397. mero*Cyanines Derived from Thio-oxindole. Part I.* mero-*Cyanines having a Dimethin Chain Attached to the* 3-*Thionaphthen Nucleus.*

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

By condensing thio-oxindole-3-aldehyde with the quaternary salts of various heterocyclic compounds having a suitable reactive methyl group, a new type of *mero*cyanine has been prepared in which the thionaphthen nucleus is linked at the 3-position to the dimethin chain.* Since certain of these compounds are active photographic sensitisers, a wide range has been prepared by variation of (*a*) the type of heterocyclic compound employed in this condensation, (*b*) the alkyl groups used for quaternisation of these compounds, (*c*) the nature and position of substituents in either or both of the heterocyclic systems present in each *mero*cyanine.

Further variation has been obtained by the insertion of methyl groups in the α- and the β-position in the dimethin chain. For comparative purposes, one compound has been prepared in which the two heterocyclic systems are directly joined, and the dimethin chain thus eliminated.

Dyes of the *mero*cyanine type containing the thionaphthen ring system linked at the 2-position in the methin chain were described by Ogata (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 556) and later appeared also in patent specifications [*e.g.*, Kodak Pathé, F.P. 793,723 (1936); Brooker–Kodak, U.S.P. 2,170,806 (1939)]. Considerably more detailed information concerning such *mero*cyanines has been provided by Sveshnikov and Levkoev [*J. Gen. Chem. U.S.S.R.*, 1940, **10**, 274; Sveshnikov, Levkoev, and Durmashkina, *ibid.*, p. 773; 1944, **14**, 198; cf. also R.P. 58,099 (1940)], who found that such compounds having the 2-benzothiazole ring as the second heterocyclic nucleus showed activity as photographic sensitisers. The colour and absorption of such *mero*cyanines have been studied by various workers (*e.g.*, Sheppard, *Rev. Mod. Phys.*, 1942, **14**, 303; Kiprianov and Timoshenko, *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 1468; Levkoev, Sveshnikov, and Lifshits, *Doklady Akad. Nauk. S.S.S.R.*, 1950, **74**, 275; Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, and White, *J. Amer. Chem. Soc.*, 1951, **73**, 5326).

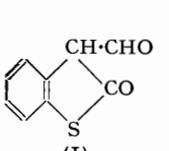
It is noteworthy, however, that the thionaphthen ring was linked solely at the 2-position in all the above compounds. We have now employed thio-oxindole-3-aldehyde (I) and its substituted derivatives (described in an earlier paper, *J.*, 1952, 2127) for the preparation of a new type of *mero*cyanine dye in which the thionaphthen ring is (necessarily) linked at the 3-position to the methin chain.

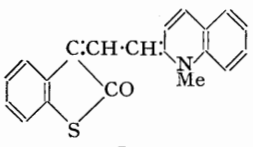
We find that for this purpose the aldehyde (I) will condense under the influence of various basic catalysts with a variety of heterocyclic quaternary salts containing suitable reactive methyl groups. For example, it condensed with quinaldine methiodide in boiling ethanol in the presence of piperidine, to give [3-(dihydro-2-ketothionaphthen)][2-(dihydro-1-methylquinoline)]dimethin*mero*cyanine (IIA), a highly crystalline compound which formed a magenta-coloured solution in ethanol. Lepidine methiodide similarly gave [3-(dihydro-2-ketothionaphthen)][4-(dihydro-1-methylquinoline)]dimethin*mero*cyanine (III) which furnished a deep blue ethanolic solution. Analogous products were obtained

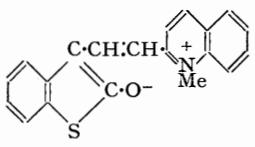
* B.P. Appln. 21,584/1950.

from 2- and 4-picoline methiodides, but more strongly basic catalysts were required to cause pronounced condensation.

It will be seen that all compounds of this type will exist as resonance hybrids, having one non-ionic canonical form (as IIA), and a second ionic form showing a charge separation (as IIB) which necessarily involves a reversal of the former conjugated system, and doubtless it is primarily to this structural feature that these *mero*cyanines owe their intense colours.


(I)


(IIA)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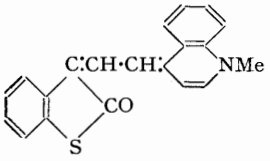
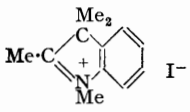
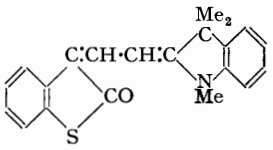

(III)

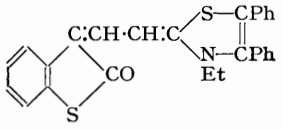

(IV)

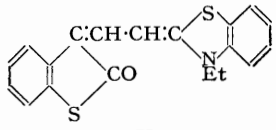

(V)

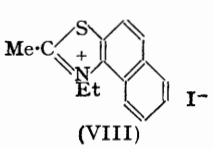
In view of the potential value of these *mero*cyanines as photographic sensitisers, we have investigated a wide range of members. The chief types will be briefly reviewed, but the complete list is given in Table 1.

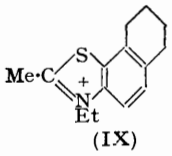
It is noteworthy that a basic catalyst was advantageous only when the quaternary salt of the heterocyclic compound was used : when, however, a suitable stable methylene base could be employed, condensation proceeded readily without a catalyst. For example, 1 : 3 : 3-trimethylindolenine methiodide (Fischer's base hydriodide) (IV) would condense with the aldehyde (I) only under the influence of a base such as piperidine, to form [3-(dihydro-2-ketothionaphthen)][2-(1 : 3 : 3-trimethylindoline)]dimethin*mero*cyanine (V), but 1 : 3 : 3-trimethyl-2-methyleneindoline condensed with the aldehyde (I) in boiling methanol without a catalyst to give this *mero*cyanine.

