298. *Some Chain-substituted Methincyanines and Styryl Dyes.*

By FRANCES M. HAMER.

Various methincyanines carrying a substituent on the chain have been prepared and their absorption maxima compared with those of the parent dyes. On substitution there are large bathochromic shifts for methyl, 2-benzothiazolyl, phenyl, and *p*-nitrophenyl; for carbethoxy, in the thiacyanine series, the shifts are also bathochromic but smaller, whilst in the thia-2′-cyanine series they are hypsochromic. Introduction of substituents into the α-position in the chain of styryl dyes causes hypsochromic shifts of the absorption maximum.

THE introduction of a substituent into the chain of a trimethincyanine has, until recently, been known to produce only slight colour changes. For example, passage from the benzothiazole dye (I; R = H) to its analogues (I; R = Me) and (I; R = Ph) caused the absorption maximum to undergo a hypsochromic shift of 145 Å, and a bathochromic shift of 25 Å, respectively.[1] Comparable with these are bathochromic shifts of 70—100 Å on passing from the same dye (I; R = H) to the analogue where R = NAcR′, whereas hypsochromic shifts of 620, 890, and 560—880 Å, respectively, on passing [2] to dyes where R = OMe, NEt_2, and NHR′ are of a different order.

In the methincyanine series, Götze [3] actually made the first chain-substituted member (II; R = Me, R′ = R″ = Et) but, because it gave a violet solution whereas the unsubstituted dye gave an orange one, he did not believe them to be so simply related; [3] the colour change produced by introduction of this methyl group in fact corresponds to a bathochromic shift of 590 Å. In another methincyanine series (III), it has been recorded [4] that replacement of :CH· by :CMe· caused a bathochromic shift of 605 Å. In another, (IV; R′ = R″ = Me), a bathochromic shift of 430 Å, or 445 Å, was recorded for this displacement.[5, 6] A striking instance is replacement [7] of :CH· by :C(OH)· in this dye (IV; R′ = R″ = Me), where the bathochromic shift amounted to 750 Å, and treatment with triethylamine caused a further such shift of 1060 Å.

In contrast with the record of these large bathochromic shifts is the statement that no change of absorption maximum occurred on passing from a dye (IV; R = H, R′ = Me, R″ uncertain) to its ethoxycarbonyl derivative (IV; R = CO_2Et, R′ = Me, R″ uncertain).[8] Because of its anomalous character, this result is particularly important and it is a pity that preparative details and analyses were not published.

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[1] Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 2480.

[2] Sveshnikov, Levkoev, Portnaya, and Lifshits, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 733.

[3] Götze, *Angew. Chem.*, 1936, **49**, 563.

[4] Brooker, White, Sprague, Dent, and van Zandt, *Chem. Rev.*, 1947, **41**, 325.

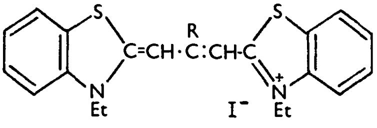
[5] Kiprianov and Ushenko, *J. Gen. Chem.* (*U.S.S.R.*), 1950, **20**, 139 (*Zhur. obshchei Khim.*, p. 134) (in this and a similar citation, the first refers to the U.S. translation, the second to the Russian original).

[6] Fry and Kendall, *J.*, 1951, 1723.

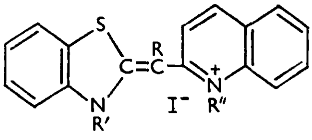
[7] Jeffreys, *J.*, 1954, 503.

[8] Van Dormael and Nys, 21st Congr. Chim. Ind., 1948, 483; *Chimie et Industrie*, 1950, **63**, 483.

In a typical thia-2′-cyanine condensation, 2-methylbenzothiazole ethiodide was condensed with 2-iodoquinoline ethiodide to give the cyanine (II; R = H, R′ = R″ = Et);[9] by modifying the conditions, the yield was increased[10] to 88%. For *meso*-substituted dyes, benzothiazole ethiodides having a substituted 2-methyl group were



(I)



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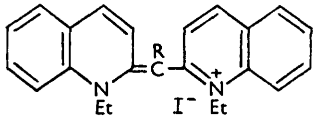

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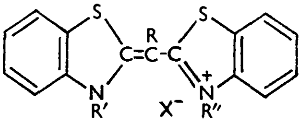

(IV)

required. When the ethiodide of pure 2-ethylbenzothiazole[11] was now condensed with 2-iodoquinoline ethiodide, the yield of *meso*-methyl dye (II; R = Me, R′ = R″ = Et) was 59% and it was unaccompanied by any dye by-product, although Götze[3] obtained one. However, when 2-ethylthioquinoline ethiodide was used instead of 2-iodoquinoline ethiodide, the yield of *meso*-methyl dye was greatly reduced and it was accompanied by the unsubstituted dye (II; R = H, R′ = R″ = Et). Similarly, reaction of 2-ethylthiobenzothiazole ethiodide with 2-ethylbenzothiazole ethiodide gave the required product (IV; R = Me, R′ = R″ = Et, X = I), accompanied by the unsubstituted dye (IV; R = H, R′ = R″ = Et, X = I). Fry and Kendall have recorded that the methyl analogue (IV; R = R′ = R″ = Me) is accompanied by its " parent " (IV; R = H, R′ = R″ = Me).[6]

By condensation of 2-benzylbenzothiazole ethiodide with 2-iodoquinoline ethiodide, the *meso*-phenyl dye (II; R = Ph, R′ = R″ = Et) was produced in 60% yield. 2-Ethyl- and 2-benzyl-benzothiazole ethiodide, respectively, with 2-iodo-5 : 6-benzoquinoline ethiodide, gave the more complex analogues (V; R = Me and Ph, R′ = R″ = Et), the yields being 67% and 42% as against 42% for the parent (V; R = H, R′ = R″ = Et). Similar condensations with 1-iodo*iso*quinoline ethiodide led to the *iso*quinoline dyes (VI; R = Me, R′ = R″ = Et, X = ClO_4) and (VI; R = Ph, R′ = R″ = Et, X = I), in 72% and 36% yield, respectively; the 41% yield for the parent (VI; R = H, R′ = R″ = Et, X = I), obtained[12] by use of sodium ethoxide, could probably be improved by use of triethylamine. The thia-2′-cyanine condensation has been successfully extended to the preparation of chain-substituted methincyanines, the yields being comparable with those of the unsubstituted parent dyes.

The thia-4′-cyanine condensation, on the other hand, could not be extended in a similar way. According to that, 2-methylbenzothiazole ethiodide was condensed with quinoline ethiodide to give the 4′-cyanine (VII; R = H, R′ = R″ = Et), acid and hydrogen being eliminated;[13] under improved conditions, the yield had been raised[14] to 63%. Use of 2-ethyl- in place of 2-methyl-benzothiazole ethiodide now gave a negative result so far as the dye (VII; R = Me, R′ = R″ = Et) was concerned; dyes were indeed produced in low yield, but they were identified as xantho- and erythro-*apo*cyanines, which are known to be formed by the action of alkali on quinoline ethiodide.[15, 16] This negative result for

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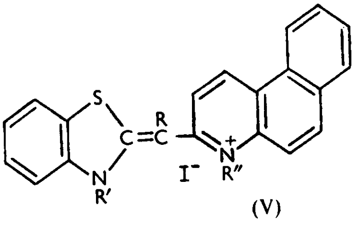
[9] Hamer, *J.*, 1928, 206.
[10] Brooker and Keyes, *J. Amer. Chem. Soc.*, 1935, **57**, 3488.
[11] Hamer, Rathbone, and Winton, *J.*, 1947, 954.
[12] Fisher and Hamer, *J.*, 1934, 1905.
[13] Braunholtz and Mills, *J.*, 1922, **121**, 2004.
[14] Keyes and Brooker, *J. Amer. Chem. Soc.*, 1937, **59**, 74.
[15] Kaufmann and Strübin, *Ber.*, 1911, **44**, 690.
[16] Mills and Ordish, *J.*, 1928, 81.

the *meso*-methylthia-4′-cyanine disagrees with a claim that 2-ethylbenzoselenazole ethiodide was condensed with *p*-toluquinoline ethiodide to give a *meso*-methylselena-4′-cyanine.[17]

Alternatively, thia-4′-cyanines had been synthesised by a modified thia-2′-cyanine condensation, in which 4-iodoquinoline ethiodide took the part of its 2-isomeride.[18] This reaction has now proved capable of extension, so that by condensing the 4-iodo-salt with 2-ethyl- and 2-benzyl-benzothiazolium salts, there were obtained the 4′-cyanines (VII; R = Me and Ph, R′ = R″ = Et).

Synthesis of further chain-substituted thia-2′-cyanines (II) required two stages: first, the preparation of other benzothiazoles and their quaternary salts, having a substituted 2-methyl group, and, secondly, their application in dye condensations.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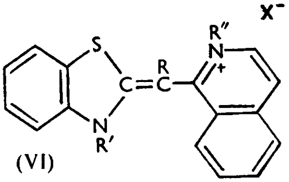
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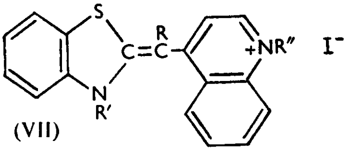
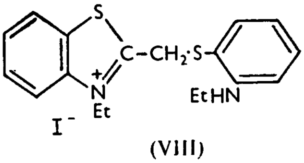

(VII)

Both steps were realised in the preparation of the ethiodide of a new base, 2-*p*-nitrobenzylbenzothiazole and, from it, of the dye (II; R = p-C_6H_4·NO_2, R′ = R″ = Et).

2-Chloromethylbenzothiazole is also described for the first time, but it could not be converted into a quaternary salt: this corresponds with a reported failure to prepare a quaternary salt of 2-bromomethylbenzothiazole.[19] However, Kiprianov and Pazenko's general method for preparing quaternary benzothiazolium salts, by the action of acid halides on *N*-substituted *o*-aminothiophenol [20] was applied by them to the preparation of 2-bromomethylbenzothiazole methobromide,[20] and it was hoped to apply it to the ethiodide of 2-chloromethylbenzothiazole. This hope was not realised, although Yagupolsky and Marenets had isolated 2-chloromethylbenzothiazole ethochloride: [21] reaction of *o*-ethylaminothiophenol with excess of chloroacetyl chloride, followed by potassium iodide, did give an ethiodide, but by analysis the product was identified as the sulphide (VIII). This resembles the product (IX) which Kiprianov and Pazenko obtained from *o*-methylaminothiophenol and dichloroacetyl chloride.[20]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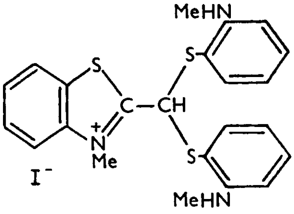
(IX)

2-Ethoxycarbonylmethylbenzothiazole was prepared by van Dormael and Nys, who used the crude base for dye condensations and made its methiodide.[22] The base has now

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[17] Dieterle, Zeh, and Agfa Ansco Corp., U.S.P. 2,051,134/1931.

[18] Hamer, *J.*, 1939, 1008.

[19] Zubarovsky, *J. Gen. Chem.* (*U.S.S.R.*). 1951, **21**, 2055.

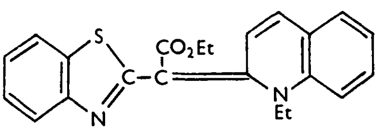
[20] Kiprianov and Pazenko, *ibid.*, 1949, **19**, 1515.

[21] Yagupolsky and Marenets, *ibid.*, 1953, **23**, 497.

