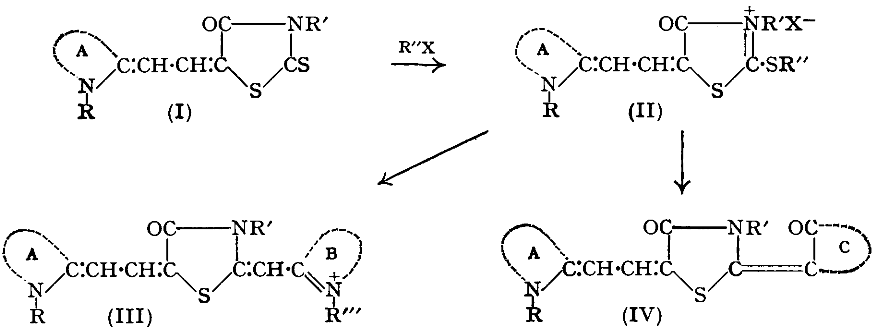
930. *The Colour of Organic Compounds. Part VII.* Complex Cyanines and* mero*Cyanines.*

By E. B. KNOTT and R. A. JEFFREYS.

Complex cyanines (III) and *mero*cyanines (IV) containing 4 : 5-disubstituted thiazole and oxazole nuclei and, as central nucleus, 3-ethylthiazolid-4-one, have been prepared and their properties compared with related dyes derived from benzoxazoles, benzothiazoles, etc. (Kendall and Fry, B.P. 489,335). It is also shown that dimethin*mero*cyanines containing the 2-ethylthiothiazol-5-one (as V) and 3-alkyl-2-thiothiazolid-5-one (VI) nuclei are readily quaternized to the salts (VII) which condense with suitable intermediates to give complex dyes (VIII and IX) which are isomeric with (III) and (IV). Observations on the absorption of these dyes are made.

KENDALL and FRY (B.P. 489,335; see also Kendall, B.P. 487,051) and Brooker, independently (Mees, "The Theory of the Photographic Process," Macmillan, 1942, p. 1038) showed that *mero*cyanines (I; $n = 0$ or 1) derived from 3-substituted rhodanines (thiazolid-4-ones) were quaternised by alkyl sulphates or alkyl toluene-*p*-sulphonates to give cationic dyes (II) containing an active $C_{(2)}$ in the thiazolidone ring. The latter dyes could then be condensed further, in the presence of a tertiary base, with a heterocyclic quaternary salt carrying a reactive methyl group to give a complex cyanine (III), or with a ketomethylene compound to give a complex *mero*cyanine (IV).



These trinuclear dyes, particularly (III) carrying a substituent in the dimethin chain are set forth as red sensitisers for colour photographic material (B.I.O.S. Final Report No. 1355, Item No. 22). A number of chain-unsubstituted dyes of types (III) and (IV) are now reported in which nuclei A and/or B are 4-aryl-5-phenylthiazoles. The series has been extended by employing 4-aryl-5-tolylthiothiazole, 4-aryl-5-aryloxythiazole, and 4 : 5-diaryloxazole intermediates, and parent dimethin*mero*cyanines have been reported in previous papers (Knott, *J.*, 1952, 4099; Jeffreys, to be published). For comparative purposes a series of such dyes derived from benzoxazoles, benzothiazoles, quinoline, etc., have been prepared.

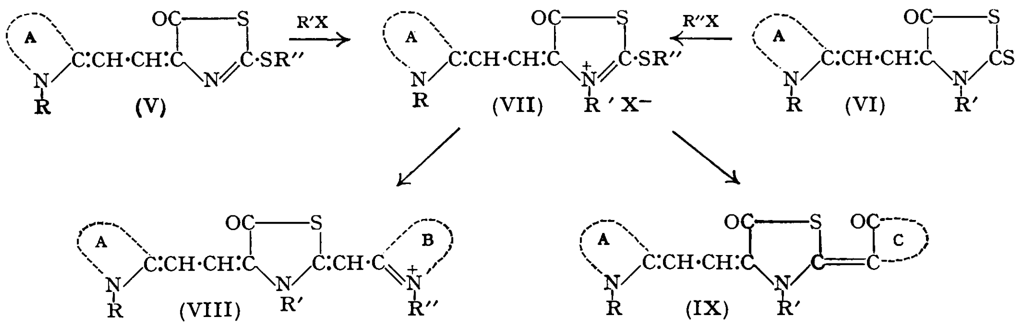
It has also been found that isomeric complex dyes (VIII and IX), in which the central nucleus is a 3-alkylthiazolid-5-one, are readily obtained by quaternizing dimethin*mero*-cyanines derived from 2-ethylthiothiazol-5-one (as V) (Cook, Harris, and Shaw, *J.*, 1949, 1435; Aubert, Knott, and Williams, *J.*, 1951, 2185) or 3-alkyl-2-thiothiazolid-5-ones (VI) (Jeffreys and Knott, *J.*, 1952, 4632) to give (VII) and treating these with a quaternary ammonium salt carrying a reactive methyl group or an amino-group to give (VIII) or (XII—XIII) respectively, or with a ketomethylene compound to give (IX).

* Part VI, *J.*, 1952, 4632.

In two cases, complex dyes (IV) were quaternized and converted into tetranuclear cyanines (X and XI) (cf. Kendall and Fry, *loc. cit.*).

Since this work was completed Doyle, Lawrence, and Kendall (B.P. 622,775) have given numerous examples of dyes of type (VI) and one example of type (VIII).

The Colour of these Dyes.—In all cases introduction of the third nucleus brings with it a profound bathochromic shift in absorption, as has already been observed by Brooker (*loc. cit.*). In the *mero*cyanine series (Table 6), with the exception of dyes derived from quinoline, it is noteworthy that in both the thiazolid-4-one and -5-one series the addition of the third nucleus (3-ethylthiazolid-4-one) causes a fairly constant shift of *ca.* 50 mμ. A similar shift is also given by the introduction of the 2-ethylthiothiazol-5-one nucleus (cf. dyes 82 and 95, 110 and 131, 100 and 129, 102 and 130). On the other hand, the 2-alkoxythiazol-5-one nucleus gives a smaller shift of *ca.* 40 mμ. The 3-methyl-2-thio-



thiazolid-5-one nucleus was introduced as the third nucleus in one case and caused a remarkable shift of 79 mμ (cf. dyes 102 and 123). This additional shift is a probable result of excessive over-crowding in the molecule which will force the thiazolid-5-one end-nucleus out of coplanarity with the rest of the molecule. This effect is considered to be additional to that produced by the higher colour value of the thiazolid-5-one nucleus compared with the 4-keto-analogue (cf. Jeffreys and Knott, *loc. cit.*).

TABLE 1. *3-Alkyl-2-alkylthio-4-(*A*-ethylidene)-5-ketothiazolinium toluene-*p*-sulphonates* (VII).

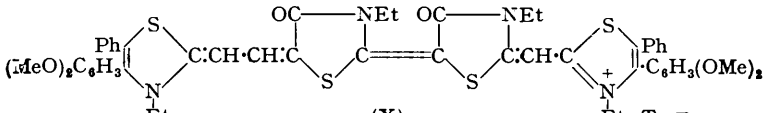
Nucleus A	R′	R″	M. p.	Appearance (from EtOH–Et$_2$O)	$\lambda_{max.}$ (mμ; MeOH)	Formula	Found : S, %	Reqd. : S, %
3-Ethylbenzoxazolin-2-ylidene	Me	Me	222°	Red prisms, blue reflex	488	$C_{23}H_{24}O_5N_2S_3$	18·65	19·0
,, ,,	Me	Et	209	Flat red needles	488	$C_{24}H_{26}O_5N_2S_3$	18·6	18·5
,, ,,	Et	Et	176	Green plates	490	$C_{18}H_{21}O_2N_2S_2I$ *	13·05	13·1
3-Ethylbenzothiazolin-2-ylidene	Me	Me	182	Maroon leaflets	522	$C_{23}H_{24}O_4N_2S_2$	23·5	23·7
1-Ethyldihydroquinol-4-ylidene	Me	Me	—	Green plates	565	$C_{25}H_{26}O_4N_2S_3$ †	18·6	18·7

* Iodide. Found: I, 26·1. Reqd.: I, 26·0%. † Found: N, 5·3. Reqd.: N, 5·45%.