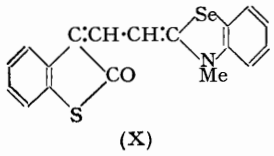
2-Methyl-4 : 5-diphenylthiazole ethiodide underwent condensation with the aldehyde (I) under the usual basic conditions to give [3-(dihydro-2-ketothionaphthen)][2-(3-ethyl-4 : 5-diphenylthiazoline)]dimethin*mero*cyanine (VI), and 2-methylbenzothiazole ethiodide similarly gave the [2-(3-ethylbenzothiazoline)]dimethin*mero*cyanine (VII). Compounds similar to (VII) have also been prepared by using 6-chloro-2-methylbenzothiazole ethiodide, 2 : 5 : 6-trimethylbenzothiazole ethiodide, 2-methylnaphtho(1′ : 2′-4 : 5)thiazole ethiodide (VIII), and 5′ : 6′ : 7′ : 8′-tetrahydro-2-methylnaphtho(2′ : 1′-4 : 5)thiazole ethiodide (IX). The use of 2-methylbenzoselenazole methiodide furnished similarly the [2-(3-methylbenzoselenazoline)]dimethin*mero*cyanine (X).


(VI)


(VII)


(VIII)


(IX)

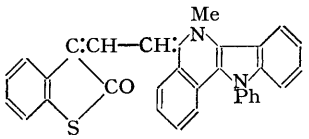

(X)

Many analogous *mero*cyanines have been prepared by condensing 6-ethoxy-, 4 : 5-benzo-, and 6-chloro-4-methyl(thio-oxindole)-3-aldehydes with the above heterocyclic

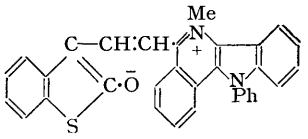
quaternary salts, so that the effect of substituents in the thionaphthen nucleus on the sensitisation could also be studied.

An additional structural feature appears in one exceptional *mero*cyanine prepared from 1-methyl-1′-phenylindolo(3′ : 2′-3 : 4)*iso*quinoline methiodide (Huang-Hsinmin and Mann, *J.*, 1949, 2903). This quaternary salt, when condensed with thio-oxindole-3-aldehyde, furnished [3-(dihydro-2-ketothionaphthen)][1-{1 : 2-dihydro-2-methyl-1′-phenylindolo(3′ : 2′-3 : 4)*iso*quinoline}]dimethin*mero*cyanine (XIA). This compound, unlike its predecessors, has two ionic forms, in one (XIB) of which the pyridine nitrogen atom, and in the second (XIC) the indolo-nitrogen atom, takes the positive charge.

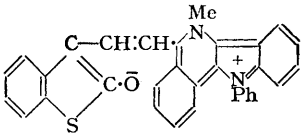
The condensation of the various quaternary salts cited above with the aldehyde (I) and its substituted derivatives proceeded with varying ease under the influence of different basic catalysts, alone or mixed. The use of piperidine or triethylamine alone was often sufficient; sometimes, however, a mixture of pyridine with either or both of these amines had to be employed, and in one case (that of 4-picoline methiodide) a solution of sodium methoxide in methanol had to be utilised. Since no reliable general rule for the choice of a catalyst can be given, the catalyst for each example is stated in the Experimental section. The anil of thio-oxindole-3-aldehyde could be used in place of the aldehyde in



(XIA)



(XIB)



(XIC)

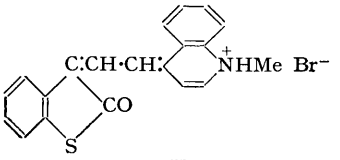
these condensations, the other conditions being unchanged, but a lower yield of the *mero*cyanine appeared to result. It is notable, however, that all attempts to isolate *mero*cyanines by the condensation of 2-methylthiazoline ethiodide or of 2-methyl-5-phenylbenzoxazole ethiodide with the aldehyde (I) failed, in spite of the employment of various combinations of these basic catalysts, although the change in colour of the reaction mixture indicated in every case that some condensation was occurring. This recalls Haworth and Mann's failure (*J.*, 1944, 670) to condense these salts with 1 : 2-disubstituted 3-nitrosoindoles, and that of Holliman and Schickerling (*J.*, 1951, 914) to condense the benzoxazole derivative with their nitrosopyrrocolines.

All the *mero*cyanines crystallise readily (when pure) in hard, well-formed, stable crystals, which usually show a bright green surface reflection. Their solutions in methanol and ethanol frequently have a lower stability, and the colour of these solutions in certain cases slowly fades in the course of several days at room temperature. The colours in ethanolic solution of the *mero*cyanines derived from the unsubstituted aldehyde (I) can be classified in accordance with the chief types of the second heterocyclic system thus: 2- and 4-pyridine, red or purple; 2-quinoline, purple; 4-quinoline, blue; indolenine, orange; benzothiazole and benzoselenazole, pink.

