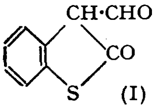
977. mero*Cyanines Derived from Thio-oxindole. Part II.** mero*Cyanines having a Tetramethin, Hexamethin, or Diazadimethin Chain attached to the 3-Thionaphthen Nucleus.*

By R. H. Glauert and Frederick G. Mann.

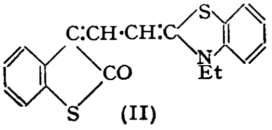
The preparation of *mero*cyanines in which the thio-oxindole nucleus is linked at the 3-position through a tetramethin, hexamethin, or diazadimethin chain to suitable heterocyclic systems is described.† The compounds with tetra- and hexa-methin chains act as photographic sensitisers, but those with diazadimethin chains do not.

We have shown in Part I* that thio-oxindole-3-aldehyde (I), or its anil, will condense under the influence of various basic catalysts with a wide variety of heterocyclic quaternary salts containing suitable reactive methyl groups, to give a new type of *mero*cyanine dye in which the thionaphthen ring is linked at the 3-position to the dimethin chain, *e.g.*, (II). Since several of these compounds proved to be valuable photographic sensitisers, we have investigated the preparation and properties of similar compounds in which the dimethin chain has been extended to a tetramethin and hexamethin chain, or replaced by a diazadimethin chain.

For the preparation of the *mero*cyanines with tetramethin and hexamethin chains, we utilised malondialdehyde dianil (III; $n = 1$) and glutacondialdehyde dianil (III; $n = 2$) (cf. Piggott and Rodd, B.P. 355,393/1930, 355,693/1930). Thio-oxindole and the former readily gave the orange-brown 3-(3-anilinoallylidene)thio-oxindole (IV; $n = 1$), which, when treated with a boiling pyridine solution of 2-methylbenzothiazole ethiodide containing triethylamine, condensed further to give the required tetramethin compound, [3-(dihydro-2-ketothionaphthen)][2-(3-ethylbenzothiazoline)]tetramethin*mero*cyanine (V), as blue crystals.



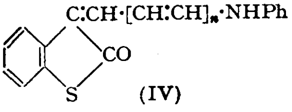
(I)



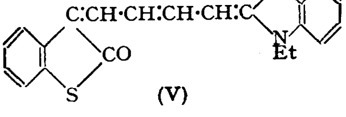
(II)

NPh:CH·[CH:CH]$_n$·NHPh

(III)



(IV)



(V)

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* *J.*, 1952, 2135.

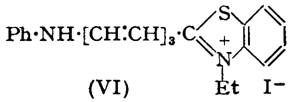
† Patent protection pending.

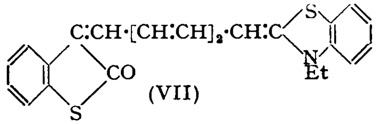
Although thio-oxindole and glutacondialdehyde dianil (III; $n = 2$) readily formed 3-(5-anilinopentadienylidene)thio-oxindole (IV; $n = 2$), this did not condense with 2-methylbenzothiazole ethiodide or lepidine methiodide in spite of wide variation of the conditions employed.

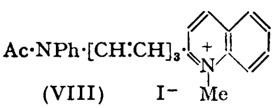
The dianil (III; $n = 2$), however, also combined readily with 2-methylbenzothiazole ethiodide in cold ethanol, to give 2-(6-anilino-1 : 3 : 5-hexatrienyl)benzothiazole ethiodide (VI) which, when shaken with thio-oxindole in ethanol containing sodium ethoxide, gave the required hexamethin*mero*cyanine (VII).

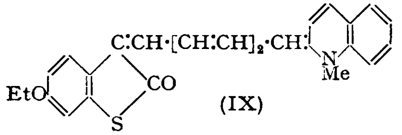
When equimolecular quantities of thio-oxindole, the hydrochloride of the dianil (III; $n = 2$) and 2-methylbenzothiazole ethiodide were treated in hot ethanolic solution with sodium ethoxide (2 mols.) the *mero*cyanine (VII) was again obtained, almost certainly through the reactive intermediate (VI).