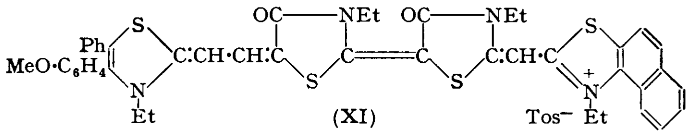
In the cyanine series the shift on introduction of the third nucleus (Tables 7 and 8) varies, as expected, with the nature of this nucleus. The shift obtained however is not consistent with the shift expected from a consideration of the intrinsic colour values of these nuclei as exhibited in simpler dyes. Thus, in (III) and (VIII), in which A is 3-ethylbenzoxazoline, the shift given by trimethylindolenine is unusually high whilst that given by the diarylazoles is similar to or less than that given by the corresponding benzazoles, benzothiazoles, etc. It would appear therefore that the stronger the $+M$ effect of nucleus B the stronger is the hypsochromic effect which offsets the expected bathochromic effect of the introduction of the nucleus.

It will also be observed that in the same series (Table 8) the shift in acetone on addition of nucleus B is greater in the 5-keto-series (VIII) than in the 4-keto-series (III), but in pyridine the 4-keto-series gives the larger shift (Table 7).

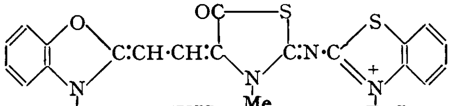
In all cases the 5-ketones (VIII, IX) are deeper than the 4-ketones (III, IV). One of the major reasons for this may be the lower degree of non-degeneracy of the resonance system in the 5-ketones, as shown by the generally higher value of $\varepsilon_{max.}$ of such dyes. In the cyanine series the 4-ketones (III) have $\varepsilon_{max.}$ *ca.* 10×10^4 whilst the values for the 5-ketones are about $15—16 \times 10^4$. There appears to be no relation between the differences in absorption of such isomeric dyes and the nature of the nuclei A, B, or C.



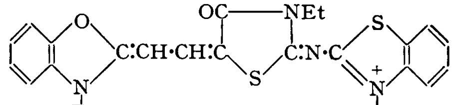
(X)



(XI)



(XII)



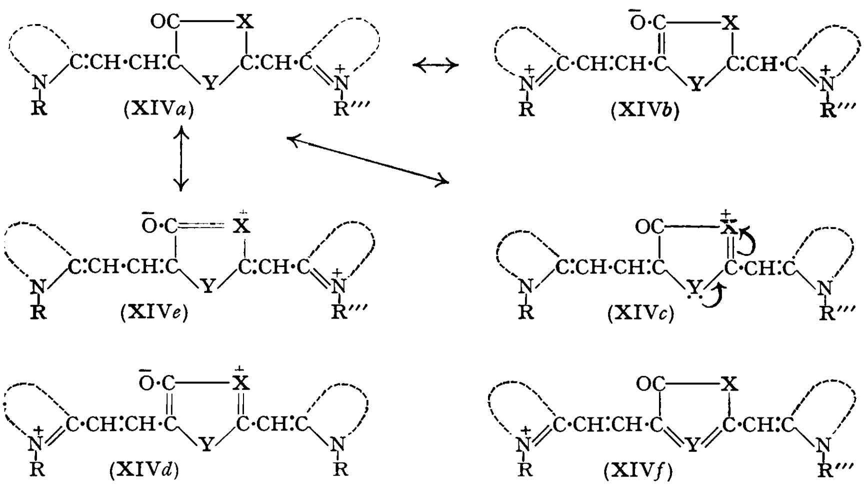
(XIII)

[Tos = p-$C_6H_4Me{\cdot}SO_3$)

In general, as found in the simpler, parent *mero*cyanines the 5-ketones show double peaks or secondary inflections. These are shown in the 4-keto-series only in one or two cases.

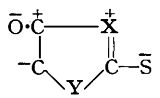
The absorption peaks of the complex 5-keto-cyanines (VIII) show some sensitivity towards solvent polarity, a gradual hypsochromic shift resulting on proceeding from pyridine through acetone to aqueous formamide. On the other hand, the 4-keto-cyanines (III) are fairly insensitive to solvent changes.

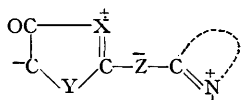
Resonance Systems in these Dyes.—For this study the resonance systems in the cyanines only are considered, the same arguments being readily applied in the *mero*cyanines. The latter cations contain two well-defined and separate resonance systems, both of which are capable of causing visible absorption. These are the amide-type resonance (XIV*a* ⟷ *b*; XIV*c* ⟷ *d*) and the cyanine-type resonance (XIV*a* ⟷ *c*; XIV*b* ⟷ *d*). The former

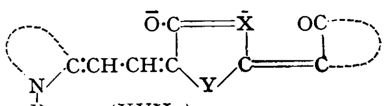


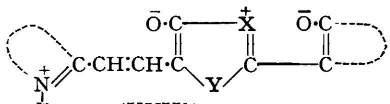
is the system present in the parent dimethin*mero*cyanine, whilst the latter is a short-path system generally associated with absorption in the blue and near-ultra-violet region of the spectrum. The powerful bathochromic shifts experienced on the addition of the third nucleus may *a priori* be a function of two major effects. (i) The system (XIV*a* ⟷ *b*) may be the fundamental resonance system and the addition of the third nucleus may then disturb this by increasing the energy of its excited structures (Knott, *J.*, 1951, 1028). (ii) There may be interaction of both resonance systems which allows the π-electrons of either system the freedom to move along the whole length of the molecule. This would be equivalent to a considerable extension of the conjugated path of the molecule. This possibility was envisaged by Brooker (*loc. cit.*, p. 1039).

Effect (i) can be analysed by considering the fragments (XV) and (XVI). These represent important excited structures of the system (XIV*a* ⟷ *b*; XIV*a* ⟷ *c*). Their importance will be decreased and a bathochromic effect will be produced as the amount of positive charge on –X– increases (adjacent charges of like sign). The replacement of thione sulphur in the parent dye by the heterocyclic cation (XVI; Z = CH) might well be expected to achieve such an increase although a shift of such a magnitude as that found would hardly be expected. On replacing Z = CH by Z = N in (XVI), *i.e.*, by increasing the importance of excited structures containing (XVI), a further increase in the amount of positive charge on –X– should also result. Such a replacement, however, results in a strong hypsochromic shift: dye No. 9 (559 mμ) ⟶ (XIII) (535 mμ), dye No. 36 (582 mμ) ⟶ (XII) (537 mμ). Effect (i), therefore, cannot be considered to be of importance.


(XV)


(XVI)


(XVII*a*)


(XVII*b*)

Effect (ii) is shown in the considerable increase in $\varepsilon_{max.}$ on proceeding from the parent dye ($\varepsilon_{max.} = 4$—8×10^4) to the trinuclear dye ($\varepsilon_{max.} = 10$—15×10^4) (cf. Brooker, *loc. cit.*, p. 1040). The responsible resonance is now considered to be represented by the extreme structures (XIV*a* ⟷ *e*) and (XIV*d*). Structure (XIV*e*) shows clearly that the central nucleus is not an insulator between the two basic resonance systems but can function as a conductor between the two halves of the molecule. Similarly the resonance in the trinuclear merocyanine may be represented by (XVII*a* ⟷ *b*).

The resonance system (XIV*a* ⟷ *f*) (Y = S), which may be assumed to be present in (III) and in which the sulphur atom functions as a resonance transmitter, appears to be of no importance since this type of resonance is excluded in (VIII; *i.e.*, XIV, Y = NR).

