308. *The Reactivity of the Alkylthio-group in Nitrogen Ring Compounds. Part II.*[1] *Cyanine Bases from* 3,3-*Dimethyl*-2-*methylthio*-3H-*indole.*

By G. E. Ficken and J. D. Kendall.

Reaction of 3,3-dimethyl-2-methylthio-3*H*-indole with heterocyclic quaternary ammonium salts gives cyanine bases. Isomeric bases are obtained by dequaternisation of unsymmetrical indocyanines with diethylaniline. The light absorption of these bases is discussed.

Amongst the methincyanine dyes described by Kendall and Suggate [1] in Part I were two, (I; R = R′ = Me, X = I) and (I; R = Me, R′ = Et, X = ClO_4), prepared by fusing 1,2,3,3-tetramethyl-3*H*-indolium iodide with 2-alkylthiobenzothiazole and an alkyl toluene-*p*-sulphonate according to the method devised by one of the present authors.[2] Before this work the use of 3,3-dimethyl-2-methylthio-3*H*-indole (II), a compound first synthesised by Brunner,[3] as the alkylthio-component in this type of reaction had been investigated in this laboratory. It was found that although it reacted normally when fused with quinaldine and methyl toluene-*p*-sulphonate to give indocyanine (III), identical with that described by Hamer,[4] the corresponding reaction with 2-methylbenzothiazole led to a rather complex mixture.

We have re-examined the latter reaction and have isolated as major components, in approximately equal amounts, the expected indothiacyanine (I; R = R′ = Me, X = I) and the cyanine base (IV), the latter largely as its hydriodide. Also formed in appreciable, but smaller, amount was the symmetrical thiacyanine (V), identical with the material described by Kendall and Suggate.[1] The structure of dye base (IV) was confirmed by reaction with methyl iodide to give cyanine (I; R = R′ = Me, X = I) and with ethyl iodide to give the analogue (I; R = Et, R′ = Me, X = I), the latter identical with a sample prepared unambiguously by reaction of 1-ethyl-2,3,3-trimethyl-3*H*-indolium iodide with 3-methyl-2-methylthiobenzothiazolium iodide.

Dye base (IV) had clearly arisen in the " fusion process " by reaction of unquaternised sulphide (II) with 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate. It was in fact found that the sulphide (II) reacted only slowly with methyl toluene-*p*-sulphonate, but that the resulting quaternary salt (VI) gave only the true cyanine (I; R = R′ = Me, X = I) by reaction with 2,3-dimethylbenzothiazolium iodide. Moreover, this dye was the sole product when 1,3,3-trimethylindoline-2-thione (VII) was used in the " fusion process," the quaternary salt (VI) being formed from (VII) by reaction with methyl toluene-*p*-sulphonate. By fusing the sulphide (II) with preformed 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate, the dye base (IV) was formed in almost quantitative yield. Various other cyanine bases were prepared similarly from quaternary salts containing a reactive methyl group. The yields were generally high, except with the quaternary salts of some of the strongly basic thiazoles and quinolines (see Table 3). Reaction apparently failed with 1,2-dimethylpyridinium and 1,2,3-trimethylbenzimidazolium toluene-*p*-sulphonate, these nuclei being amongst the most strongly basic according to Brooker *et al.*[5,6] With heterocyclic ketomethylene compounds, the sulphide gave merocyanines such as (VIII) (from *N*-ethylrhodanic acid).

The formation of a dye base by reaction of a 2-alkylthio-substituted nitrogen heterocycle with the quaternary salt of a reactive methyl compound was first described by

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[1] Part I, Kendall and Suggate, *J.*, 1949, 1503.

[2] Kendall, B.P. 438,420/1934.

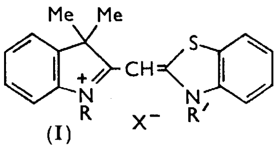
[3] Brunner, *Monatsh.*, 1933, **62**, 373.

[4] Hamer, *J.*, 1928, 206.

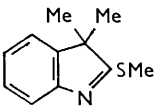
[5] Brooker, Sklar, Cressman, Keyes, Smith, Sprague, VanLare, VanZandt, White, and Williams, *J. Amer. Chem. Soc.*, 1945, **67**, 1875.

[6] Brooker, White, and Sprague, *ibid.*, 1951, **73**, 1087.

Hamer.[7] This was a modification of the method devised by one of the present authors,[8] in which a 2- or 4-methylquinoline was fused with a 2-alkylthio-substituted quaternary salt. Beilenson, Hamer, and Rathbone [9] have reported that 2-methylthio-4*H*-3,1-benzothiazine when fused with 2-methylbenzothiazole and methyl toluene-*p*-sulphonate gave only the cyanine base and none of the expected dye, owing to the resistance of the sulphide to quaternisation. The behaviour of compound (II) in the " fusion " process represents a less extreme case of the same phenomenon.