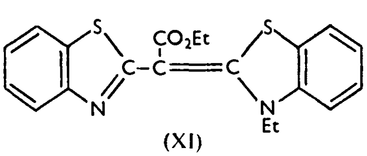
[22] Van Dormael and Nys, *Bull. Soc. chim. belges*, 1948, **57**, 355.

been distilled and obtained analytically pure. Their preparation of the methiodide by heating the base with methyl iodide in a sealed tube at 65° was confirmed, but at 100° the product was 2-methylbenzothiazole methiodide. When the base was heated with ethyl iodide in a sealed tube at 65°, salt formation did not occur, whilst at 100° the product was 2-methylbenzothiazole ethiodide, but 2-ethoxycarbonylmethylbenzothiazole ethiodide was arrived at by applying the general method of Kiprianov and Pazenko,[20] the reactants in this case being *o*-ethylaminothiophenol and ethoxycarbonylacetyl chloride. Unfortunately attempts to convert this ethiodide into methincyanines having a *meso*-ethoxycarbonyl group (II and IV; R = CO_2Et, R′ = R″ = Et) were unsuccessful. At first sight this is surprising, since it was noted long ago that quaternary salts undergo certain condensations more readily than do the corresponding bases,[23] and indeed the whole chemistry of cyanines may be regarded as based on that theorem. However, there are exceptions and it has recently been recorded [24] that 2-ethylpyridine, but not its methiodide, condensed with aldehydes.

As its ethiodide could not be used, 2-ethoxycarbonylmethylbenzothiazole was condensed with the ethosulphates of 2-ethylthioquinoline and 2-ethylthiobenzothiazole severally to give the dye bases (X) and (XI), the condensations being effected as indicated by van Dormael and Nys [8] for the *N*-methyl analogue of the latter. The bases were purified through their perchlorates. Attempts to use similarly 2-(ethoxycarbonylformyl)methylbenzothiazole,[25] in order to reach analogues of (X) and (XI) having a *meso*-ethoxalyl group,



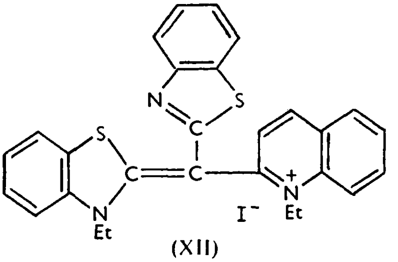
(X)



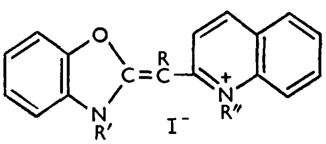
(XI)

led only to the corresponding unsubstituted bases; in an attempt to condense 2-chloromethylbenzothiazole with 2-ethylthioquinoline ethosulphate, dye formation did not take place. By the action of alkyl halides on the bases (X) and (XI), two pairs of chain-substituted methincyanines were prepared, *viz.*, (II; R = CO_2Et, R′ = Me or Et, R″ = Et) and (IV; R = CO_2Et, R′ = Me or Et, R″ = Et).

By reaction of di(benzothiazolyl)methane ethiodide [26] with 2-iodoquinoline ethiodide there was prepared the cyanine (XII), in which the *meso*-substituent is particularly large. Use of a quaternary salt of di(benzothiazolyl)methane in a cyanine-dye condensation has



(XII)



(XIII)

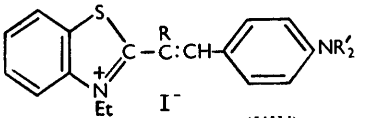
not previously been described, although the base itself was used for making trinuclear *mero*cyanines.[27]

Condensing quaternary salts of 2-ethyl- and 2-benzyl-benzoxazole with 2-iodoquinoline ethiodide gave the cyanines (XIII; R = Me or Ph, R′ = R″ = Et), which are the benzoxazole analogues of (II; R = Me or Ph, R′ = R″ = Et). The benzoxazole

[23] Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736.
[24] Phillips, *J. Amer. Chem. Soc.*, 1954, **76**, 3986.
[25] Borsche and Doeller, *Annalen*, 1939, **537**, 53.
[26] Mills, *J.*, 1922, **121**, 455.
[27] Anish and General Aniline and Film Corp., B.P. 620,482/1945.

analogues of (V and VII; R = Ph, R′ = R″ = Et) and that of (VI; R = Ph, R′ = R″ = Et, X = I) were also obtained. Owing to their instability, the benzoxazole analogues were more difficult to isolate than the benzothiazole dyes.

In the styryl series, the parent ethiodide (XIV; R′ = Me, R = H) is known.[28] Kiprianov and Ushenko [29] prepared the corresponding perchlorate and made an interesting study of chain-substituted styryl dyes, including the perchlorates corresponding with the iodides (XIV; R′ = Me, R = Me or Ph). Five chain-substituted styryl dyes have now been made, namely, (XIV; R′ = Me, R = Me, Ph, *p*-$C_6H_4{\cdot}NO_2$, CO_2Et, or 2-benzothiazolyl).



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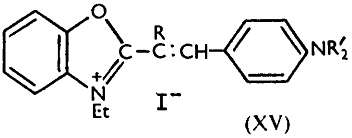
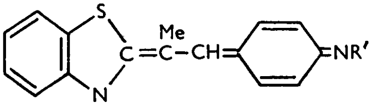


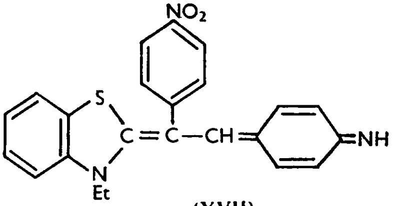
(XV)

Another unsubstituted parent dye and its methyl derivative (XIV; R′ = Et, R = H and Me) were also made. In the benzoxazole series there were prepared the parent dye (XV; R′ = Me, R = H) and two derivatives (XV; R′ = Me, R = Me or Ph).

It was noticed that the dye (XIV; R′ = R = Me) was accompanied by a basic by-product. So also was the closely related product (XIV; R′ = Et, R = Me) whereas the unsubstituted parent (XIV; R′ = Et, R = H) was not. These by-products were purified and analysed; it was concluded that both *N*-methyl groups, but only one *N*-ethyl group, was lost in formation of the by-products, which were the imines (XVI; R = H or Et).



(XVI)



(XVII)

The latter by-product may be simply derived from (XIV; R′ = Et, R = Me) by elimination of ethyl iodide; to arrive at the former by-product from (XIV; R′ = R = Me), methyl iodide may be eliminated, hydrogen iodide added, and methyl iodide again eliminated. A basic by-product also accompanied the dye (XIV; R′ = Me, R = *p*-$C_6H_4{\cdot}NO_2$), and it was concluded from analysis that it had structure (XVII). Methanolic solutions of the three bases had each a sharp absorption maximum, for which the chain of conjugated double bonds is doubtless responsible.

Tables 1 and 2 contain the absorption maxima of methanolic solutions of the methincyanines and styryl dyes respectively, as well as the shifts which occur on substitution, and the molecular extinction coefficients. A connection between departure from planarity of the molecule and decreased intensity of absorption was deduced with *o*-substituted diphenyls [30] and with certain dimethylanilines.[31] In the cyanine series, intensity of absorption is diminished by substitution on the chain and has been ascribed to non-planarity,[4, 5] as also with styryl dyes.[29] All the chain-substituted dyes recorded in the Tables show decreased intensity of absorption.

With the dimethylanilines, non-planarity of the molecule led to absorption at a shorter wavelength.[31] Other instances of absorption at a shorter wavelength due to steric effects have been recorded; [32] even in the cyanine series, four methincyanines, each of which had a 3 : 4-benzoquinoline nucleus and could not have planar molecules,[33] absorbed at a shorter

[28] Bloch and Hamer, *Phot. J.*, 1930, **54**, 374.
[29] Kiprianov and Ushenko, *J. Gen. Chem.* (*U.S.S.R.*), 1950, **20**, 543 (*Zhur. obshchei Khim.*, p. 514).
[30] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906.
[31] Remington, *ibid.*, 1945, **67**, 1838.
[32] Förster, *Z. Elektrochem.*, 1939, **45**, 548.
[33] Sheppard, Lambert, and Walker, *Nature*, 1940, **145**, 386.

wavelength than the analogues having a 5 : 6-benzoquinoline nucleus.[34] On the other hand, a bathochromic shift of absorption maximum was ascribed to steric deformation with the dipyrrylmethenes [35] and with *N*-methyl*ætio*porphyrin II.[36] Instances of bathochromic shifts caused by chain-substitution of methincyanines, and attributed to non-planarity of the molecule, have been recorded.[4, 5] Vittum and Brown [37] pointed out that steric factors may produce sometimes an increase and sometimes a decrease of the wavelength of maximum absorption, depending on their effects on the ground state and on the excited state.

TABLE 1. *Methincyanines.*

R	Abs. max. (Å)	Bathochromic shift on substn. (Å)	ε	Ref.
Formula (II; R′ = R″ = Et)				
H	4860	—	51,200	*a*, *b*
Me	5450	590	25,900	
Ph	5520	660	31,400	
p-$C_6H_4{\cdot}NO_2$	5480 (4500)	620	24,400 (11,560)	
CO_2Et	4780	− 80	10,700	
2-Benzothiazolyl	5470	610	11,500	
Formula (II; R′ = Me, R″ = Et)				
H	4850	—	50,200	*a*
CO_2Et	4750	−100	15,000	
Formula (V; R′ = R″ = Et)				
H	4980	—	50,000	*b*
Me	5470	490	24,200	
Ph	5560	580	25,800	
Formula (VI; R′ = R″ = Et)				
H	5020	—	24,800	*c*
Me	5230	210	5,590	
Ph	5480	460	6,960	
Formula (VII; R′ = R″ = Et)				
H	5030	—	52,600	13, *b*
Me	5770	740	26,000	
Ph	5810	780	31,100	

R	Abs. max. (Å)	Bathochromic shift on substn. (Å)	ε	Ref.
Formula (IV; R′ = R″ = Et)				
H	4220	—	86,700	*d*
Me	4770	550	40,000	
CO_2Et	4370	150	11,500	
Formula (IV; R′ = Me, R″ = Et)				
H	4220	—	86,500	
CO_2Et	4320	100	21,780	
Formula (XIII; R′ = R″ = Et)				
H	4370	—	53,000	10, *b*
Me	4960	590	24,600	
Ph	5050 (4900 inflexion)	680	30,200 (27,000)	
O-Analogues of (V; R′ = R″ = Et)				
H	4630 (4450)	—	50,300 (49,400)	*b*
Ph	5140	510	27,300	
O-Analogues of (VI; R′ = R″ = Et)				
H	4550	—	28,000	
Ph	5080	530	7,000	
O-Analogues of (VII; R′ = R″ = Et)				
H	4700	—	64,400	*b*, *e*
Ph	5320	620	33,300	

[a] Hamer, *J.*, 1928, 206. [b] Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138. [c] Fisher and Hamer, *J.*, 1934, 1905. [d] *Idem, Proc. Roy. Soc.*, 1936, *A*, **154**, 703. [e] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906.

TABLE 2. *Styryl compounds.*

R	Abs. max. (Å)	Hypsochromic shift on substn. (Å)	ε
Formula (XIV; R′ = Me)			
H	5250 *	—	79,000
Me	4600 *	650	21,000
Ph	4910 *	340	25,300
p-$C_6H_4{\cdot}NO_2$	4820	430	28,000
CO_2Et	4180 †	1070	25,000
2-Benzothiazolyl	4380	870	32,800

R	Abs. max. (Å)	Hypsochromic shift on substn. (Å)	ε
Formula (XIV; R′ = Et)			
H	5380	—	81,500
Me	4670	710	25,400
Formula (XV; R′ = Me)			
H	4920	—	70,000
Me	4670	250	30,880
Ph	4910	10	58,200

* For the corresponding perchlorates (XIV; R′ = Me, R = H, Me, and Ph), Kiprianov and Ushenko [29] give 5300, 4810, and 5080 Å, respectively, but their solvent is not recorded.

† Van Dormael and Nys [8] said that the corresponding methiodide decomposed during recrystallisation, so that $\lambda_{max.}$ could not be determined exactly, but was about 4860 Å.

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[34] Brooker and Keyes, *J. Amer. Chem. Soc.*, 1936, **58**, 659.

[35] Brunings and Corwin, *ibid.*, 1942, **64**, 593.

[36] Ellingson and Corwin, *ibid.*, 1946, **68**, 1112.

[37] Vittum and Brown, *ibid.*, 1947, **69**, 152.