Experimental

Microanalyses are by Dr. Weiler and Dr. Strauss, Oxford.

Quaternized Dimethinmerocyanines (II and VII).—These were obtained in solid or tar form by fusing the dyes (I, V, or VI) (cf. Knott, *loc. cit.*; Jeffreys, *loc. cit.*; Jeffreys and Knott, preceding paper) (1 mol.) with alkyl sulphate or toluene-*p*-sulphonate (1·0—1·1 mols.) at 120—130° for 30—60 minutes or until the maximum water-solubility was achieved. In general the quaternary salts were not isolated (see, however, Table 1) before proceeding to the next step.

Trinuclear Dyes.—These were all obtained by dissolving the quaternized dyes (II or VII) (1 mol.) in ethanol (*ca.* 10 c.c./g.), adding the ketonic heterocyclic compound (1 mol.) or 2-methylheterocycle quaternary salt (1 mol.) and triethylamine (1·1 mols.), and heating the whole on the steam bath for 2—5 minutes. In some cases better yields were obtained by keeping the solution at room temperature overnight. The mero*cyanines* (IV, IX) (see Tables 4 and 5) usually separated rapidly, but it was often necessary to precipitate the *cyanines* (III, VIII) (see Tables 2 and 3) by a little aqueous potassium iodide. The dyes were collected and washed with ethanol until the washings were free from impurities. This point was shown by observing the

TABLE 2. [B][3-*ethyl*-5-(A-*ethylidene*)-2-*thiazol*-4-*one*]*methincyanine iodides* (III).

No.	Nuclei B (first) and A (second)	M. p.	Solvent	Appearance	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
1	1 : 3 : 3-Trimethyl-2-indolenine 1 : 3 : 3-Trimethylindolin-2-ylidene	241°	EtOH	Violet	585	$C_{30}H_{34}O_5N_3ClS$ [b]	N, 6·9	S, 5·5	N, 6·85	S, 5·5
2	3-Ethyl-2-benzoxazole 3-Ethylbenzoxazolin-2-ylidene	269	,,	Gold leaflets	542	$C_{26}H_{26}O_3N_3IS$	N, 7·2	I, 21·8	N, 7·15	I, 21·65
3	3-Ethyl-2-benzothiazole 3-Ethylbenzothiazolin-2-ylidene	260	C_5H_5N	Green	586	$C_{26}H_{26}ON_3IS_3$	S, 15·5	I, 20·7	S, 15·5	I, 20·5
4	3-Ethyl-2-benzoselenazole 3-Ethylbenzoselenazolin-2-ylidene	271	,,	Steel-blue	592	$C_{26}H_{26}ON_3ISSe_2$	I, 17·6	—	I, 17·8	—
5	1-Ethyl-2-quinoline 1-Ethyldihydroquinol-2-ylidene	285 201	NH_2Ph EtOH	Gold threads ,,	642 (660) —	$C_{30}H_{30}ON_3IS$ $C_{37}H_{37}O_4N_3S_2$ [c]	N, 6·95 C, 68·1	I, 21·1 H, 5·8	N, 6·9 C, 68·0	I, 20·9 H, 5·7
6	1-Ethyl-4-quinoline 1-Ethyldihydroquinolin-4-ylidene	271 [a]	C_5H_5N	Sepia threads	702	$C_{30}H_{30}ON_3IS$	N, 7·05	I, 20·7	N, 6·9	I, 20·9
7	1 : 3 : 3-Trimethyl-2-indolenine 3-Ethylbenzoxazolin-2-ylidene	261 [a]	EtOH–Et_2O	Green needles	581	$C_{28}H_{30}O_2N_3IS$	C, 56·2 I, 21·2	H, 4·9 —	C, 56·05 I, 21·2	H, 5·0 —
8	3-Methyl-2-thiazoline 3-Ethylbenzoxazolin-2-ylidene	295 [a]	C_5H_5N–MeOH	Chocolate leaflets	532	$C_{21}H_{24}O_2N_3IS_2$	I, 23·5	—	I, 23·5	—
9	3-Ethyl-2-benzothiazole 3-Ethylbenzoxazolin-2-ylidene	269	MeOH	Green needles	559	$C_{26}H_{26}O_2N_3IS_2$	I, 21·3	—	I, 21·05	—
10	3-Ethyl-2-benzoselenazole 3-Ethylbenzoxazolin-2-ylidene	270 [a]	C_5H_5N	Moss-green needles	563	$C_{26}H_{26}O_2N_3ISSe$	N, 6·5	I, 19·7	N, 6·45	I, 19·55
11	1-Ethyl-2-quinoline 3-Ethylbenzoxazolin-2-ylidene	257 [a]	NH_2Ph–MeOH	Sepia	590	$C_{28}H_{28}O_2N_3IS$	C, 56·4	H, 4·5	C, 56·25	H, 4·7
12	1-Ethyl-4-quinoline 3-Ethylbenzoxazolin-2-ylidene	285 [a]	C_5H_5N–MeOH	Sepia prisms	613	$C_{28}H_{28}O_2N_3IS$	I, 21·4	S, 5·5	I, 21·3	S, 5·35
13	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-oxazole 3-Ethylbenzoxazolin-2-ylidene	253 [a]	MeOH	Brown leaflets	538	$C_{35}H_{34}O_4N_3IS$	N, 5·9	I, 17·8	N, 5·85	I, 17·65
14	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethylbenzoxazolin-2-ylidene	283	C_5H_5N–MeOH	Green needles (gold reflex)	552	$C_{35}H_{34}O_3N_3IS_2$	N, 5·85	I, 17·2	N, 5·7	I, 17·3
15	1-Ethyl-4-quinoline 3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene	298	$CHCl_3$–pet [d]	Sepia needles	648	$C_{37}H_{36}O_3N_3IS$	S, 4·3	I, 17·55	S, 4·4	I, 17·4
16	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethylbenzothiazolin-2-ylidene	264	C_5H_5N	Gold	584	$C_{34}H_{32}ON_3IS_3$	I, 17·5	—	I, 17·6	—

TABLE 2 (*continued*).

No.	Nuclei B (first) and A (second)	M. p.	Solvent	Appearance	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
17	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	275°	C_5H_5N–Et_2O	Gold	615	$C_{42}H_{38}ON_3IS_3$	S, 11·6	I, 15·7	S, 11·65	I, 15·45
18	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 4-*p*-Methoxyphenyl-3-methyl-5-phenylthiazolin-2-ylidene	282	MeOH	Violet needles	613	$C_{50}H_{47}O_6N_3S_4$ [c]	N, 4·6	S, 13·9	N, 4·6	S, 14·05
19	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethylbenzothiazolin-2-ylidene	285	C_5H_5N	Green	583	$C_{35}H_{34}O_2N_3IS_3$	N, 5·6	I, 16·7	N, 5·6	I, 16·9
20	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 4-*p*-Methoxyphenyl-3-methyl-5-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxythiazolin-2-ylidene	228	C_5H_5N–MeOH	Purple needles	608	$C_{51}H_{54}O_4N_3IS_3$	C, 61·3 I, 12·6	H, 5·3 —	C, 61·5 I, 12·75	H, 5·4 —
21	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	210	Et_2O–EtOH	Brown needles	575	$C_{43}H_{40}O_3N_3IS_2$	I, 15·2	—	I, 15·2	—
22	4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenyl-2-thiazole 4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenylthiazolin-2-ylidene	227	C_5H_5N–Et_2O	Golden-brown	616 (588i)	$C_{46}H_{46}O_5N_3IS_3$	S, 10·4	I, 13·5	S, 10·2	I, 13·45
23	3-Methyl-5-phenyl-4-*p*-xylyl-2-thiazole 3-Methyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	240	EtOH	Bronze	613	$C_{44}H_{42}ON_3IS_3$	S, 11·45	I, 15·1	S, 11·3	I, 14·9
24	3-Ethyl-5-phenyl-4-*p*-xylyl-2-thiazole 3-Ethyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	260—262	,,	Bronze	614	$C_{46}H_{46}ON_3IS_3$	I, 14·3	—	I, 14·45	—
25	4-*p*-Methoxyphenyl-3-methyl-5-phenoxy-2-thiazole 4-*p*-Methoxyphenyl-3-methyl-5-phenoxythiazolin-2-ylidene	266	MeOH	Green needles	605	$C_{49}H_{45}O_8N_3S_3$ [c]	N, 4·7	S, 10·7	N, 4·65	S, 10·7
26	3-Methyl-4-*β*-naphthyl-5-*p*-tolylthio-2-thiazole 3-Ethyl-4-*β*-naphthyl-5-*p*-tolylthiothiazolin-2-ylidene	241	C_5H_5N–Et_2O	Violet threads	613	$C_{51}H_{43}ON_3IS_5$	I, 12·6	—	I, 12·7	—
27	3-Ethyl-4 : 5-diphenyl-2-oxazole 3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	284	EtOH–Et_2O	Maroon leaflets	560 (536i)	$C_{42}H_{38}O_3N_3IS$	I, 15·9	—	I, 16·05	—