(I)



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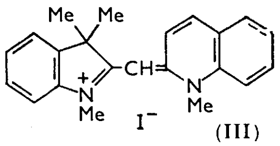

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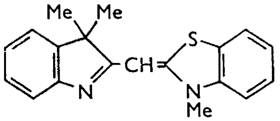

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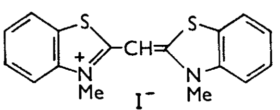

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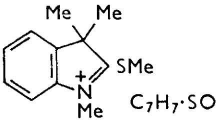
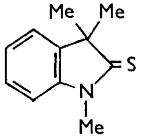
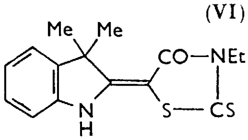


(VI)

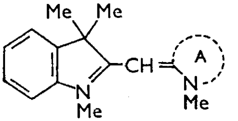
(VII)



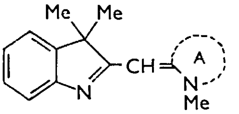


(VIII)

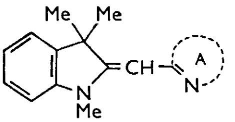
Cyanine bases have also been prepared by the dequaternisation of true cyanines, the first recorded example being that of a substituted 2,4′-quinoline cyanine which was found by Kaufmann and Vonderwahl [10] to give one of the two possible bases on pyrolysis. It was subsequently found that alkyl halide could be smoothly removed from a cyanine by heating it with a high-boiling amine.[11] Though initially used only with symmetrical dyes, the method was later extended to a few unsymmetrical dyes by Hamer,[7] who usually obtained only one of the two possible bases, although both bases were formed in one case. We have applied the reaction to a series of *NN*′-dimethylindocyanines (IX), and have in every case obtained only one base. This was invariably different from the base (X) obtained by reaction of the methylthio-3*H*-indole (II) with the appropriate methyl heterocyclic quaternary salt. The bases obtained by the dequaternisation must consequently be assigned structure (XI), which was proved in the case of the product from cyanine (I; R = R′ = Me, X = I) by conversion into the salt (I; R = Me, R′ = Et, X = ClO_4), identical with Kendall and Suggate's material.[1] Also, the base from cyanine (IX; A = 3-methylnaphtho[1,2]thiazole-2) was synthesised by reaction of the quaternary salt (VI) with 2-methylnaphtho[1,2]thiazole.



I⁻ (IX)



(X)



(XI)

Brooker *et al.*[12] have pointed out that in the cation of an unsymmetrical cyanine the sharing of the positive charge between the two nitrogen atoms is unequal owing to resonance between forms (XIIa and b). These authors defined the " basicity " of heterocyclic nuclei in cyanines as the tendency to acquire a positive charge, *i.e.*, B is more basic

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[7] Hamer, *J.*, 1940, 799.

[8] Kendall, B.P. 456,362/1935; Barent and Kendall, B.P. 477,983/1936.

[9] Beilenson, Hamer, and Rathbone, *J.*, 1945, 222.

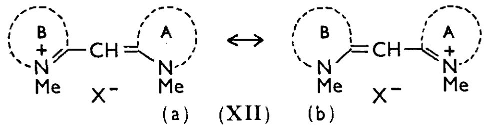
[10] Kaufmann and Vonderwahl, *Ber.*, 1912, **45**, 1404.

[11] Gevaert Photo-Producten N.V., B.P. 477,990/1935.

[12] Brooker, Keyes, and Williams, *J. Amer. Chem. Soc.*, 1942, **64**, 199.

than A if (XIIa) makes a greater contribution than (XIIb) to the resonance hybrid. On Brooker's definition 3*H*-indole is only weakly basic,[5] and it is the less basic component in all of the cyanines (IX) examined in the present work. Clearly, dequaternisation of these dyes has occurred at the more basic nitrogen atom in every case. This conclusion can be readily explained by the fact that, whatever the detailed mechanism may be, dequaternisation effectively involves transfer of a methyl cation (Me^+) from the dye cation to the diethylaniline molecule. This carbonium ion would be expected to be lost from the nitrogen atom carrying the greater positive charge, *i.e.*, from the more basic nitrogen. It is to be noted that in the case described by Hamer,[7] in which both isomeric bases were obtained, the nuclei (benzothiazole and 2-quinoline) were of very similar basicity in Brooker's series.

