mero*Cyanines Derived from Thio-oxindole. Part III.* Trinuclear* mero*Cyanines.*

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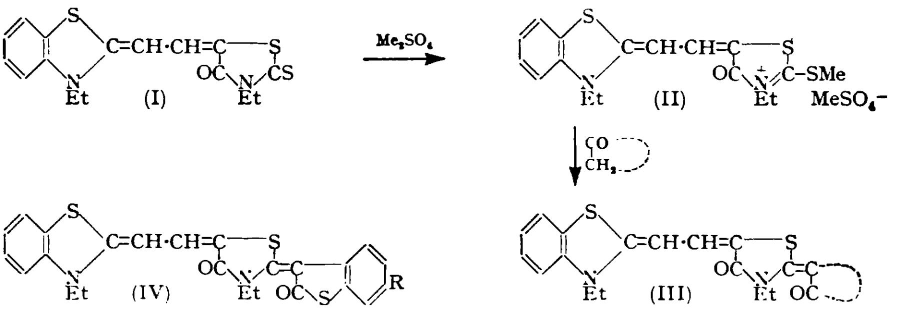
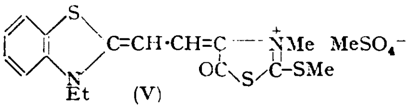
Four trinuclear *mero*cyanines containing the thio-oxindole nucleus have been prepared. The dyes are compared briefly with their isomers derived from thioindoxyl.

PARTS I and II of this series * describe the preparation of *mero*cyanines which all contain the thio-oxindole nucleus linked in the 3-position to suitable heterocyclic systems but differ in the nature of the latter systems, in the nature and length of the connecting chain, and in the degree of substitution of the thionaphthen ring. As many of these compounds proved to be active photographic sensitisers, the preparation and properties of some trinuclear *mero*cyanines containing the thio-oxindole nucleus have now been examined.

Kendall and Brooker discovered independently (Mees, " The Theory of the Photographic Process," Macmillan, London, 1942, pp. 1037—1040) that a *mero*cyanine containing the rhodanine nucleus, *e.g.*, 3-ethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-thiothiazolid-4-one (I), may be quaternised with, for example, dimethyl sulphate, to give a quaternary salt (II) which on treatment with a suitable cyclic ketomethylene compound forms a complex *mero*cyanine (III). Trinuclear dyes of the latter type are also photographic sensitisers.



We find that in the presence of a basic catalyst the deep red intermediate (II), in ethanol, readily condenses with thio-oxindole, at room temperature, with evolution of methanethiol and the formation of the deep purple dye (IV; R = H) in high yield. The use of 6-ethoxy(thio-oxindole) similarly affords the substituted dye (IV; R = OEt).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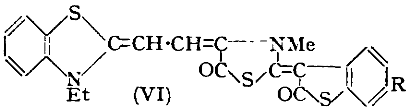
(VI)

Knott and Jeffreys (*J.*, 1952, 4762) have recently shown that a series of reactions analogous to that of (I) ⟶ (III) may be carried out with *mero*cyanines derived from *iso*rhodanines (thiazolid-5-ones). Thus quaternisation of the *N*-methyl*iso*rhodanine analogue of (I) gives the salt (V) which with a ketomethylene compound forms a trinuclear *mero*cyanine. Using thio-oxindole we have thus obtained the deep blue *mero*cyanine (VI; R = H) and from 6-ethoxy(thio-oxindole) the ethoxy-derivative (VI; R = OEt).

For comparative purposes we prepared the thioindoxyl analogues of (IV and VI; R = H), *i.e.*, (VII) (cf. Kendall, B. P. 487,051/1936) and (VIII). These are less soluble in ethanol and acetone than their thio-oxindole isomers.

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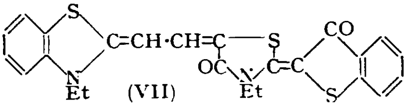
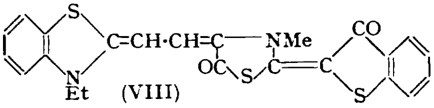
* Parts I and II, *J.*, 1952, 2135, 5012.

The absorption maxima of the new *iso*rhodanine dyes lie at appreciably longer wavelengths than those of the corresponding rhodanine compounds (cf. Knott and Jeffreys, *loc. cit.*). Thus, in 2-ethoxyethanol, (IV; R = H) has $\lambda_{max.}$ 577 mμ and (VI; R = H) $\lambda_{max.}$ 600 mμ; replacement of the thio-oxindole nucleus by that of thioindoxyl results in a bathochromic shift, *e.g.*, (VII) has $\lambda_{max.}$ 583 mμ, and (VIII) has $\lambda_{max.}$ 615 mμ; a similar effect is observed in the dimethin*mero*cyanines [cf. Glauert and Mann, *J.*, 1952, 2135; Kiprianov and Timoshenko, *Zhur. obshchey Khim.*, 1947, **17**, 1468; *Chem. Abs.*, 1948, **42**, 8475].