This remarkable difference in reactivity of the intermediate compounds (IV; $n = 2$) and (VI) is not an isolated example. Thus, 6-ethoxy(thio-oxindole) and the dianil (III; $n = 2$) gave 3-(5-anilinopentadienylidene)-6-ethoxy(thio-oxindole) (as IV; $n = 2$), which, however, did not condense with quinaldine methiodide. On the other hand, although the dianil (III; $n = 2$) did not condense satisfactorily with quinaldine methiodide in ethanol, yet it did so readily in acetic anhydride, forming (VIII), which with 6-ethoxy(thio-oxindole) in hot ethanol containing triethylamine afforded the hexamethin*mero*cyanine (IX). In this case, it was not surprising that when an equimolecular mixture of 6-ethoxy(thio-oxindole), the hydrochloride of the dianil (III; $n = 2$), and quinaldine methiodide was heated in ethanol with sodium ethoxide, the *mero*cyanine could not be isolated; the purple-red colour of the solution indicated that the inactive anilo-compound (as IV; $n = 2$) was preferentially formed.

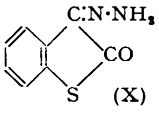

(VI)

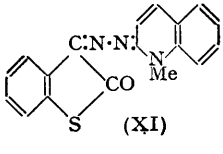

(VII)

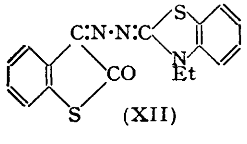

(VIII)

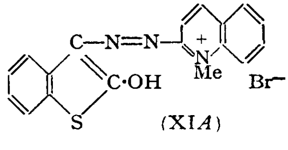

(IX)

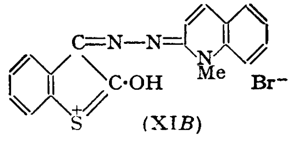
For the preparation of *mero*cyanines having a diazadimethin chain, we have utilised thionaphthenquinone 3-hydrazone (X) (Glauert and Mann, *J.*, 1952, 2127). In boiling ethanol containing triethylamine this condensed with 2-iodoquinoline methiodide to form the reddish-brown [3-(dihydro-2-ketothionaphthen)][2-(1 : 2-dihydro-1-methylquinoline)]-diazadimethin*mero*cyanine (XI), and with 2-ethylthiobenzothiazole ethiodide to form orange crystals of the corresponding [2-(3-ethylbenzothiazoline)]*mero*cyanine (XII). These


(X)


(XI)


(XII)


(XI*A*)


(XI*B*)

compounds represent the first *mero*cyanines to be prepared in which the two heterocyclic nuclei are linked by a diazadimethin chain.

It is noteworthy that compound (XI), when treated in acetone solution with aqueous hydrogen bromide, gave an orange-yellow crystalline hydrobromide, which, however, readily dissociated on exposure to damp air, regenerating the parent *mero*cyanine. The colour of this salt, compared with that of (XI), indicates that, as in the case of the dimethin-*mero*cyanines (cf. Part I), proton addition has occurred, not on the nitrogen atom of the second heterocyclic system, but on the oxygen atom, and that the hydrobromide has probably the structure (XI*A*), of which (XI*B*) is a second canonical form. If this is so, this salt is systematically analogous to a true cyanine, and should therefore be termed [2-hydroxy-3-thionaphthen][1-methyl-2-quinoline]diazadimethincyanine bromide. The compound (XII) when similarly treated was however converted into an isomer; this behaviour will be investigated more fully later.

The photographic sensitivity of the above *mero*cyanines has been kindly investigated by Imperial Chemical Industries Limited, Dyestuffs Division, who find that the tetramethin and hexamethin members are photographic sensitisers, but that the diazadimethin members and also the anil (IV; $n = 1$) are not. The absorption maxima of the dyes in solution and their sensitisation maxima when applied to a bromo-iodide emulsion are tabulated and briefly discussed on p. 5016.