The absorption spectra of both series of bases have been measured in neutral and in acid solution, and the results are given in Table 1, together with the relevant data for the corresponding monomethincyanines. The nuclei A in the first column are arranged in order of increasing basicity, as determined by Brooker[5] for a series of styryl dyes [these nuclei are named in Table 1 in the form in which they occur in the bases of series (XI); the names do not strictly apply to the isomeric bases (X) or to the cyanines (IX)]. Where A is 3,3-dimethyl-3*H*-indole, bases (X) and (XI) are identical, and the data here refer to the compound obtained by reaction of the sulphide (II) with 1,2,3,3-tetramethyl-3*H*-indolium toluene-*p*-sulphonate; this base could not be obtained by dequaternisation of the symmetrical indocyanine.


(XII)

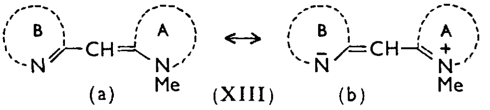

(XIII)

TABLE 1. *Light absorption of cyanines and bases,* $\lambda_{max.}$ (Å) *and* log ε.

Nucleus (A)	Cyanine (IX)	Base (X) Neutral	Base (X) Acid	Base (XI) Neutral	Base (XI) Acid
3,3-Dimethyl-3*H*-indole-2	4325	3870	4230	3870	4230
	4·56	4·52	4·58	4·52	4·58
2-Benzoxazole	3960	3780	3850	3630	3890
	4·77	4·63	4·69	4·64	4·69
2-Benzoselenazole	4350	3985	4270	3830	4390
	4·68	4·62	4·70	4·64	4·69
2-Benzothiazole	4300	4000	4225	3780	4315
	4·86	4·58	4·68	4·61	4·69
Naphtho[1,2]thiazole-2	4440	4145	4400	3950	4450[a]
	4·66	4·67	4·74	4·62	4·67
2-Quinoline	4710	4630	4700	4030	4700
	4·64	4·42	4·61	4·44	4·64
4-Phenyl-2-thiazole	4175	4050	4080	3685	4300
	4·67	4·59	4·64	4·46	4·47
4-Methyl-2-thiazole	4140	4050	4025	3620	4190
	4·52	4·55	4·59	4·42	4·58
4-Quinoline	5020	4890	4950	4020	4920
	4·72	4·55	4·67	4·26	4·71

[a] Second maximum at 4600 Å (log ε 4·67).

Previous workers have found that, with very few exceptions, cyanine bases absorb at lower wavelengths than the corresponding cyanines; also that addition of acid to a solution of a base generally causes a bathochromic shift of the wavelength maximum, the protonated base absorbing close to the parent cyanine.[7,9,13,14] These conclusions are confirmed by the results given in Table 1. It has been deduced by Brooker *et al.*[13] that in a

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[13] Brooker, Sprague, Smyth, and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116.

[14] Beilenson and Hamer, *J.*, 1942, 98; Hamer and Rathbone, *J.*, 1943, 487.

pair of isomeric bases, differing only in the location of the alkyl group on one or other of the heterocyclic nitrogen atoms, that base which carries this alkyl group on the more basic nitrogen atom will absorb at longer wavelength. This is again confirmed by the results of Table 1, where a base of structure (X) invariably absorbs at longer wavelength than the isomeric base (XI).

TABLE 2. *Wavelength shifts* (Å) *for bases.*

Nucleus (A)	$\Delta_X{}^H$	$\Delta_X{}^{Me}$	$\Delta_{XI}{}^H$	$\Delta_{XI}{}^{Me}$	$\Delta_{XI}{}^{Me} - \Delta_X{}^{Me}$
Benz[*cd*]indole-2	560	450	150	200	−250
3,3-Dimethyl-3*H*-indole-2	360	455	360	455	0
2-Benzoxazole	70	180	260	330	150
2-Benzoselenazole	285	365	560	520	155
2-Benzothiazole	225	300	535	520	220
Naphtho[1,2]thiazole-2	255	295	500 [a]	490	195
2-Quinoline	70	80	670	680	600
4-Phenyl-2-thiazole	30	125	615	490	365
4-Methyl-2-thiazole	−25	90	570	520	430
4-Quinoline	60	130	900	1000	870

[a] The maximum at 4600 Å for the protonated base gives a value of 650 Å.

By using the data given in Table 1, the following values have been calculated and recorded in Table 2: (i) the shift in wavelength (Δ^H) on acidification of an ethanolic solution of the base, corresponding to the addition of a proton, (ii) the shift (Δ^{Me}) on proceeding from the base to the corresponding cyanine, and (iii) the difference between the wavelengths of maximum absorption of a dye base (X) and the isomeric base (XI), equal to $\Delta_{XI}{}^{Me} - \Delta_X{}^{Me}$. The values for the bases containing the benz[*cd*]indole nucleus are taken from Part III (following paper), where evidence is presented that this ring system is less basic than 3*H*-indole. Benz[*cd*]indole is consequently placed first in Table 2, where the nuclei A are again arranged in order of increasing basicity.