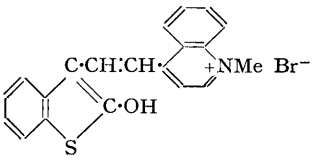
One sharp differentiation between our *mero*cyanines and most true cyanine salts is provided by the action of acids. The true cyanines are usually decolourised in solution by the addition of strong mineral acids, since the latter by salt formation thrust a positive charge on the nitrogen atoms of both heterocyclic nuclei, and the characteristic structural features of the original cyanine are thus profoundly changed. These acids react, however, with our *mero*cyanines to give highly coloured and rather unstable salts, which systematically are themselves true cyanines. For example, when the *mero*cyanine (III) in concentrated acetone solution was treated with hydrobromic acid, the deep blue colour of the *mero*cyanine was replaced by red, and deep brick-red crystals of the hydrobromide separated. This hydrobromide was sufficiently stable to allow crystallisation from acetic acid, but when the crystals were exposed to air at room temperature for two days, they then gave a blue solution in acetic acid, showing that considerable dissociation to the *mero*cyanine had occurred. The deep red colour of the hydrobromide indicates almost certainly that salt formation had not occurred by simple proton addition to the nitrogen atom, as in (XII), but that the hydrogen atom had added on to the oxygen atom, and the

hydrobromide is consequently a resonance hybrid of the two forms (XIIIA) and (XIIIB); it therefore now possesses true cyanine characteristics and should be termed [2-hydroxy-3-thionaphthen][1-methyl-4-quinoline]dimethincyanine bromide. The corresponding hydrochloride and hydriodide of the *mero*cyanine (III) were dull red and reddish-brown respectively, and were rather more unstable than the hydrobromide.

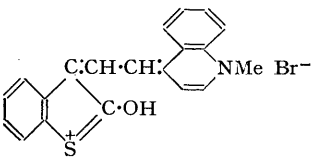
Similarly, the orange indolenine *mero*cyanine (V) gave a red crystalline hydrobromide which also could be recrystallised from acetic acid, but on attempted recrystallisation from ethanol furnished the original *mero*cyanine : the hydrobromide was thus stable only in acid solution.



(XII)

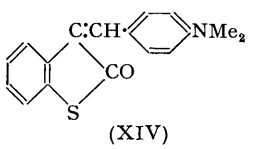


(XIIIA)

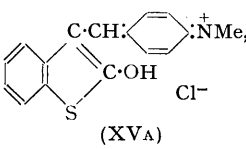


(XIIIB)

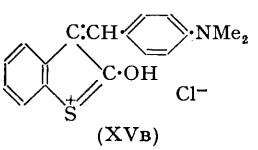
The properties of these salts recall the red compound (XIV) which Marschalk (*J. pr. Chem.*, 1913, **88**, 244) obtained by condensation of *p*-dimethylaminobenzaldehyde and thio-oxindole, and which gave a yellow hydrochloride. The compound (XIV) is clearly related to our *mero*cyanines, and its hydrochloride is presumably a similar resonance hybrid of the forms (XVA) and (XVB).



(XIV)



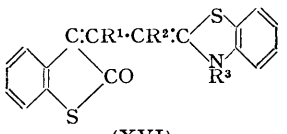
(XVA)



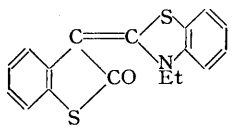
(XVB)

In order to obtain further correlation between structure and sensitising action, we have also investigated the effect of (*a*) introducing substituents into the dimethin chain, and (*b*) eliminating this chain altogether.

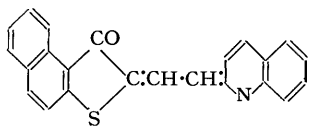
For the first purpose, 3-acetyl(thio-oxindole)[1] (*J.*, 1952, 2127) was condensed with 2-methylbenzothiazole ethiodide to give [3-(dihydro-2-ketothionaphthen)][2-(3-ethylbenzothiazoline)]-α-methyldimethin*mero*cyanine (XVI; $R^1 = Me$, $R^2 = H$, $R^3 = Et$), which gave a purple-red solution in methanol. When thio-oxindole-3-aldehyde was condensed with 2-ethylbenzothiazole methiodide, the [2-(3-methylbenzothiazoline]-β-methyldimethin*mero*cyanine (XVI; $R^1 = H$, $R^2 = R^3 = Me$) was obtained : both this compound and its 3-ethyl homologue ($R^1 = H$, $R^2 = Me$, $R^3 = Et$) gave magenta solutions in methanol. Finally, the condensation of 3-acetyl(thio-oxindole) with 2-ethylbenzothiazole methiodide furnished the [2-(3-methylbenzothiazoline)]-αβ-dimethyldimethin*mero*cyanine (XVI; $R^1 = R^2 = R^3 = Me$), which gave an orange-yellow solution in methanol, in marked contrast to the colours provided by the other methyl derivatives. In all these condensations the yield was considerably lower than that usually obtained with *mero*cyanines containing the unmethylated dimethin chain.



(XVI)



(XVII)



(XVIII)

For the second purpose, an ethanolic solution of thio-oxindole and 2-ethylthiobenzothiazole ethiodide was boiled with triethylamine, ethanethiol being steadily evolved, and the solution ultimately deposited [3-(dihydro-2-ketothionaphthen)][2-(3-ethylbenzothiazoline)]*mero*cyanine (XVII) in high yield. This compound also gave an orange-yellow solution in ethanol.

A complete list of the *mero*cyanines thus prepared is given in Table 1, together with the absorption maxima which they show in various solvents and the sensitisation maxima

in a bromo-iodide emulsion : the choice of a solvent was determined, of course, by the solubility of the dye, but it was observed that, in general, a dye having the >NEt group in the second heterocyclic system was more soluble than the corresponding compound having the >NMe group.

From the full data obtained from the absorption spectrograms, which are only briefly summarised in Table 1, the following generalisations can be made. Very feeble sensitisation is usually shown by those dyes which contain (*a*) the 4 : 5-benzo- and the 6-chloro-4-methyl substituents in the thionaphthen system, irrespective of the second heterocyclic system present, (*b*) the 1 : 3 : 3-trimethylindoline system, (*c*) one or two methyl groups in the dimethin chain, or (*d*) no dimethin chain. Those other *mero*cyanines, however, which contain either the unsubstituted or the 6-ethoxythionaphthen system show varying degrees of sensitisation, and certain of these members appear to be of great promise as photographic sensitisers.