[a] With decomp. [b] Perchlorate. [c] Toluene-*p*-sulphonate. [d] Pet = light petroleum (b. p. 60—80°). i = inflexion.

TABLE 3. [B][3-*alkyl*-4-(A-*ethylidene*)-2-*thiazole*-5-*one*]*methincyanine iodides* (VIII).

No.	Nuclei B (first) and A (second)	R′	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
28	1 : 3 : 3-Trimethyl-2-indolenine 1 : 3 : 3-Trimethylindolin-2-ylidene	Me	245°	Olive-green needles (M)	592 (556i)	$C_{29}H_{32}ON_3IS$	N, 7·05	I, 21·2	N, 7·05	I, 21·3
29	3-Ethyl-2-benzoxazole 3-Ethylbenzoxazolin-2-ylidene	Me	300	Grey prisms (M)	554 (524)	$C_{25}H_{24}O_3N_3IS$	N, 7·4	—	N, 7·5	—
30	3-Ethyl-2-benzothiazole 3-Ethylbenzothiazolin-2-ylidene	Me	278	Green needles (P)	613 (570)	$C_{25}H_{24}ON_3IS_3$	S, 15·7	—	S, 15·85	—
31	3-Ethyl-2-benzoselenazole 3-Ethylbenzoselenazolin-2-ylidene	Me	277	Green powder (A)	621 (575)	$C_{25}H_{24}ON_3ISSe_2$	I, 17·8	—	I, 17·55	—
32	1-Ethyl-2-quinoline 1-Ethyldihydroquinol-2-ylidene	Me	282	Green (P)	682 (632)	$C_{36}H_{35}O_4N_3S_2$ [c]	C, 68·1 S, 10·2	H, 5·6 —	C, 67·8 S, 10·05	H, 5·5 —
33	1-Ethyl-4-quinoline 1-Ethyldihydroquinol-4-ylidene	Me	234	Olive-green (NH_2Ph)	691	$C_{29}H_{28}ON_3SI$	I, 21·6	—	I, 21·4	—
34	1 : 3 : 3-Trimethyl-2-indolenine 3-Ethylbenzoxazolin-2-ylidene	Me	271	Green-gold threads (AE)	620	$C_{27}H_{28}O_2N_3IS$	N, 7·1	I, 21·9	N, 7·2	I, 21·7
35	3-Methyl-2-thiazoline 3-Ethylbenzoxazolin-2-ylidene	Me	298	Bronze prisms (M)	548	$C_{20}H_{22}O_2N_3IS_2$	S, 12·3	I, 24·4	S, 12·15	I, 24·1
36	3-Ethyl-2-benzothiazole 3-Ethylbenzoxazolin-2-ylidene	Me	292	Green needles (P)	582 (542)	$C_{25}H_{24}O_2N_3IS_2$	C, 51·2 N, 7·2 I, 21·7	H, 4·0 S, 10·7 —	C, 51·0 N, 7·15 I, 21·6	H, 4·1 S, 10·85 —
37	3-Ethyl-2-benzoselenazole 3-Ethylbenzoxazolin-2-ylidene	Me	285	Green threads (G)	578 (542i)	$C_{25}H_{24}O_2N_3ISSe$	N, 6·55	I, 20·1	N, 6·6	I, 19·95
38	1-Ethyl-2-quinoline 3-Ethylbenzoxazolin-2-ylidene	Me	268	Green (AE)	610	$C_{27}H_{26}O_2N_3IS$	I, 21·8	S, 5·3	I, 21·8	S, 5·5
39	1-Ethyl-2-quinoline 2-Ethylbenzoxazolin-2-ylidene	*n*-C_7H_{15}	244	Green prisms (ME)	614	$C_{33}H_{38}O_2N_3SI$	I, 18·85	—	I, 19·0	—
40	1-Ethyl-4-quinoline 3-Ethylbenzoxazolin-2-ylidene	Me	277	Green threads (AE)	646	$C_{27}H_{26}O_2N_3IS$	I, 22·0	—	I, 21·8	—
41	1-Ethyl-4-quinoline 3-Ethylbenzoxazolin-2-ylidene	Et	272	Blue-black (ME)	643 (612i)	$C_{28}H_{28}O_2N_3IS$	N, 7·3	I, 21·7	N, 7·05	I, 21·3
42	1-Ethyl-4-quinoline 3-Ethylbenzoxazolin-2-ylidene	*n*-C_7H_{15}	184	Moss-green needles (ME)	649 (616i)	$C_{33}H_{38}O_2N_3SI$	I, 19·2	—	I, 19·0	—
43	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-oxazole 3-Ethylbenzoxazolin-2-ylidene	Me	278 [b]	Green needles (A)	559 (528i)	$C_{34}H_{32}O_4N_3IS$	C, 58·1 I, 18·3	H, 4·7 —	C, 57·95 I, 18·0	H, 4·55 —
44	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethylbenzoxazolin-2-ylidene	Me	278	Green (PE)	583 (538i)	$C_{34}H_{32}O_3N_3IS_2$	I, 17·8	S, 9·05	I, 17·6	S, 8·85

TABLE 3 (*continued*).