Hamer [15] has stated that, apart from the generally observed hypsochromic shifts, the light-absorption of cyanine bases seemed erratic compared with that of the related cyanine dyes. Inspection of Table 2 shows that this is clearly not the case with the bases described in the present paper. Whilst there are individual discrepancies, there is nevertheless a tendency in series (X) for the value of Δ^H (or Δ^{Me}) to decrease as the basicity of A is increased; in series (XI) the opposite trend is apparent. These changes are more clearly brought out when the isomeric bases are compared by the use of the function $\Delta_{XI}{}^{Me} - \Delta_X{}^{Me}$. With one exception, the increase in this function closely parallels the increase in basicity of A. The chief discrepancy in this relationship concerns the 2-quinoline nucleus, since the base of series (XI) has a Δ^{Me} value greater than those of the two thiazole bases higher in the series. The benzoxazole bases are also anomalous, since the Δ values for both bases, but particularly that in series (X), are lower than would be expected from the position of benzoxazole in the basicity series. Brooker *et al.*,[16] however, found benzoxazole to behave somewhat anomalously also in merocyanine dyes.

Brooker *et al.*[13] discussed the colour of cyanine bases in terms of resonance between the non-polar form (XIIIa) and a dipolar form (XIIIb) and have by this means satisfactorily accounted for the usual hypsochromic shift on going from a cyanine to the base. They found, however, that if nucleus A was very strongly basic compared with B, then base XIII) might absorb at longer wavelength that the cyanine (XII). If these arguments are applied to a series of bases (XIII) in which B, a weakly basic nucleus, is kept constant throughout, it follows that (i) when A is also weakly basic Δ^{Me} should have its usual fairly large positive value but (ii) when A is very strongly basic Δ^{Me} should be negative. It

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[15] Hamer, *Quart. Rev.*, 1950, **4**, 327.

[16] Brooker, Keyes, Sprague, VanDyke, VanLare, VanZandt, White, Cressman, and Dent, *J. Amer. Chem. Soc.*, 1951, **73**, 5332.

might therefore be expected that as A is increased in basicity from (i) to (ii) the value of Δ^{Me} would decrease fairly steadily through zero to a negative value. Such a series is provided by bases (X), where the value of Δ^{Me} does indeed decrease in this manner, and would no doubt become negative with nuclei more basic than 4-quinoline. Similar considerations can account for the change of $\Delta_{XI}{}^{Me}$ in the opposite direction.

It should be noted that although basicity is undoubtedly the chief factor influencing the colour of cyanines and bases, other factors must be invoked to account for the anomalies discussed above. In particular, Brooker *et al.*[17] pointed out that steric effects must be particularly serious in the monomethincyanine series.

EXPERIMENTAL

Except where otherwise stated, light petroleum refers to the fraction of b. p. 60—80°.

3,3-*Dimethylindoline*-2-*thione* (2-*mercapto*-3,3-*dimethyl*-3H-*indole*).—Brunner's preparation of this material[3] has been improved by carrying out the reaction of 3,3-dimethyloxindole[18] (20 g.) with phosphorus pentasulphide (20 g.) in dry pyridine (50 ml.). After 3 hours' boiling, the solution was poured into warm water, and the mixture was cooled and acidified with hydrochloric acid. The oil which separated initially soon solidified, and the product was washed with cold water to leave the pale yellow thione (19·3 g., 88%), m. p. 105—108°. Crystallisation from ethanol gave colourless crystals, m. p. 109—110° (Brunner[3] gives m. p. 108—109°).

3,3-*Dimethyl*-2-*methylthio*-3H-*indole* (II).—(*a*) The following method is simpler than Brunner's.[3] The thione (10 g.) and methyl iodide (10 ml.) were refluxed gently together, a vigorous reaction occurring after a few minutes; the hydriodide of the sulphide was obtained by washing the solid with dry ether, and had m. p. 167—168° (decomp.) on crystallisation from ethanol (Brunner gives m. p. 165°). Treatment of a methanolic solution of the hydriodide with a slight excess of aqueous sodium hydroxide caused the sulphide to separate. After being washed with water and dried, it had m. p. 55—57°, the yield being almost quantitative.

(*b*) Dimethyl sulphate (10·8 ml.) was added slowly and with stirring to a solution of the thione (20 g.) in 10% aqueous sodium hydroxide (50 ml.), the temperature being maintained between 10° and 15°. After 1 hr. the oil which had separated was taken up in benzene, and the dried (K_2CO_3) solution was distilled. 3,3-Dimethyl-2-methylthio-3*H*-indole (17·3 g., 80%) had b. p. 95—110°/0·6 mm., m. p. 56—57°. Repeated recrystallisation from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 57·5—58° (Found: S, 16·75. Calc. for $C_{11}H_{13}NS$: S, 16·8%); Brunner's m. p. of 65° could not be reproduced.