TABLE 1. 3-(*Dihydro*-2-*ketothionaphthen*)mero*cyanines*.

[Col. 2 indicates whether the 3-(dihydro-2-ketothionaphthen) system is unsubstituted (" unsubtd.") or whether it carries the 6-ethoxy-, the 4 : 5-benzo-, or the 6-chloro-4-methyl substituents. Col. 3 shows the nature of the dimethin chain, and col. 4 shows the second heterocyclic system present. Col. 6 gives the absorption maxima (mμ) of solutions, the solvent and concentration of which are shown in col. 5, where M = methanol, E = ethanol, D = dioxan, and G = glycol monoethyl ether. The last column shows the sensitisation maxima (mμ) of the dyes when applied to a bromo-iodide emulsion.]

No.	Thionaphthen system	Chain	Second heterocyclic system	Solvent and concn.	Max. in solution	Max. in emulsion
1	Unsubtd.	:CH·CH:	2-(1-Me-dihydropyridine)	D 1 : 2000	535	550
2	,,	,,	4-(2-Me- ,,)	G 1 : 4000	555	560
3	,,	,,	2-(1-Me-dihydroquinoline)	M 1 : 5000	553	560
4	,,	,,	2-(1-Et- ,,)	M 1 : 3000	554	620
5	,,	,,	4-(1-Me- ,,)	M 1 : 5000	628	665
6	,,	,,	4-(1-Et- ,,)	G 1 : 2000	636	670
7	,,	,,	2-(1-Me-dihydro-5 : 6-benzoquinoline)	Not tested		
8	,,	,,	2-(1 : 3 : 3-Trimethylindoline)	M 1 : 2000	504	560
9	,,	,,	2-(3-Et-4 : 5-di-Ph-thiazoline)	E 1 : 4000	551	580
10	,,	,,	2-(3-Et-benzothiazoline)	M 1 : 5000	531	575
11	,,	,,	2-(3-Et-6-Cl-benzothiazoline)	G 1 : 2000	536	570
12	,,	,,	2-(3-Et-5 : 6-di-Me-benzothiazoline)	E/G 1 : 6000	541	570
13	,,	,,	2-[3-Et-naphtho(1′ : 2′-4 : 5)-thiazoline]	G 1 : 4000	553	590
14	,,	,,	2-[3-Et-5′ : 6′ : 7′ : 8′-tetrahydronaphtho(2′ : 1′-4 : 5)thiazoline]	E/G 1 : 6000	539	580
15	,,	,,	2-(3-Me-benzoselenazoline)	D 1 : 2000	532	570
16	,,	,,	2-(3-Et- ,,)	G 1 : 2000	536	580
17	,,	,,	1-[2-Me-1′-Ph-1 : 2-dihydroindolo-(3′ : 2′-3 : 4)*iso*quinoline]	G 1 : 2000	610	660
18	6-EtO	,,	2-(1-Me-dihydroquinoline)	D 1 : 2000	569	610
19	,,	,,	4-(1-Me- ,,)	D 1 : 2000	600	690
20	,,	,,	4-(1-Et- ,,)	G 1 : 4000	609	700
21	,,	,,	2-(1 : 3 : 3-Trimethylindoline)	M 1 : 2000	507	560
22	,,	,,	2-(3-Et-benzothiazoline)	E 1 : 4000	528	580
23	4 : 5-Benzo	,,	2-(1-Me-dihydroquinoline)	D 1 : 2000	583	530, 635
24	,,	,,	4-(1-Me- ,,)	G 1 : 6000	626	(550), (680)
25	,,	,,	2-(3-Et-benzothiazoline)	E/G 1 : 8000	560	(540), 600
26	6-Cl-4-Me	,,	2-(1-Me-dihydroquinoline)	D 1 : 2000	557	(600)
27	,,	,,	4-(1-Me- ,,)	D 1 : 600	594	655
28	,,	,,	2-(3-Et-benzothiazoline)	E/G 1 : 6000	526	(560)
29	Unsubtd.	:CMe·CH:	2-(3-Et- ,,)	G 1 : 5000	526	—
30	,,	:CH·CMe:	2-(3-Me- ,,)	Not tested		
31	,,	,,	2-(3-Et- ,,)	E 1 : 20,000	544	600
32	,,	:CMe·CMe:	2-(3-Et- ,,)	G 1 : 2000	400	—
33	,,	None	2-(3-Et- ,,)	G 1 : 2000	418	—

Since supplies of 4 : 5-benzo- and 6-chloro-4-methyl-thioindoxyl-2-aldehydes were available (see *J.*, 1952, 2127), we have utilised them to prepare a number of *mero*cyanines, *e.g.*, [2-(dihydro-3-keto-4 : 5-benzothionaphthen)][2-(dihydro-1-methylquinoline)]dimethin-*mero*cyanine (XVIII), for direct comparison with the isomeric 3-(2-keto)*mero*cyanines described above. These 2-(dihydro-3-ketothionaphthen)*mero*cyanines are similar in type

to those prepared by earlier workers, but members carrying substituents in the thionaphthen ring have not apparently been previously recorded.

We are now investigating further variations in the structure of the above 3-(dihydro-2-ketothionaphthen)*mero*cyanines, in particular those in which the dimethin chain is replaced by (*a*) a tetramethin or a hexamethin chain, or (*b*) a diaza-chain.

Experimental

For ready correlation of preparation, identity, and absorption, the number allotted in arabic numerals to each *mero*cyanine in Tables 1 and 2 (pp. 2139, 2141) is quoted immediately before the name in the description of the preparation of the dye. In most preparations, the effect of various basic catalysts was tested: only the most effective catalyst in each case is quoted below. Unless otherwise stated, one molecular proportion of the basic catalyst was employed. Since the colour of the crystalline *mero*cyanines usually differed markedly from that of their solutions, both colours are given in Table 2.