EXPERIMENTAL

Malondialdehyde Dianil (III; $n = 1$).—Propargylaldehyde diethyl acetal, prepared from acraldehyde by Grard's method (*Ann. Chim.*, 1930, **13**, 336), was converted into the dianil hydrochloride by reaction with aniline hydrochloride (cf. Claisen, *Ber.*, 1903, **36**, 3668). The free anil was obtained by basifying a methanolic suspension of the hydrochloride with dilute aqueous potassium hydroxide and then precipitating the base by further dilution with water.

Glutacondialdehyde Dianil (III; $n = 2$).—The hydrochloride was prepared by Fisher and Hamer's modification (*J.*, 1933, 189) of the method of Zincke, Heuser, and Möller (*Annalen*, 1904, **333**, 296): the free base was isolated as above.

[3-(*Dihydro-2-ketothionaphthen*)][(2-(3-*ethylbenzothiazoline*)]*tetramethin*mero*cyanine* (V).—Solutions of thio-oxindole (1 g.) and of malondialdehyde dianil (1·48 g., 1 mol.) in warm ethanol (5 and 10 c.c.) were mixed, boiled under reflux for 5 minutes, and cooled. The deposit of 3-(3-*anilinoallylidene*)*thio-oxindole* (IV; $n = 1$) furnished orange-brown crystals (1·24 g.), m. p. 243—245°, from ethanol (Found: C, 73·0; H, 4·4; N, 5·0. $C_{17}H_{13}ONS$ requires C, 73·1; H, 4·7; N, 5·0%). This (0·5 g.) was boiled with 2-methylbenzothiazole ethiodide (0·545 g., 1 mol.) in pyridine (10 c.c.) containing triethylamine (0·25 c.c.) under reflux for 3 hours, developing a deep blue colour. The solvent was evaporated under reduced pressure, and the residue triturated with methanol; the crystalline product, when recrystallised from methanol, gave the mero*cyanine* (V) as small blue crystals, m. p. 173—174° (Found: C, 69·4; H, 5·2; N, 3·8. $C_{21}H_{17}ONS_2$ requires C, 69·4; H, 4·7; N, 3·9%): yield, 0·38 g., 57%.

The compound (IV; $n = 1$) did not condense with 2-methylthiazoline ethiodide in boiling pyridine–triethylamine or in boiling ethanolic triethylamine, unchanged (IV) being recovered.

[3-(*Dihydro-2-ketothionaphthen*)][2-(3-*ethylbenzothiazoline*)]*hexamethin*mero*cyanine* (VII).—(*a*) Solutions of thio-oxindole (1 g.) and glutacondialdehyde dianil (1·65 g., 1 mol.), both in cold ethanol (25 and 100 c.c.), when mixed, rapidly became deep red and deposited crystals, which after 24 hours were collected and recrystallised from methanol, giving 3-(5-*anilinopentadienylidene*)*thio-oxindole* (IV; $n = 2$), purple, m. p. 176—177° (1·5 g.) (Found: C, 7·45; H, 4·5; N, 4·6. $C_{19}H_{15}ONS$ requires C, 74·7; H, 4·95; N, 4·6%). No *mero*cyanine was isolated from equimolecular quantities of this anil and 2-methylbenzothiazole ethiodide in (*a*) methanol containing triethylamine, with 3 hours' boiling, (*b*) pyridine containing triethylamine, the solution being set aside at room temperature for 48 hours or boiled for 6 hours, or (*c*) ethanol containing sodium ethoxide, the solution being set aside for 24 hours, or boiled for 30 minutes.

(*b*) The dianil (0·815 g.) and 2-methylbenzothiazole ethiodide (1 g., 1 mol.) in cold ethanol readily formed 2-(6-anilino-1 : 3 : 5-hexatrienyl)benzothiazole ethiodide (VI) (0·6 g.), dark greenish-brown needles, m. p. 216—217° (Found: C, 54·7; H, 5·1. Calc. for $C_{21}H_{21}N_2IS$: C, 54·8; H, 4·6%). Brooker, White, Keyes, Smyth, and Oesper (*J. Amer. Chem. Soc.*, 1941, **63**, 3192) give m. p. 161—163°: the reason for the wide discrepancy is not obvious. The product (VI) (0·307 g.) and thio-oxindole (0·1 g., 1 mol.) were shaken in ethanol (30 c.c.), to which a solution of sodium ethoxide (0·015 g., 1 mol.) in ethanol (15 c.c.) was added, the mixture becoming blue. After 48 hours, the mero*cyanine* (VII) was collected and recrystallised from ethanol, giving bright blue crystals (70%), m. p. 172° (Found: C, 70·5; H, 4·5; N, 3·6. $C_{23}H_{19}ONS_2$ requires C, 70·9; H, 4·9; N, 3·6%).