(VII)


(VIII)

The absorption and sensitisation data are briefly summarised below.

EXPERIMENTAL

*Quaternised Dimethin*mero*cyanines.*—The dimethin*mero*cyanine was fused with methyl sulphate (2—4 mols.) at 130—135° for 15—30 min. The metho(methyl sulphate) was dissolved in warm methanol and precipitated by the addition of ether. The crystalline products were used without further purification.

3-Ethyl-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-methylthio-4-oxothiazolonium methosulphate (II) formed crystals with a brown reflex, m. p. 207—208°; van Dormael (*Bull. Soc. chim. Belg.*, 1949, **58**, 403) gives m. p. 210—213°.

4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-3-methyl-2-methylthio-5-oxothiazolonium methosulphate (V) separated as a red microcrystalline powder, m. p. 179° (decomp.), which, recrystallised from methanol-ether, gave the *hydrate*, small magenta needles, m. p. 194—196° (decomp.) (Found: C, 42·7; H, 4·5; N, 5·7. $C_{17}H_{20}O_5N_2S_4,H_2O$ requires C, 42·7; H, 4·6; N, 5·9%).

Trinuclear mero*Cyanines.*—A solution of the quaternised *mero*cyanine and the thio-oxindole or thioindoxyl (1 mol.) in warm ethanol was cooled to 25—30°, some crystallisation occurring. Triethylamine (1 mol.) was quickly added, and the mixture stirred and set aside overnight. Methanethiol was steadily evolved and the mixture darkened rapidly as the dye separated. The dye was collected, washed with a small quantity of ethanol, then with much water and again ethanol, and recrystallised by dissolution in a minimum of warm pyridine and addition of a tenfold volume of methanol.

3-Ethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-(2 : 3-dihydro-2-oxothionaphthen-3-ylidene)thiazolid-4-one (IV; R = H) formed small dark purple rods (72%), m. p. 221—222°, when inserted at 205° (Found: C, 62·15; H, 4·0; N, 5·8. $C_{24}H_{20}O_2N_2S_3$ requires C, 62·0; H, 4·3; N, 6·0%).

The *6-ethoxy*-derivative (IV; R = OEt) formed flat dark purple plates (77%), m. p. 226—227° with softening at 200° (Found: C, 61·85; H, 5·0; N, 5·8. $C_{26}H_{24}O_3N_2S_3$ requires C, 61·4; H, 4·75; N, 5·5%).

4-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-2-(2 : 3-dihydro-2-oxothionaphthen-3-ylidene)-3-methylthiazolid-5-one (VI; R = H) formed a *monohydrate* (78%), olive-green needles with golden reflex, m. p. 236—237° (Found: C, 58·8; H, 4·15; N, 6·2. $C_{23}H_{18}O_2N_2S_3,H_2O$ requires C, 58·95; H, 4·3; N, 6·0%).

The *6-ethoxy*-derivative (VI; R = OEt) separated as green prismatic needles (68%), m. p. 257—258° (inserted at 240°) (Found: C, 60·4; H, 4·5; N, 5·5. $C_{25}H_{22}O_3N_2S_3$ requires C, 60·7; H, 4·5; N, 5·7%).

3-Ethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-(2 : 3-dihydro-3-oxothionaphthen-2-ylidene)thiazolid-4-one (VII) formed green prisms (58%), m. p. 301—303° (Found: C, 62·1; H, 4·7; N, 6·3. $C_{24}H_{20}O_2N_2S_3$ requires C, 62·0; H, 4·3; N, 6·0%).

4-(3-*Ethylbenzothiazolin-2-ylidene-ethylidene*)-2-(2 : 3-*dihydro*-3-*oxothionaphthen*-2-*ylidene*)-3-*methylthiazolid*-5-*one* (VIII) formed blue-green prisms (46%) (from pyridine), m. p. 282—283° with previous softening (Found: C, 61·0; H, 4·4; N, 6·4. $C_{23}H_{18}O_2N_2S_3$ requires C, 61·3; H, 4·0; N, 6·2%).

We are greatly indebted to Imperial Chemical Industries Limited, Dyestuffs Division, for

the following report on the optical data of the *mero*cyanines and for the gift of intermediate compounds.

" The absorption values were determined in 2-ethoxyethanol solution. The *mero*cyanines (IV; R = H) and (VI; R = H) show quite good, although broad, sensitising action in positive (chlorobromide), but poor sensitisation in negative emulsions. The ethoxy-derivatives are inferior in both these respects to the corresponding unsubstituted compounds."

Compound	Absorption max. (mμ)	Sensitising max. (mμ)	Sensitising range (mμ)
(IV; R = H)	577	620	525—695
(IV; R = OEt)	576	620	520—700
(VI; R = H)	600	630	520—730
(VI; R = OEt)	610	600	525—740

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