Intermediates used in the Preparation of the mero*Cyanines.*—Of the various quaternary salts employed, the following are new: all were prepared by heating the cyclic tertiary amine with an excess of the appropriate alkyl iodide under reflux for the time stated. 2-*Methyl*-4 : 5-*diphenylthiazole ethiodide*, after 13 hours' heating, was collected, triturated with acetone, and then recrystallised from ethanol: it formed pale yellow crystals (yield 33%), m. p. 184° (Found: N, 3·6. $C_{18}H_{18}NIS$ requires N, 3·4%). 2 : 5 : 6-*Trimethylbenzothiazole ethiodide* (3 hours' heating) on recrystallisation from ethanol gave colourless needles (yield 54%), m. p. 231° (decomp.) (Found: N, 4·4. $C_{12}H_{16}NIS$ requires N, 4·2%). 5′ : 6′ : 7′ : 8′-*Tetrahydro*-2-*methylnaphtho*(2′ : 1′-4 : 5)*thiazole ethiodide* (IX) (7·5 hours' heating) on recrystallisation from ethanol and then acetone gave colourless crystals (yield 18%), m. p. 214° (decomp.) (Found: C, 46·4; H, 4·8. $C_{14}H_{18}NIS$ requires C, 46·8; H, 5·05%). 2-*Ethylbenzothiazole methiodide* (2 hours' heating), when recrystallised from ethanol–light petroleum (b. p. 60—80°), formed colourless crystals (yield, 28%), m. p. 180—181° (Found: N, 4·7. $C_{10}H_{12}NIS$ requires N, 4·6%). The *ethiodide* (8 hours' heating) (yield, 21%) had m. p. 195° (from ethanol) (Found: N, 4·2. $C_{11}H_{14}NIS$ requires N, 4·4%). 2-*Methyl*-5-*phenylbenzoxazole ethiodide* (13 hours' heating) formed colourless crystals (yield 42%), m. p. 182—183°, from acetone (Found: C, 52·4; H, 4·6. $C_{16}H_{16}ONI$ requires C, 52·6; H, 4·4%).

mero*Cyanines derived from Thio-oxindole*-3-*aldehyde* (I).

(1) [3-(*Dihydro*-2-*ketothionaphthen*)][2-(*dihydro*-1-*methylpyridine*)]*dimethin*mero*cyanine*. A mixture of the aldehyde (I) (0·3 g.), 2-picoline methiodide (0·4 g., 1 mol.), piperidine (0·5 c.c., 3 mols.), triethylamine (10 c.c.), and methanol (5 c.c.) was boiled under reflux for 15 hours. The mero*cyanine* separated from the cold mixture in 17% yield.

(2) *The* [4-(*dihydro*-1-*methylpyridine*)]mero*cyanine*. A mixture of the above aldehyde (0·34 g.), 4-picoline methiodide (0·45 g., 1 mol.), piperidine (0·19 c.c.), and methanol (10 c.c.) was boiled under reflux for 12 hours, but when the bright red solution was evaporated to dryness, the residue consisted almost entirely of the unchanged solid components. A solution of the residue in methanol (5 c.c.) was therefore shaken for 1 hour with a 10% methanolic sodium methoxide solution, when a purple precipitate of the mero*cyanine* rapidly formed; after being set aside for 2 days, this precipitate was collected (yield 22%).

(3) *The* [2-(*dihydro*-1-*methylquinoline*)]mero*cyanine* (II A–B). When the aldehyde (0·5 g.), quinaldine methiodide (0·84 g., 1 mol.), piperidine (0·28 c.c.), and methanol (10 c.c.) were heated under reflux for 12 hours, the mero*cyanine* was deposited in 21% yield.

(4) The 1-*ethyl* homologue was similarly prepared from triethylamine (1 mol.) and piperidine (2 mols.), and obtained in 36% yield. When the aldehyde and the ethiodide in ethanol were boiled for 24 hours without a catalyst, a small yield of the dye, m. p. 210·5°, was obtained.

(5) The [4-(*dihydro*-1-*methylquinoline*)]mero*cyanine* (III) was prepared as for (3) using lepidine methiodide with 4 hours' heating, and obtained in 63% yield.

When 48% hydrobromic acid was added to a cold concentrated acetone solution of this *mero*cyanine, the deep blue colour changed to deep red, and crystals of the *hydrobromide* (XIII, A–B) separated. These were collected, washed with acetone containing hydrobromic acid, and then recrystallised from acetic acid, from which the hydrobromide separated as small dull-red needles, m. p. 194° (decomp., preliminary softening) containing 3 mols. of acetic acid of crystallisation (Found: C, 54·0; H, 4·7; N, 2·2. $C_{20}H_{16}ONBrS,3C_2H_4O_2$ requires C, 54·0; H, 4·9; N, 2·4%). The hydrochloride and hydriodide are described on p. 2138.

TABLE 2. 3-(*Dihydro*-2-*ketothionaphthen*)mero*cyanines*.

[In Col. 4 the solvent (S.) used for recrystallisation is indicated as M = methanol and E = ethanol, E, M indicating that these solvents were used consecutively. The solvent in Col. 6 was ethanol, except when marked * when methanol was used.]

