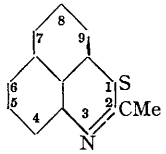
131. *Thiazinocyanines. Part III. Carbocyanines containing the* peri-*Naphtha-*1 : 3-*thiazine Nucleus.*

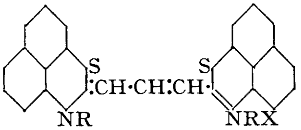
By Frances M. Hamer and Russell J. Rathbone.

From 2-methyl*peri*naphtha-1 : 3-thiazine, the carbocyanines of Joy and Bogert were obtained free from solvent and an unsubstituted dicarbocyanine was prepared : these dyes are abnormal in being decolorised by alkali. In view of the difficulty of making its quaternary salts, the base itself was condensed with suitable salts, to give the bases of six unsymmetrical carbocyanines. Two carbocyanines were made from one of these. Absorption data for methyl-alcoholic solutions of the dyes are recorded, and comparisons made with the dihydro-1 : 3-thiazine, 2 : 4-benzthiazine, and naphthathiazole series. Styryl compounds also were prepared.

The preparation of quaternary salts of 2-methylbenzthiazole and of 1-methyl-α-naphthathiazole proceeds smoothly; it is well known that some of the cyanine dyes prepared from these salts are outstandingly valuable photographic sensitisers. By synthesising 2-methyl*peri*naphtha-1 : 3-thiazine (I), Bogert and Bartlett obtained a promising intermediate (*J. Amer. Chem. Soc.*, 1931, **53**, 4046). Joy and Bogert's observation that the new base only with difficulty undergoes quaternary salt formation (*J. Org. Chem.*, 1936, **1**, 236) is interesting because so unexpected. They succeeded in making two symmetrical carbocyanines (II; R = Me or Et, X = I) containing the new nucleus, but, unlike the isomeric carbocyanines containing two α- or two β-naphthathiazole nuclei, these were devoid of photographic sensitising action (*loc. cit.*).

(I.)



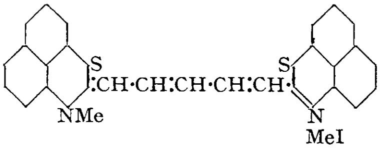


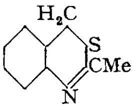
(II.)

In preparing the methiodide of 2-methyl*peri*naphtha-1 : 3-thiazine, we confirmed Joy and Bogert's observation as to the beneficial effect of adding a little quinol, which we added also in preparing the ethiodide. The instability of the methiodide was shown by the drop in yield on recrystallisation. We too were unable to prepare the ethiodide in a state of purity but we prepared a pure specimen of the *hydriodide*. We prepared the two symmetrical carbocyanine iodides (II; R = Me or Et, X = I) by Joy and Bogert's method and confirmed their observation that only short heating can be applied. By modifying their procedure, we succeeded in obtaining both specimens free from solvent, whereas theirs contained chloroform of crystallisation. Starting from the methomethylsulphate of (I), the formation of the *carbocyanine methylsulphate* (II; R = Me, X = SO_4Me) proceeded smoothly, the dye being obtained in 71% yield. Not only were these carbocyanines devoid of sensitising action, but they depressed the original blue sensitivity of the photographic emulsion. A peculiarity is that their alcoholic solutions are reversibly bleached by alkali. In attempts to carry out titrations, sharp end-points were not obtained and it appeared that considerable excess of alkali, over the molecular proportion, was required to effect bleaching.

Joy and Bogert tried to prepare the 12-chloro-derivative of the dicarbocyanine (III) by applying the method of Beattie, Heilbron, and Irving (J., 1932, 260) to 2-methyl*peri*naphtha-1 : 3-thiazine methiodide, but the dye was not obtained pure (*loc. cit,*). We obtained a pure specimen of the unsubstituted dicarbocyanine (III) by carrying out its preparation at a low temperature. Its behaviour with alkali resembles that of the carbocyanines (II). Thus its blue chloroform solution was turned yellow by caustic alkali. At first the blue was readily restored by addition of traces of acid or by dilution with methyl alcohol, but, after the chloroform solution had been evaporated to dryness, the brown residue no longer gave a blue colour with acid, indicating

(III.)

