

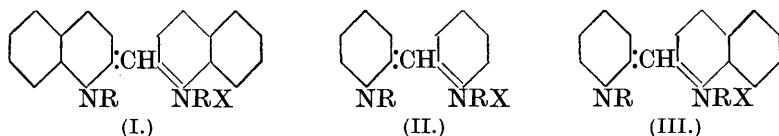
CVIII.— $\psi$ -Cyanine Dyes containing Pyridine or  $\beta$ -Naphthaquinoline Nuclei.

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THE  $\psi$ -cyanines, or 2 : 2'-cyanines (I), are prepared by the action of alkali on a solution containing the alkyl iodides of 2-iodoquinoline and quinaldine. The formation of a dye in this way was first observed by Kaufmann (*Ber.*, 1912, **45**, 1417), but Fischer and Scheibe were the first to isolate a  $\psi$ -cyanine and to assign the constitution (I) (*J. pr. Chem.*, 1919, **100**, 86). Several new  $\psi$ -cyanines were subsequently prepared by a modification of the method, and, by employing an alkyl iodide of lepidine, 1-methylbenzthiazole, or 2 : 3 : 3-trimethylindolenine in place of quinaldine alkyl iodide, other types of dyes were prepared, and the generality of the method was demonstrated (Hamer, *J.*, 1928, 206). Just as the quinaldine alkyl iodide, which is employed in the  $\psi$ -cyanine condensation, may be replaced by other salts, so also should the 2-iodoquinoline alkyl iodide be replaceable, *e.g.*, by the alkyl iodides of 2-iodopyridine or of  $\beta$ -naphthaquinoline, respectively.

Attempts to apply the general method to the preparation of

$\psi$ -cyanines (II) containing two pyridine nuclei, by treating an absolute-alcoholic solution containing  $\alpha$ -picoline methiodide, or



ethiodide, and 2-iodopyridine methiodide, or *ethiodide*, with alcoholic potassium hydroxide were unsuccessful. This is not altogether surprising, because it has already been recognised that the simplest cyanines are especially difficult to prepare: for instance, the general method for preparing carbocyanines, consisting in the use of pyridine and ethyl orthoformate, failed completely in the case of those derived from  $\alpha$ -picoline alkyl iodides (Hamer, J., 1927, 2796) and gave a remarkably poor yield in the case of those derived from 2:4-dimethylthiazole alkyl iodides (Fisher and Hamer, J., 1930, 2502).

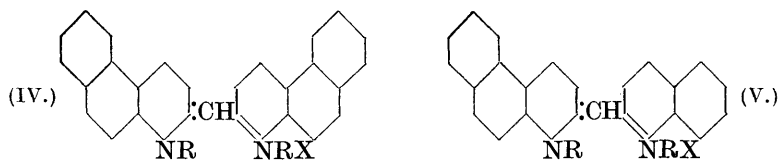
$\psi$ -Cyanines containing one pyridine nucleus and one quinoline nucleus (III) have not previously been prepared. Theoretically, they are obtainable by two methods. One of these, consisting in condensing  $\alpha$ -picoline alkyl iodide with 2-iodoquinoline alkyl iodide, was fruitless. The other—the condensation of 2-iodopyridine alkyl iodide with quinaldine alkyl iodide—yielded dyes of the new type, but *isocyanine* was produced simultaneously and fractional crystallisation was necessary in order to isolate the new, more soluble, dyes. Three of them were obtained in a state of analytical purity.

Mr. O. F. Bloch has examined the absorption of spirit solutions of all the dyes described in this paper and has tested the sensitivity of gelatino-bromide plates bathed in their solutions. The absorption of the new dyes (III) is 270—500 Å. nearer to the blue than with  $\psi$ -cyanines containing two quinoline nuclei (I). They extend the sensitivity of the plate, but the extra-sensitivity is less strong than its normal sensitivity. The extreme delicacy of these optical and photographic tests is illustrated by the fact that, in two instances, a faint unexpected band revealed the presence of a trace of impurity, undetectable by analysis.

Three  $\psi$ -cyanines containing two  $\beta$ -naphthaquinoline nuclei (IV) were prepared by condensing an *alkyl iodide* of 2-iodo- $\beta$ -naphthaquinoline with  $\beta$ -naphthaquinaldine alkyl iodide: the condensations proceeded normally. As compared with the  $\psi$ -cyanines containing two quinoline nuclei (I), the absorption bands of their spirit solutions are usually somewhat shifted towards the red end of the spectrum. These three dyes are powerful photographic sensitizers.