Table 1 shows that in four instances the bathochromic shift on passing from ⁚CH· to ⁚CMe· varies from 490 to 590 Å, whilst for the *iso*quinoline dye (VI) it is smaller (210 Å) and for the 4-linked quinoline dye (VII) it is larger (780 Å). In six instances, the shift on passing from ⁚CH· to ⁚CPh· varies from 510 to 680 Å, but again is smaller in (VI) (460 Å) and larger in (VII) (780 Å). In each of five instances, substitution of hydrogen by phenyl produces a bigger shift than its substitution by methyl. The *p*-nitrophenyl group causes a rather smaller shift than does the phenyl group, which implies that the effect is not electronic. The large 2-benzothiazolyl group causes a shift which is again a little less. With two pairs represented by (IV), the introduction of the ethoxycarbonyl group produces bathochromic shifts of 150 and 100 Å, respectively. On the other hand, in two pairs represented by (II), the shifts on passing from ⁚CH· to ⁚C(CO_2Et)· are hypsochromic, of 80 and 100 Å. Van Dormael and Nys recorded the absence of shift in a pair represented by (IV), whence they concluded that the two benzothiazole nuclei lie in one plane and the ethoxycarbonyl group in another.[8] However, in making a Courtauld model of the compound (X), of which the dye (IV; R = CO_2Et, R′ = R″ = Et) is the ethiodide, a fairly stable arrangement was attained when the ethoxycarbonyl group and one benzothiazole nucleus lay in one plane and the second benzothiazole nucleus in another.

Although there are hypsochromic shifts on passing from two parent methincyanines represented by (II) to the corresponding *meso*-ethoxycarbonylmethincyanines, and bathochromic shifts on passing from two parent methincyanines represented by (IV) to the corresponding *meso*-ethoxycarbonylmethincyanines, just the opposite occurs, in each instance, on passing to the *meso*-ethoxycarbonyl bases (X) and (XI) from the parent bases. The magnitude of these two shifts cannot be stated, since more than one value of $\lambda_{max.}$ was recorded for each parent base; [38] possibly those different values corresponded with different stereoisomeric forms.

The striking observation that, in the styryl series, substitution on the chain causes a hypsochromic shift of absorption maximum [29] is borne out by the examples in Table 2. Here, in two instances, a change from ⁚CH· to ⁚CMe· in the benzothiazole series caused hypsochromic shifts of 650 and 710 Å, that in the benzoxazole series being smaller (250 Å). In the benzothiazole series the hypsochromic shifts on replacing ⁚CH· by ⁚CR· increase as R represents the groups Ph, *p*-C_6H_4·NO_2, Me, 2-benzothiazolyl, CO_2Et, reaching the figure 1070 Å for the last.

Of nineteen chain-substituted methincyanines that were tested photographically, fourteen had no sensitising action; nine of the eleven unsubstituted parent dyes are strong sensitisers, but not the two containing the *iso*quinoline nucleus.[39] Extremely weak sensitising of a chlorobromide emulsion was shown by the remaining five chain-substituted methincyanines, *viz.*, (IV; R = Me, R′ = R″ = Et), (II; R = CO_2Et, R′ = Me or Et, R″ = Et), and (IV; R = CO_2Et, R′ = Me or Et, R″ = Et).

Of the eight chain-substituted styryl dyes, seven were photographic sensitisers, but weaker than the corresponding unsubstituted dyes, of which there were three. In comparison with the sensitisation by the *meso*-phenyl dye (XIV; R′ = Me, R = Ph), it is interesting that the *p*-nitrophenyl analogue was not a sensitiser and strongly depressed the normal sensitivity of the emulsion.

EXPERIMENTAL

A, Bases and Salts.

Phenylacetyl Chloride.—As the preparation by use of phosphorus pentachloride [40] could not be reproduced, thionyl chloride [41] was used. To boiling thionyl chloride (18 c.c., 1·25 mols.), phenylacetic acid (27·2 g., 1 mol.) was added during 10 min. After a further 30 minutes' boiling, the liquid was distilled. The fraction, b. p. 96—98°/17 mm., comprised a 77% yield.

2-Benzylbenzothiazole.[42]—This was prepared by mixing phenylacetyl chloride (17·80 g., 1 mol.)

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

[39] Fisher and Hamer, *J.*, 1934, 1905.

[40] Schott, *Ber.*, 1896, **29**, 1985.

[41] Meyer, *Monatsh.*, 1901, **22**, 415.

[42] Hofmann, *Ber.*, 1880, **13**, 1223.

with *o*-aminothiophenol hydrochloride (1 mol.), stirring in phosphoric oxide (0·33 mol.), and heating the mixture in an oil-bath. After 8 min. at 160—175°, the product was warmed with sodium hydroxide solution, and the base extracted with ether. After removal of the solvent from the dried extract, the viscous yellow oil had b. p. 157°/0·5 mm., and the fraction of b. p. 157—163°/0·5 mm. amounted to a 29% yield. Skraup and Böhm[43] recorded b. p. 204—205°/13 mm.

2-*Benzylbenzothiazole Ethiodide.*—2-Benzylbenzothiazole (9·82 g., 1 mol.) and ethyl iodide (1·2 mols.) were heated at 100° for 48 hr. The acetone-treated product (71% yield) was recrystallised from ethanol (7 c.c. per g.), giving a 57% yield. The pale yellow crystals of *ethiodide* had m. p. 181° (Found: C, 50·2; H, 4·4. $C_{16}H_{16}NIS$ requires C, 50·4; H, 4·25%).

p-*Nitrophenylacetic Acid.*—Phenylacetic acid was nitrated by Borsche's method;[44] he records a 50—60% yield of *p*-nitro-compound, m. p. 152°. The present yield of crude acid was 76% but the m. p. was 95—140° and four recrystallisations from water were required (one from 20 c.c. per g. and three from 100 c.c. per g.) for the m. p. to reach 151°, at which point the yield was only 22%.

p-Nitrophenylacetyl chloride, prepared by use of phosphorus pentachloride,[45] had m. p. 47°. In our work, thionyl chloride (10·4 c.c., 3 mols.) was boiled, *p*-nitrophenylacetic acid (8·72 g., 1 mol.) gradually added, and boiling continued for 30 min. Excess of thionyl chloride was distilled off and the residual oil extracted with light petroleum (b. p. 40—60°; 1500 c.c.). The chloride (44% yield) had m. p. 48°. Pyman[46] gives m. p. 48°.

2-4'-*Nitrobenzylbenzothiazole.*—To *p*-nitrophenylacetyl chloride (3·28 g., 1 mol.) and *o*-aminothiophenol (1 mol.) at 115°, phosphoric oxide (1 mol.) was stirred in. After 15 min. at 145—170° the brown glass was heated with sodium hydroxide solution and benzene. From the dried extract the benzene was removed. The crystalline residue was dissolved in hot ethanol (30 c.c.), and the solution treated with hot water (30 c.c.). The resultant oil solidified (88% yield). After recrystallisation from ethanol (10 c.c. per g.) the yield of sand-coloured *benzothiazole* was 73%, and the m. p. 115°. Another such recrystallisation (17 c.c. per g.) gave a 58% yield, but no change of m. p. (Found: C, 62·05; H, 3·65. $C_{14}H_{10}O_2N_2S$ requires C, 62·15; H, 3·75%).

The thiazole (2·7 g., 1 mol.) and ethyl iodide (1·2 mols.) were heated at 100° for 24 hr. Treatment with acetone (total 30 c.c.) gave a pale yellow salt (88%). This was recrystallised from methanol (100 c.c. per g.), contact with water being avoided, and gave a 67% yield of pale beige *ethiodide*, m. p. 249° (decomp.) with previous darkening (Found: C, 45·05; H, 3·7. $C_{16}H_{15}O_2N_2IS$ requires C, 45·05; H, 3·55%).

Ethoxycarbonylacetyl Chloride.—The method of Staudinger and Becker[47] required modification, possibly because of the present smaller scale. Potassium ethyl malonate (32·49 g., 1 mol.) was gradually added to boiling thionyl chloride (1·25 mols.), and the mixture was further boiled for a few minutes, then, without filtering, distilled. The yield was 64%, and the b. p. 75—78°/21 mm.

2-*Ethoxycarbonylmethylbenzothiazole.*—In a repetition of the method of van Dormael and Nys,[22] a suspension of the zinc salt (20·85 g., 0·5 mol.) of *o*-aminothiophenol in boiling dry benzene (90 c.c.) was treated gradually with ethoxycarbonylacetyl chloride (1 mol.) in dry benzene (120 c.c.); the mixture was boiled for 6 hr., lumps of zinc salt being broken up at intervals. The solid was filtered off hot and boiled out with benzene (2 × 30 c.c.). After being washed with water, it amounted to a 23% recovery of zinc salt. The benzene extract was shaken with excess of aqueous sodium hydrogen carbonate, washed with water, and dried (Na_2SO_4). The solvent was taken off under reduced pressure. Van Dormael and Nys thus obtained a 70% yield of base, which they subjected to condensations. In the present work, the crude product was distilled, giving a pale yellow *base*, b. p. 121—126°/0·5 mm. (Found: C, 59·65; H, 5·05. $C_{11}H_{11}O_2NS$ requires C, 59·7; H, 5·0%). Taking account of the recovered zinc salt, the yield was 53%.

This thiazole (0·64 g., 1 mol.) and methyl iodide (1·25 mols.) were heated in a sealed tube at 65° for 15 hr. and then treated with anhydrous ether and acetone (2 : 1), as described by van Dormael and Nys.[22] The *methiodide* was obtained in their yield (70%), but with much lower m. p. On recrystallisation from methanol–acetone (1 : 3) (16 c.c. per g.), the yield dropped

[43] Skraup and Böhm, *Ber.*, 1926, **59**, 1007.
[44] Borsche, *Ber.*, 1909, **42**, 3596.
[45] Wedekind, Häussermann, Weisswange, and Miller, *Annalen*, 1911, **378**, 261.
[46] Pyman, *J.*, 1917, **111**, 169.
[47] Staudinger and Becker, *Ber.*, 1917, **50**, 1016.

to 28%; the m. p. was 175° (decomp.) with previous darkening (Found : C, 40·05; H, 4·15. $C_{12}H_{14}O_2NIS$ requires C, 39·7; H, 3·9%). Van Dormael and Nys give m. p. 170—171° (decomp.) but do not record the yield at this stage or an analysis. Addition of ether to the filtrate from the recrystallisation precipitated a solid (0·09 g.), which was recrystallised from ethanol (4 c.c.; 0·06 g. obtained). Although this had m. p. 172° (decomp.), a colour-test showed contamination with 2-methylbenzothiazole methiodide.

In an attempted preparation where the reactants were heated at 100° for 24 hr., treatment with dry acetone gave a 54% yield of crystals; after two recrystallisations from ethanol (12 c.c. per g.), the yield was 22%, and the m. p. 210° (decomp.). By the colour-test and by analysis (Found : C, 37·0; H, 3·7. Calc. for $C_9H_{10}NIS$: C, 37·1; H, 3·45%), this salt was identified as 2-methylbenzothiazole methiodide.

2-*Ethoxycarbonylmethylbenzothiazole Ethiodide*.—(*a*) When 2-ethoxycarbonylmethylbenzothiazole and ethyl iodide were heated in a sealed tube at 65° for 15 hr., salt formation did not occur. The base and ethyl iodide were heated at 100° for 24 hr., the supernatant liquid was poured off, and the gum treated with acetone; a 51% yield of crystals resulted. After two recrystallisations from ethanol (7 c.c. per g.), the yield was 23%; the m. p., 190° (decomp.), was unchanged by the second recrystallisation. From m. p., mixed m. p., analysis (Found : C, 39·4; H, 4·2. Calc. for $C_{10}H_{12}NIS$: C, 39·35; H, 3·95%), and the colour test, the salt was identified as 2-methylbenzothiazole ethiodide.

(*b*) (Cf. Kiprianov and Pazenko.[20]) To a solution of *o*-ethylaminothiophenol (0·81 g., 1 mol.) in dry benzene (4 c.c.) was added one of ethoxycarbonylacetyl chloride (1·1 mols.) in dry benzene (2 c.c.). After cooling to room temperature, the liquid was decanted and the gum washed twice with benzene, dissolved in hot methanol (2 c.c.), and treated with a warm solution of potassium iodide (2 mols.) in water (4 c.c.). The *ethiodide* crystallised and was filtered off and washed (49% yield). After recrystallisation from methanol (5 c.c. per g.), the yield was 32%. The white crystals had m. p. 155° (decomp.), with previous yellowing, but the m. p. depended on the rate of heating (Found : C, 41·55; H, 4·6. $C_{13}H_{16}O_2NIS$ requires C, 41·4; H, 4·3%).

