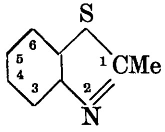
CCCXLIX.—*Cyanine Dyes from Quaternary Salts of Methyl-α- and -β-naphthathiazoles.*

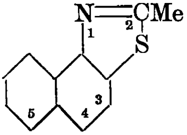
By Frances Mary Hamer.

THREE types of cyanine dyes derived from β-naphthaquinaldine have been described : (*a*) a carbocyanine with two β-naphthaquinaldine nuclei (Mees and Gutekunst, *J. Ind. Eng. Chem.*, 1922, **14**, 1060), (*b*) a carbocyanine with one β-naphthaquinaldine nucleus and one quinaldine nucleus (Mills and Raper, J., 1925, **127**, 2466), and (*c*) ψ-cyanines with one β-naphthaquinaldine and one quinoline nucleus (Hamer, J., 1928, 206). In the same way it should be possible to use methylnaphthathiazoles as the starting points for the preparation of cyanine dyes, which dyes would be expected to have their absorption bands shifted towards the red region of the spectrum as compared with those of the analogous cyanines derived from 1-methylbenzthiazole.

Corresponding to 1-methylbenzthiazole (I), there are three possible methylnaphthathiazoles, two of which (II and III) are dealt with here. 2-Methyl-β-naphthathiazole (II) was first prepared by Jacobson (*Ber.*, 1887, **20**, 1897), and 1-methyl-α-naphthathiazole (III) by Jacobson and Süllwald (*Ber.*, 1888, **21**, 2624) and subsequently by Jacobson and Schwarz (*Annalen*, 1893, **277**, 257). Rupe and Schwarz (*Z. Farb. Textilchem.*, 1904, **3**, 397) also prepared (II) and (III) under the names μ-methyl-α-naphthathiazole and μ-methyl-β-naphthathiazole respectively.



(I.)



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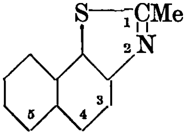


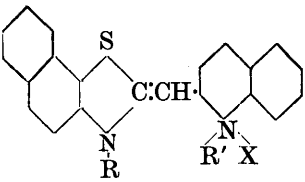
(III.)

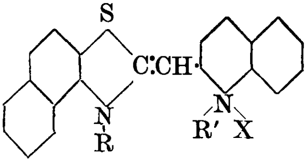
The constitution of the new cyanine dyes derived from naphthathiazoles is rendered explicit by referring to them as derivatives of benzthiazole, the same numbering being used as in (I).

The methiodides, already described by Smith (J., 1923, **123**, 2288), and the *ethiodides* of the two methylnaphthathiazoles form the starting points for the present new dyes. It is an interesting point in connexion with the difference in the spatial surroundings of the nitrogen atom in (II) and (III), respectively, that (III) gives a better yield of methiodide, under the same conditions, than does (II). The point is more strikingly exemplified in the case of the ethiodides : with (III), the method of heating with ethyl iodide in a sealed tube gave an 81% yield of ethiodide, after recrystallisation; but the same method, after removal, by ether extraction, of unaltered base, gave less than 1% of the ethiodide of (II). This ethiodide was, however, prepared, although only in 31% yield, by the use of ethyl *p*-toluenesulphonate under suitable conditions.