Repetition of this experiment with triethylamine (1 mol.) in place of sodium ethoxide gave the *mero*cyanine in 46% yield.

Thio-oxindole (0·75 g.), the hydrochloride of the dianil (III; $n = 2$) (1·42 g., 1 mol.), and 2-methylbenzothiazole ethiodide (1·525 g., 1 mol.) were dissolved in boiling ethanol (40 c.c.), to which was then added a solution of sodium ethoxide (sodium, 0·23 g., 2 atoms; ethanol, 10 c.c.). The solution, which became purple-blue and deposited crystals, was set aside for 24 hours; recrystallisation from ethanol then gave the above *mero*cyanine (23%), m. p. 172°, alone and when mixed with the previous sample.

[3-(*Dihydro-6-ethoxy-2-ketothionaphthen*)][2-(*dihydro-1-methylquinoline*)]*hexamethin*mero*cyanine* (IX).—(*a*) 6-Ethoxy(thio-oxindole) reacted with the dianil (III; $n = 2$) under the conditions previously described, to give 3-(5-*anilinopentadienylidene*)-6-*ethoxythio-oxindole*, which after recrystallisation from ethanol and acetone (deep purple solution) formed dark blue rods (48%), m. p. 185° (Found: C, 72·2; H, 5·6. $C_{21}H_{19}O_2NS$ requires C, 72·2; H, 5·5%). Condensation of this with quinaldine methiodide was attempted under conditions similar to those described for the unsubstituted anil, but in all cases it was recovered unchanged and the absence of a blue colour in the various reaction mixtures showed that not more than a trace of the required *mero*cyanine could have been formed.

(*b*) (i) Cold solutions of the dianil (III; $n = 2$) (1 g.) and quinaldine methiodide (1·14 g., 1 mol.) in ethanol (35 and 25 c.c.) were mixed and set aside for 24 hours. The purple deposit (0·25 g.) of indefinite m. p. could not be satisfactorily recrystallised. Reaction in boiling ethanol gave no better results.

(ii) A solution of the above reagents (same quantities) in acetic anhydride (10 c.c.) was boiled for 15 minutes and cooled. The 2-(6-*acetanilido*-1 : 3 : 5-*hexatrienyl*)*quinoline methiodide* (VIII) which separated was recrystallised from ethanol, and apparently formed a stable *diethanol* solvate, dark brown crystals, m. p. 189—190° with softening from 147° (Found: C, 58·7; H, 6·0; after heating at 60°/0·1 mm., C, 58·5; H, 5·7; N, 5·4. $C_{24}H_{23}ON_2I,2C_2H_6O$ requires C, 58·5; H, 6·1; N, 4·9%).

When a few drops of triethylamine were added to a solution of this methiodide (0·2 g.) and 6-ethoxy(thio-oxindole) (0·08 g., 1 mol.) in a minimum of boiling ethanol, the orange-brown solution became dark blue and crystals separated. The solution when boiled for 5 minutes became green. The crystals (0·12 g.), when then recrystallised from benzene, gave the mero*cyanine* (IX) as green prisms, m. p. 199° (Found: C, 75·65; H, 5·9; N, 3·1. $C_{26}H_{23}ONS$, requires C, 75·5; H, 5·6; N, 3·4%).