2-*Chloromethylbenzothiazole*.—Chloroacetyl chloride [48] (8·28 g.; 1 mol.) was cooled with ice, and *o*-aminothiophenol (1 mol.) was gradually stirred in. Phosphoric oxide (0·33 mol.) was added and the mixture heated in an oil-bath. After 45 min. at 140—150°, the product was heated with water, benzene, and sodium hydroxide solution. After repeated benzene extraction, the dark extract was dried (Na_2SO_4). The solvent was taken off and the residue distilled. The *product* (18%), b. p. 79—91°/0·2 mm., solidified. On recrystallisation of this from light petroleum (b. p. 40—60°; 8 c.c. per g.), the yield dropped to 6% and there was a residue. The colourless crystals had m. p. 34° (Found : C, 52·55; H, 3·55. C_8H_6NClS requires C, 52·3; H, 3·3%).

2-(o-*Ethylaminophenylthiomethyl*)*benzothiazole Ethiodide* (VIII).—An attempt to prepare 2-chloromethylbenzothiazole ethiodide, by heating the base with ethyl iodide in a sealed tube, was unsuccessful, so Kiprianov and Pazenko's general method [20] was tried. A solution of *o*-ethylaminothiophenol (1·58 g., 1 mol.) in dry benzene (5 c.c.) was treated with one of chloroacetyl chloride (2 mols.) in dry benzene (4 c.c.), with slight cooling. Heat was evolved and a pale yellow solid separated. After cooling, the liquid was decanted and the solid washed twice with dry benzene. It was dissolved in hot methanol (6 c.c.) and the solution was treated with hot aqueous potassium iodide. After cooling, the brown and tacky product was twice washed with water, by decantation, and then treated with acetone (3 c.c.), whereupon a yellow solid separated. This was filtered off and washed with acetone (4 × 1 c.c.). The yield amounted to 19%, but in a preparation on a scale half as large again it was only 11%; another preparation on the larger scale decomposed completely on treatment with potassium iodide. Recrystallisation from methanol (14 c.c. per g.) decreased the 19% yield to 17%, and a second recrystallisation to 13%, but the m. p., 158° (decomp.), was unaltered by the second recrystallisation (Found : C, 47·15; H, 4·65; N, 6·3; I 27·85; S, 14·2. $C_{18}H_{21}N_2IS_2$ requires C, 47·35; H, 4·65; N, 6·15; I, 27·8; S, 14·05%). It was concluded that the *ethiodide* must be that named above. Although the precautions recommended [20] in preparing 2-bromomethylbenzothiazole methobromide were observed, decomposition occurred at the stage of addition of potassium iodide.

3-*Ethyl*-2-*oxobenzothiazoline*.—This, b. p. 170°/14 mm., was prepared by Fuchs and Grauaug from 3-ethyl-2-nitrosoiminobenzothiazoline.[49] Hunter [50] described it as an oil. Sexton [51] prepared its 3-methyl homologue from 2-methylthiobenzothiazole methosulphate and alkali.

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[48] Barnett, *Chem. News*, 1921, **122**, 220.

[49] Fuchs and Grauaug, *Ber.*, 1928, **61**, *B*, 57.

[50] Hunter, *J.*, 1930, 125.

[51] Sexton, *J.*, 1939, 470.

Kiprianov and Pazenko[52] claim to have prepared similarly the 3-ethyl compound and, by treatment with ligroin, to have obtained it with m. p. 58°. In the present work 2-ethylthiobenzothiazole (19·93 g., 1 mol.) was heated with neutral ethyl sulphate (1 mol.) at 110—120° for 8 hr. Although the gum sometimes crystallised spontaneously, its solution in water (120 c.c.) was cloudy and acid. It was cleared by extraction with ether and was then stirred and cooled with ice during addition of an ice-cold solution of sodium hydroxide (2·2 mols.) in water (40 c.c.). The oil from the dried ether extract (Na_2SO_4) was distilled in a vacuum. The yield varied, in eight experiments, from 30 to 83% (average 53%). An analytically pure sample of the 2-oxo-compound was clear and colourless and had b. p. 101°/0·5 mm. (Found : C, 60·25; H, 5·0. Calc. for C_9H_9ONS : C, 60·3; H, 5·05%), and could not be induced to solidify. When crude, it tends to distil cloudy, which is attributed to contamination by 2-thio-compound since that was isolated by treating the highest-boiling fraction with ether and light petroleum (Found, after two recrystallisation from light petroleum : C, 55·25; H, 4·8. Calc. for $C_9H_9NS_2$: C, 55·35; H, 4·65%); its identity was confirmed by its m. p., 78°, and mixed m. p., and the yield was of the order 6—14%.

3-Ethyl-2-thiobenzothiazoline.—This was originally prepared, with m. p. 75°, by heating 3-ethyl-2-nitrosoiminobenzothiazoline with phosphorus pentasulphide,[50] secondly, with m. p. 78—79°, by refluxing 2-ethylthiobenzothiazole ethotoluene-*p*-sulphonate with pyridine and pouring into water,[53] and thirdly, with m. p. 73—75°, by heating 2-ethylthiobenzothiazole with iodine.[52] On repetition of the second method, 2-ethylthiobenzothiazole (19·5 g., 1 mol.) and ethyl sulphate (1 mol.) were heated together at 110—120° for 8 hr. A solution of the salt in pyridine (100 c.c.) was boiled for an hour, then poured into warm water (1 l.). The washed thione (93% yield) was recrystallised from methanol (3 c.c. per g.), giving an 82% yield (m. p. 77—78°). In another experiment, freshly prepared 2-ethylthiobenzothiazole ethiodide (0·63 g.) was boiled with pyridine (3 c.c.) for 10 min. and the solution poured into water (12 c.c.). On recrystallisation of the product (83%) from light petroleum (b. p. 60—80°; 25 c.c. per g.), the yield dropped to 68%. This material had m. p. 78° (Found: C, 55·2; H, 4·7. Calc. for $C_9H_9NS_2$: C, 55·35; H, 4·65%).

2-Ethylthiobenzothiazole Ethiodide.—When a sample which had been prepared some months previously was converted by pyridine into the thione, the impossibly high yield led to the conclusion that partial conversion had already occurred. Calculated from the carbon content (Found: C, 48·3; H, 4·4. Calc. for $C_{11}H_{14}NIS_2$: C, 37·6; H, 4·0%. Calc. for $C_9H_9NS_2$: C, 55·35; H, 4·65%), the proportion of ethiodide was 40% and of thione 60%. A similar sample of ethiodide (2 g.) was thrice ground with anhydrous benzene (3 × 5 c.c.). The residue of ethiodide amounted to 28%, whilst the quantity of thione obtained on removal of the benzene was 64%; after recrystallisation from light petroleum it was 56% (m. p. 78°). This deterioration of the ethiodide may explain why alkiodides appeared less satisfactory for preparation of dye bases than did alkotoluene-*p*-sulphonates.[38]

o-*Ethylaminothiophenol*.—This, b. p. 129—130°/20 mm., was prepared from crude 3-ethyl-2-oxobenzothiazoline by boiling with alcoholic potassium hydroxide and the yield, based on the quaternary salt used for making the 2-oxo-compound, was claimed[52] to be 73%. On repetition, only a 47% yield was obtained, perhaps owing to the variability of crude 2-oxo-compound. Preferably distilled 2-oxo-compound (12·10 g., 1 mol.), in ethanol (24 c.c.), was boiled with a solution of potassium hydroxide (6 mols.) in ethanol (70 c.c.) for 1 hr. After cooling, the potassium carbonate was filtered off and washed with ethanol, and the filtrate and washings were evaporated to dryness. The residue was dissolved in water (100 c.c.), and the solution was cooled during addition of concentrated hydrochloric acid. The precipitated oil was extracted with benzene, and the extract dried (Na_2SO_4). After removal of solvent, the yield of pale yellow oil, b. p. 57—60°/0·5 mm., was 77% (Found : C, 62·8; H, 7·3. Calc. for $C_8H_{11}NS$: C, 62·7; H, 7·25%).

This compound is better prepared from 3-ethyl-2-thiobenzothiazoline, since the preparation of that is straightforward. Thus this 2-thione (19·53 g., 1 mol.), in ethanol (40 c.c.), was boiled with potassium hydroxide (6 mols.) in ethanol (105 c.c.) for 6 hr. After cooling, the solid was filtered off and washed with ethanol, and the filtrate and washings were concentrated to a paste. This was treated with water (130 c.c.), and the solution was extracted with benzene and neutralised with hydrochloric acid. The oil was extracted with benzene. The yield was 70%, and the b. p. 56—64°/0·4 mm. Kiprianov and Pazenko[52] claimed 77%. When only 4 mols. of

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[52] Kiprianov and Pazenko, *J. Gen. Chem.* (*U.S.S.R.*), 1949, **19**, 1523.
[53] Kendall, B.P. 475,647/1936.

potassium hydroxide were used, there was a 24% recovery of thione, which was filtered off with the potassium salt and freed from it by washing with water.

2-Ethylbenzoxazole.—By a procedure similar to that for 2-methylbenzoxazole,[54] *o*-aminophenol (42·6 g., 1 mol.) was gradually added to propionic anhydride (3 mols.). The liquid was heated on a water-bath for 30 min. and then in an oil-bath, to remove propionic acid and anhydride. The latter fraction, b. p. 150—168°, and the residue were distilled under a vacuum. The distillate was subjected to prolonged treatment with 10% sodium carbonate solution, extracted with ether, and redistilled, giving a 28% yield of material, b. p. 40—43°/0·3—0·5 mm. Skraup and Moser,[55] who prepared it from *o*-aminophenol and propionitrile under pressure, give b. p. 210°.

2-Ethylbenzoxazole (16·25 g.) and ethyl iodide were heated together at 100° for 8 hr. After treatment with anhydrous acetone (40 c.c.), the yield was 58%. Recrystallisation from ethanol (3 c.c. per g.) gave a 40% yield of colourless *ethiodide*, m. p. 198° (decomp.) (Found : C, 43·5; H, 4·85. $C_{11}H_{14}ONI$ requires C, 43·55; H, 4·65%).

2-Benzylbenzoxazole.[56]—Prepared from *o*-aminophenol and benzyl cyanide, this had b. p. 325°/750 mm. According to the present method, *o*-aminophenol (10·9 g., 1 mol.) and phenylacetic acid (1 mol.) were heated for 3 hr. at 200—225°, in a flask allowing the escape of water vapour. The product was treated with aqueous sodium hydroxide and extracted with benzene, which gave a yellowish oil, b. p. 118—125°/0·3 mm. (48%).

An attempt to prepare the ethiodide at 100° was unsuccessful. The ethotoluene-*p*-sulphonate was prepared as a gum, which was dissolved by dry acetone (1 c.c. per g.), instead of being induced to solidify; it was used for dye condensations.

B, Methincyanine Dyes.

[2-(*3-Ethylbenzothiazole*)][2-(*1-ethylquinoline*)]*methylmethincyanine Iodide* (II; R = Me, R′ = R″ = Et).—To 2-ethylbenzothiazole ethiodide (0·80 g., 1 mol.) and 2-iodoquinoline ethiodide (1 mol.) in ethanol (3 c.c.), triethylamine (2·1 mols.) was added and the mixture was boiled and stirred for 1 min. Ether precipitated a tar, which was washed with ether and then crystallised from hot acetone (4 c.c.). The yield of acetone-washed dye was 72% and a chromatogram with chloroform on alumina gave no indication of coloured by-product. After recrystallisation from ethanol (7 c.c. per g.), the olive-green *dye* (54%) melted about 148°, with softening from 125° (Found : C, 55·45; H, 5·35. $C_{22}H_{23}N_2IS$ requires C, 55·65; H, 4·9%). Towards a photographic emulsion the dye had a slight desensitising action.