The general method previously described for the preparation of thio-ψ-cyanines (Hamer, *loc. cit.*) has been extended to the preparation of such dyes containing one naphthathiazole and one quinoline nucleus. Thus by condensation of methyl-α- or -β-naphthathiazole methiodide or ethiodide with 2-iodoquinoline methiodide or ethiodide, it is possible to prepare eight different *thio-ψ-cyanines* of the general formulæ (IV) and (V). In writing their chemical names, the former convention (*ibid.*, p. 208) of appending dashes to the numerals in the quinoline nucleus has been followed. The four dyes of structure (V) were obtained in yields varying from 19% to 26% after recrystallisation and were somewhat more soluble in methyl alcohol than those of structure (IV), which were obtained in yields varying from 27% to 32%. The absorption spectra, determined in spirit solution throughout this work, of all eight thio-ψ-cyanines are practically identical, the crest of the one absorption band showing, as compared with that of the chief band of the parent thio-ψ-cyanines containing a benzthiazole instead of a naphthathiazole nucleus, a shift towards the red region of 150 Å. Mr. O. F. Bloch has tested the dyes described in this paper for photographic sensitising properties by bathing gelatino-bromide plates in their solutions. He found that the eight thio-ψ-cyanines all impart sensitivity to the blue-green. In some cases the curve of normal sensitivity of the plate receives an almost uniform extension into the blue-green. Details are given in the experimental part of the paper, but it may be noted that in each case the sensitising maximum, as compared with the chief maximum of the thio-ψ-cyanines containing a benzthiazole nucleus, lies 100—200 Å. nearer to the red.

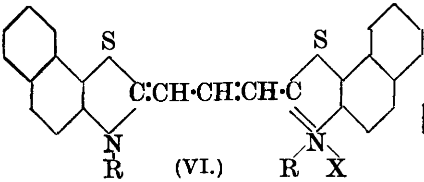
(IV.)



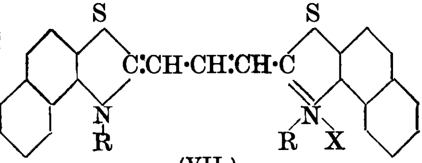


(V.)

The general method for the preparation of carbocyanines (Hamer, J., 1927, 2796), consisting in the action of ethyl orthoformate, in the presence of pyridine, on quaternary salts containing reactive methyl groups, was applied to the methiodide and ethiodide of methyl-α- and -β-naphthathiazoles. In this way four new *thiocarbocyanines*, two belonging to type (VI), and two belonging to type (VII), were prepared. The yields, after purification, of the thiocarbocyanines of type (VII) were less than those of the thiocarbocyanines of type (VI) (57% and 64% as compared with 78% and 79%). The *bromide* corresponding to one of the new iodides was also prepared. The position of the chief absorption maximum is nearly the same for each of the new thiocarbocyanines, lying 350—400 Å. nearer to the red than the maximum of the principal absorption band of 2 : 2′-diethylthiocarbocyanine iodide. That the shift towards the red of the absorption bands would be greater for the new thiocarbocyanines than for the new thio-ψ-cyanines was, of course, to be expected, since in the former case two naphthathiazole nuclei have replaced two benzthiazole nuclei, whereas in the latter only one such replacement has occurred. The maxima of extra-sensitivity of the new thiocarbocyanines lie 500—600 Å. nearer to the red than does that of 2 : 2′-diethylthiocarbocyanine iodide. It is a striking fact that the two of these thiocarbocyanines which are ethiodides sensitise powerfully, whereas the two methiodides show only a feeble sensitising action. Such a difference between the methiodide and the ethiodide is not infrequently observed with carbocyanines. For example, 1 : 1′-diethyl-2 : 2′-carbocyanine iodide (pinacyanol) is one of the most powerful sensitisers known, but the corresponding methiodide is valueless.



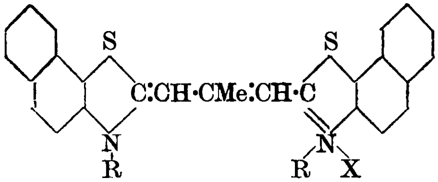
(VI.)



(VII.)

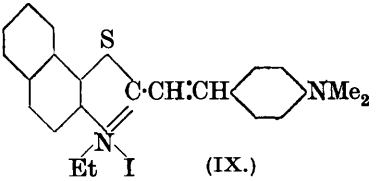
It might be supposed that, just as 1-methylbenzthiazole quaternary salts can be condensed with ethyl orthoacetate in the presence of pyridine (Hamer, J., 1928, 3160), forming thiocarbocyanines with the chain :CH·CMe:CH·, so also this condensation would be applicable to methyl-α- and -β-naphthathiazole quaternary salts. The result of actually trying to effect the reaction is surprising. For, whereas the condensation proceeds normally with the methiodide or ethiodide of 1-methyl-α-naphthathiazole, giving the two *dyes* of type (VIII), it completely fails with the corresponding salts of 2-methyl-β-naphthathiazole. This result had been foreshadowed, in that, with both the present thio-ψ-cyanines and the thiocarbocyanines, the yield from salts of methyl-α-naphthathiazole is somewhat better than that from salts of methyl-β-naphthathiazole, but a difference between the two so striking as this was quite unexpected. With the new pair of thiocarbocyanines, with

(VIII.

