodide (1.02 g.; 1 mol.), 3-ethylrhodanine (1.5 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (15 c.c.) were stirred together at 140—150° for 5 minutes. Ether-precipitation was effected, followed by washing with water, and the residue, on recrystallisation from methyl alcohol (25 c.c.), gave a 58% yield (Found: I, 21.75. $C_{20}H_{26}ON_3IS_4$ requires I, 21.9%). The purple crystals had m. p. 214° (decomp.). The absorption curve had its maximum at 5360 Å. and an inflexion at 5000 Å. The substance sensitised weakly to 6200 Å., the maximum lying at 5900 Å., but considerably diminished the normal sensitivity.

[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)][$\beta\beta'$ -dimethin-2'-(3'-ethylbenzthiazolium iodide)]dimethinmerocyanine (XVI).—[5-(1-Phenyl-3-ethyl-2-thiohydantoin)][2-(4-methyl-3-ethyl- Δ^4 -thiazoline)]- β -anilomethyl-dimethinmerocyanine (1.19 g.; 1 mol.), 2-methylbenzthiazole ethiodide (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (30 c.c.) were stirred together at 145—150° for 5 minutes. The product was precipitated with ether and washed with warm water; after boiling out with, and recrystallising from, methyl alcohol (10 c.c., 60 c.c.), the yield was 31% (Found: I, 18.5. $C_{30}H_{31}ON_4IS_3$ requires I, 18.5%). The dark green crystals had m. p. 225° (decomp.). The broad absorption curve had its maximum at 5765 Å. and an inflexion at 5400 Å. The substance depressed the sensitivity of a photographic plate.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzselena-zoline)][$\beta\beta'$ -dimethin-2'-(3'-ethylbenzthiazolium iodide)]dimethinmerocyanine (XVIII; X = S).—[5-(3-Ethylrhodanine)][2-(3-ethylbenzselena-zoline)]- β -anilomethyl-dimethinmerocyanine (0.50 g.; 1 mol.), 2-methylbenzthiazole ethiodide (2 mols.), anhydrous sodium acetate (4 mols.), and acetic anhydride (15 c.c.) were stirred together at 145—150° for 3 minutes. The product was precipitated with ether, washed with water (84% yield left), and recrystallised from methyl alcohol (600 c.c. per g.), whereupon the yield was 71% (Found: I, 18.0. $C_{27}H_{26}ON_3IS_3Se$ requires I, 17.85%). The dark purple crystals had m. p. 235° (decomp.). The broad absorption curve had its maximum at 5800 Å. and an inflexion at 5410 Å. The dye strongly depressed the normal sensitivity of a plate and did not confer extra-sensitivity.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzselena-zoline)][$\beta\beta'$ -dimethin-2'-(3'-ethyl-6':7'-benzbenzthiazolium iodide)]dimethinmerocyanine.—This was similarly prepared but 2-methyl-6':7'-benzbenzthiazole ethiodide took the place of 2-methylbenzthiazole ethiodide. The ether-precipitated, water-washed dye was boiled out with, and recrystallised from, methyl alcohol (15 c.c., 300 c.c.), the hot filtrate being concentrated to $\frac{1}{2}$ volume to give a 43% yield (Found: I, 16.7. $C_{31}H_{28}ON_3IS_3Se$ requires I, 16.7%). The blue-green crystals had m. p. 240° (decomp.). The broad absorption curve had its maximum at 5930 Å. and an inflexion at 5300 Å. The dye decreased the blue sensitivity and did not confer extra-sensitivity.

[5-(3-Ethylrhodanine)][2-(3-ethylbenzselena-zoline)][$\beta\beta'$ -dimethin-2'-(3'-ethylbenzselena-zolium iodide)]dimethinmerocyanine (XVIII; X = Se).—This was similarly prepared but the quaternary salt was 2-methylbenzselena-zole ethiodide. The precipitated, washed solid (0.65 g.) was recrystallised from methyl alcohol (550 c.c.) and gave a 71% yield (Found: I, 16.8. $C_{27}H_{26}ON_3IS_2Se_2$ requires I, 16.75%). The dark purple crystals had m. p. 245° (decomp.). The broad absorption curve had its maximum at 5820 Å. and an inflexion at 5400 Å. There was no sensitisation but very strong desensitisation.

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