With 30 minutes' heating, the yields were 84% and 59%, and again no dye by-product was detected. In a similar experiment with 2-ethylbenzothiazole ethotoluene-*p*-sulphonate, with heating for 1 min., the tar precipitated by ether was heated with aqueous potassium iodide. After cooling, the liquid was decanted and the tar heated with acetone, giving a 66% yield, which dropped to 48% on recrystallisation. Götze obtained two dyes by condensation of 2-ethylbenzothiazole ethiodide with 2-iodoquinoline methiodide,[3] but the present products were homogeneous.

On the other hand, when 2-ethylbenzothiazole ethiodide (0·80 g., 1 mol.), 2-ethylthioquinoline ethiodide (1 mol.), ethanol (5 c.c.), and triethylamine (1·1 mols.) were boiled together for 10 min., the dye precipitated by ether, washed with water, and obtained in 30% yield by boiling with acetone (6 c.c.) was a mixture. By chromatography with chloroform, containing ethanol (1%), on alumina, the chain-substituted purple dye was washed through; the extract was concentrated in a vacuum and the residue, on treatment with acetone, gave a 12% yield (3% on recrystallisation from ethanol). The alumina from the upper part of the column was extracted with hot methanol, and the extract taken to dryness and treated with acetone. The residue (0·005 g.) had the same m. p. and mixed m. p. as had [2-(3-ethylbenzothiazole)][2-(1-ethylquinoline)]methincyanine iodide (II; R = H, R′ = R″ = Et); also the absorption maxima of their methanolic solutions were identical.

Bis-2-(3-ethylbenzothiazole)methylmethincyanine Iodide (IV; R = Me, R′ = R″ = Et, X = I).—To a hot solution of 2-ethylbenzothiazole ethiodide (1·60 g., 1 mol.) and 2-ethylthiobenzothiazole ethiodide (1 mol.) in ethanol (20 c.c.) was added triethylamine (1·1 mols.) and the whole was boiled for 35 min. The mixture of salts and dyes, precipitated by ether, was ground with water, whereby the dyes were left in 16% yield (0·38 g.). They were boiled out with ethanol

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[54] Phillips, *J. Soc. Chem. Ind.*, 1937, **56**, 474T.
[55] Skraup and Moser, *Ber.*, 1922, **55**, 1080.
[56] Skraup, *Annalen*, 1919, **419**, 1.

(8 c.c.), which left a yellow residue (0·08 g.). The filtrate was boiled with charcoal (0·04 g.), then refiltered, and from it the desired dye separated in 8% yield. It recrystallised from ethanol (20 c.c. per g.; charcoal) in 5% yield. The brick-red *cyanine* had m. p. about 214° (decomp.), with previous darkening and shrinking (Found: C, 50·15; H, 4·75. $C_{20}H_{21}N_2IS_2$ requires C, 50·0; H, 4·4%). The dye was inert in a bromoiodide photographic emulsion but sensitised a chlorobromide emulsion extremely weakly to 5400 Å. It has been claimed[57] that this condensation is effected with sodium ethoxide in 24% yield, dropping on recrystallisation to 13% (m. p. 232°).

The yellow residue was recrystallised from methanol (250 c.c. per g.; 0·06 g. obtained). By m. p., mixed m. p., and identity of absorption maxima, it was established as bis-2-(3-ethylbenzothiazole)methincyanine iodide (IV; R = H, R′ = R″ = Et, X = I).

[2-(3-*Ethylbenzothiazole*)][2-(1-*ethylquinoline*)]*phenylmethincyanine Iodide* (II; R = Ph, R′ = R″ = Et).—2-Benzylbenzothiazole ethiodide (0·95 g., 1 mol.), 2-iodoquinoline ethiodide (1 mol.), ethanol (5 c.c.), and triethylamine (2·1 mols.), boiled and stirred for 3 min., gave a 79% yield of washed dye. Recrystallisation from ethanol (25 c.c. per g.) gave a 60% yield (Found: C, 60·15; H, 4·7. $C_{27}H_{25}N_2IS$ requires C, 60·4; H, 4·7%). The *dye* strongly desensitised a bromoiodide photographic emulsion.

[2-(1-*Ethyl*-5 : 6-*benzoquinoline*)][2-(3-*ethylbenzothiazole*)]*methincyanine Iodide* (V; R = H, R′ = R″ = Et).—2-Methylbenzothiazole ethiodide (3·05 g.) and 2-iodo-5 : 6-benzoquinoline ethiodide in ethanol (120 c.c.) with triethylamine were boiled and stirred for 30 min. The washed dye (68% yield) was obtained in a 42% yield after two recrystallisations from methanol (170 c.c. per g.) (Found: I, 24·9. Calc. for $C_{23}H_{23}N_2IS$: I, 24·85%). The reddish-orange crystals had m. p. 258° (decomp.).

[2-(1-*Ethyl*-5 : 6-*benzoquinoline*)][2-(3-*ethylbenzothiazole*)]*methylmethincyanine Iodide* (V; R = Me, R′ = R″ = Et).—2-Ethylbenzothiazole ethiodide (0·80 g.), 2-iodo-5 : 6-benzoquinoline ethiodide, ethanol (8 c.c.), and triethylamine were boiled together for 15 min. From the hot filtrate, the *dye* crystallised in 89% yield and was obtained in 67% yield after recrystallisation from ethanol (70 c.c. per g.). The dark purplish crystals underwent violent decomposition at about 225° (Found: C, 59·15; H, 4·95. $C_{26}H_{25}N_2IS$ requires C, 59·55; H, 4·8%). The substance strongly desensitised a bromoiodide photographic emulsion.

[2-(1-*Ethyl*-5 : 6-*benzoquinoline*)][2-(3-*ethylbenzothiazole*)]*phenylmethincyanine Iodide* (V; R = Ph, R′ = R″ = Et).—By use of 2-benzylbenzothiazole ethiodide (0·95 g.) instead of 2-ethylbenzothiazole ethiodide above, the product separated as tar, which eventually crystallised. The washed *dye* (58% yield) was recrystallised from ethanol (15 c.c. per g.) and obtained in 42% yield. The purple crystals had m. p. about 175° (decomp.) (Found: C, 63·3; H, 4·8. $C_{31}H_{27}N_2IS$ requires C, 63·45; H, 4·65%). The dye slightly desensitised a chlorobromide and a bromoiodide emulsion.

[2-(3-*Ethylbenzothiazole*)][1-(2-*ethyl*iso*quinoline*)]*methylmethincyanine Perchlorate* (VI; R = Me, R′ = R″ = Et, X = ClO_4).—A mixture of 2-ethylbenzothiazole ethiodide (0·80 g.), 1-iodo*iso*quinoline ethiodide, ethanol (3 c.c.), and triethylamine, boiled for 3 min., gave a purple filtrate and no residue. Ether precipitated the dye iodide as tar, which was washed with ether and with water. Its solution in hot ethanol gave with hot aqueous sodium perchlorate an 89% yield of washed *dye perchlorate*. After recrystallisation from ethanol (20 c.c. per g.), the yield was 72%. The vermilion crystals had m. p. about 164° (decomp.), with previous softening (Found: C, 59·0; H, 5·5. $C_{22}H_{23}O_4N_2ClS$ requires C, 59·1; H, 5·2%). The dye slightly desensitised a chlorobromide and a bromoiodide emulsion.

[2-(3-*Ethylbenzothiazole*)][1-(2-*ethyl*iso*quinoline*)]*phenylmethincyanine Iodide* (VI; R = Ph, R′ = R″ = Et, X = I).—When the 2-ethylbenzothiazole ethiodide above was replaced by 2-benzylbenzothiazole ethiodide (0·95 g.), the reaction mixture very slowly deposited crystals, the yield of washed dye iodide being 79% (1·06 g.). Half the product was dissolved in chloroform (5 c.c.) and subjected to chromatography on alumina with chloroform. A blue impurity was washed through first, with loss of some purple dye, and the desired purple dye was then extracted from the column with methanol. Concentration gave a 45% yield. Recrystallisation from ethanol (10 c.c. per g.) gave a 36% yield. The maroon crystals partly melted at 135° when quickly heated, with violent decomp. at about 227° (Found: C, 60·65; H, 4·8. $C_{27}H_{25}N_2IS$ requires C, 60·4; H, 4·7%). The *dye* slightly desensitised a chlorobromide and a bromoiodide emulsion.

[2-(3-*Ethylbenzothiazole*)][4-(1-*ethylquinoline*)]*methylmethincyanine Iodide* (VII; R = Me,

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[57] Kendall, Fry, and Ilford Ltd., B.P. 660,408/1949.

R′ = R″ = Et).—2-Ethylbenzothiazole ethotoluene-*p*-sulphonate (0·91 g.), 4-iodoquinoline ethiodide, and ethanol, with triethylamine were boiled for 2 min., then treated with hot aqueous potassium iodide. With acetone the tar gave a 56% yield of crystals. Chromatography with chloroform on alumina on a test portion revealed no dye other than the blue one. Recrystallisation from ethanol (6 c.c. per g.) reduced the yield to 49%. The olive-green crystals had m. p. 185° (decomp.) (Found: I, 26·7; S, 6·6. $C_{22}H_{23}N_2IS$ requires I, 26·75; S, 6·75%). The *dye* slightly desensitised a chlorobromide and a bromoiodide photographic emulsion.

In an attempted preparation by a modified thia-4′-cyanine condensation, 2-ethylbenzothiazole ethiodide (1·60 g., 1 mol.) and quinoline ethiodide (3 mols.), dissolved in ethanol (35 c.c.), were boiled with potassium hydroxide (3 mols.) in ethanol (20 c.c.) for 30 min. The washed product amounted to a 14% yield of *apo*cyanines. These were boiled with ethanol (25 c.c.) and the residue was washed with hot ethanol (5 c.c.). From the filtrate and washings there separated an 8% yield, which had the same m. p. and mixed m. p. as erythro*apo*cyanine, and the absorption maxima were the same. The undissolved residue, after recrystallisation from ethanol (35 c.c.), amounted to a ½% yield; like xantho*apo*cyanine, it and their mixture all darkened below 100° but remained unmelted at 300°, and the absorption maxima were the same.

[3-(1-*Ethylquinoline*)][4-(1-*ethylquinoline*)]*cyanine Iodide* (*Erythro*apo*cyanine*).—On reaction of methanolic potassium hydroxide with quinoline ethiodide,[15, 16] the yield of crude, washed *apo*cyanines was in our work 31%. They were boiled with ethanol four times (each, 6 c.c. per g.). The residue was recrystallised from ethanol and gave a ½% yield of xantho*apo*cyanine. The crystalline product obtained from the extracts and by their concentration amounted to 20% of erythro*apo*cyanine. Recrystallisation from ethanol (23 c.c. per g.) with charcoal (0·1 g. per g.) reduced the yield to 14%, and a further two recrystallisations from methanol (20 c.c. per g.; charcoal) to 6% (a chromatogram with chloroform on alumina showed no yellow contaminant) (Found: C, 59·8; H, 5·5. Calc. for $C_{22}H_{23}N_2I$: C, 59·7; H, 5·25%). The m. p. was 215—220° (decomp.). The absorption maximum of a methanolic solution was at 5160 Å (ε 31,600). A chlorobromide emulsion was very weakly sensitised to about 6000 Å, whilst a bromoiodide emulsion was slightly desensitised.

[2-(1-*Ethylquinoline*)][3-(1-*ethylquinoline*)]*cyanine Iodide* (*Xantho*apo*cyanine*).—Kaufmann and Strübin[15] said that, by modified conditions, the yield of xantho*apo*cyanine may be increased to 15%. To reproduce this, quinoline ethiodide (7 g., 2 mols.) in ethanol (140 c.c.) was treated with sodium (1·2 atom-equivs.) dissolved in ethanol (20 c.c.), and the solution was boiled for 1 hr. The yield of washed dye was 20%. Recrystallisation from methanol (200 c.c. per g.) gave a 5% yield of orange crystals, which remained unmelted at 305° (Found: C, 59·7; H, 5·5. Calc. for $C_{22}H_{23}N_2I$: C, 59·7; H, 5·25%). Kaufmann and Strübin give m. p. 320° (decomp.). The maxima of a methanolic solution were at 4610 (ε 19,900) and 3620 Å (ε 6200). A chlorobromide emulsion was weakly sensitised, with maxima at 5200 and 5400 Å and a bromoiodide emulsion showed a very weak extension of sensitivity.