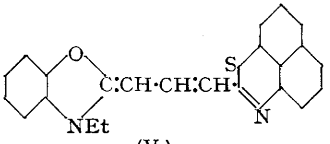




(IV.)

that decomposition had occurred. The bleached dye was free from iodine. Like the carbocyanines (II), the dicarbocyanines (III) did not sensitise but depressed the original blue sensitivity of a photographic plate. The absorption maximum of a methyl-alcoholic solution of the dicarbocyanine (III) is 1100 A. further towards the red than that of the carbocyanine (II; R = Me, X = I).

The difficulties which Joy and Bogert experienced in preparing quaternary salts of 2-methyl*peri*naphtha-1 : 3-thiazine (I) (*loc. cit.*) were intensified in the case of the related 3-methyl-2 : 4-benzthiazine (IV), as has been recorded in the first paper of this series (Beilenson and Hamer, J., 1942, 98). However, following the failure to prepare quaternary salts of (IV), it proved possible to condense the base itself with heterocyclic quaternary ammonium salts containing a substituted β-aminovinyl group, cyanine bases thus being obtained, from which carbocyanine dyes could be produced by the action of esters (Beilenson and Hamer, *loc. cit.*). Following this procedure and starting from the base (I), we have now prepared *bases* of unsymmetrical carbocyanines containing the *peri*naphtha-1 : 3-thiazine nucleus. Thus the new base (V) was prepared in 38% yield, by fusing (I) with 2-β-acetanilidovinylbenzoxazole ethiodide, followed by treatment with alkali. Its 4 : 5- and 6 : 7-benz-derivatives were prepared analogously, in 24% and 20% yields. (VI) was prepared in 54% yield and its 4 : 5- and 6 : 7-benz-derivatives in 36% and 35% yields. The *hydrochlorides* of (V) and of the 6 : 7-benz-derivative of (VI) were prepared. By the action of methyl iodide and ethyl iodide, respectively, on (V), two *carbocyanines* (VII; R = Me or Et) were prepared. These new dyes, whether carbocyanines or carbocyanine bases, sensitised weakly and depressed the normal blue sensitivity of the photographic plate.



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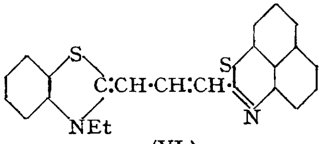

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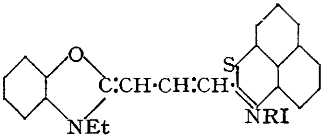


(VII.)

The six carbocyanine bases of the *peri*naphtha-1 : 3-thiazine series give, in methyl-alcoholic solution, very broad absorption curves, with indefinite maxima. In the 2 : 4-benzthiazine series (Beilenson and Hamer, *loc. cit.*), the carbocyanine bases gave rounded, but much less broad, absorption curves, and the effect of adding acid was to make each curve narrower and the maxima more sharply defined. In the present group, addition of acid has a similar effect; the resultant curves consist of two or more bands, of which the one nearest the red is, in general, the strongest. On passing from the acid salt of (V) to the acid salt of (VI), the absorption maximum shifts 300 A. towards the red end of the spectrum. The effect of introducing the 4 : 5- or 6 : 7-benz-group into the acid salt of (V) or (VI) is to produce a shift of 200 to 250 A. in the same direction. Acid solutions of four unsymmetrical carbocyanine bases containing the 2 : 4-benzthiazine nucleus (*ibid., loc. cit.*) may be compared with those of four in the present series, in which the place of the 2 : 4-benzthiazine nucleus is taken by the *peri*naphtha-1 : 3-thiazine nucleus : this shifts the absorption maximum towards the red, the amount of the shift varying from 100 to 250 A.

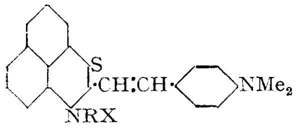
The absorption curves of the carbocyanines (VII; R = Me or Et) are well defined, with the maximum 550 or 600 A. nearer to the red than that of the base (V) and only 50 or 100 A. nearer to the blue than that of the acidified solution of (V). With the unsymmetrical carbocyanine, replacement of the 2 : 4-benzthiazine nucleus (*ibid., loc. cit.*) by the *peri*naphtha-1 : 3-thiazine nucleus, giving (VII; R = Et), is accompanied by a bathochromic shift of 100 A. Replacement of the dihydro-1 : 3-thiazine nucleus (Hamer and Rathbone, this vol., p. 243) by the *peri*naphtha-1 : 3-thiazine nucleus, giving (VII; R = Me), is accompanied by a bathochromic shift of 450 A.