No.	Formula	M. p.	S.	Colour of crystals	Colour in solution	Found, % C	Found, % H	Found, % N	Required, % C	Required, % H	Required, % N
1	$C_{16}H_{13}ONS$	240°	E	Green	Red	71·7	4·9	5·1	71·9	4·9	5·2
2	$C_{16}H_{13}ONS$	259—261	E	Purple	Magenta	72·1	4·75	5·2	71·9	4·9	5·2
3	$C_{20}H_{15}ONS$	256—257	E	Green	Magenta	75·7	4·65	4·3	75·7	4·8	4·4
4	$C_{22}H_{17}ONS$	210—211	E	Blue-green	Magenta	76·35	5·2	4·25	76·9	5·0	4·1
5	$C_{20}H_{15}ONS$	244—245	E	Green	Blue	75·7	4·6	4·0	75·7	4·8	4·4
6	$C_{21}H_{17}ONS$	226	E	Green	Blue	76·0	5·2	4·2	76·1	5·2	4·1
7	$C_{24}H_{17}ONS,\frac{1}{2}C_2H_6O$ [1]	292—293	E	Dark green	Purple	76·55	4·8	2·5	76·9	5·2	3·6
8	$C_{21}H_{19}ONS$	180—181	E	Purple-red	Orange	76·0	5·6	4·1	75·7	5·7	4·2
9	$C_{27}H_{21}ONS$	234—235	E	Green	Purple	73·9	4·9	3·3	73·75	4·8	3·2
10	$C_{19}H_{15}ONS_2$	230—231	E	Brown	Orange-pink	67·3	4·2	4·0	67·6	4·5	4·15
11	$C_{19}H_{14}ONClS_2$	201	M	Purple-red	Orange-pink *	61·3	3·8	4·1	61·4	3·8	3·8
12	$C_{21}H_{19}ONS_2$	258—259	E	Purple	Reddish-pink	69·2	5·4	4·2	69·0	5·2	3·8
13	$C_{23}H_{17}ONS$	252—254	E	Dark purple	Purple	70·9	4·85	3·7	71·3	4·4	3·6
14	$C_{23}H_{21}ONS_2$	246—248	E	Purple-red	Purple	70·6	5·8	3·8	70·6	5·4	3·6
15	$C_{18}H_{13}ONSSe$	227—228	E, M	Yellow-green	Reddish-pink *	58·5	3·7	3·9	58·4	3·6	3·8
16	$C_{19}H_{15}ONSSe$	209—211	E	Blue-grey	Reddish-pink	59·5	3·3	3·6	59·4	3·9	3·6
17	$C_{32}H_{22}ON_2S$	249—250	E	Dark-green	Purple-blue	79·4	4·7	5·7	79·7	4·6	5·8
18	$C_{22}H_{19}O_2NS$	248—249	E	Green	Purple	73·45	5·3	3·8	73·1	5·3	3·9
19	$C_{22}H_{19}O_2NS$	192—193	E	Purple	Blue	73·3	5·5	3·8	73·1	5·3	3·9
20	$C_{23}H_{21}O_2NS$	175	E	Green	Blue	73·6	5·8	3·7	73·5	5·6	3·7
21	$C_{23}H_{23}O_2NS$	168—169	E, M	Orange-red	Orange *	73·5	6·3	3·6	73·2	6·1	3·7
22	$C_{21}H_{19}O_2NS_2$	207	E	Greenish-brown	Reddish-pink	66·2	5·2	4·0	66·1	5·0	3·7
23	$C_{24}H_{17}ONS$	250	E	Dark green	Violet	78·3	5·3	3·5	78·4	4·7	3·8
24	$C_{24}H_{17}ONS,\frac{1}{2}C_2H_6O$ [1]	307—309	E	Greenish-brown	Pale blue	76·9	4·8	3·8	76·9	5·2	3·6
25	$C_{23}H_{17}ONS_2,\frac{1}{2}C_2H_6O$ [1]	264—266	E	Brown	Purple-red	70·3	4·9	3·5	70·2	4·9	3·4
26	$C_{21}H_{16}ONClS$	258—260	M	Blue-green	Magenta	69·25	4·9	4·0	68·9	4·4	3·8
27	$C_{21}H_{16}ONClS,C_2H_6O$ [2]	299—300	E	Purple-black	Blue	67·0	4·75	3·5	67·1	5·4	3·5
28	$C_{20}H_{16}ONClS$	269—270	E	Purple	Reddish-pink	62·15	4·2	3·7	62·2	4·2	3·6
29	$C_{20}H_{17}ONS_2$	174—175	M	Blue-green	Purple-red *	68·3	5·2	—	68·3	4·9	—
30	$C_{19}H_{15}ONS_2$	193—194	M	Steel blue	Magenta *	67·8	4·9	—	67·6	4·5	—
31	$C_{20}H_{17}ONS_2$	173	M	Green	Magenta *	68·4	5·2	—	68·3	4·9	—
32	$C_{20}H_{17}ONS_2$	191	M	Orange	Orange-yellow *	68·5	4·8	—	68·3	4·9	—
33	$C_{17}H_{13}ONS_2$	175—176	E	Yellow-brown	Orange-yellow	65·7	4·0	4·4	65·55	4·2	4·5

[1] Hemiethanolates. [2] Ethanolate.

(6) *The* 1-*ethyl homologue.* This was similarly prepared, but with 12 hours' heating, and was isolated in 64% yield.

(7) *The* [2-(*dihydro*-1-*methyl*-5 : 6-*benzoquinoline*)]mero*cyanine.* The aldehyde (0·24 g.), 5 : 6-benzoquinaldine methiodide (0·45 g., 1 mol.), piperidine (0·5 c.c., 3·7 mols.), and methanol (10 c.c.) were boiled for 6 hours, the mero*cyanine* rapidly separating (yield, 33%).

(8) *The* [2-(1 : 3 : 3-*trimethylindoline*)]mero*cyanine* (V). (*a*) The aldehyde (0·34 g.), 1 : 3 : 3-trimethyl-2-methyleneindoline (Fischer's base) (0·33 g., 1 mol.) and methanol (10 c.c.) were boiled for 12 hours without a catalyst. The mero*cyanine*, m. p. 180—181°, separated in 47% yield.