No.	Nuclei B (first) and A (second)	R′	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	%	Reqd.: %	%
45	3-Ethyl-2-benzoxazole 3-Ethylbenzothiazolin-2-ylidene	Me	280°	Gold-green needles (M)	593 (560)	$C_{25}H_{24}O_2N_3IS_2$	I, 21·4	—	I, 21·6	—
46	3-Ethyl-2-benzothiazole 3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	Me	269	Green (PE)	629 (595i)	$C_{33}H_{30}ON_3IS_3$	S, 13·55	—	S, 13·6	—
47	3-Ethyl-2-benzothiazole 3-Ethyl-4-*p*-methoxyphenyl-5-phenylthiazolin-2-ylidene	Me	272	Green needles (P)	630 (590i)	$C_{34}H_{33}O_2N_3IS_3$	I, 17·3	—	I, 17·2	—
48	1-Ethyl-4-quinoline 3-Ethylbenzothiazolin-2-ylidene	Me	292	Green needles (P)	676 (640i)	$C_{27}H_{26}ON_3IS_2$	S, 10·5	I, 20·9	S, 10·7	I, 21·2
49	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethylbenzothiazolin-2-ylidene	Me	246	Green (PE)	620 (585i)	$C_{35}H_{34}O_5N_3S_4$ [d]	C, 59·3 S, 18·3	H, 3·5 —	C, 59·6 S, 18·15	H, 3·5 —
50	3-Ethyl-4 : 5-diphenyl-2-thiazole 5-Chloro-3-ethylbenzothiazolin-2-ylidene	Me	249	Violet (M)	621 (585i)	$C_{40}H_{36}O_4N_3ClS_4$ [c]	N, 5·3 S, 16·2	Cl, 4·5 —	N, 5·35 S, 16·2	Cl, 4·5 —
51	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethylbenzoselenazolin-2-ylidene	Me	268	Bronze flakes (PM)	624 (588i)	$C_{40}H_{37}O_4N_3S_3Se$ [c]	C, 60·5 N, 5·3	H, 4·7 —	C, 60·2 N, 5·25	H, 4·65 —
52	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin-2-ylidene	Me	263	Green (M)	643 (600i)	$C_{44}H_{39}O_4N_3S_4$ [c]	N, 5·15	S, 16·0	N, 5·25	S, 16·0
53	3-Ethyl-4 : 5-diphenyl-2-thiazole 3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	Me	243	Green (PE)	643 (605i)	$C_{41}H_{36}ON_3IS_3$	N, 15·1	S, 11·9	N, 5·2	S, 11·9
54	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethylbenzothiazolin-2-ylidene	Me	269	Green needles (PW)	624 (585i)	$C_{34}H_{33}O_2N_3IS_3$	I, 17·3	—	I, 17·2	—
55	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethylbenzoselenazolin-2-ylidene	Me	271	Green (P)	624 (590i)	$C_{41}H_{39}O_5N_3S_3Se$ [c]	C, 59·7 N, 5·1	H, 4·9 —	C, 59·5 N, 5·05	H, 4·7 —
56	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	Me	247	Green needles (AE)	598 (565)	$C_{42}H_{38}O_3N_3IS_2$	I, 15·5	—	I, 15·45	—
57	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-thiazole 3-Ethyl-4-*p*-methoxyphenyl-5-phenylthiazolin-2-ylidene	Me	263	Green (PW)	643 (600i)	$C_{43}H_{40}O_3N_3IS_3$	S, 10·9	I, 14·5	S, 11·05	I, 14·6
58	3-Methyl-5-phenyl-4-*p*-xylyl-2-thiazole 3-Methyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	Me	220	Green flakes (M)	642 (600i)	$C_{43}H_{40}ON_3IS_3$	S, 11·3	I, 15·1	S, 11·45	I, 15·15
59	4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenyl-2-thiazole 4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenylthiazolin-2-ylidene	Me	265	Bronze (PE)	651	$C_{45}H_{44}O_5N_3IS_3$	S, 10·1	I, 13·7	S, 10·35	I, 13·7
60	3-Methyl-5-phenoxy-4-phenyl-2-thiazole 3-Ethylbenzothiazolin-2-ylidene	Me	242	Coppery-violet threads (P)	619 (580i)	$C_{32}H_{28}O_2N_3IS_3$	N, 6·6 I, 20·6	S, 15·7 —	N, 6·9 I, 20·85	S, 15·75 —

TABLE 3 (*continued*).

No.	Nuclei B (first) and A (second)	R′	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
61	3-Methyl-5-phenoxy-4-phenyl-2-thiazole 3-Ethylbenzoselenazolin-2-ylidene	Me	263°	Green (P)	622 (585i)	$C_{32}H_{28}O_2N_3IS_2Se$	I, 16·85	—	I, 16·8	—
62	3-Methyl-5-phenoxy-4-phenyl-2-thiazole 3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin-2-ylidene	Me	264	Violet threads (P)	636 (595i)	$C_{43}H_{37}O_5N_3S_4$ [c]	S, 16·1	—	S, 15·95	—
63	5-*p*-Bromophenoxy-4-*p*-bromophenyl-3-methyl-2-thiazole 5-*p*-Bromophenoxy-4-*p*-bromophenyl-3-ethyl-thiazolin-2-ylidene	Me	190	Green flakes (M)	629 (595i)	$C_{40}H_{30}O_3N_3Br_4IS_3$	S, 8·4	—	S, 8·4	—
64	3-Methyl-4-phenyl-5-*p*-tolylthio-2-thiazole 3-Methyl-4-phenyl-5-*p*-tolylthiothiazolin-2-ylidene	Me	205	Violet threads (PME)	633 (596i)	$C_{41}H_{36}ON_3IS_5$	I, 14·3	S, 18·1	I, 14·45	S, 18·3
65	3-Methyl-4-β-naphthyl-5-*p*-tolylthio-2-thiazole 3-Methyl-4-β-naphthyl-5-*p*-tolylthiothiazolin-2-ylidene	Me	222	Bronze-violet (PME)	635 (600i)	$C_{49}H_{39}ON_3IS_5$	I, 13·1	S, 16·4	I, 13·05	S, 16·45
66	3-Ethyl-4 : 5-diphenyl-2-oxazole 3-Ethylbenzothiazolin-2-ylidene	Me	295	Green (A)	593 (560i)	$C_{40}H_{37}O_5N_3S_3$ [c]	S, 13·2	—	S, 13·1	—
67	3-Ethyl-4 : 5-diphenyl-2-oxazole 5-Chloro-3-ethylbenzothiazolin-2-ylidene	Me	210	Green (AE)	597	$C_{33}H_{29}O_2N_3ClIS_2$	S, 9·05	—	S, 8·85	—
68	3-Ethyl-4 : 5-diphenyloxazole 3-Ethylbenzoselenazolin-2-ylidene	Me	260	Green (AE)	599 (566i)	$C_{33}H_{30}O_2N_3ISSe$	I, 17·3	—	I, 17·2	—
69	3-Ethyl-4 : 5-diphenyl-2-oxazole 3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin-2-ylidene	Me	249	Green (PE)	615 (578i)	$C_{37}H_{32}O_2N_3IS_2$	I, 16·9	S, 8·5	I, 17·1	S, 8·65
70	3-Ethyl-4 : 5-diphenyl-2-oxazole 3-Ethyl-4-*p*-methoxyphenyl-5-phenylthiazolin-2-ylidene	Me	186	Green needles (M)	616 (578i)	$C_{42}H_{38}O_3N_3IS_2$	S, 7·85	I, 15·7	S, 7·8	I, 15·45
71	3-Ethyl-4 : 5-diphenyl-2-oxazole 3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	Me	265	Green (AE)	569 (540)	$C_{41}H_{36}O_3N_3IS$	I, 16·5	—	I, 17·0	—
72	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-oxazole 3-Ethylbenzothiazolin-2-ylidene	Me	263	Green (PM)	598 (565i)	$C_{34}H_{32}O_3N_3IS_2$	I, 17·3	—	I, 17·6	—
73	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-2-oxazole 3-Ethylbenzoselenazolin-2-ylidene	Me	263	Green needles (PM)	603 (566i)	$C_{34}H_{32}O_3N_3ISSe$	N, 5·7	S, 16·7	N, 5·45	S, 16·55
74	4-*p*-Dimethylaminophenyl-3-ethyl-5-phenyl-2-oxazole 3-Ethylbenzothiazolin-2-ylidene	Me	277	Blue (PM)	604 (560)	$C_{35}H_{35}O_6N_4ClS_2$ [e]	Cl, 5·0	S, 9·2	Cl, 5·05	S, 9·05

[a] M = methanol; A = ethanol, E = ether, P = pyridine, G = ethyleneglycol, W = water.
[b] With decomp. [c] Toluene-*p*-sulphonate. [d] Ethosulphate. [e] Perchlorate.

TABLE 4. 3-*Ethyl*-5-(A-*ethylidene*)-2-(C)-*thiazolid*-4-*ones* (IV).