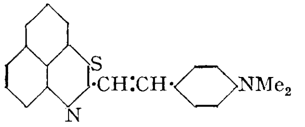
The base (V) has its sensitising maximum in the same position as that of its hydrochloride, methiodide (VII; R = Me) and ethiodide (VII; R = Et); the other dye base and hydrochloride show the same abnormality, which was observed also in the 2 : 4-benzthiazine series (Beilenson and Hamer, *loc. cit.*). As in that series, so also here, the abnormality is considered to lie with the bases and not with the carbocyanines, because with five of the present bases the shift on passing from absorption maximum to sensitising maximum is as much as 900 to 1250 A., whereas with the two carbocyanines it has the more usual values of 350 and 400 A.

As the *peri*naphtha-1 : 3-thiazine nucleus is isomeric with the naphthathiazole nucleus, a comparison of absorption spectra of dyes of these series is of interest. The absorption maxima of the symmetrical thiacarbocyanines, having two α- or two β-naphthathiazole nuclei (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703) lie 530 and 570 A., respectively, nearer to the red end of the spectrum than that of the thiacarbocyanine having two *peri*naphtha-1 : 3-thiazine nuclei. Those of the symmetrical thiadicarbocyanines having two α- or two β-naphthathiazole nuclei (*idem, ibid.*) lie 470 and 510 A., respectively, nearer to the red than that of the thiadicarbocyanine having two *peri*naphtha-1 : 3-thiazine nuclei (here two ethiodides are compared with a methiodide). The absorption maxima of the oxathiacarbocyanines having an α- or β-naphthathiazole nucleus (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138) lie 260 and 270 A., respectively, nearer to the red end of the spectrum than that of the oxathiacarbocyanine having a *peri*naphtha-1 : 3-thiazine nucleus.

By condensing the methiodide and the hydriodide, respectively, of (I) with *p*-dimethylaminobenzaldehyde, Joy and Bogert obtained two styryl compounds (VIII; R = Me or H, X = I) (*loc. cit.*). We prepared the corresponding methomethylsulphate (VIII; R = Me, X = SO_4Me) but found that its absorption maximum did not agree with that published for the methiodide. We repeated the preparation of the hydriodide and found a similar divergence there : the solvent used for the published absorption data has not been recorded. We also prepared the styryl *base* (IX). On acidification of a methyl-alcoholic solution of the base, the absorption maximum shifted 1260 A. towards the region of longer wave-length. On passing from the base to the hydriodide, and to the methomethylsulphate, the shifts were 1260 and 1350 A., respectively.

(VIII.)





(IX.)

EXPERIMENTAL.

8-*Nitronaphthalene*-1-*sulphonyl Chloride*.—In following the directions for nitrating naphthalene-1-sulphonyl chloride (Erdmann and Süvern, *Annalen*, 1893, **275**, 230; Reissert, *Ber.*, 1922, **55**, 858), the yields of 8 : 1-isomer, from its mixture with the 5 : 1-isomer, were variable. The modification of Joy and Bogert (*J. Org. Chem.*, 1936, **1**, 236) was preferred, as the variations were less. Benzene (3 c.c. per g.) was used for the separation, and the resultant yield of 8 : 1-compound, m. p. 149°, was 28%. They obtained a 16% yield, m. p. 154°.