$\psi$ -Cyanines containing one quinoline nucleus and one  $\beta$ -naphtha-

quinoline nucleus (V) are obtainable (a) by the condensation of 2-iodoquinoline alkyliodide with  $\beta$ -naphthaquinaldine alkyliodide,



and two members of this series have already been thus prepared (Hamer, J., 1928, 206), (b) by condensing quinaldine alkyliodide with 2-iodo- $\beta$ -naphthaquinoline alkyliodide, which method is applied now for the first time. The dye prepared from quinaldine methiodide and 2-iodo- $\beta$ -naphthaquinoline methiodide proves, as would be expected from what is known of the virtual tautomerism of the cyanine dyes (Mills and Braunholtz, J., 1922, **121**, 1489; Hamer, *loc. cit.*; Kuhn, Winterstein, and Balsler, *Ber.*, 1930, **63**, 3176), to be identical with that previously prepared from 2-iodoquinoline methiodide and  $\beta$ -naphthaquinaldine methiodide. The second method was also applied to the preparation of two new  $\psi$ -cyanines of the same type, which are powerful photographic sensitisers.

Two new thio- $\psi$ -cyanines were prepared by condensing 2-iodo- $\beta$ -naphthaquinoline alkyliodide with 1-methylbenzthiazole alkyliodide. They also have photosensitising properties.

#### EXPERIMENTAL.

*1-Methyl-2-pyridone.*—On trying the method of Fargher and Furness (J., 1915, **107**, 688) it was found that (1) much of the potassium ferricyanide separated when its solution in the given amount of water cooled, (2) the ferrocyanide crystallised as a fine powder not easily filterable, (3) the quantity of potassium hydroxide required for true saturation was very large. The success of the present method depends upon the use of the minimum quantity of water as solvent; instead of potassium ferricyanide solution, the powdered solid is employed.

Pyridine (80 c.c.; 1 mol.) and methyl *p*-toluenesulphonate (182 g.; 1 mol.) were heated together on the water-bath for an hour. The pyridine metho-*p*-toluenesulphonate, dissolved in water (300 c.c.), was gradually added to a well-cooled solution of potassium hydroxide (192 g.) in water (600 c.c.), and finely powdered potassium ferricyanide (848 g.; 2 mols. + 30% excess) was gradually stirred in, with continued cooling. The mixture was then kept below 35° while powdered potassium hydroxide (1800 g.) was gradually stirred in. Hot extraction was effected with successive quantities of benzene (2 l., 2 l., 1 l., 1 l.), the filtered extracts being dried with

potassium hydroxide. The pyridone was obtained in 69% yield (74.5 g.) as an almost colourless liquid, b. p. 249°/767 mm., which darkens in the light.

*1-Ethyl-2-pyridone*.—To prepare pyridine etho-*p*-toluenesulphonate, pyridine (80 c.c.; 1 mol.) and ethyl *p*-toluenesulphonate (198 g.; 1 mol.) were heated together on the water-bath for 2¼ hours. A solution of the salt in water (200 c.c.) was added as before to a solution of potassium hydroxide (192 g.) in water (500 c.c.). The mixture was covered with benzene (2 l.) before the addition of powdered potassium ferricyanide (1300 g.; 2 mols. + 100% excess), and then of powdered potassium hydroxide (1550 g.). During the addition of the various reagents the mixture was cooled with ice, and subsequently the pyridone was extracted with hot benzene. It was obtained in 81% yield, b. p. 247°/767 mm. Both air and light cause it to darken.

*Pyridine Benzochloride*.—Pyridine (10 c.c.; 1 mol.) and benzyl chloride (15 c.c.; 1.1 mols.) were heated together at 140–150° for 6 hours, and the product was treated with water and benzene. Evaporation of the aqueous extract to dryness left pyridine benzochloride as a deliquescent, sometimes crystalline, product. The compound is merely mentioned by Fischer (*Ber.*, 1899, **32**, 1297).

*Pyridine benzoferricyanide*, (C<sub>5</sub>H<sub>5</sub>N·C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>Fe(CN)<sub>6</sub>, was prepared by adding pyridine benzochloride (prepared from 3 c.c. of pyridine; 1 mol.), dissolved in water (10 c.c.), to a solution of potassium ferricyanide (12 g.; 1 mol.) in water (31 c.c.). The solid product (7.8 g.) was twice recrystallised from spirit and dried in a vacuum at 60–80°; m. p. 102–103° (Found: N, 17.4. C<sub>42</sub>H<sub>36</sub>N<sub>9</sub>Fe requires N, 17.5%).