1,3,3-*Trimethylindoline*-2-*thione* (VII).—1,3,3-Trimethyloxindole[19] (12·5 g.) and phosphorus pentasulphide (12·5 g.) were refluxed together in pyridine (30 ml.) for 3 hr. The oil which separated when the solution was poured into water was taken up in benzene, and the dried ($CaCl_2$) extracts were distilled, the fraction (9·7 g., 71%) boiling at 122°/1·0 mm. to 133°/1·6 mm. being collected. 1,3,3-*Trimethylindoline*-2-*thione*, b. p. 102°/0·3 mm., $n_D^{19\cdot8}$ 1·6400, solidified on strong cooling to colourless crystals, m. p. 29° (Found: S, 17·0. $C_{11}H_{13}NS$ requires S, 16·8%). The *mercuric chloride complex* formed colourless needles, m. p. 200—200·5°, from ethanol (Found: N, 2·95. $C_{11}H_{13}NCl_2SHg$ requires N, 3·0%).

Preparation of Dyes via *the Quaternary Salt* (VI).—The sulphide (1·91 g.) and methyl toluene-*p*-sulphonate (1·86 g.) were fused together at 120° for 2 hr. Extraction of the product several times with boiling benzene left a viscous brown oil (2·04 g.) which did not crystallise. This quaternary salt (0·75 g.) and 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate (1·86 g.) were refluxed together in ethanol (15 ml.) containing sodium acetate (0·50 g.) for 2 hr. The resulting solution was poured into aqueous potassium iodide to precipitate the dye (0·16 g.), which was obtained as orange prisms from ethanol; the m. p. and mixed m. p. 263—264° were identical with that of an authentic sample of (1,3,3-trimethyl-3*H*-indole-2)(3-methyl-2-benzothiazole)-methincyanine iodide, for which Kendall and Suggate[1] give m. p. 262°.

A similar non-crystalline quaternary salt was obtained by fusion of 1,3,3-trimethylindoline-2-thione with methyl toluene-*p*-sulphonate; this material gave the same dye in similar yield.

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[17] Brooker, Sprague, and Cressman, *J. Amer. Chem. Soc.*, 1945, **67**, 1889.

[18] Brunner, *Monatsh.*, 1897, **18**, 98.

[19] Brunner, *Monatsh.*, 1896, **17**, 481.

Preparation of Dyes by the "Fusion Process."—(a) *Quinaldine and sulphide* (II) [with D. J. Fry]. A mixture of the sulphide (0·96 g.), quinaldine (0·74 g.), and methyl toluene-*p*-sulphonate (1·86 g.) was heated at 140° for 3 hr. The resulting melt was refluxed in pyridine (5 ml.) for 3 hr. and the solution poured into aqueous potassium iodide. The precipitated solid was collected and crystallised from ethanol to yield dye (III), m. p. 256—257° (decomp.), identical with material prepared by Hamer's method [4] (cf. Table 4).