2-*Methyl*peri*naphtha*-1 : 3-*thiazine* (I).—The tin chloride addition compound of 1-thiol-8-acetonaphthalide was prepared from 8-nitronaphthalene-1-sulphonyl chloride, and cyclisation was effected by the method of Bogert and Bartlett (*J. Amer. Chem. Soc.*, 1931, **53**, 4046; cf. Joy and Bogert, *loc. cit.*). The base was recrystallised from spirit (5 c.c. per g.), being obtained in 66% yield, m. p. 93—94°, and base of this quality was used for subsequent work. Recrystallisation from acetone (3 c.c. per g.) brought the m. p. up to 96°, whilst the yield fell to 48%. The substance was dried in a vacuum at 60° and analysed by the method of Carius, which method of analysis was used throughout this work, except where otherwise stated (Found : S, 16·3. Calc. for $C_{12}H_9NS$: S, 16·1%). Bogert and Bartlett record m. p. 96·5—97·5° and their yield, calculated from the same starting point, is 53%.

2-*Methyl*peri*naphtha*-1 : 3-*thiazine Methomethylsulphate*.—2-Methyl*peri*naphtha-1 : 3-thiazine (1·99 g.; 1 mol.) and methyl sulphate (1·4 c.c.; 1·5 mols.), which had been purified by means of sodium bicarbonate and sodium sulphate, were heated together on a steam-bath for 10 minutes. The resultant solid was ground with absolute ether and then with acetone, and was dried in a vacuum desiccator (92% yield), and was used without further purification.

2-*Methyl*peri*naphtha*-1 : 3-*thiazine Methiodide*.—2-Methyl*peri*naphtha-1 : 3-thiazine (3 g.; 1 mol.), methyl iodide (1·2 c.c.; 1·2 mols.), and quinol (0·006 g.) were heated together in a sealed tube at 100°, according to the method of Joy and Bogert (*J. Org. Chem.*, 1936, **1**, 236), but 4 hours was found to be the best time of heating, whereas they heated for 12 hours. Their observation, that addition of quinol has a favourable effect upon the yield, was confirmed by three pairs of comparative experiments. The yield of chloroform-washed product was 60% (2·7 g.) and this was used for subsequent work; Joy and Bogert obtained 62%. After rapid recrystallisation from absolute alcohol (30 c.c. per g.), the yield dropped to 24%. Before analysis, the iodide was dried to constant weight in a vacuum at 60—80°, which method of drying was employed throughout this work, except where otherwise stated (Found : I, 37·0. Calc. for $C_{13}H_{12}NIS$: I, 37·2%). M. p. 177° (decomp.), but Joy and Bogert give m. p. 222—230° (decomp.).

2-*Methyl*peri*naphtha*-1 : 3-*thiazine Ethiodide*.—2-Methyl*peri*naphtha-1 : 3-thiazine (1·99 g.; 1 mol.) and ethyl iodide (1·6 c.c.; 2 mols.) were heated together in a sealed tube at 100°, with addition of quinol (0·006 g.), since Joy and Bogert found this addition useful in the case of the methiodide. The best yield of chloroform-washed product was 40% (1·51 g.) and this was attained by 4 days' heating, whereas they heated for 1 day, without quinol, and got a 39% yield. The yellow powder had m. p. 269—270° (decomp.), with softening from 230°, but the presence of hydriodide was suggested by its acidity to litmus. It was, however, used for preparing the carbocyanine.

2-*Methyl*peri*naphtha*-1 : 3-*thiazine Hydriodide*.—2-Methyl*peri*naphtha-1 : 3-thiazine (1 g.; 1 mol.) was dissolved in hot acetic acid (5 c.c.) and treated with a hot aqueous solution of potassium iodide (3 g.; 3 mols.) in water (5 c.c.). The yield of ether-washed product was 31% (Found : I, 38·7. $C_{12}H_{10}NIS$ requires I, 38·8%). The bright orange crystals had m. p. 260° (decomp.). Joy and Bogert record m. p. 259° (decomp.) for a specimen of hydriodide containing ethiodide.

Bis-2-(3-*methyl*peri*naphtha*-1 : 3-*thiazine*)*trimethincyanine Iodide* (II; R = Me, X = I).—2-Methyl*peri*naphtha-1 : 3-thiazine methiodide (2 g.; 2 mols.), ethyl orthoformate (2 c.c.; 4 mols.), and pyridine (20 c.c.) were boiled together for 4 minutes and the product (0·5 g.; 30% yield) was ground with acetone until the washings were a clean purple. A 28% yield (0·45 g.) of pure dye was thus obtained, m. p. 223° (decomp.) (Found : I, 22·5; S, 11·5. Calc. for $C_{27}H_{21}N_2IS_2$: I, 22·5; S, 11·4%). Its absorption maximum was at 5300 A. Joy and Bogert used half the amount of pyridine and boiled for 5 minutes; by repeated boiling of the filtrate, they obtained more dye and their total yield of washed dye (43%) was higher than ours; we failed to obtain further yields by reheating. After recrystallisation from chloroform, their product, m. p. 221° (decomp.), apparently contained chloroform of crystallisation.