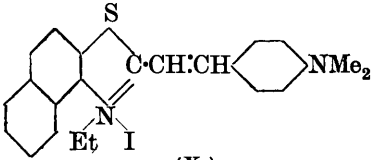


the chain :CH·CMe:CH· and containing two naphthathiazole nuclei, the absorption maximum lies 350 Å. nearer to the red than with the parent thiocarbocyanines containing two benzthiazole nuclei. The new methiodide is a weak sensitiser and the ethiodide a powerful one, its maximum effect occurring 300 Å. nearer to the red than is the case with the parent thiocarbocyanine.

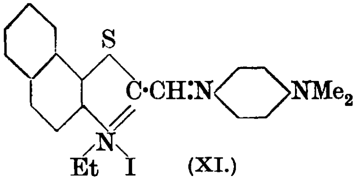
Condensation of the ethiodides of methyl-α- and -β-naphthathiazole with *p*-dimethylaminobenzaldehyde gave the *styryl* compounds (IX) and (X). Condensation of the ethiodides with *p*-nitrosodimethylaniline gave the *anils* (XI) and (XII). With both pairs, the methyl-α-naphthathiazole salt gave a better yield than did the methyl-β-naphthathiazole salt: 67% as compared with 46% for



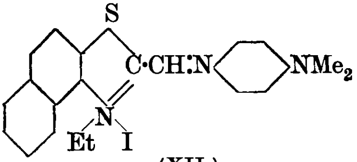
(IX.)



(X.)



(XI.)



(XII.)

the styryl compounds, and 61% as compared with 24% for the anils. In the case of such pairs of styryl compounds and anils, it has been observed that the styryl compounds are sensitisers, whereas the anils desensitise (Smith, *loc. cit.*; Hamer, J., 1924, **125**, 1348)—an observation which has recently been shown to be general (Hamer, *Phot. J.*, 1929, **69**, 409): the phenomenon occurs in the present instance.

EXPERIMENTAL.

2-*Methyl*-β-*naphthathiazole Methiodide.*—The base (II), prepared from α-naphthylamine, was supplied by Boots Pure Drug Company and melted at 95—96°, with softening from 93°; Jacobson (*loc. cit.*) gives m. p. 94·5—95·5° and Rupe and Schwarz (*loc. cit.*) give m. p. 94—95°. It was heated (5 g.; 1 mol.) with methyl iodide (1·9 c.c.; 1·2 mols.) in a sealed tube at 100° for 2 days. The product was extracted with ether in a Soxhlet apparatus, and the undissolved residue (89% yield) recrystallised from spirit (350 c.c.). The yield (5·9 g.) was 69%. The salt was dried in a vacuum at 100—110°, until of constant weight, and was analysed by the method of Carius, which was used throughout this work (Found: I, 37·3. Calc. for $C_{13}H_{12}NIS$: I, 37·2%). It melted at 222—229° with evolution of gas, the exact m. p. depending upon the rate of heating. Smith (*loc. cit.*) obtained a 60% yield of crude substance and gives the m. p. of the recrystallised salt as 234° (decomp.).