(b) *Methylbenzothiazole and sulphide* (II). The sulphide (3·82 g.), 2-methylbenzothiazole (2·98 g.), and methyl toluene-*p*-sulphonate (7·44 g.) were fused together at 140—145° for 4 hr. The resulting melt was refluxed for 1 hr. with pyridine (20 ml.), and the solution poured into aqueous potassium iodide. The solid which separated was washed thoroughly with water, dried, and then boiled with benzene. The dried (Na_2SO_4) extract was concentrated and chromatographed on activated alumina. The main yellow band was eluted and the eluate evaporated to yield 3,3-*dimethyl*-2-(3-*methyl*-2-*benzothiazolinylidene*)*methyl*-3H-*indole* (0·53 g.), yellow needles, m. p. 157·5—158·5°, from benzene–light petroleum (Found: C, 74·6; H, 5·6; N, 9·3; S, 10·4. $C_{19}H_{18}N_2S$ requires C, 74·5; H, 5·9; N, 9·1; S, 10·5%). The mixture of dyes remaining after extraction with benzene was boiled with ethanol (50 ml.), and the mixture cooled and filtered, the residual solid being washed with more ethanol (50 ml.). The combined filtrates and washings yielded on evaporation a solid (1·51 g.), m. p. 247—248°, raised to 262—263°, by recrystallisation from ethanol and undepressed on admixture with authentic indothiacyanine (I; R = R′ = Me, X = I) (Found: N, 6·0; I, 28·1; S, 7·2. Calc. for $C_{20}H_{21}N_2IS$: N, 6·25; I, 28·3; S, 7·15%). Recrystallisation from methanol (400 ml.) of the solid remaining after extraction with ethanol gave a mixture of two crystalline solids, which were separated by flotation in methanol. The lighter, yellow material (0·6 g.) gave bis-(3-methyl-2-benzothiazole)-methincyanine iodide, m. p. and mixed m. p. 312—313° (decomp.), by crystallisation from 2-methoxyethanol (Kendall and Suggate [1] give m. p. 306°). The heavier, orange crystals (0·8 g.) had m. p. 220—222° (decomp.), and a further crop (1·26 g.) of slightly less pure material was obtained from the mother-liquors. 3,3-*Dimethyl*-2-(3-*methyl*-2-*benzothiazolinylidene*)-*methyl*-3H-*indole hydriodide monohydrate* was obtained as golden-yellow plates, m. p. 228—229° (decomp.), from 2-methoxyethanol (Found: C, 50·1; H, 4·4; I, 28·0; S, 7·3. $C_{19}H_{21}ON_2IS$ requires C, 50·45; H, 4·7; I, 28·1; S, 7·1%). The hydriodide (0·42 g.) was boiled with a solution of sodium (0·03 g.) in methanol (25 ml.) for 45 min. The resulting clear solution was evaporated to dryness and the product washed with water. The dried solid was extracted with light petroleum to give the dye base (0·24 g.), identical in m. p. and mixed m. p. with that isolated in an earlier stage of the experiment.

(c) *Methylbenzothiazole and thione* (VII). The thione (0·48 g.), 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate (0·84 g.), and methyl toluene-*p*-sulphonate (0·46 g.) were fused together at 150—160° for 2½ hr. and then refluxed with pyridine for ½ hr. The resulting solution was poured into aqueous potassium iodide solution to precipitate the dye (I; R = R′ = Me, X = I), m. p. 253—254°, raised to 262—263° by recrystallisation from ethanol, and undepressed by an authentic sample.

Quaternisation of Dye Base (IV).—The base (0·42 g.) was refluxed for 16 hr. with methyl iodide, and the product was washed with hot benzene to yield indothiacyanine (I; R = R′ = Me, X = I), m. p. and mixed m. p. 261—262°. Obtained similarly, with ethyl iodide, was (1-*ethyl*-3,3-*dimethyl*-3H-*indole*-2)(3-*methyl*-2-*benzothiazole*)*methincyanine iodide* (yellow) m. p. 247—248° (from 30 parts of ethanol) (Found: I, 27·1. $C_{21}H_{23}N_2IS$ requires I, 27·45%). The dye, prepared by reaction of 1-ethyl-2,3,3-trimethyl-3*H*-indolium iodide (0·63 g.) with 3-methyl-2-methylthiobenzothiazolium iodide (0·65 g.) in ethanol (6 ml.) containing sodium acetate (0·30 g.), had the same m. p. and the mixed m. p. was undepressed.

Preparation of Dye Bases (X).—The dye base (IV) was preferably prepared by fusing 3,3-dimethyl-2-methylthio-3*H*-indole (1·91 g.) with 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate (3·35 g.) at 150° for 4 hr. The product was shaken with chloroform and excess of dilute aqueous sodium hydroxide. The solid remaining after evaporation of the dried (Na_2SO_4) chloroform solution was washed with a little cold light petroleum to yield dye base (IV) (2·8 g.), m. p. 152—156°; the m. p. was raised to 157·5—158·5° by crystallisation from benzene–light petroleum.

The other *dye bases* given in Table 3 were prepared similarly by fusion of equivalent amounts of 3,3-dimethyl-2-methylthio-3*H*-indole with the appropriate methyl heterocyclic quaternary toluene-*p*-sulphonate. When the yield was low it was necessary to isolate the dye base from

TABLE 3. 3,3-*Dimethyl*-2-(A)-*methyl*-3H-*indoles* (X).