Bis-2-(3-*methyl*peri*naphtha*-1 : 3-*thiazine*)*trimethincyanine Methylsulphate* (II; R = Me, X = SO_4Me).—2-Methyl*peri*naphtha-1 : 3-thiazine methomethylsulphate (2·17 g.; 2 mols.), ethyl orthoformate (4 mols.), and pyridine (10 c.c.) were boiled together for 5 minutes. The purple solution was quickly cooled, and the solid filtered off and washed with ether, being obtained in 71% yield, as green crystals with a golden reflex. M. p. 232° (decomp.). On recrystallising from methyl alcohol (30 c.c. per g.), the yield dropped to 53% but the m. p. was unchanged (Found : S, 17·35. $C_{28}H_{24}O_4N_2S_3$ requires S, 17·5%).

Bis-2-(3-*ethyl*peri*naphtha*-1 : 3-*thiazine*)*trimethincyanine Iodide* (II; R = Et, X = I).—2-Methyl*peri*naphtha-1 : 3-thiazine ethiodide was caused to react with ethyl orthoformate, potassium acetate, and acetic anhydride, and the product was precipitated with ethyl acetate and washed with water, all according to the method of Joy and Bogert (*loc. cit.*), except that 10 times their amount of potassium acetate was used. Instead of boiling out with methyl alcohol, whereby they obtained a 9% yield, we washed exhaustively with ether and thus obtained a pure specimen, free from solvent (Found : I, 21·3. Calc. for $C_{29}H_{25}N_2IS_2$: I, 21·4%), in 10% yield. Its absorption maximum was at 5400 A. M. p. 212° (decomp.). They give m. p. 243° (decomp.) for a sample recrystallised from chloroform and apparently containing solvent of crystallisation.

Bis-2-(3-*methyl*peri*naphtha*-1 : 3-*thiazine*)*pentamethincyanine Iodide* (III).—2-Methyl*peri*naphtha-1 : 3-thiazine methiodide (2·28 g.; 2 mols.), β-anilinoacraldehyde anil hydrochloride (0·86 g.; 1 mol.), anhydrous potassium acetate (2·4 g.; 8 mols.), and acetic anhydride (30 c.c.) were stirred together at 0° and kept in the ice-chest, with occasional stirring, for 7 days. Water was added, and the mixture left overnight in the ice-chest. Next day the product was filtered off and washed with water and with ether. It was ground with successive lots of a mixture of equal volumes of acetone and ether (10 c.c. × 16) until the filtrates were blue. The undissolved residue amounted to a 30% yield (0·59 g.)

(Found : I, 21·6. $C_{29}H_{23}N_2IS_2$ requires I, 21·5%). The dull green crystals had m. p. 183° (decomp.). The methyl-alcoholic solution had a well-defined absorption band with maximum at 6400 A.

An attempt to prepare this dicarbocyanine by using sodium dissolved in alcohol as condensing agent was unsuccessful.

Trimethin[2-(3-*ethyldihydrobenzoxazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)] (V).—2-Methyl*peri*naphtha-1 : 3-thiazine (3·98 g. ; 1 mol.) and 2-*β*-acetanilidovinylbenzoxazole ethiodide (8·68 g. ; 1 mol.) were fused together at 125° for 30 minutes. The reaction mixture was heated with sodium hydroxide solution, and the *base* extracted with chloroform. After removal of solvent, the residue was recrystallised from ethyl acetate (120 c.c.) and thus obtained in 38% yield (3·08 g.) (Found : S, 8·5. $C_{23}H_{18}ON_2S$ requires S, 8·7%). The dark red crystals had m. p. 165—168° (decomp.). Their pyridine or methyl-alcoholic solution had an absorption band which extended from 4000 to 4900 A., with maxima at 4300 and 4550 A. Addition of sulphuric acid to the latter (5 g. per 100 c.c.) resulted in an absorption curve with definite maxima at 4900 and 5200 A. The dye is a weak sensitiser, giving a broad band which extends past 6000 with an indefinite maximum at 5500 A.