2-*Methyl*-β-*naphthathiazole Ethiodide*.—The base (5 g.; 1 mol.) and ethyl *p*-toluenesulphonate (5 g.; 1 mol.) were heated together for 5 hours in an oil-bath at 180—190° and the product was treated with benzene and water. (By distilling off the benzene from the extract and acidifying, steam-distilling, and making the residue alkaline with ammonia, a not inconsiderable amount of base was recovered.) The aqueous solution was evaporated on the water-bath and treated with a concentrated aqueous solution of potassium iodide (8·5 g.). The *ethiodide* crystallised on cooling and was filtered off, being well washed with water in order to remove potassium iodide. It was extracted with ether, and the undissolved residue (3·3 g.; 37% yield) recrystallised from spirit (60 c.c.). The product (2·8 g.; 31% yield) formed crystals containing solvent of crystallisation. On drying in a desiccator (Found: I, 33·5%), or even in a vacuum at 90—105°, they showed no change in appearance (Found: I, 34·0. $C_{14}H_{14}NIS,H_2O$ requires I, 34·0%). Loss of weight occurred on drying in a vacuum at 100—120° or at 120—130°, and the substance lost its crystalline form and became powdery, but constancy of weight was not attained, owing to sublimation (Found: I, 35·3. $C_{14}H_{14}NIS$ requires I, 35·7%). There were signs of decomposition from 200° and melting occurred at 209° with violent decomposition.

1-*Methyl*-α-*naphthathiazole Methiodide*.—The base (III), prepared from β-naphthylamine, was supplied by Boots Pure Drug Company, who recrystallised it until the m. p. was constant at 81°. It was distilled in a vacuum in order to get the anhydrous base, which melted at 57—58° with previous softening; Jacobson and Süllwald (*loc. cit.*) give m. p. 81°; Jacobson and Schwarz (*loc. cit.*) give m. p. 80°, with softening from 68—70°, for the base containing water of crystallisation, and m. p. 48° for the anhydrous base.

The preparation of the methiodide from the base (5 g.) was effected by a method identical with that used with the isomeric base, but the yield was higher, being 91% (7·8 g.) after ether extraction and 75% after recrystallisation from spirit (250 c.c.). For analysis, the salt was dried in a vacuum at 100—120°; it then melted at 262° (decomp.) (Found : I, 37·3. Calc. for $C_{13}H_{12}NIS$: I, 37·2%). Smith (*loc. cit.*) describes the m. p. as 245° (decomp.) and the yield of crude product as almost quantitative.

1-*Methyl-α-naphthathiazole Ethiodide.*—The base (5 g.; 1 mol.) and ethyl iodide (2·4 c.c.; 1·2 mols.) were heated together for 2 days in a sealed tube at 100°. The product was extracted with ether, and the residue (8·5 g.; 95% yield) recrystallised from spirit (100 c.c.). The yield of almost colourless crystals was 81% (7·2 g.). They were dried for analysis in a vacuum at 100—120° (Found : I, 35·8. $C_{14}H_{14}NIS$ requires I, 35·7%). M. p. 235° (decomp.).

1′ : 2-*Dimethyl*-3 : 4-*benzthio-ψ-cyanine Iodide.*—2-Iodoquinoline methiodide (2 g.; 1 mol.) and 2-methyl-β-naphthathiazole methiodide (1·72 g.; 1 mol.) were boiled with 99% spirit (100 c.c.) and treated with a solution of potassium hydroxide (0·7 g.; *ca.* 90%; more than 2 mols.) in 99% spirit (10 c.c.). Separation of the *dye* began almost at once, but the mixture was boiled and stirred mechanically for an hour. The crude product (1·60 g.; 66% yield) was recrystallised from methyl alcohol (150 c.c. per g.) and the crystals (0·63 g.; 26% yield) were dried for analysis in a vacuum at 100—120°, until of constant weight, which method of drying was also applied to the seven analogous dyes (Found : I, 26·2. $C_{23}H_{19}N_2IS$ requires I, 26·3%). M. p. 248° (decomp.).

This and the following seven thio-ψ-cyanines all form small red crystals, which show only slight variations in shade amongst the different members of the series. The absorption spectra of all eight in spirit solution are practically identical, there being one band with its maximum at λ 5000 Å. Photographic plates which have been bathed in a solution of any of the eight thio-ψ-cyanines show an extra-sensitivity extending to about λ 6000 Å. for moderate exposures. For this particular dye, the band is almost uniform, but with a maximum at λ 5500 Å.