(*b*) The above experiment was repeated, but with 2 : 3 : 3-trimethylindolenine methiodide (IV) (1 mol.), but no *mero*cyanine could be isolated from the orange-red solution. When, however, piperidine (1 mol.) was added to the solution, boiling soon caused the separation of the *mero*cyanine (yield 55%), m. p. 179—180°, unchanged by admixture with the previous sample.

When 48% hydrobromic acid (0·25 g.) was added to an orange solution of the *mero*cyanine (0·1 g.) in cold acetone (6 c.c.), red crystals of the hydrobromide rapidly separated : these were collected, washed with acetone containing hydrobromic acid, recrystallised from acetic acid, and dried in a desiccator at 1 atm. for 2 days. The *hydrobromide* then had m. p. 239—240° (decomp., with liberation of orange-brown vapour) (Found : C, 60·6; H, 5·0; N, 3·5. $C_{21}H_{20}ONBrS$ requires C, 60·8; H, 4·9; N, 3·4%) ; when set aside in a specimen tube for 2 months the compound had m. p. 232—234°, and after 11 months, m. p. 229—231°. Recrystallisation of a freshly prepared sample from ethanol gave crystals of the original mero*cyanine*, m. p. 178—180°, unchanged by admixture with an authentic sample ; complete dissociation of the hydrobromide had thus occurred. The hydrobromide is systematically named [2-*hydroxy*-3-*thionaphthen*][1 : 3 : 3-*trimethyl*-2-*indolenine*]*dimethincyanine bromide.*

(9) The [2-(3-*ethyl*-4 : 5-*diphenylthiazoline*)]mero*cyanine* (VI) was prepared using piperidine in methanol with 5 hours' heating, in 69% yield.

(10) The [2-(3-*ethylbenzothiazoline*)]mero*cyanine* (VII) was prepared using piperidine in methanol with 13 hours' heating, and obtained in 45% yield. When the anil of thio-oxindole-3-aldehyde was used in place of the free aldehyde in this preparation, with 6 hours' heating, the mero*cyanine* (m. p. 230°) was obtained in 18% yield.

(11) The [2-(6-*chloro*-3-*ethylbenzothiazoline*)]mero*cyanine* was prepared using triethylamine in ethanol with 5 hours' heating; yield, 19%.

(12) The [2-(3-*ethyl*-5 : 6-*dimethylbenzothiazoline*)]mero*cyanine* was prepared using piperidine in methanol with 1 hour's heating; yield, 34%.

(13) The [2-(3-*ethylnaphtho*(1′ : 2′-4 : 5)*thiazoline*)]mero*cyanine* was prepared using the iodide (VIII) and triethylamine in ethanol with 12 hours' heating; yield, 11%.

(14) The [2-(3-*ethyl*-5′ : 6′ : 7′ : 8′-*tetrahydronaphtho*(2′ : 1′-4 : 5)*thiazoline*)]mero*cyanine* was prepared using the iodide (IX) and piperidine in methanol with 3 hours' heating; yield, 48%.

(15) The [2-(3-*methylbenzoselenazoline*)]mero*cyanine* (X) was prepared by boiling a solution of the aldehyde (0·4 g.), the methiodide (0·76 g., 1 mol.) and piperidine in pyridine (10 c.c.) for 6 hours, and then evaporating the mixture to dryness under reduced pressure, and recrystallising the residue : yield, 13%.

(16) The 3-*ethyl* homologue was similarly prepared using triethylamine in pyridine with 18 hours' boiling; yield, 13%.

(17) The [1-{1 : 2-*dihydro*-2-*methyl*-1′-*phenylindolo*(3′ : 2′-3 : 4)iso*quinoline*}]mero*cyanine* (XI, A—C) was prepared using piperidine in ethanol with 6 hours' heating, the solution being then set aside for 3 days whilst crystallisation proceeded; yield, 42%.

mero*Cyanines derived from* 6-*Ethoxy*(*thio-oxindole*)-3-*aldehyde.*

(18) [3-(6-*Ethoxydihydro*-2-*ketothionaphthen*)][2-(*dihydro*-1-*methylquinoline*)]*dimethin*mero*cyanine* was prepared in the usual way, piperidine in methanol being used with 11 hours' heating, although crystals rapidly separated : yield, 51%.

(19) The [4-(*dihydro*-1-*methylquinoline*)]mero*cyanine* was similarly prepared : yield, 23%.

(20) The 1-*ethyl* homologue was similarly prepared using piperidine in ethanol with 24 hours' boiling : the solution when set aside at 0° overnight deposited a dark oil which solidified on rubbing; yield, 26%.

(21) The [2-(1 : 3 : 3-*trimethylindoline*)]mero*cyanine* was prepared from the aldehyde and 1 : 3 : 3-trimethyl-2-methyleneindoline (1 mol.), with 16 hours' boiling in methanol, and was collected after the mixture had been set aside for 2 days; yield, 26%.

(22) The [2-(3-*ethylbenzothiazoline*)]mero*cyanine* was prepared with piperidine in methanol with 6 hours' boiling; yield, 53%.

mero*Cyanines derived from* 4 : 5-*Benzothio-oxindole*-3-*aldehyde.*

(23) [3-(*Dihydro*-2-*keto*-4 : 5-*benzothionaphthen*)][2-(*dihydro*-1-*methylquinoline*)]*dimethin*mero*cyanine* was prepared by using piperidine in methanol with 6 hours' heating; yield, 23%.

(24) The [4-(*dihydro*-1-*methylquinoline*)]mero*cyanine* was prepared by means of piperidine in methanol and boiling for 10 hours : yield, 23%.