No.	Nuclei A	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
	C = 3-*Ethyl-4-keto-2-thiothiazolidin-5-ylidene.*								
75	1 : 3 : 3-Trimethylindolin-2-ylidene	290° [b]	Brown leaflets, green reflex (PM)	544	$C_{23}H_{25}O_2N_3S_3$	S, 20·4	—	S, 20·4	—
76	3-Ethylbenzoxazolin-2-ylidene	320 [b]	Red-bronze leaflets (PM)	537(504i)	$C_{21}H_{21}O_3N_3S_3$	N, 8·75	S, 19·95	N, 8·65	S, 19·8
77	3-Ethylbenzothiazolin-2-ylidene	318 [b]	Chocolate leaflets (P)	566	$C_{21}H_{21}O_2N_3S_4$	S, 27·2	—	S, 27·0	—
78	3-Ethylbenzoselenazolin-2-ylidene	313 [b]	Green prisms (P)	562	$C_{21}H_{21}O_2N_3S_3Se$	N, 8·3	—	N, 8·05	—
79	3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin-2-ylidene	307	Sepia (PM)	584	$C_{25}H_{23}O_2N_3S_4$	S, 24·45	—	S, 24·4	—
80	1-Ethyldihydroquinol-2-ylidene	310 [b]	Green threads (P)	600(566)	$C_{23}H_{23}O_2N_3S_3$	C, 59·05 S, 20·7	H, 4·7 —	C, 58·9 S, 20·45	H, 4·9 —
81	1-Ethyldihydroquinol-4-ylidene	310 [b]	Green threads (P)	643(600i)	$C_{23}H_{23}O_2N_3S_3$	S, 20·3	—	S, 20·45	—
82	3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	298	Magenta flakes (PW)	594(556)	$C_{24}H_{27}O_2N_3S_4$	C, 60·4 N, 7·25	H, 4·7 S, 22·5	C, 60·0 N, 7·3	H, 4·7 S, 22·2
83	3-Ethyl-4-*p*-methoxyphenyl-5-phenylthiazolin-2-ylidene	286	Bronze (B)	595	$C_{30}H_{29}O_3N_3S_4$	N, 6·7	S, 19·1	N, 6·9	S, 18·8
84	4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenylthiazolin-2-ylidene	243	Green (PM)	594	$C_{31}H_{31}O_4N_3S_4$	N, 6·7	S, 20·0	N, 6·6	S, 20·1
85	3-Methyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	indef.	Olive-green (PM)	594	$C_{30}H_{29}O_2N_3S_4$	N, 7·15	S, 21·8	N, 7·1	S, 21·65
86	3-Ethyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	indef.	Green (PM)	596	$C_{31}H_{31}O_2N_3S_4$	S, 21·1	—	S, 21·2	—
87	3-Ethyl-5-phenoxy-4-phenylthiazolin-2-ylidene	274	Green (PM)	584	$C_{29}H_{27}O_3N_3S_4$	S, 26·1	—	S, 26·0	—
88	4-*p*-Methoxyphenyl-3-methyl-5-phenoxythiazolin-2-ylidene	240	Green (PM)	584	$C_{29}H_{27}O_4N_3S_4$	N, 6·6	S, 20·8	N, 6·9	S, 21·0
89	3-Ethyl-4-*p*-methoxyphenyl-5-phenoxythiazolin-2-ylidene	278	Coppery (PM)	586	$C_{30}H_{29}O_4N_3S_4$	S, 20·4	—	S, 20·55	—
90	4-*p*-Methoxyphenyl-3-methyl-5-*p*-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxythiazolin-2-ylidene	252	Green needles (PM)	585	$C_{37}H_{43}O_4N_3S_4$	C, 61·9 S, 17·6	H, 6·1 —	C, 61·5 S, 17·75	H, 5·95 —
91	5-*p*-Chlorophenoxy-4-*p*-chlorophenyl-3-ethylthiazolin-2-ylidene	246	Green-brown (PM)	584	$C_{29}H_{25}O_3N_3Cl_2S_4$	Cl, 10·5	S, 19·5	Cl, 10·7	S, 19·3
92	3-Ethyl-4-β-naphthyl-5-*p*-tolylthiothiazolin-2-ylidene	247	Green needles (PM)	585	$C_{34}H_{31}O_2N_3S_5$	S, 23·7	—	S, 23·8	—
93	3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	310	Green leaflets (PM)	562	$C_{29}H_{27}O_3N_3S_3$	S, 16·9	—	S, 17·1	—
94	3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene	287	Brown-green needles (PM)	564	$C_{30}H_{29}O_4N_3S_3$	S, 16·3	—	S, 16·25	—
	C = 2-*Ethylthio-5-ketothiazolin-4-ylidene.*								
95	3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	246	Green needles (PW)	593(550i)	$C_{29}H_{27}O_2N_3S_4$	S, 22·3	—	S, 22·2	—
	C = 3-*Ethyl-4-keto-2-thio-oxazolidin-5-ylidene.*								
96	3-Ethyl-4-*p*-methoxyphenyl-5-phenoxythiazolin-2-ylidene	276	Green needles (PM)	574	$C_{30}H_{29}O_5N_3S_2$	S, 15·75	—	S, 15·8	—
97	4-*p*-Methoxyphenyl-3-methyl-5-*p*-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxythiazolin-2-ylidene	201	,, (PM)	572	$C_{37}H_{43}O_5N_3S_3$	S, 13·4	—	S, 13·6	—
98	3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	271	Blood-red needles (PM)	548	$C_{29}H_{27}O_4N_3S_2$	S, 11·4	—	S, 11·7	—

[a] B = benzene, P = pyridine, M = methanol, W = water. [b] With decomp.

TABLE 5. 3-*Alkyl*-4-(A-*ethylidene*)-2-(C)*thiazolid*-5-*ones* (IX).