[2-(3-*Ethylbenzothiazole*)][4-(1-*ethylquinoline*)]*phenylmethincyanine Iodide* (VII; R = Ph, R′ = R″ = Et).—To a mixture of 2-benzylbenzothiazole ethiodide (1·91 g., 1 mol.) and 4-iodoquinoline ethiodide in ethanol (20 c.c.) was added anhydrous potassium carbonate (180-mesh; 2·1 mols.), and the mixture was boiled for 2 min. The yield of washed *dye* was 99%; after one recrystallisation from ethanol (19 c.c. per g.) and a second from methanol (25 c.c. per g.), it was 56% (Found: I, 23·65; S, 5·8. $C_{27}H_{25}N_2IS$ requires I, 23·65; S, 6·0%). The m. p. was about 222° (decomp.). It desensitised a bromoiodide emulsion without sensitising.

[2-(3-*Ethylbenzothiazole*)][2-(1-*ethylquinoline*)]-p-*nitrophenylmethincyanine Iodide* (II; R = *p*-C_6H_4·NO_2, R′ = R″ = Et).—*p*-Nitrobenzylbenzothiazole (0·54 g., 1 mol.) and ethyl toluene-*p*-sulphonate (1 mol.) were heated together at 165—175° for 4 hr. The gum resulting was dissolved in hot ethanol (8 c.c.), treated with powdered 2-iodoquinoline ethiodide and triethylamine, and boiled for 2 min. Hot filtration removed a little 2-iodo-salt, and two washings with ethanol were given. The tar deposited was treated with ether, then dissolved in hot methanol (10 c.c.) and treated with hot aqueous potassium iodide. The tar hardened and was washed with water, and dried in a vacuum-desiccator (0·58 g. obtained, 40% yield). It was purified by two chromatograms. In the first it was treated with chloroform containing ethanol (1%) on alumina and this gave incomplete removal of a brown forerun; the purplish dye was then collected (23% yield), leaving three coloured impurities in the column. In the second chromatogram, pure chloroform was used to remove a brown forerun; the dye was then washed out (13% yield) with chloroform containing ethanol (1%). Its solution in hot ethanol (6 c.c.), with ether (45 c.c.), gave a 6% yield. Recrystallisation from ethanol (28 c.c. per g.) reduced the yield to 3%. The dark purple crystals had m. p. 216° (decomp.) (Found: C, 55·6; H, 4·5.

$C_{27}H_{24}O_2N_3IS$ requires C, 55·75; H, 4·15%). The *dye* strongly desensitised a bromoiodide emulsion.

Ethoxycarbonylmethin[2-*benzothiazole*][2-(1-*ethyldihydroquinoline*)] (X).—2-Ethylthioquinoline (0·95 g.) and ethyl sulphate were heated together at 110—120° for 8 hr. The salt was dissolved in hot ethanol (5 c.c.), and 2-ethoxycarbonylmethylbenzothiazole (1 mol.) and then triethylamine (2·2 mols.) were added. After 5 minutes' boiling the solution was acidified with hydrochloric acid and treated with sodium perchlorate in hot water (50 c.c.). After cooling, the liquid was decanted from the orange tar. This was washed by melting under hot water, cooling, and decantation. On a second treatment with hot water, the tar did not melt and, after cooling, the solid was filtered off. Whilst still wet, it was dissolved in hot methanol (15 c.c.). A red *perchlorate* crystallised in 66% yield [56% after recrystallisation from methanol (17 c.c. per g.)], and had m. p. 195° (decomp.) (Found : C, 55·6; H, 4·65; N, 5·8. $C_{22}H_{21}O_6N_2ClS$ requires C, 55·4; H, 4·45; N, 5·9%). The perchlorate was ground with water and with aqueous sodium hydroxide. The *base* was extracted with benzene and the extract dried (Na_2SO_4). After removal of solvent, the residue (54%) was taken up in hot benzene (14 c.c.), and the filtered solution treated with hot light petroleum (b. p. 60—80°; 28 c.c.). The yield of almost black crystals was 51% [m. p. 179° (decomp.)] (Found : C, 70·05; H, 5·4. $C_{22}H_{20}O_2N_2S$ requires C, 70·15; H, 5·35%). The absorption maximum of a methanolic solution containing ammonia was at 5170 Å (ε 13,500). A methanolic solution containing sulphuric acid had its maxima at 3290 (ε 41,500) and 4780 Å (ε 8100). The substance sensitised a chlorobromide emulsion extremely weakly.

The base was also prepared by fusing 2-ethylthioquinoline ethotoluene-*p*-sulphonate with 2-ethoxycarbonylmethylbenzothiazole but, under these conditions, was liable to break down partly to the corresponding unsubstituted base.

Ethoxycarbonylmethin[2-*benzothiazole*][2-(3-*ethyl*-2 : 3-*dihydrobenzothiazole*)] (XI).—2-Ethylthiobenzothiazole (0·98 g.) and ethyl sulphate were heated together at 110—120° for 8 hr., the resulting salt in ethanol was similarly boiled with 2-ethoxycarbonylmethylbenzothiazole and triethylamine, and the product was converted into the yellow *perchlorate* [79% yield; 66% after recrystallisation from methanol (30 c.c. per g.)], m. p. 137° (decomp.) (Found : C, 48·7; H, 4·5; N, 5·75. $C_{20}H_{19}O_6N_2ClS_2,\frac{1}{2}H_2O$ requires C, 48·8; H, 4·1; N, 5·7%).

The derived pale yellow *base* (65% yield), which was recrystallised from benzene (8 c.c. per g.) with light petroleum (b. p. 60—80°; 16 c.c. per g.), had m. p. 127° (47% yield) (Found: C, 62·9; H, 4·8. $C_{20}H_{18}O_2N_2S_2$ requires C, 62·8; H, 4·75%). The absorption maximum of a methanolic solution containing ammonia was at 3430 Å (ε 17,500). That of a methanolic solution containing sulphuric acid was at 4230 Å (ε 9110). The base sensitised a chlorobromide emulsion extremely weakly and was inert towards a chloride emulsion.

It was also prepared by the fusion method, which was less reliable.

[2-(1-*Ethylquinoline*)][2-(3-*methylbenzothiazole*)]*ethoxycarbonylmethincyanine Iodide* (II; R = CO_2Et, R′ = Me, R″ = Et).—Ethoxycarbonylmethin[2-benzothiazole][2-(1-ethyldihydroquinoline)] (0·38 g., 1 mol.) and methyl iodide (1·5 mols.) were heated at 100° for 24 hr. After four extractions with hot benzene (4 × 8 c.c.), the residue of salt amounted to a 59% yield. To remove dye hydriodide, it was shaken with benzene and aqueous sodium hydrogen carbonate (42% yield of residue). The recovery of crude base was 26% at the original benzene extraction and 13% at the second. After two recrystallisations of the *dye* from methanol (9 c.c. per g.), the yield was 25%. The red crystals had m. p. 206° (decomp.) (Found : C, 53·05; H, 4·65; O, 6·4; N, 5·2. $C_{23}H_{23}O_2N_2IS$ requires C, 53·3; H, 4·45; O, 6·15; N, 5·4%). In a chlorobromide emulsion the substance produced extremely weak sensitisation to 5400 Å and very slightly desensitised a bromide emulsion.

[2-(3-*Ethylbenzothiazole*)][2-(1-*ethylquinoline*)]*ethoxycarbonylmethincyanine Iodide* (II; R = CO_2Et, R′ = R″ = Et).—Ethoxycarbonylmethin[2-benzothiazole][2-(1-ethyldihydroquinoline)] (0·75 g., 1 mol.) and ethyl iodide (2 mols.) were heated at 100° for 48 hr. After extraction with hot benzene (4 × 10 c.c.), the residue (77%) was shaken with benzene and sodium hydrogen carbonate solution (58% yield); the ethiodide was taken up in hot methanol (2 c.c.) and the solution treated with hot water (2 c.c.). The yield of crystals was 43%, and after a second such treatment was 32%. The orange *iodide* had m. p. 190° (decomp.) (Found : C, 54·05; H, 4·9. $C_{24}H_{25}O_2N_2IS$ requires C, 54·15; H, 4·75%). The dye produced extremely weak sensitisation of a chlorobromide emulsion and very slight desensitisation of a bromoiodide emulsion.

[2-(3-*Ethylbenzothiazole*)][2-(3-*methylbenzothiazole*)]*methincyanine Iodide* (IV; R = H, R′ = Me, R″ = Et, X = I).—2-Ethylthiobenzothiazole (0·98 g.) was heated with ethyl sulphate, and 2-methylbenzothiazole with methyl toluene-*p*-sulphonate, at 110—120° for 8 hr. A solution of the salts in hot ethanol (10 c.c.), with triethylamine (2·2 mols.), was boiled for 15 min., then added to hot aqueous potassium iodide. The washed dye iodide was heated with acetone (20 c.c.), cooled, filtered off, and further washed with acetone (yield 72%). The dye was boiled with methanol (20 c.c.) and recrystallised from it (250 c.c.). The yield was 52% and after a second recrystallisation from methanol (150 c.c. per g.) was 41%. The salt was purified by heating it with potassium iodide in aqueous ethanol (40% yield), then further recrystallised from ethanol (280 c.c. per g.) (33% yield). The pale yellow crytals had m. p. 287° (decomp.) (Found : C, 47·8; H, 4·0. Calc. for $C_{18}H_{17}N_2IS_2$: C, 47·8; H, 3·8%). In a chlorobromide emulsion the sensitising maximum was at 4700 Å, the strong sensitisation extending to 5100 Å. Kiprianov and Grigor'eva [58] prepared this dye from 2-methylthiobenzothiazole methiodide, 2-methylbenzothiazole ethiodide, and sodium acetate in alcohol and give m. p. 270·5°.

[2-(3-*Ethylbenzothiazole*)][2-(3-*methylbenzothiazole*)]*ethoxycarbonylmethincyanine Iodide* (IV; R = CO_2Et, R′ = Me, R″ = Et, X = I).—Ethoxycarbonylmethin[2-benzothiazole][2-(3-ethyl-2 : 3-dihydrobenzothiazole)] (0·38 g., 1 mol.) and methyl iodide (1·5 mols.) were heated at 100° for 24 hr. The 40% yield, insoluble in hot benzene, fell to 35% on treatment of the *product* with benzene and sodium hydrogen carbonate solution. Recrystallisation from methanol (28 c.c. per g.) further decreased it to 25%. The pale yellow crystals had m. p. 224° (decomp.) (Found : C, 48·0; H, 4·15; O, 6·1. $C_{21}H_{21}O_2N_2IS_2$ requires C, 48·1; H, 4·05; O, 6·1%). In a chlorobromide or bromoiodide emulsion there was an extremely weak extension of the sensitivity.

[*Bis*-2-(3-*ethylbenzothiazole*)]*ethoxycarbonylmethincyanine Iodide* (IV; R = CO_2Et, R′ = R″ = Et, X = I).—Ethoxycarbonylmethin[2-benzothiazole][2-(3-ethyl-2 : 3-dihydrobenzothiazole)] (0·765 g., 1 mol.) and ethyl iodide (2 mols.) were heated at 100° for 48 hr. Treatment with hot benzene, followed by benzene and sodium hydrogen carbonate solution, left an 80% yield, reduced to 45% on two recrystallisations from methanol (12 c.c. per g.). The yellow *iodide* had m. p. 218° (decomp.), with previous darkening (Found: C, 49·15; H, 4·1. $C_{22}H_{23}O_2N_2IS_2$ requires C, 49·05; H, 4·3%). There was an extremely weak extension of photographic sensitivity, as with the preceding dye.