2-*Methyl*-1′-*ethyl*-3 : 4-*benzthio-ψ-cyanine iodide*, similarly prepared from 2-iodoquinoline ethiodide and 2-methyl-β-naphthathiazole methiodide, was obtained crude in 41% yield, and 22% after recrystallisation (using 100 c.c. of methyl alcohol per g.) (Found : I, 25·5. $C_{24}H_{21}N_2IS$ requires I, 25·6%). M. p. 243° (decomp.). It is a good sensitiser, but the band shows a gap; the maximum sensitisation is at λ 5500 Å.

1′-*Methyl*-2-*ethyl*-3 : 4-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline methiodide and 2-methyl-β-naphthathiazole ethiodide, was obtained crude in 40% yield, and 19% after recrystallisation (using 300 c.c. of methyl alcohol per g.) (Found : I, 25·7. $C_{24}H_{21}N_2IS$ requires I, 25·6%). M. p. 270° (decomp.). The position of the sensitising maximum is the same as with the two preceding dyes and the band is nearly uniform.

1′ : 2-*Diethyl*-3 : 4-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline ethiodide and 2-methyl-β-naphthathiazole ethiodide, was obtained crude in 36% yield, and 24% after recrystallisation (using 390 c.c. of methyl alcohol per g.) (Found : I, 24·8. $C_{25}H_{23}N_2IS$ requires I, 24·9%). M. p. 265° (decomp.). The sensitising action is like that of the preceding compound.

1′ : 2-*Dimethyl*-5 : 6-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline methiodide and 1-methyl-α-naphthathiazole methiodide, was obtained crude in 66% yield, and 27% after recrystallisation (using 320 c.c. of methyl alcohol per g.) (Found : I, 26·2. $C_{23}H_{19}N_2IS$ requires I, 26·3%). M. p. 293° (decomp.). This is not such a powerful sensitiser; the maximum lies at λ 5400 Å.

2-*Methyl*-1′-*ethyl*-5 : 6-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline ethiodide and 1-methyl-α-naphthathiazole methiodide, was obtained crude in 53% yield, and 29% after recrystallisation (using 320 c.c. of methyl alcohol per g.) (Found : I, 25·5. $C_{24}H_{21}N_2IS$ requires I, 25·6%). M. p. 296° (decomp.). The sensitising maximum lies at λ 5400 Å. and there is very little gap between the regions of normal and extra-sensitivity.

1′-*Methyl*-2-*ethyl*-5 : 6-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline methiodide and 1-methyl-α-naphthathiazole ethiodide, was obtained crude in 63% yield, and 32% after recrystallisation (using 320 c.c. of methyl alcohol per g.) (Found : I, 25·5. $C_{24}H_{21}N_2IS$ requires I, 25·6%). M. p. about 293° (decomp.). The sensitivity curve is almost uniform, with a maximum at λ 5500 Å.

1′ : 2-*Diethyl*-5 : 6-*benzthio-ψ-cyanine iodide*, prepared from 2-iodoquinoline ethiodide and 1-methyl-α-naphthathiazole ethiodide, was obtained crude in 44% yield, and 30% after recrystallisation (using 410 c.c. of methyl alcohol per g.) (Found : I, 24·8. $C_{25}H_{23}N_2IS$ requires I, 24·9%). M. p. 296° (decomp.). The sensitising maximum lies at λ 5400 Å. and the action is not so powerful as with some of the analogous dyes.