*1-Benzyl-2-pyridone*.—Pyridine benzochloride (from 10 c.c. of pyridine) was dissolved in water and added to a thoroughly cooled solution of potassium hydroxide (24 g.) in water (50 c.c.); sufficient water was added to redissolve the oil which separated. With continued cooling, powdered potassium ferricyanide (10.6 g.) was stirred in, and then potassium hydroxide (twice the weight of water present), and the pyridone was extracted with hot benzene. The product was recrystallised from petrol (yield, 10 g.; 38%). The pale yellow plates obtained on a second recrystallisation were dried in a vacuum desiccator; m. p. 72° (Fischer, *loc. cit.*, gives m. p. 75–76°) (Found: N, 7.6. Calc. for C<sub>12</sub>H<sub>11</sub>ON: N, 7.6%).

*2-Chloropyridine*.—1-Methyl-2-pyridone (104 g.) was treated by the method of Fargher and Furness (*loc. cit.*), but heating for 14 hours was necessary. The 2-chloropyridine obtained (yield, 73–76%) had b. p. 171–172° [Found: Cl, 32.4 (which corresponds with 7% of dichloropyridine). Calc. for C<sub>5</sub>H<sub>4</sub>NCl: Cl, 31.2%.

Calc. for  $C_5H_3NCl_2$ : Cl, 47.9%]. The analysis shows the presence of the by-product which Steinhäuser and Diepolder (*J. pr. Chem.*, 1916, **93**, 387) observed to be formed at higher temperatures. In one case, the base was treated with concentrated hydrochloric acid until nearly all had dissolved; on cooling and stirring, a white solid crystallised; the filtrate was made alkaline with sodium hydroxide, and the base extracted with ether and distilled (Found: Cl, 30.9%). In other instances, however, either the solid would not separate, or it melted before it could be removed by filtration.

2-Chloropyridine is similarly prepared from 1-ethyl-2-pyridone as starting point.

*2-Iodopyridine Methiodide*.—Pure 2-chloropyridine (1 c.c.) and methyl iodide (2.8 c.c.) were heated in a sealed tube at  $100^\circ$  for 24 hours. The product was extracted with ether, and the undissolved residue (3.0 g.; 82% yield) recrystallised from dry spirit (40 c.c. per g.). It was dried in a vacuum at  $60$ – $80^\circ$  and analysed by the method of Carius, which method was employed throughout this work (Found: I, 73.25. Calc. for  $C_5H_3NI_2$ : I, 73.2%). M. p.  $203$ – $211^\circ$  (decomp.); Fischer gives m. p.  $207^\circ$  (decomp.). A similar preparation carried out with less pure 2-chloropyridine (Found: Cl, 32.4%) gave a satisfactory specimen of 2-iodopyridine methiodide (Found, after recrystallisation: I, 73.6%).

*2-Iodopyridine ethiodide* was similarly prepared. The residue insoluble in ether (85% yield) was dried in a vacuum at  $80$ – $100^\circ$  (Found: I, 70.3.  $C_7H_9NI_2$  requires I, 70.3%) and recrystallised from water (1 c.c. per g.) (Found: I, 70.5%).

By heating 2-chloropyridine (1 c.c.) with ethyl iodide (4 c.c.) under reflux for 5 days, and washing the product with ether, the yield obtained was 91% (Found: I, 70.4%). After recrystallisation, the almost colourless product melted at  $156$ – $157^\circ$  with previous softening (Found: I, 70.1%).

*$\psi$ -Cyanine from 2-Iodopyridine Methiodide and Quinaldine Methiodide*.—2-Iodopyridine methiodide (6.0 g.; 1 mol.) and quinaldine methiodide (5.0 g.; 1 mol.), dissolved in hot absolute alcohol (64 c.c.), were treated with a hot solution of potassium hydroxide (2.4 g.) in absolute alcohol (48 c.c.), and the mixture was boiled for 40 minutes. The product was washed with water and extracted with ether. The undissolved residue (3.7 g.) was fractionally recrystallised, five lots of methyl alcohol (5 c.c., 10 c.c.  $\times$  3, 15 c.c.) being used, after which there remained a small purplish residue, presumably of isocyanine. The crystals from fractions (1)–(4) gave golden-brown spirit solutions (1 part in 2000), but that from (5) was of the isocyanine colour. For analysis, the specimens were dried in a vacuum at  $115$ – $125^\circ$ , and fractions (3) and (4) (1.08 g.

in all; 17% yield) proved analytically pure (Found: I, 33.5.  $C_{17}H_{17}N_2I$  requires I, 33.75%); m. p. 238—241° (decomp.). The dye forms brown crystals with a steely lustre. There is a feeble extension of the sensitivity of a gelatino-bromide plate to  $\lambda$  5600 Å. for moderate exposures, with an ill-defined maximum at  $\lambda$  5200 Å.