Nucleus (A)	Yield (%)	M. p.	Appearance (solvent [a])	Formula	Found (%) C	Found (%) H	Found (%) N	Reqd. (%) C	Reqd. (%) H	Reqd. (%) N
1,3,3-Trimethyl-2-indolinylidene	48	184°	Yellow plates (E)	$C_{22}H_{24}N_2$	83·4	7·3	8·8	83·5	7·65	8·9
1,2-Dihydro-1-methyl-2-quinolylidene	9	151—151·5	Red needles (EW)	$C_{21}H_{20}N_2$	—	—	9·0	—	—	9·3
1,4-Dihydro-1-methyl-4-quinolylidene	4	154	Red needles (C)	$C_{21}H_{20}N_2$	—	—	9·1	—	—	9·3
3,4-Dimethyl-2-thiazolinylidene	20	237	Yellow plates (A)	$C_{16}H_{18}N_2S$		[b]			[b]	
3-Methyl-4-phenyl-2-thiazolinylidene	12	182—183	Yellow prisms (BP)	$C_{21}H_{20}N_2S$		[c]			[c]	
3-Methyl-2-benzoxazolinylidene	22	96—98	Pale yellow needles (C)	$C_{19}H_{18}ON_2$	78·8	6·4	—	78·6	6·25	—
3-Methyl-2-benzoselenazolinylidene	55	164—165	Brown prisms, blue reflex (E)	$C_{19}H_{18}N_2Se$	—	—	8·05	—	—	7·9
3-Methylnaphtho[1,2]thiazolin-2-ylidene	50	222—223	Yellow plates (A)	$C_{23}H_{20}N_2S$		[d]			[d]	

[a] A = Ethyl acetate, B = benzene, C = cyclohexane, E = ethanol, P = light petroleum, W = water. [b] Found: S, 12·3. Reqd.: S, 11·9%. [c] Found: S, 9·65. Reqd.: S, 9·6%. [d] Found: S, 9·05. Reqd.: S, 9·0%.

TABLE 4. (1,3,3-*Trimethyl*-3H-*indole*-2) (A) *methincyanine iodides* (IX).

Nucleus (A)	Method *	M. p.	Appearance (solvent [b])	Formula	Found (%) I	Found (%) S	Reqd. (%) I	Reqd. (%) S
1,3,3-Trimethyl-3*H*-indole	Q	233—234°	Orange prisms (EW)	$C_{23}H_{27}N_2I$	27·45	—	27·7	—
1-Methyl-2-pyridine	S	219	Red plates (E)	$C_{18}H_{21}N_2I$	32·2	—	32·35	—
1-Methyl-2-quinoline	S	256—257 [ac]	Red plates (E)	—	—	—	—	—
1-Methyl-4-quinoline	QS	258	Red plates, green reflex (EW)	$C_{22}H_{23}N_2I$	28·4	—	28·7	—
3,4-Dimethyl-2-thiazole	S	244—245	Pale yellow needles (E)	$C_{17}H_{21}N_2IS$	30·7	7·8	30·8	7·8
3-Methyl-4-phenyl-2-thiazole	S	224—225 [a]	Yellow plates (EW)	$C_{22}H_{23}N_2IS$	26·4	7·1	26·75	6·8
3-Methyl-2-benzoxazole	S	298—299 [ad]	Yellow plates (E)	—	—	—	—	—
3-Methyl-2-benzoselenazole	Q	243—244	Yellow-brown plates (E)	$C_{20}H_{21}N_2ISe$	(N, 5·7)		(N, 5·7)	
3-Methylnaphtho[1,2]thiazole-2	Q	202—203	Yellow needle clusters (E)	$C_{24}H_{23}N_2IS$	25·0	6·8	25·5	6·4

[a] With decomp. [b] E = ethanol, M = methanol, W = water. [c] Hamer [4] gives m. p. 247° (decomp.). [d] Found: I, 29·2. Calc. for $C_{20}H_{21}ON_2I$: I, 29·4%. Kendall [2] gives m. p. 296° (decomp.). * See text.

TABLE 5. 1,3,3-*Trimethyl*-2-(A)-*methyleneindolines* (XI).

Nucleus (A)	Yield (%)	M. p.	Appearance (solvent [a])	Formula	Found (%)	Reqd. (%)
2-Quinolyl	66	144—145°	Yellow plates (E)	$C_{21}H_{20}N_2$	N, 8·8	9·3
4-Quinolyl	59	121	Yellow needles (P)	$C_{21}H_{20}N_2$	N, 9·25	9·3
4-Methyl-2-thiazolyl	46	133	Pale yellow prisms (C)	$C_{16}H_{18}N_2S$	S, 12·2	11·9
4-Phenyl-2-thiazolyl	83	206	Pale yellow plates (BC)	$C_{21}H_{20}N_2S$	S, 9·8	9·6
2-Benzoxazolyl	74	131—132	Pale yellow prisms (BP)	$C_{19}H_{18}ON_2$	N, 9·7	9·65
2-Benzoselenazolyl	14	137—138	Yellow prisms (P)	$C_{19}H_{18}N_2Se$	N, 8·0	7·9
Naphtho[1,2]thiazolyl-2	37	185	Yellow needles (E)	$C_{23}H_{20}N_2S$	S, 9·1	9·0

[a] B = benzene, C = cyclohexane, E = ethanol, P = light petroleum.

the crude reaction product by extraction (Soxhlet) with light petroleum followed by purification by chromatography in chloroform on activated alumina.