[2-(3-*Ethylbenzothiazole*)][2-(1-*ethylquinoline*)](2-*benzothiazolyl*)*methincyanine Iodide* (XII).—A mixture of dibenzothiazolylmethane ethiodide (1·10 g.), 2-iodoquinoline ethiodide, ethanol (10 c.c.), and triethylamine was boiled for 30 min. The *dye*, precipitated by ether and washed, was in 38% yield. A chromatogram, with chloroform on alumina, showed it to be homogeneous. Twice recrystallised from methanol (35 c.c. per g.) (yield 20%), the purple crystals had m. p. 232° (decomp.) (Found: C, 56·4; H, 4·35. $C_{28}H_{24}N_3IS_2$ requires C, 56·65; H, 4·1%). The dye caused slight desensitisation of a chlorobromide and a bromoiodide emulsion.

[2-(3-*Ethylbenzoxazole*)][2-(1-*ethylquinoline*)]*methincyanine Iodide* (XIII; R = H, R′ = R″ = Et).—2-Iodoquinoline ethiodide (0·82 g.), 2-methylbenzoxazole ethiodide, ethanol (4 c.c.), and triethylamine were boiled together for 3 min. The yield of washed dye was 33%, whereas a 56% yield had been claimed for 10 minutes' boiling.[10] After two recrystallisations of our product from ethanol (70 c.c. per g.; charcoal), the yield was 15%. The yellow crystals had m. p. 277° (decomp.) [Brooker and Keyes gave m. p. 290—292° (decomp.)] (Found : C, 56·7; H, 4·95. Calc. for $C_{21}H_{21}ON_2I$: C, 56·75; H, 4·75%).

[2-(3-*Ethylbenzoxazole*)][2-(1-*ethylquinoline*)]*methylmethincyanine Iodide* (XIII; R = Me, R′ = R″ = Et).—2-Ethylbenzoxazole ethiodide (3·03 g.), 2-iodoquinoline ethiodide, ethanol (25 c.c.), and triethylamine were boiled for 1 min. The blood-red solution was filtered hot from unchanged iodo-salt, which was washed with hot ethanol (3 c.c.). The filtrate and washings were treated with ether (280 c.c.); the ether-washed tar, dissolved in hot methanol (6 c.c.), was treated with potassium iodide (4 mols.) in hot water (66 c.c.). The tar was washed with water and dried in a vacuum-desiccator (25% yield). The crude dye was chromatographed with chloroform containing 1% of ethanol, on alumina. The blood-red dye was collected first (22% yield), leaving five coloured impurities in the column. The chromatogram was repeated with pure chloroform : this time there was a yellow forerun, then the red dye came through (17% yield). Two recrystallisations from ethanol [4 c.c. (charcoal) and 10 c.c. per g., respectively] reduced the yield to 3%. The maroon crystals shrank suddenly at 110° and decomposed violently at 133° (Found : C, 57·6; H, 5·5. $C_{22}H_{23}ON_2I$ requires C, 57·6; H, 5·05%). The *dye* is very unstable and not all preparations succeeded; a crystalline sample had changed to tar after seven months.

[2-(3-*Ethylbenzoxazole*)][2-(1-*ethylquinoline*)]*phenylmethincyanine Iodide* (XIII; R = Ph, R′ = R″ = Et).—2-Benzylbenzoxazole (0·65 g.) was heated with ethyl toluene-*p*-sulphonate at

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[58] Kiprianov and Grigor'eva, *Chem. Abs.*, 1940, **34**, 3274.

150—165° for 4 hr. To the crude salt were added 2-iodoquinoline ethiodide, ethanol (7 c.c.), and triethylamine, and the mixture was boiled for 2 min. The red solution was treated whilst hot with one of potassium iodide (4 mols.) in water (14 c.c.). The water-washed product (1·03 g.) was recrystallised from ethanol (20 c.c.; with charcoal). The yield of dark maroon crystals was 26% (Found: C, 62·1; H, 5·0. $C_{27}H_{25}ON_2I$ requires C, 62·3; H, 4·85%). A chromatogram with chloroform on alumina did not show any coloured by-product. The *dye*, m. p. 227° (decomp.) with previous shrinking, had a slight desensitising effect on a bromoiodide emulsion.

[2-(1-*Ethyl*-5 : 6-*benzoquinoline*)][2-(3-*ethylbenzoxazole*)]*methincyanine Iodide*.—2-Methyl-5 : 6-benzoquinoline (1·93 g., 1 mol.), 2-ethylthiobenzoxazole (1 mol.), and ethyl toluene-*p*-sulphonate (2 mols.) were heated together at 150—160° for 3½ hr. The gum was dissolved in hot alcohol (15 c.c.) and treated with potassium iodide (4 mols.) in hot water (30 c.c.). The resultant oil solidified and was washed with water. After treatment with cold acetone (20 c.c.), the residue amounted to a 34% yield [17% after two recrystallisations from methanol (75 c.c. per g.)]. The orange dye had m. p. 275° (decomp.), with previous shrinking (Found: C, 59·05; H, 5·05; I, 24·05. Calc. for $C_{25}H_{23}ON_2I,CH_3{\cdot}OH$: C, 59·3; H, 5·15; I, 24·15%). Although the recorded absorption maximum is 4450 Å (ref. *b*, Table 1), the values now found are 4630 (ε 50,300) and 4450 Å (ε 49,400).

Alternatively, a hot mixture of 2-iodo-5 : 6-benzoquinoline ethiodide (1·15 g.), 2-methylbenzoxazole ethiodide, ethanol (10 c.c.), and triethylamine was boiled for 3 min. The solid was filtered off hot and washed with hot ethanol (2 × 1 c.c.); it consisted of unchanged iodo-compound, together with green crystals. The filtrate and washings slowly crystallised, giving a 13% yield of (washed) dye. After two recrystallisations of this from methanol (75 c.c. per g.), the first being with charcoal, the yield was 3%. The m. p. and mixed m. p. were those of the sample prepared by the first method, and the absorption maxima were identical (Found: C, 59·05; H, 4·95%). A solution of the washed residue (0·06 g.) from the original mother-liquor, in methanol (100 c.c.), was filtered hot and concentrated to 33 c.c., these being the conditions for recrystallising bis-2-(1-ethyl-5 : 6-benzoquinoline)methincyanine iodide, m. p. 310° (decomp.).[59] Green crystals (0·02 g.) separated, which remained unmelted at 302° (Found: C, 67·3; H, 4·9. Calc. for $C_{31}H_{27}N_2I$: C, 67·1; H, 4·9%). Methanolic solutions of the two dyes gave the same absorption maxima.

[2-(1-*Ethyl*-5 : 6-*benzoquinoline*)][2-(3-*ethylbenzoxazole*)]*phenylmethincyanine Iodide*.—2-Benzylbenzoxazole (0·62 g.) and ethyl toluene-*p*-sulphonate were heated at 155—165° for 4 hr. The resulting gum was dissolved in hot ethanol (8 c.c.), 2-iodo-5 : 6-benzoquinoline ethiodide was added, then triethylamine, and the mixture was boiled for 2 min. Hot filtration removed unchanged iodo-compound, which was washed with hot ethanol (2 c.c.). The filtrate and washings were treated with ether (100 c.c.), and the precipitated tar was washed with ether. Its solution in hot methanol (2 c.c.) was treated with potassium iodide (4 mols.) in water (25 c.c.). The washed solid (56% yield) was dissolved in chloroform, containing 1% of ethanol, and washed with this solvent on a column of alumina. A little yellow impurity was removed, the red dye was then collected (31% yield), and a yellow residue remained in the column. The dye was boiled in hot ethanol (20 c.c.) with charcoal, and the filtrate was treated hot with aqueous potassium iodide. The tar solidified when ground with ice and was dried (9% yield). After two crystallisations of this material from ethanol, with charcoal in the first, the red crystals (2%) had m. p. about 183° (decomp.), with shrinking from 150° (Found: C, 64·85; H, 5·1. $C_{31}H_{27}ON_2I$ requires C, 65·25; H, 4·75%). The *dye* was inert towards a chlorobromide and a bromoiodide emulsion.

[2-(3-*Ethylbenzoxazole*)][1-(2-*ethyl*iso*quinoline*)]*methincyanine Iodide*.—2-Methylbenzoxazole ethotoluene-*p*-sulphonate (0·83 g.), 1-iodo*iso*quinoline ethiodide, ethanol (8 c.c.), and triethylamine were boiled for 15 min. Potassium iodide (4 mols.) in hot water (16 c.c.) was added. The washed, red *dye* (46%) on recrystallisation from ethanol (20 c.c. per g.) was obtained in 37% yield and had m. p. 228° (decomp.) (Found: C, 56·85; H, 5·1. $C_{21}H_{21}ON_2I$ requires C, 56·75; H, 4·75%).

[2-(3-*Ethylbenzoxazole*)][1-(2-*ethyl*iso*quinoline*)]*phenylmethincyanine Iodide*.—To the quaternary salt from 2-benzylbenzoxazole (0·50 g.) and ethyl toluene-*p*-sulphonate were added 1-iodo-*iso*quinoline ethiodide, ethanol (7 c.c.), and triethylamine, and the mixture was boiled for 3 min. Potassium iodide (4 mols.) in hot water (32 c.c.) was added. The tar was washed with water and then with ether. It separated from hot ethanol (5 c.c.) in 27% yield [12% after two recrystallisations from water (100 c.c. per g.)]. The vermilion crystals had m. p. about 180° (decomp. from

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[59] Hamer and Kelly, *J.*, 1931, 777.

<100°) (Found: C, 60·0; H, 5·0; I, 23·8. $C_{27}H_{25}ON_2I,H_2O$ requires C, 60·2; H, 5·05; I, 23·6%). The *dye* slightly desensitised a bromoiodide emulsion.

[2-(3-*Ethylbenzoxazole*)][4-(1-*ethylquinoline*)]*phenylmethincyanine Iodide*.—To the salt from 2-benzylbenzoxazole (1·08 g.) and ethyl toluene-*p*-sulphonate were added 4-iodoquinoline ethiodide, ethanol (10 c.c.), and triethylamine and the mixture was boiled for 3 min. A hot solution of potassium iodide precipitated the dye *iodide* as tar, which was washed with water, and dissolved in acetone (8 c.c.), whence it crystallised (16% yield) [4% after 3 recrystallisations from ethanol (10 c.c. per g.)]. The maroon crystals had m. p. 224° (decomp.) with previous softening (Found: C, 61·2; H, 5·1. $C_{27}H_{25}ON_2I$ requires C, 62·3; H, 4·85%). The dye slightly desensitised a bromoiodide emulsion.

C, *Styryl Dyes*.

2-4′-*Diethylaminostyrylbenzothiazole Ethiodide* (XIV; R = H, R′ = Et).—A mixture of 2-methylbenzothiazole ethiodide (3·05 g., 1 mol.), *p*-diethylaminobenzaldehyde (1 mol.), and acetic anhydride (20 c.c.) was boiled for 20 min., then poured into a hot solution of potassium iodide (4 mols.) in water (200 c.c.). The washed product (4·28 g.) was extracted with ether (4·18 g. left; 90% yield). After two recrystallisations from methanol (25 c.c. per g.) and one from ethanol (20 c.c. per g.) (yields 83, 73, and 62%), the indigo-blue crystals had m. p. 225° (decomp.), after losing solvent below 100° (Found: C, 54·3; H, 5·65. $C_{21}H_{25}N_2IS$ requires C, 54·3; H, 5·45%). The *dye* sensitised a bromoiodide emulsion to 6500 Å, with maxima at 5700 and 6100 Å.

2-(4-*Dimethylamino-α-methylstyryl*)*benzothiazole Ethiodide* (XIV; R = R′ = Me).—A solution of 2-ethylbenzothiazole ethiodide (3·19 g.) and *p*-dimethylaminobenzaldehyde in acetic anhydride was similarly boiled and treated with aqueous potassium iodide. The product (3·56 g.) was washed with water and extracted with ether; the residue (3·07 g.; 68%) was thrice extracted with hot benzene (66% yield left), then recrystallised from ethanol (40 c.c. per g.). The dark blue *dye* (57%) had m. p. 197° (decomp.) (Found: C, 53·1; H, 5·35. $C_{20}H_{23}N_2IS$ requires C, 53·3; H, 5·15%). Towards a chlorobromide emulsion there was weak sensitisation to 6300 Å, with maxima at 5300 and 5700 Å.