[3-(*Dihydro-2-ketothionaphthen*)][2-(*dihydro-1-methylquinoline*)]*diazadimethin*mero*cyanine* (XI).—The reddish solution of thionaphthenquinone-3-hydrazone (0·4 g.) and 2-iodoquinoline methiodide (0·69 g., 1 mol.) (Roser, *Annalen*, 1894, **182**, 376) in boiling ethanol (50 c.c.), when diluted with triethylamine (0·64 c.c., 2 mols.), became deep blood-red and deposited crystals. The mixture was boiled for 10 minutes and the crystals, when collected from the cold product and recrystallised from ethanol, afforded the reddish-brown mero*cyanine* (XI) (0·33 g.), m. p. 225—226° (Found: C, 67·9; H, 4·3; N, 13·1. $C_{18}H_{13}ON_3S$ requires C, 67·7; H, 4·1; N, 13·15%).

When 48% aqueous hydrobromic acid (4 c.c.) was added to a suspension of (XI) (0·08 g.) in warm acetone (8 c.c.), the greater part of the dye dissolved to give a yellow-orange solution, which, when filtered, concentrated, and cooled, deposited the crystalline *hydrobromide* (XI*A*–*B*). When recrystallised from acetic acid and dried in a desiccator at atmospheric pressure this formed thin orange-yellow crystals, m. p. 210—211°, which contained one molecule of acetic acid and which on exposure to damp air soon darkened as the *mero*cyanine was regenerated (Found: C, 52·2; H, 4·15; N, 9·25. $C_{18}H_{14}ON_3BrS,C_2H_4O_2$ requires C, 52·2; H, 3·9; N, 9·1%).

The 2-(3-*ethylbenzothiazoline*) analogue (XII) was prepared as (XI) from 2-ethylthiobenzothiazole ethiodide (0·7 g., 1 mol.) and recrystallised from ethanol as orange needles, m. p. 175—176° (Found: C, 60·05; H, 3·7; N, 12·1. $C_{17}H_{13}ON_3S_2$ requires C, 60·2; H, 3·9; N, 12·4%): 0·45 g., 59%.

When a solution of (XII) (*a*) in cold acetic acid was treated with hydrobromic acid, (*b*) in acetic acid was boiled for a few minutes, (*c*) in ethanol or benzene was set aside for several hours, a bright orange isomer, m. p. 259—260° unchanged by recrystallisation from acetic acid, was deposited (Found: C, 60·3; H, 4·1; N, 12·1%). A mixture of the two forms when rapidly heated melted at *ca.* 230—250°, and when slowly heated melted at *ca.* 260°, in each case with some softening at *ca.* 170°.

Ethanolic solutions of (XI) and (XII) were both orange, whereas the corresponding dimethin compounds give magenta and orange-pink solutions respectively (cf. Part I).

Physical Characteristics.—In the Table below, the second column gives the colour of the dye in solution (E = ethanol, M = methanol); the third column gives the concentration in 2-ethoxyethanol at which the absorption maxima (mμ) in the fourth column were determined; the last column shows the sensitisation maxima (mμ) of the dyes when applied to a bromo-iodide emulsion.

No.	Solvent and colour in solution	Concn.	Max. in solution	Max. in emulsion
(V)	M Purple-blue	1 : 2000	619	685
(VII)	E Blue	1 : 10,000	644	780
(IX)	E Blue	Not tested		—
(XI)	E Orange	,,		—
(XII)	E Orange-red	1 : 2000	454	—
(IV, *n* = 1)	E Orange	1 : 2000	471	—

The absorption maximum of the *mero*cyanine having the 3-thionaphthen and the 2-(3-ethylbenzothiazoline) nuclei directly joined (cf. Part I) is 418 mμ, and those of the corresponding compounds having these nuclei joined through a di-, tetra-, and hexa-methin chain are 531, 619, and 644 mμ respectively, whilst that of the compound with these nuclei joined by the diazadimethin chain is 454 mμ. Increasing the methin chain therefore causes the expected bathochromic shift in the absorption (the four maxima forming a convergent series), whereas replacement of the dimethin by the diazadimethin chain causes a hypsochromic shift.

We are greatly indebted to Imperial Chemical Industries Limited, Dyestuffs Division, for the determination of the above absorption and sensitisation maxima, and for the gift of various compounds.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August* 14*th*, 1952.]