Reaction of the Sulphide with Ketomethylene Compounds.—A mixture of 3,3-dimethyl-2-methylthio-3*H*-indole (0·96 g.) and 3-ethyl-2-thiothiazolid-4-one (*N*-ethylrhodanic acid) (0·81 g.) was heated at 190—200° for 6 hr., methanethiol being slowly evolved. The cooled melt was stirred with a little cold ethanol, and the resulting solid was crystallised from ethanol (50 ml./g.) to give 5-(3,3-*dimethylindolin*-2-*ylidene*)-3-*ethyl*-2-*thiothiazolid*-4-*one* (VIII) (0·52 g.) as orange plates, m. p. 163—164° (Found: S, 21·4. $C_{15}H_{16}ON_2S_2$ requires S, 21·1%), $\lambda_{max.}$ 4200 Å (log ε 4·73). Similarly prepared was 4-(3,3-*dimethylindolin*-2-*ylidene*)-3-*methyl*-1-*phenylpyrazol*-5-*one* (81% yield), yellow plates, m. p. 166—167°, from ethanol (Found: N, 13·6. $C_{20}H_{19}ON_3$ requires N, 13·2%), $\lambda_{max.}$ 3600 Å (log ε 4·34).

2-2′-*Benzothiazolylmethylene*-1,3,3-*trimethylindoline*.—Indothiacyanine (I; R = R′ = Me, X = I) (2·60 g.) and redistilled *NN*-diethylaniline (100 ml.) were refluxed together for 1 hr. After removal of the amine by steam-distillation, the solid was collected and washed with water. Crystallisation from benzene–light petroleum gave pale yellow crystals of 2-2′-*benzothiazolylmethylene*-1,3,3-*trimethylindoline*, m. p. 142° (Found: S, 10·2. $C_{19}H_{18}N_2S$ requires S, 10·5%). The dye base (0·10 g.) was fused with ethyl toluene-*p*-sulphonate (1·0 g.) at 180° for 2 hr., and a solution of the resulting melt in ethanol was poured into aqueous sodium perchlorate solution. The precipitated dye (0·10 g.) was crystallised from methanol to yield (1,3,3-trimethyl-3*H*-indole-2)(3-ethyl-2-benzothiazole) methincyanine perchlorate, m. p. 239—240° (decomp.), identical with Kendall and Suggate's material.[1]

Dequaternisation of 3H-*Indolecyanines.*—The 3H-*indolmethincyanines* (IX) required for this work are described in Table 4, two methods of preparation being used: (i) quaternisation of the appropriate cyanine base of structure (X) by refluxing it with excess of methyl iodide for 2—16 hr.: the crude dye was washed with boiling benzene before crystallisation (method Q in Table 4); (ii) synthesis by Kendall's method,[20] by refluxing 1,2,3,3-tetramethyl-3*H*-indolium iodide and the appropriate 2(or 4)-methylthio-heterocyclic quaternary methiodide with triethylamine in ethanolic solution; the dye generally crystallised on cooling, or it was precipitated by addition of aqueous potassium iodide solution (method S in Table 4). In the case of the 4-quinoline dye, where both methods were used, the products were identical.

The cyanines were dequaternised, and the *bases* (XI) isolated, as described above for the benzothiazole base, the results being given in Table 5. In general, refluxing for 1 hr. with diethylaniline was satisfactory, except in the case of the 4-quinoline dye, where the yield of base was negligible owing to decomposition. In this case only 5 minutes' heating was used, and the product was purified by chromatography. No base could be isolated by heating the 2-pyridine cyanine with diethylaniline for either 1 hr. or 5 min.

Alternative Preparation of 1,3,3-*Trimethyl*-2-(*naphtho*[1,2]*thiazolyl*-2)-*methyleneindoline*.—Quaternary salt (VI) (0·77 g.), prepared by fusing together equimolar quantities of the sulphide (II) and methyl toluene-*p*-sulphonate, was heated at 150—160° for 3 hr. with 2-methylnaphtho-[1,2]thiazole (0·40 g.). The resulting oil was shaken with chloroform and dilute aqueous sodium hydroxide. Evaporation of the chloroform solution yielded a solid which was washed with a little cold ethanol. Crystallisation of the product (0·03 g.) from ethanol gave the dye base, identical in m. p. and mixed m. p. with the material described in the last line of Table 5.

Absorption spectra were measured in ethanolic solution (10 mg./l.) on a Unicam SP 500 spectrophotometer. The acidified solution of a base was prepared by addition of concentrated hydrochloric acid (1 drop) to a solution (100 ml.) of the above concentration.

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[20] Kendall, B.P. 424,559/1933.