No.	Nuclei	R′	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
				C = 3-*Ethyl*-4-*keto*-2-*thiothiazolidin*-5-*ylidene*.						
	Nucleus A									
99	1 : 3 : 3-Trimethylindolin-2-ylidene	Me	283°	Steel-blue (PM)	571(540i)	$C_{22}H_{23}O_2N_3S_3$	S, 21·1	—	S, 21·0	—
100	3-Ethylbenzoxazolin-2-ylidene	Me	310	Mauve needles (P)	564(535i)	$C_{20}H_{19}O_3N_3S_3$	N, 9·4	S, 21·9	N, 9·45	S, 21·6
101	,,	Et	278	Steel-blue needles (B)	566(525i)	$C_{21}H_{21}O_3N_3S_3$	S, 21·1	—	S, 20·9	—
102	3-Ethylbenzothiazolin-2-ylidene	Me	300	Indigo needles (P)	592(560i)	$C_{20}H_{19}O_2N_3S_4$	N, 9·1	S, 27·6	N, 9·1	S, 27·8
103	,,	Et	292	Gold-green (P)	599(566i)	$C_{21}H_{21}O_2N_3S_4$	S, 26·95	—	S, 27·0	—
104	,,	n-C_7H_{15}	239	Grass-green needles (BG)	593(560i)	$C_{25}H_{27}O_2N_3S_4$	N, 7·7	S, 23·4	N, 7·8	S, 23·75
105	5-Chloro-3-ethylbenzothiazolin-2-ylidene	Me	307	Violet threads (P)	589(564i)	$C_{20}H_{18}O_2N_3ClS_4$	Cl, 7·35	S, 25·8	Cl, 7·2	S, 25·85
106	3-Ethylnaphtho(1′: 2′-4 : 5)thiazolin-2-ylidene	Me	308	Green threads (P)	612(572i)	$C_{24}H_{21}O_2N_3S_4$	S, 24·95	—	S, 25·05	—
107	3-Ethylbenzoselenazolin-2-ylidene	Me	306	Green (P)	594(564i)	$C_{20}H_{19}O_2N_3S_3Se$	C, 47·5 N, 8·1	H, 3·5 —	C, 47·25 N, 8·25	H, 3·75 —
108	1-Ethyldihydroquinol-2-ylidene	Me	307	Green threads (P)	645(605)	$C_{22}H_{21}O_2N_3S_3$	N, 9·1	S, 21·1	N, 9·25	S, 21·0
109	1-Ethyldihydroquinol-4-ylidene	Me	311	,, (A)	692(647)	$C_{22}H_{21}O_2N_3S_3$	S, 20·8	—	S, 21·0	—
110	3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	Me	298	Green needles (P)	622(586i)	$C_{28}H_{25}O_2N_3S_4$	N, 7·3	S, 24·85	N, 7·45	S, 24·9
111	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-thiazolin-2-ylidene	Me	288	Green-gold threads (B)	623(590i)	$C_{29}H_{27}O_3N_3S_4$	S, 21·4	—	S, 21·6	—
112	4-(3 : 4-Dimethoxyphenyl)-3-ethyl-5-phenyl-thiazolin-2-ylidene	Me	288	Green threads (P)	622(585i)	$C_{30}H_{29}O_4N_3S_4$	N, 6·4	S, 20·6	N, 6·75	S, 20·55
113	3-Methyl-5-phenyl-4-*p*-xylylthiazolin-2-ylidene	Me	277	Green (PM)	624(590i)	$C_{29}H_{27}O_2N_3S_4$	S, 22·25	—	S, 22·2	—
114	4-*p*-Methoxyphenyl-3-methyl-5-phenoxy-thiazolin-2-ylidene	Me	286	Green (P)	613(575i)	$C_{28}H_{25}O_4N_3S_4$	S, 21·7	—	S, 21·5	—
115	3-Ethyl-4-*p*-methoxyphenyl-5-phenoxy-thiazolin-2-ylidene	Me	253	Green needles (PM)	617(580i)	$C_{29}H_{27}O_4N_3S_4$	N, 6·85	S, 21·0	N, 6·9	S, 21·3
116	4-*p*-Methoxyphenyl-3-methyl-5-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxythiazolin-2-ylidene	Me	258	Green flakes (PM)	613(580i)	$C_{36}H_{41}O_4N_3S_4$	S, 18·2	—	S, 18·1	—
117	5-*p*-Chlorophenoxy-4-*p*-chlorophenyl-3-ethyl-thiazolin-2-ylidene	Me	275	Green needles (PM)	600(576i)	$C_{28}H_{23}O_3N_3Cl_2S_4$	S, 19·7	—	S, 19·75	—
118	5-*p*-Bromophenoxy-4-*p*-bromophenyl-3-ethyl-thiazolin-2-ylidene	Me	236	Green threads (PM)	618(584i)	$C_{28}H_{23}O_3N_3Br_2S_4$	S, 17·5	—	S, 17·35	—
119	3-Ethyl-4-phenyl-5-*p*-tolylthiothiazolin-2-ylidene	Me	224	Green needles (PM)	615(585i)	$C_{29}H_{27}O_2N_3S_5$	S, 26·5	—	S, 26·3	—
120	3-Methyl-4-β-naphthyl-5-*p*-tolylthiothiazolin-2-ylidene	Me	276	Violet (PM)	613(578i)	$C_{32}H_{29}O_2N_3S_5$	N, 6·55	S, 24·9	N, 6·5	S, 24·8
121	3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	Me	293	Green needles (P)	580(550i)	$C_{28}H_{25}O_3N_3S_3$	S, 16·4	—	S, 16·7	—

TABLE 5 (*continued*).

No.	Nuclei	R′	M. p.	Appearance (solvent [a])	$\lambda_{max.}$ (mμ; $COMe_2$)	Formula	Found: %	Found: %	Reqd.: %	Reqd.: %
	Nucleus A (first), C (second)									
122	1-Ethyldihydroquinol-2-ylidene 3-Carboxymethyl-4-keto-2-thiothiazolidin-5-ylidene	Me	270	Green (A)	645	$C_{22}H_{19}O_4N_3S_3$	N, 8·6	S, 19·7	N, 8·65	S, 19·85
123	3-Ethylbenzothiazolin-2-ylidene 5-Keto-3-methyl-2-thiothiazolidin-4-ylidene	Me	274	Green (C)	616(560i)	$C_{19}H_{17}O_2N_3S_4$	S, 28·5	—	S, 28·7	—
124	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-thiazolin-2-ylidene 3-Ethyl-4-keto-2-thio-oxazolidin-5-ylidene	Me	281	Green-black needles (PM)	613(575i)	$C_{29}H_{27}O_4N_3S_3$	N, 7·1	S, 16·8	N, 7·25	S, 16·6
125	3-Ethyl-4-*p*-methoxyphenyl-5-phenoxy-thiazolin-2-ylidene 3-Ethyl-4-keto-2-thio-oxazolidin-5-ylidene	Me	233	Green needles (PM)	607(570i)	$C_{29}H_{27}O_5N_3S_3$	S, 16·35	—	S, 16·2	—
126	4-*p*-Methoxyphenyl-3-methyl-5-(1 : 1 : 3 : 3-tetramethylbutyl)phenoxythiazolin-2-ylidene 3-Ethyl-4-keto-2-thio-5-oxazolidin-5-ylidene	Me	248	Green needles (PM)	608(570i)	$C_{36}H_{41}O_4N_3S_4$	S, 14·1	—	S, 13·9	—
127	3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene 3-Ethyl-4-keto-2-thio-oxazolidin-2-ylidene	Me	280	Indigo threads (PM)	564(540i)	$C_{28}H_{25}O_4N_3S_2$	C, 63·5 S, 12·1	H, 4·8 —	C, 63·3 S, 12·05	H, 4·7 —
128	3-Ethylbenzoxazolin-2-ylidene 5-Keto-2-phenyloxazolin-4-ylidene	Me	308	Blue needles (P)	560(530i)	$C_{24}H_{19}O_4N_3S$	N, 9·4	S, 7·1	N, 9·1	S, 7·2
129	3-Ethylbenzoxazolin-2-ylidene 5-Keto-2-*n*-octylthiothiazolin-4-ylidene	*cyclo*-Hexyl	150	Yellow-green prisms (L)	560(528i)	$C_{31}H_{39}O_3N_3S_3$	S, 16·05	—	S, 16·1	—
130	3-Ethylbenzothiazolin-2-ylidene 2-*n*-Heptylthio-5-ketothiazolidin-4-ylidene	Me	200	Green (B)	594(560i)	$C_{25}H_{29}O_2N_3S_4$	C, 56·8 S, 24·1	H, 5·55 —	C, 56·5 S, 24·1	H, 5·45 —
131	3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene 2-Ethylthio-5-ketothiazolin-4-ylidene	Me	284	Green (PW)	621(585i)	$C_{28}H_{25}O_2N_3S_4$	S, 24·8	—	S, 24·9	—
132	3-Ethyl-4-*p*-methoxyphenyl-5-phenyl-thiazolin-2-ylidene 2-Ethylthio-5-ketothiazolin-4-ylidene	Me	247	Gold (B)	620(585i)	$C_{29}H_{27}O_3N_3S_4$	S, 21·6	—	S, 21·6	—
133	3-Ethylbenzothiazolin-2-ylidene 5-Keto-2-*n*-octyloxythiazolin-4-ylidene	Me	155	Green leaflets (BG)	585(550i)	$C_{26}H_{31}O_3N_3S_3$	S, 18·2	—	S, 18·1	—
134	3-Ethyl-4-*p*-methoxyphenyl-5-phenoxy-thiazolin-2-ylidene 2-Diphenylamino-4-ketothiazolin-5-ylidene	Me	193	Green needles (PM)	600(570i)	$C_{39}H_{32}O_4N_4S_3$	S, 13·2	—	S, 13·4	

[a] B = benzene, P = pyridine, G = light petroleum, L = ligroin, W = water, E = ether, A = aniline.

colour of the filtrate which for the pure dyes were blue, blue green, or purple whilst the impurities imparted brown, yellow, or red colours to the filtrate. The yields of dye were, in general, 20—40%.

TABLE 6. *Shifts on proceeding from* (I) *or* (VI) *to* (IV) *or* (IX) (C = 3-*ethyl*-2-*thiothiazolid*-4-*one*).

$\lambda_{max.}$ (mμ) in acetone. Minor peaks and inflections (i) in parentheses.