2 : 2′-*Dimethyl*-3 : 4 : 3′ : 4′-*dibenzthiocarbocyanine Iodide*.—2-Methyl-β-naphthathiazole methiodide (2 g.; 2 mols.) and ethyl orthoformate (2 c.c.; 4 mols.) were boiled in pyridine solution (20 c.c.) for 1½ hours. The dye (1·52 g.; 92% yield) was recrystallised from methyl alcohol (2250 c.c.) and was obtained as a dark crystalline powder in 57% yield. Decomposition occurs on drying in a vacuum at 100—120°, but on drying at 60—80° constancy in

weight is attained. This and all the following dyes were dried for analysis in a vacuum at 60—80°, except in two instances, where the different temperature is stated (Found: I, 22·2. $C_{27}H_{21}N_2IS_2$ requires I, 22·5%). M. p. about 240° (decomp.). The maximum of the chief absorption band lies at λ 6000 Å. and there is a weaker band with its crest at λ 5600 Å. The feeble extra-sensitisation conferred by the dye extends to about λ 6700 Å. for moderate exposures, with a maximum at λ 6300 Å.

2 : 2′-*Diethyl*-3 : 4 : 3′ : 4′-*dibenzthiocarbocyanine iodide* was similarly prepared from 2-methyl-β-naphthathiazole ethiodide (2 g.), the time of heating, as also for the next three thiocarbocyanines, being 3 hours. The crude product (1·35 g.; 81% yield) was recrystallised from methyl alcohol (1750 c.c.) and was thus obtained, in 64% yield, in small green and gold crystals (Found : I, 21·4. $C_{29}H_{25}N_2IS_2$ requires I, 21·4%). M. p. 263° (decomp.). The absorption is like that of the preceding compound, but, unlike it, this dye is a powerful sensitiser, its action extending to λ 7200 Å. with its maximum at λ 6400 Å.

2 : 2′-*Dimethyl*-5 : 6 : 5′ : 6′-*dibenzthiocarbocyanine iodide* was prepared from 1-methyl-α-naphthathiazole methiodide (2 g.), but on account of the insolubility of the dye more pyridine than usual was taken (100 c.c.). The product (1·48 g.; 90% yield) was so sparingly soluble that its recrystallisation was practically impossible. It was boiled three times with methyl alcohol (100 c.c. × 3) and the dark green residue (78% yield) was analysed (Found : I, 22·4. $C_{27}H_{21}N_2IS_2$ requires I, 22·5%). M. p. 300° (decomp.). The chief absorption maximum lies at λ 5950 Å. and the secondary one at λ 5500 Å. A feeble extra-sensitisation extended to λ 6400 Å., but the testing was difficult, as the substance tended to precipitate instead of dyeing the emulsion.

2 : 2′-*Diethyl*-5 : 6 : 5′ : 6′-*dibenzthiocarbocyanine iodide* was prepared from 1-methyl-α-naphthathiazole ethiodide (2 g.) and the crude product (1·71 g.; quant. yield) was recrystallised from methyl alcohol (1000 c.c.); the yield of small steely crystals was 79% (Found: I, 21·2. $C_{29}H_{25}N_2IS_2$ requires I, 21·4%). M. p. 294° (decomp.). The absorption is like that of the first two thiocarbocyanines and the substance is a powerful sensitiser, showing its maximum action at λ 6350 Å.; the extra-sensitisation extends to λ 6900 Å., with a gap at λ 5100 Å.

2 : 2′ - *Diethyl* - 5 : 6 : 5′ : 6′ - *dibenzthiocarbocyanine Bromide.*—1-Methyl-α-naphthathiazole ethochloride (1·9 g.) was prepared from the ethiodide by the action of silver chloride and was used for the preparation of the thiocarbocyanine chloride. This, being too soluble to be readily recrystallised from methyl alcohol, was con-

verted into the corresponding *bromide* by addition of aqueous sodium bromide to its methyl-alcoholic solution. The crude dye bromide (86% yield) was recrystallised from methyl alcohol (100 c.c.) and dull green crystals resulted in 60% yield (Found: Br, 14·5. $C_{29}H_{25}N_2BrS_2$ requires Br, 14·65%). M. p. 274° (decomp.).