Trimethin[2-(3-*ethyldihydrobenzoxazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)] *Hydrochloride*.—A suspension of trimethin-[2-(3-ethyldihydrobenzoxazole)[2-(*peri*naphtha-1 : 3-thiazine)] (0·5 g.) in spirit (5 c.c.) was stirred and heated with concentrated hydrochloric acid (3 c.c.) and water (10 c.c.). The resultant *hydrochloride* (0·55 g.) was dissolved in absolute alcohol (5 c.c.) and by precipitation with ether was obtained in 85% yield (Found : Cl, 8·8. $C_{23}H_{19}ON_2SCl$ requires Cl, 8·7%). The bright red crystals had m. p. 200° (decomp.). Its methyl-alcoholic solution absorbed from 4200 to 5400 A. ; a strong absorption band had its maximum at 4800 and an inflexion at 4400 A., whilst a weaker one had its maximum at 5200. The distribution of sensitising is very like that of the base but the base is the stronger sensitiser. The maximum of the hydrochloride lies at 5500 A. and the sensitivity extends past 6100 A.

Trimethin[2-(3-*ethyldihydro*-4 : 5-*benzbenzoxazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)].—2-Methyl*peri*naphtha-1 : 3-thiazine and 2-*β*-acetanilidovinyl-4 : 5-benzbenzoxazole ethiodide were fused together at 140° for an hour, the product was heated with alkali, and the base extracted with chloroform. The crude *base* was purified by heating and stirring with caustic alkali and benzene, and it crystallised from the concentrated benzene extract in 24% yield (Found : S, 7·85. $C_{27}H_{20}ON_2S$ requires S, 7·65%). The bright red solid had m. p. 190° (decomp.). Its pyridine or methyl-alcoholic solution had a very broad absorption band, extending from 4000 to 5400 A., with its maximum at 4750 A. After addition of sulphuric acid to the latter (5 g. per 100 c.c.), the curve had maxima at 4800, 5050, and 5400 A. The dye is a weak sensitiser with its maximum action at 5650 A. ; it causes considerable depression of blue sensitivity.

Trimethin [2-(3-*ethyldihydro*-6 : 7-*benzbenzoxazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)].—The preparation was carried out as in the preceding instance, except that 2-*β*-acetanilidovinyl-6 : 7-benzbenzoxazole ethiodide was used and heating was for 30 minutes at 130°. Purification was by heating and stirring with caustic alkali and benzene. From the concentrated benzene extract the *base* was precipitated by ether in 20% yield (Found : S, 7·8. $C_{27}H_{20}ON_2S$ requires S, 7·6%). The dark red solid had m. p. 155° (decomp.), with shrinking from 135°. Its pyridine or methyl-alcoholic solution absorbed from the ultra-violet up to about 5400, with a maximum at 4700 A. After addition of sulphuric acid to the latter solution (5 g. per 100 c.c.), the maximum was at 5400 A. with a secondary one at 5050 A. It is a weak sensitiser with maximum at 5700 A. ; it depresses blue sensitivity a little.

Trimethin[2-(3-*ethyldihydrobenzthiazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)] (VI).—2-Methyl*peri*naphtha-1 : 3-thiazine (1·99 g.) and 2-*β*-acetanilidovinylbenzthiazole ethiodide were fused together at 130—140° for an hour and the product was stirred on the steam-bath with 40% sodium hydroxide solution (15 c.c.) for 5 minutes. The base was extracted with chloroform and, after removal of the solvent, the residue was stirred on the steam-bath for 30 minutes with benzene (50 c.c.) and 20% sodium hydroxide solution (50 c.c.). The benzene solution was separated, washed with water, and concentrated; by addition of spirit the dye *base* was precipitated in 54% yield (Found : S, 16·5. $C_{23}H_{18}N_2S_2$ requires S, 16·6%). The dull red solid had m. p. 196° (decomp.). In methyl alcohol or pyridine solution, the dye had a broad absorption band, extending from the ultra-violet up to 5500 A. with its maximum at about 4600. On addition of sulphuric acid to the methyl-alcoholic solution (5 g. per 100 c.c.), the band became much narrower, with its maximum at 5550 A. It sensitised a gelatino-bromide photographic emulsion very weakly from 5500 to 6100 A. with the maximum effect at 5850.