(25) The [2-(3-*ethylbenzothiazoline*)]mero*cyanine* was prepared by means of piperidine in methanol with 12 hours' heating; yield, 20%.

mero*Cyanines derived from* 6-*Chloro*-4-*methyl*(*thio-oxindole*)-3-*aldehyde.*

(26) [3-(6-*Chlorodihydro*-2-*keto*-4-*methylthionaphthen*)][2-(*dihydro*-1-*methylquinoline*)]*dimethin*mero*cyanine* was prepared using piperidine in methanol with 6 hours' heating, although crystallisation rapidly started : yield, 30%.

(27) The [4-(*dihydro*-1-*methylquinoline*)]mero*cyanine* was similarly prepared; yield, 21%.

(28) The [2-(3-*ethylbenzothiazoline*)]mero*cyanine* was also similarly prepared with 12 hours' heating; yield, 17%.

mero*Cyanines having Methyl-substituted Dimethin Chains.*

(29) [3-(*Dihydro*-2-*ketothionaphthen*)][2-(3-*ethylbenzothiazoline*)]-α-*methyldimethin*mero*cyanine* (XVI; $R^1 = Me$; $R^2 = H$, $R^3 = Et$). A solution of 3-acetyl(thio-oxindole) (1 g.), 2-methylbenzothiazole ethiodide (1·58 g., 1 mol.) and triethylamine (0·72 c.c., 1 mol.) in pyridine (20 c.c.) was boiled under reflux for 1·5 hours, rapidly developing a deep purple colour. The solvent was removed under reduced pressure, and the residue dissolved in hot methanol (25 c.c.) and set aside at 0° for 24 hours. The mero*cyanine* separated in 6% yield.

(30) [3-(*Dihydro*-2-*ketothionaphthen*)][2-(3-*methylbenzothiazoline*)]-β-*methyldimethin*mero*cyanine* (XVI; $R^1 = H$, $R^2 = R^3 = Me$). This was prepared precisely as (29) using, however, thio-oxindole-3-aldehyde (1 g.) and 2-ethylbenzothiazole methiodide (1·72 g., 1 mol.) with 1 hour's heating. The mero*cyanine* separated (yield 10%) when the methanolic solution was set aside for 3 days.

(31) The 3-*ethyl* homologue (XVI; $R^1 = H$, $R^2 = Me$, $R^3 = Et$) was prepared by using 2-ethylbenzothiazole ethiodide and 1 hour's heating. The hot deep purple solution was however poured with stirring into water (100 c.c.), then set aside for 24 hours (ice-chest), the pale red aqueous layer decanted, and the sticky purple residue well stirred with water which was again decanted. The residue when recrystallised from methanol gave the mero*cyanine* (yield 5%).

(32) [3-(*Dihydro*-2-*ketothionaphthen*)][2-(3-*methylbenzothiazoline*)]-αβ-*dimethyldimethin*mero*cyanine* (XVI; $R^1 = R^2 = R^3 = Me$). This was prepared as (29) but from the ketone (1 g.) and 2-ethylbenzothiazole methiodide (1·5 g., 1 mol.), with 25 hours' heating, giving a pale orange-brown solution. The mero*cyanine* (yield, 3·3%) separated when the methanolic solution of the residue was set aside for 3 days (ice-chest).

mero*Cyanine with no Dimethin Chain.*

(33) [3-(*Dihydro*-2-*ketothionaphthen*)][2-(3-*ethylbenzothiazoline*)]mero*cyanine* (XVII). A mixture of thio-oxindole (0·43 g.), 2-ethylthiobenzothiazole ethiodide (1 g., 1 mol.), triethylamine (0·4 c.c., 1 mol.), and ethanol (10 c.c.) was boiled under reflux for 6 hours, ethanethiol being evolved. The mero*cyanine* separated on cooling (yield 90%).

mero*Cyanines derived from* 4 : 5-*Benzothioindoxyl*-2-*aldehyde.*

[2-(*Dihydro*-3-*keto*-4 : 5-*benzothionaphthen*)][2-(*dihydro*-1-*methylquinoline*)]*dimethin*mero*cyanine* (XVIII) was prepared from the above aldehyde by using piperidine in ethanol with 6 hours' heating, and after recrystallisation from ethanol (pale violet solution) formed purple-black needles (yield, 65%), m. p. 302° (Found : C, 77·9; H, 4·6; N, 4·0. $C_{24}H_{17}ONS$ requires C, 78·4; H, 4·7; N, 3·8%).

The [4-(*dihydro*-1-*methylquinoline*)]mero*cyanine* was similarly prepared, crystals rapidly forming ; owing to its low solubility in alcohols, it was recrystallised from benzene (dark purple-blue solution), giving yellowish-green needles (yield, 52%), m. p. 284—285° (Found : C, 78·3; H, 5·8; N, 3·85. $C_{24}H_{17}ONS$ requires C, 78·4; H, 4·7; N, 3·8%).

The [2-(3-*ethylbenzothiazoline*)]mero*cyanine* was prepared with 13 hours' heating, and when recrystallised from ethanol (pinkish-red solution) gave deep green crystals (yield 15%), m. p. 251—253° (Found : C, 71·6; H, 4·6; N, 3·5. $C_{23}H_{17}ONS_2$ requires C, 71·3; H, 4·4; N, 3·6%).

mero*Cyanine derived from* 6-*Chloro*-4-*methylthioindoxyl*-2-*aldehyde*.

[2-(6-*Chlorodihydro*-3-*keto*-4-*methylthionaphthen*)][2-(*dihydro*-1-*methylquinoline*)]*dimethin*-mero*cyanine* was prepared by using piperidine in methanol with 4 hours' heating. The dye, which readily separated, was recrystallised from ethanol (magenta solution) giving purple needles (yield 41%), m. p. 293—295° (Found: C, 68·7; H, 4·3; N, 3·7. $C_{21}H_{16}ONClS$ requires C, 68·9; H, 4·4; N, 3·8%).

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