2 : 2′ : 8-*Trimethyl*-5 : 6 : 5′ : 6′-*dibenzthiocarbocyanine Iodide*.—1-Methyl-α-naphthathiazole methiodide (2 g.; 2 mols.) and ethyl orthoacetate (2·2 c.c.; 4 mols.) were boiled with pyridine (20 c.c.) for ½ hour. The product (0·94 g.; 56% yield), being too sparingly soluble to be recrystallised, was boiled with methyl alcohol (100 c.c. × 3); the dull green residue (0·72 g.) amounted to a 43% yield (Found: I, 22·1. $C_{28}H_{23}N_2IS_2$ requires I, 21·95%). M. p. about 298° (decomp.). The principal absorption maximum lies at λ 5750 Å.; there is some extra-sensitisation extending to λ 6600 Å.

8-*Methyl*-2 : 2′-*diethyl*-5 : 6 : 5′ : 6′-*dibenzthiocarbocyanine iodide*, similarly prepared by the action of ethyl orthoacetate on 1-methyl-α-naphthathiazole ethiodide (2 g.), was obtained crude in 60% yield, and 38% after recrystallisation from methyl alcohol (850 c.c.). When the dull green crystals were dried for analysis in a vacuum at 60—80°, the percentage of iodine was found to be low (20·1%), but approached the theoretical value when drying was effected in a vacuum at 110—120° (Found: I, 20·7. $C_{30}H_{27}N_2IS_2$ requires I, 20·9%). M. p. about 298° (decomp.). The chief absorption band has its crest at λ 5750 Å. and there is a weaker band with its maximum at λ 5400 Å. The dye exerts a powerful sensitising action, which extends to λ 6800 Å., and has one maximum at λ 6200 Å. and a less well-defined one at λ 5400 Å.

2-p-*Dimethylaminostyryl*·β-*naphthathiazole Ethiodide*.—2-Methyl-β-naphthathiazole ethiodide (2 g.; 1 mol.) and *p*-dimethylaminobenzaldehyde (0·84 g.; 1 mol.) were boiled with absolute alcohol (15 c.c.) and piperidine (0·5 c.c.) for 6 hours. The product (1·63 g.; 60% yield), after recrystallisation from methyl alcohol (200 c.c.), was obtained in 46% yield, as a dark purple powder (Found: I, 26·05. $C_{23}H_{23}N_2IS$ requires I, 26·1%). M. p. 213° (decomp.). The substance confers a fairly powerful sensitivity extending to λ 6900 Å.; there is a badly-defined maximum at about λ 6100 Å.

1-p-*Dimethylaminostyryl*-α-*naphthathiazole ethiodide* was similarly prepared from 1-methyl-α-naphthathiazole ethiodide (2 g.), and the crude product (2·25 g.; 82% yield), on recrystallisation from methyl alcohol (1000 c.c.), gave a 67% yield of purple crystals (Found: I, 26·2. $C_{23}H_{23}N_2IS$ requires I, 26·1%). M. p. 256° (decomp.). The extra-sensitivity extends to λ 6600 Å., but is less than in the case of the preceding compound, and there is no very clear maximum.

p-*Dimethylaminoanil of* β-*Naphthathiazole*-2-*aldehyde Ethiodide*.—2-Methyl-β-naphthathiazole ethiodide (2 g.; 1 mol.) and *p*-nitrosodimethylaniline (0·85 g.; 1 mol.) were boiled for 7 hours in absolute alcoholic solution (30 c.c.) with 2 drops of piperidine. The *anil* (0·90 g.; 33% yield) was recrystallised from methyl alcohol (200 c.c.), the yield being 24%. A second recrystallisation was effected (Found: I, 25·7. $C_{22}H_{22}N_3IS$ requires I, 26·05%). The green crystals melted at about 214° (decomp.), but the exact m. p. depends upon the rate of heating.

p-*Dimethylaminoanil of* α-*Naphthathiazole*-1-*aldehyde Ethiodide*.—This was similarly prepared from 1-methyl-α-naphthathiazole ethiodide (2 g.), and was obtained crude in 61% yield (1·66 g.) and, after recrystallisation from methyl alcohol (250 c.c.), in 43% yield. After a second recrystallisation, the dark green crystals were dried at 100—110° (Found: I, 25·9. $C_{22}H_{22}N_3IS$ requires I, 26·05%). M. p. 220° (decomp.).

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