Trimethin[2-(3-*ethyldihydro*-4 : 5-*benzbenzthiazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)].—2-Methyl*peri*naphtha-1 : 3-thiazine and 2-*β*-acetanilidovinyl-4 : 5-benzbenzthiazole ethiodide were fused together at 140° for 1 hour. The product was heated with alkali and extracted with chloroform and the resultant *base* was purified by boiling and stirring for 30 minutes with benzene and 20% sodium hydroxide solution. The benzene layer was washed with water and concentrated, and dark red crystals separated in 36% yield (0·79 g.) (Found : S, 14·7. $C_{27}H_{20}N_2S_2$ requires S, 14·7%). M. p. 215° (decomp.). A pyridine or methyl-alcoholic solution showed a broad absorption band, extending from 4300 to 5700 A. On addition of sulphuric acid to the latter (5 g. per 100 c.c.), the absorption band became narrower and moved towards the red, two practically equal maxima being discernible, at 5350 and 5750 A. It was a weak sensitiser, causing much depression of blue sensitivity; sensitising was practically uniform from 5000 to 6100, extending to 6700 A.

Trimethin [2-(3-*ethyldihydro*-6 : 7-*benzbenzthiazole*)][2-(peri*naphtha*-1 : 3-*thiazine*)].—The preparation was effected as in the previous case, but with use of 2-*β*-acetanilidovinyl-6 : 7-benzbenzthiazole ethiodide, and fusion was at 150°. After the product had been heated with alkali and benzene, the benzene extract was concentrated to small volume, and the *base* precipitated with ether. It was obtained in 35% yield (Found : S, 14·6. $C_{27}H_{20}N_2S_2$ requires S, 14·7%). The dark red solid had m. p. 212° (decomp.) with shrinking from 190°. Its pyridine or methyl-alcoholic solution showed a very broad absorption band from 4400—5500 A., with maxima at 4800 and 5200 A. On addition of sulphuric acid to the latter (5 g. per 100 c.c.), the absorption band moved towards the red and showed well-defined maxima at 5350 and 5700 A. The dye is a weak sensitiser to about 6400 with the maximum effect at 6150 A. ; it depresses blue sensitivity.

Trimethin [2-(3-*ethyldihydro*-6 : 7-*benzbenzthiazole*)][2-peri*naphtha*-1 : 3-*thiazine*)] *Hydrochloride*.—A suspension of trimethin [2-(3-ethyldihydro-6 : 7-benzbenzthiazole)][2-(*peri*naphtha-1 : 3-thiazine)] (0·5 g.) in spirit (5 c.c.) was heated, concentrated hydrochloric acid (3 c.c.) and water (10 c.c.) added, and the mixture boiled for 3 minutes. The solution was cooled, and the crystals filtered off and washed with water and benzene. After recrystallisation from methyl alcohol (300 c.c. per g.), the yield was 59% (Found : Cl, 7·3. $C_{27}H_{21}N_2S_2Cl$ requires Cl, 7·5%). The dark product had m. p. 218° (decomp.). In methyl-alcoholic solution it seemed to dissociate, since the broad absorption band was like that of the parent base, but on acidification of the solution with hydrochloric acid the band moved towards the red and became narrower, showing a well-defined maximum at 5750 A. and a weaker one at 5250 A. The distribution of sensitising was similar to that of the base, but it gave weaker sensitising and less depression of blue sensitivity than did the base.