Nucleus A	I	IV	No.	Shift	VI	IX	No.	Shift
Trimethylindolenine	490	544	75	54	(506i) 502	571 (540)	99	55 (38)
Benzoxazole	483	537 (504i)	76	54 (21)	(506) 489	564 (535)	100	58 (46)
Benzothiazole	513	566	77	53	537	592 (560i)	102	55
Benzoselenazole	515	562	78	47	541	594	107	53
2-Quinoline	538 (561i)	600 (566)	80	39 (28)	573 (543)	645 (605)	108	72 (62)
4-Quinoline	(604) 569	643 (600i)	81	39 (31)	639 (598)	692 (647)	109	53 (49)
Diphenylthiazole	546	594 (556)	82	48	(573) 544	622 (586)	77	49 (42)
Diphenyloxazole	508	562	93	54	529 (503)	580 (550i)	121	51 (47)

TABLE 7. *Shifts on proceeding from* (I) *or* (VI) *to* (III) *or* (VIII).

$\lambda_{max.}$ (mμ) in benzene (I, VI) and pyridine (III, VIII). Minor peaks and inflexions (i) in parentheses.

Nuclei A and B	I	III	No.	Shift	VI	VIII	No.	Shift
Trimethylindolenine	490	605	1	115	(516i) 502	608	28	(92) 106
Benzoxazole	483	558	2	75	(506) 489	562 (532i)	29	56 (43)
Benzothiazole	513	605	3	92	537	625 (585)	30	88
Benzoselenazole	515	612	4	97	541	632 (585)	31	91
2-Quinoline	(565i) 538	668	5	(103) 130	573 (543)	695 (650)	32	122 (107)
4-Quinoline	(604) 569	736	6	(132) 167	(639) 598	786	33	147
Diphenylthiazole	546	623	17	77	(573) 544	652 (605)	53	79 (61)
Diphenyloxazole	508	573	27	65	529 (503)	580 (545)	71	51 (42)

TABLE 8. *Shifts on proceeding from* (I) *or* (VI) *to* (III) *or* (VIII) (A = 3-*ethylbenzoxazoline*).

$\lambda_{max.}$ (mμ) in acetone.

Nucleus B	(III)	(No.)	Shift from (I) (490)	(VIII)	(No.)	Shift from (VI) (500)
Trimethylindolenine	581	(7)	91	620	(34)	120
Thiazoline	532	(8)	42	548	(35)	48
Benzoxazole	542	(2)	52	554	(29)	54
Benzothiazole	559	(9)	69	582	(36)	82
Benzoselenazole	563	(10)	73	578	(37)	78
2-Quinoline	590	(11)	100	610	(38)	110
4-Quinoline	613	(12)	123	646	(40)	146
p-Methoxyphenylphenylthiazole	552	(14)	62	583	(44)	83
p-Methoxyphenylphenyloxazole	538	(13)	48	559	(43)	59

[3-*Ethyl*-4-(3-*ethylbenzoxazolin*-2-*ylidene*-*ethylidene*)-2-*thiazol*-5-*one*][3-*methyl*-2-*benzothiazole*]-*azamethincyanine Iodide* (XII).—3-Ethyl-4-(3-ethylbenzoxazolin-2-ylidene-ethylidene)-2-thiothiazolid-5-one (Jeffreys and Knott, *loc. citl*) (1·65 g.) and methyl toluene-*p*-sulphonate (0·95 g.) were fused at 130° for 1 hour. 2-Aminobenzothiazole ethotoluene-*p*-sulphonate (1·75 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were added and the whole was heated for 2 hours on the steam-bath. The *product* (0·45 g.) was obtained as a red powder on addition of a little aqueous potassium iodide. It formed a red microcrystalline powder, m. p. 196°, from *iso*-propyl alcohol (Found: N, 9·6; S, 11·1; I, 21·7. $C_{24}H_{23}O_2N_4IS_2$ requires N, 9·5; S, 10·85; I, 21·5%).

[3-*Ethyl*-5-(3-*ethylbenzoxazolin*-2-*ylidene-ethylidene*)-2-*thiazol*-4-*one*][3-*ethyl*-2-*benzothiazole*]-*azamethincyanine Iodide* (XIII).—Obtained similarly from 3-ethyl-5-(3-ethylbenzoxazolin-2-ylidene-ethylidene)-2-thiothiazolid-4-one (1·65 g.) and ethyl toluene-*p*-sulphonate (1·0 g.) by fusion at 130° for 1 hour, followed by 10 minutes' refluxing with 2-aminobenzothiazole ethotoluene-*p*-sulphonate (1·75 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.), the *dye* (1·8 g., 60%) formed soft brown needles, m. p. 227—228°, from pyridine–ethanol (Found: N, 9·2; I, 21·1. $C_{25}H_{25}O_2N_4IS_2$ requires N, 9·3; I, 21·0%).

{4-3′ : 4′-*Dimethoxyphenyl*-3-*ethyl*-5-*phenyl*-2-*thiazole*}{5-[5-(4-3′ : 4′-*dimethoxyphenyl*-3-*ethyl*-5-*phenylthiazolin*-2-*ylidene-ethylidene*)-3-*ethyl*-4-*ketothiazolidin*-2-*ylidene*]-3-*ethyl*-2-*thiazol*-4-*one*}-*methincyanine Toluene*-p-*sulphonate* (X).—3-Ethyl-5-(4-3′:4′-dimethoxyphenyl-3-ethyl-5-phenylthiazolin-2-ylidene-ethylidene)-2-(3-ethyl-4-keto-2-thiothiazolidin-5-ylidene)thiazolid-4-one (1 g.) and methyl toluene-*p*-sulphonate (0·3 g.) were fused at 150° for 1 hour with good mixing. 4-3′ : 4′-Dimethoxyphenyl-2-methyl-5-phenylthiazole (0·5 g.) and ethyl sulphate (0·25 g.) were fused similarly, and the two mixtures were united in ethanol (15 c.c.) and triethylamine (0·5 c.c.), and refluxed for 30 minutes. Sodium toluene-*p*-sulphonate (0·5 g.) was added to the hot blue solution and the latter chilled overnight. The *dye* (0·8 g.) separated. It was obtained as soft, bronze crystals, m. p. 192° (shrinks at 172°) after twice recrystallizing from methanol (Found: C, 62·4; H, 5·4; N, 4·95; S, 14·3. $C_{58}H_{58}O_9N_4S_5$ requires C, 62·5; H, 5·2; N, 5·05; S, 14·35%), $\lambda_{max.}$ 650 mμ in methanol.

{3-*Ethyl*-2-*naphtho*(1′ : 2′-4 : 5)*thiazole*}{5-[5-(3-*ethyl*-4-p-*methoxyphenyl*-5-*phenyloxazolin*-2-*ylidene-ethylidene*)-3-*ethyl*-4-*ketothiazolidin*-2-*ylidene*]-3-*ethyl*-2-*thiazol*-4-*one*}*methincyanine Toluene*-p-*sulphonate* (XI).—3-Ethyl-2-(3-ethyl-4-keto-2-thiothiazolidin-5-ylidene)-5-(3-ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)thiazolid-4-one (0·6 g.) and methyl toluene-*p*-sulphonate (0·28 g.) were fused at 150° for 1 hour, to give a solid green quaternary salt. This was ground and dissolved in ethanol (10 c.c.) with 2-methylnaphtho(1′ : 2′-4 : 5)-thiazole ethotoluene-*p*-sulphonate (0·41 g.) and triethylamine (0·15 c.c.), and the whole refluxed for 30 minutes. The solution was chilled, to give 0·5 g. of *dye*, washed with ethanol and then boiling benzene. It formed small olive-green leaflets, m. p. 266°, from pyridine–ether (Found: N, 5·85; S, 13·6. $C_{51}H_{48}O_2N_4S_4$ requires N, 5·85; S, 13·4%), $\lambda_{max.}$ 620 mμ in methanol.

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