The *base* (0·36 g., 12%), which had been extracted by ether, was dissolved in hot benzene (10 c.c. per g.), and the solution treated with light petroleum (b. p. 60—80°; 10 c.c. per g.). After a second recrystallisation from acetic anhydride (17 c.c. per g.) (6% yield), the yellow crystals had m. p. 160° [Found: C, 73·2; H, 6·3; N, 9·5; S, 10·8%; *M* (Rast), 278. $C_{18}H_{18}N_2S$ requires C, 73·45; H, 6·15; N, 9·5; S, 10·9%; *M*, 294]. The base was thus 3-*ethyl*-2-[2-(4-*imino*cyclo*hexa*-2 : 5-*dienylidene*)-1-*methylethylidene*]*benzothiazoline* (XVI; R′ = H). The absorption maximum of a methyl-alcoholic solution was at 3840 Å (ε 15,400). The base produced slight desensitisation of a chlorobromide and a bromoiodide emulsion and was inert towards a pure chloride emulsion.

2-(4-*Diethylamino-α-methylstyryl*)*benzothiazole Ethiodide* (XIV; R = Me, R′ = Et).—A solution of 2-ethylbenzothiazole ethiodide (3·19 g., 1 mol.) and *p*-diethylaminobenzaldehyde in acetic anhydride (20 c.c.) was boiled for 30 min., then poured into water (100 c.c.). After cooling, the solid was filtered off and washed with water (0·74 g. obtained). By treatment of the filtrate with potassium iodide solution, a further 2·72 g. were obtained.

Recrystallisation of the second crop from water (20 c.c.; charcoal) gave inhomogeneous crystals. These were ground with cold water and left a terracotta residue (0·30 g.). Concentration of the filtrate to about 8 c.c. gave buff crystals (1·24 g.). By repeated extraction of the charcoal with methanol, concentration (to 5 c.c.), and treatment with ether, a further yield (0·14 g.) of terracotta solid resulted. The required dye (0·30 + 0·14 = 0·44 g.) (9% yield) recrystallised from ethanol (5 c.c.) (7% yield). It was boiled with benzene (2 × 10 c.c.), and the residue recrystallised from ethanol (4 c.c.) (6% yield). The red *product* had m. p. 192° (decomp.) (Found: C, 55·15; H, 5·95. $C_{22}H_{27}N_2IS$ requires C, 55·2; H, 5·7%). Sensitisation of a chlorobromide emulsion was from 4800 to 6100 Å with an indistinct maximum. The crystals (1·24 g.) from the aqueous extract were dissolved in hot water (20 c.c.), and the orange solution was treated with ammonia. The washed crystals (0·90 g.) made a further 19% yield of the dye, which was recrystallised from ethanol (10 c.c.) (a 12% yield) and had the same m. p. and mixed m. p. as the analytically pure dye (total yield 18%).

The original first crop (0·74 g.) was twice extracted with benzene (2 × 20 c.c.). The residue was dissolved in hot methanol, and this extract taken to small volume and treated with ether. The resultant dye (0·08 g.) was twice recrystallised from methanol (37 c.c. and 75 c.c. per g., respectively) (0·02 g. obtained) (Found: C, 52·45; H, 6·05. Calc. for $C_{21}H_{25}N_2IS,H_2O$: C, 52·25; H, 5·65%. The dark blue crystals had m. p. 225° (decomp.). This m. p. and the mixed m. p. were the same as that of 2-4′-diethylaminostyrylbenzothiazole ethiodide; identity was confirmed, since they had the same absorption maximum.

The preceding benzene extract gave a base (0·61 g., 19%). This was dissolved in hot benzene (3 c.c.), treated with light petroleum (b. p. 60—80°; 3 c.c.), decanted from some dark oil, and treated with more benzene and light petroleum (3 c.c. of each), yielding yellow crystals (11%). After two recrystallisations from ethanol (55 c.c. per g.) (7% yield), the m. p. was 137° (Found: C, 74·4; H, 6·95; N, 8·8; S, 9·65. $C_{20}H_{22}N_2S$ requires C, 74·45; H, 6·85; N, 8·7; S, 9·95%). The base was believed to be 3-*ethyl*-2-[2-(4-*ethyliminocyclohexa*-2 : 5-*dienylidene*)-1-*methylethylidene*]*benzothiazoline* (XVI; R′ = Et). Its methanolic solution had its absorption maximum at 3930 Å (ε 13,600). It was inert towards a chlorobromide, a bromoiodide, and a pure chloride emulsion.

2-(4-*Dimethylamino-α-phenylstyryl*)*benzothiazole Ethiodide* (XIV; R = Ph, R′ = Me).—2-Benzylbenzothiazole ethiodide (0·76 g.), *p*-dimethylaminobenzaldehyde, and acetic anhydride (10 c.c.) were boiled for 30 min. The product was precipitated by ether, washed with water, and boiled with benzene (3 × 25 c.c.). The residual dye (63%) recrystallised from acetic acid (10 c.c. per g.) (56% yield). When the red crystals were heated, solvent was eliminated about 120° and there was shrinking; the m. p., about 180° (decomp.), depended on the rate of heating (Found: C, 58·65; H, 4·8. $C_{25}H_{25}N_2IS$ requires C, 58·55; H, 4·9%). The *dye* weakly sensitised a chlorobromide emulsion from 4800 to 6300 Å, with a maximum at 5800 Å.

2-(4-*Dimethylamino-α*-p-*nitrophenylstyryl*)*benzothiazole Ethiodide* (XIV; R = *p*-$C_6H_4{\cdot}NO_2$, R′ = Et).—2-*p*-Nitrobenzylbenzothiazole ethiodide (0·85 g.), *p*-dimethylaminobenzaldehyde, and acetic anhydride (10 c.c.) were boiled for 20 min., and added to potassium iodide (4 mols.) in water (100 c.c.). The washed solid (0·93 g.) was extracted with ether (61% yield of residue). It was recrystallised from methanol (10 c.c. per g.) (40% yield), boiled with benzene (2 × 45 c.c. per g.) (36% yield of residue), and recrystallised from methanol (26% yield) (Found: C, 53·45; H, 4·4. $C_{25}H_{24}O_2N_3IS$ requires C, 53·8; H, 4·35%). The terracotta *salt* had m. p. 203° (decomp.). It strongly desensitised a chlorobromide and a bromoiodide photographic emulsion.

The *base* (0·24 g., 30% yield), which had been extracted by ether, was dissolved in hot benzene (5 c.c.), and the solution treated with light petroleum (b. p. 60—80°; 5 c.c.) (15% yield). After recrystallisation from acetic anhydride (40 c.c. per g.), the yellow crystals (11% yield) had m. p. 220°. The m. p. was unchanged after another recrystallisation from acetic anhydride [Found: C, 68·35; H, 4·85; N, 10·45; S, 7·8%; *M* (Rast), 318·6. $C_{23}H_{19}O_2N_3S$ requires C, 68·8; H, 4·75; N, 10·45; S, 8·0%; *M*, 401·5]. The analysis indicates the structure 3-*ethyl*-2-(2-4′-*iminocyclohexa*-2′ : 5′-*dienylidene*-1-p-*nitrophenylethylidene*)*benzothiazoline* (XVII). The absorption maximum of a methanolic solution was at 4040 Å (ε 37,900). The base was photographically inert when tested in a chlorobromide and in a bromoiodide emulsion.

2-(4-*Dimethylamino-α-ethoxycarbonylstyryl*)*benzothiazole Ethiodide* (XIV; R = CO_2Et, R′ = Me).—A solution of 2-ethoxycarbonylmethylbenzothiazole ethiodide (1·89 g., 1 mol.), *p*-dimethylaminobenzaldehyde (1 mol.), and triethylamine (1·2 mols.) in ethanol (15 c.c.) was boiled for 5 hr. and filtered hot (no residue). The dye crystallised on cooling and more was obtained by concentration (total 51%). It was boiled with ethanol (20 c.c. per g.; charcoal), and the filtrate was concentrated to 7 c.c. and allowed to crystallise. A further similar recrystallisation, followed by simple recrystallisation from ethanol (7 c.c. per g.), afforded a 24% yield. The orange crystals had m. p. 199° (decomp.) (Found: C, 52·2; H, 5·15. $C_{22}H_{25}O_2N_2IS$ requires C, 51·95; H, 4·95%). The *dye* sensitised a chlorobromide emulsion very weakly to 5600 Å with the maximum at 5250 Å.

2-(α-2′-*Benzothiazolyl*-4-*dimethylaminostyryl*)*benzothiazole Ethiodide* (XIV; R = 2-benzothiazolyl, R′ = Me).—A solution of dibenzothiazolylmethane ethiodide (1·46 g.) and *p*-dimethylaminobenzaldehyde in acetic anhydride (20 c.c.) was boiled for 10 min. The washed dye (84% yield) was recrystallised from methanol (38 c.c. per g.) (74% yield), then from acetic acid (47 c.c. per g.) (57%) and from methanol (54 c.c. per g.) (43%). The red crystals darkened about 100° and had m. p. 210° (decomp.) (Found: C, 54·55; H, 4·6. $C_{26}H_{24}N_3IS_2$ requires C, 54·85; H, 4·25%). On a chlorobromide emulsion the *dye* conferred weak sensitising to 5600 Å, tailing to 6000 Å, with the maximum at 5200 Å.

2-4′-*Dimethylaminostyrylbenzoxazole Ethiodide* (XV; R = H, R′ = Me).—To a hot solution of 2-methylbenzoxazole ethotoluene-*p*-sulphonate (1·67 g., 1 mol.) and *p*-dimethylaminobenzaldehyde (1 mol.) in ethanol (6 c.c.), triethylamine (0·12 mol.) was added, and the solution was boiled for 3 hr. Ether (60 c.c.) precipitated a red tar, which crystallised. Its solution in hot methanol (5 c.c.) was treated with potassium iodide (4 mols.) in hot water (50 c.c.). The water-washed product (42%) was recrystallised from ethanol (50 c.c. per g.). The red crystals (30%) had m. p. 251° (decomp.) (Found : C, 54·3; H, 5·15. $C_{19}H_{21}ON_2I$ requires C, 54·25; H, 5·05%). The *dye* sensitised a bromoiodide emulsion weakly up to 6000 Å.

2-(4-*Dimethylamino-α-methylstyryl*)*benzoxazole Ethiodide* (XV; R = R′ = Me).—A solution of 2-ethylbenzoxazole ethiodide (1·52 g.) and *p*-dimethylaminobenzaldehyde in acetic anhydride (10 c.c.) was boiled for 5 min. The washed crystals (74%) were thrice extracted with hot benzene (total: 20 c.c.) (71% yield left). After recrystallisation from methanol (20 c.c. per g.) the bright red crystals (57%) had m. p. 210° (decomp.) (Found : C, 55·2; H, 5·4. $C_{20}H_{23}ON_2I$ requires C, 55·3; H, 5·35%). The *dye* weakly sensitised a chlorobromide emulsion to 5900 Å, with a maximum at 5400 Å.

2-(4-*Dimethylamino-α-phenylstyryl*)*benzoxazole Ethiodide* (XV; R = Ph, R′ = Me).—2-Benzylbenzoxazole (2·09 g.) and ethyl toluene-*p*-sulphonate were heated at 150—160° for 4 hr. The gum was dissolved in hot ethanol (10 c.c.), *p*-dimethylaminobenzaldehyde and triethylamine (0·12 g.) were added, and boiling was continued for 4 hr. The oil precipitated by ether was dissolved in hot methanol (8 c.c.) and added to a solution of potassium iodide (4 mols.) in hot water (40 c.c.). The washed product became brittle when dried (2·59 g. obtained). Much impurity was removed by treatment with acetone (7 c.c.). The 9% yield (0·44 g.) was reduced to 7% by recrystallisation from ethanol (30 c.c. per g.). The vermilion crystals had m. p. 223° (decomp.), with previous darkening (Found : C, 60·45; H, 5·2. $C_{25}H_{25}ON_2I$ requires C, 60·5; H, 5·35%). The *dye* sensitised a chlorobromide emulsion from 4900 to 5800 Å, with the maximum at 5500 Å.

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