[2-(3-*Ethylbenzoxazole*)][2-(3-*methyl*peri*naphtha*-1 : 3-*thiazine*)]*trimethincyanine Iodide* (VII ; R = Me).—Trimethin-[2-(3-ethyldihydrobenzoxazole)][2-(*peri*naphtha-1 : 3-thiazine)] (V) (0·74 g. ; 1 mol.) was heated with methyl iodide (0·25 c.c. ; 2 mols.) in a sealed tube at 100° for 2 days. The resultant *methiodide* was boiled out with benzene (15 c.c.) and washed with ether. After recrystallisation from methyl alcohol (30 c.c.), it was obtained in 39% yield (0·4 g.) (Found : I, 24·65. $C_{24}H_{21}ON_2IS$ requires I, 24·8%). The dark red substance had m. p. 202° (decomp.). Its absorption maximum is at 5150 A. It is a very weak sensitiser, with maximum at 5500 A., and causes considerable depression of blue sensitivity.

[2-(3-*Ethylbenzoxazole*)][2-(3-*ethyl*peri*naphtha*-1 : 3-*thiazine*)]*trimethincyanine Iodide* (VII; R = Et).—Trimethin-[2-(3-ethyldihydrobenzoxazole)][2-(*peri*naphtha-1 : 3-thiazine)] (1 g.) was heated with ethyl iodide in a sealed tube at 100° for 2 days. After boiling out with benzene and grinding with ether, the *ethiodide* (1·16 g.) was recrystallised from methyl alcohol (30 c.c.) and obtained in 46% yield (0·65 g.) (Found : I, 24·1. $C_{25}H_{23}ON_2IS$ requires I, 24·1%). The dark crystalline substance had m. p. 173° (decomp.). The absorption maximum is at 5100 A., with a secondary maximum at 4850. It is a weak sensitiser, with maximum at 5500 A., and depresses the blue sensitivity.

2-p-*Dimethylaminostyryl*peri*naphtha*-1 : 3-*thiazine Methomethylsulphate* (VIII; R = Me, X = SO_4Me).—2-Methyl-*peri*naphtha-1 : 3-thiazine methomethylsulphate (3·25 g.; 1 mol.), *p*-dimethylaminobenzaldehyde (1·49 g.; 1 mol.), and absolute ethyl alcohol (40 c.c.) were boiled together for 15 minutes. The product (2·4 g.; 53% yield) was purified by grinding first with ether and then with acetone, after which the yield was 48% (Found : S, 14·2. $C_{23}H_{24}O_4N_2S_2$ requires S, 14·05%). The dark solid had m. p. 116° (decomp.). The absorption maximum of a methyl-alcoholic solution is at 5520 A. The dye gave practically no sensitising and depressed the blue speed of the plate. Joy and Bogert (*J. Org. Chem.*, 1936, **1**, 236) give 4700 A. as the absorption maximum of the methiodide.

2-p-*Dimethylaminostyryl*peri*naphtha*-1 : 3-*thiazine Hydriodide* (VIII; R = H, X = I).—2-Methyl*peri*naphtha-1 : 3-thiazine hydriodide (2 g.; 1 mol.), *p*-dimethylaminobenzaldehyde (1 g.; 1·1 mols.) and absolute ethyl alcohol (25 c.c.) were boiled together for 5 minutes. The crude solid was purified by grinding with ether and resulted in 38% yield (1·09 g.) (Found : I, 27·9. Calc. for $C_{21}H_{19}N_2IS$: I, 27·7%). M. p. 235—240° (decomp.). The absorption maximum of a methyl-alcoholic solution, acidified with hydrochloric acid to prevent dissociation, is at 5430 with a weaker one at 5100 A. Joy and Bogert give the absorption maximum as 4500 A. (*loc. cit.*).

2-p-*Dimethylaminostyryl*peri*naphtha*-1 : 3-*thiazine* (IX).—2-Methyl*peri*naphtha-1 : 3-thiazine (1·99 g.; 1 mol.), *p*-dimethylaminobenzaldehyde (1·49 g.; 1 mol.), and concentrated hydrochloric acid (15 c.c.; 1·1 mols.) were heated together on the steam-bath for 30 minutes. The solid product was taken up in hot methylated spirit, and the filtered solution treated with excess of ammonia. The base was filtered off, washed (2·97 g. obtained), and crystallised from benzene (90 c.c.). The yield of orange crystals was 59% (Found : S, 9·8. $C_{21}H_{18}N_2S$ requires S, 9·7%). M. p. 213° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4170 A., and on addition of sulphuric acid (5 g. per 100 c.c.) moved to 5430 A.

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