*$\psi$ -Cyanine from 2-Iodopyridine Ethiodide and Quinaldine Methiodide.*—2-Iodopyridine ethiodide (2.92 g.) and quinaldine methiodide were similarly condensed. The product was ground with water, and the residue extracted with ether. The yield of undissolved solid (0.86 g.) amounted to 27%. By using a 70% excess of quinaldine methiodide the yield (1.53 g.) was 49%. Fractional crystallisation from methyl alcohol (7 c.c., 10 c.c.  $\times$  2, 20 c.c.) gave three fractions (0.19 g., 0.28 g., and 0.21 g.; solutions in spirit, golden-brown), a fourth fraction (0.05 g.; purple solution), and a residue (0.10 g.). The dye (0.49 g.) from fractions (2) and (3) was recrystallised from methyl alcohol (12 c.c.), and the product (0.35 g.) dried as was the preceding  $\psi$ -cyanine; m. p. 249° (decomp.) (Found: I, 32.3.  $C_{18}H_{19}N_2I$  requires I, 32.5%). The crystals are terra-cotta, with a steely lustre. There is a broad absorption band with its maximum at  $\lambda$  4800 Å. The extra-sensitivity extends to  $\lambda$  6000 Å. and there is one maximum at  $\lambda$  5200 Å. and a much feebler one at  $\lambda$  5700 Å.

*$\psi$ -Cyanine from 2-Iodopyridine Ethiodide and Quinaldine Ethiodide.*—Equimolecular amounts of 2-iodopyridine ethiodide (3.0 g.) and quinaldine ethiodide (2.5 g.) in boiling absolute ethyl alcohol (60 c.c.) were condensed by means of potassium hydroxide. The colourless crystals were filtered off, the filtrate concentrated, and the product washed with water, extracted with ether, and (0.75 g.; 22% yield) recrystallised from methyl alcohol (3 c.c.), leaving a small residue. The resultant crystals (0.35 g.; 10% yield) were dried in a vacuum at 100—120° (Found: I, 31.3.  $C_{19}H_{21}N_2I$  requires I, 31.4%). The chief absorption band has its crest at  $\lambda$  4950 Å.; but there is a weaker one at  $\lambda$  5500 Å., indicating that the dye is not pure, a conclusion which was confirmed by its sensitising curve.

*1-Methyl- $\beta$ -naphtha-2-quinolone.*— $\beta$ -Naphthaquinoline (50 g.; 1 mol.) and methyl *p*-toluenesulphonate (51.7 g.; 1 mol.) were heated together for 3 hours at 140—150°. The  $\beta$ -naphthaquinoline metho-*p*-toluenesulphonate was fairly readily soluble in hot water but separated as an oil on cooling. Hence its solution in warm water (220 c.c.) was gradually added to an ice-cold solution of potassium hydroxide (63 g.) in water (125 c.c.), to which powdered potassium ferricyanide (240 g.) had just been added, and which had been covered with benzene (3 l.). The mixture was well cooled and stirred during the addition of the quaternary salt, and during the

subsequent addition of powdered potassium hydroxide (700 g.). The mixture was finally heated, the hot benzene extract filtered with the aid of a pump, and further extractions with hot benzene (3 l., 2½ l., 1½ l.) effected. The extract, after drying over potassium hydroxide, gave a 79% yield (46.2 g.) of the *quinolone*. This was twice recrystallised from spirit, being obtained almost colourless, and was dried in a vacuum desiccator (Found: N, 6.65.  $C_{14}H_{11}ON$  requires N, 6.7%). M. p. 174° with previous shrinking and darkening. This *quinolone* is mentioned by Fischer (*loc. cit.*), but there is no account of its preparation or properties.

1-*Ethyl- $\beta$ -naphtha-2-quinolone*.— $\beta$ -Naphthaquinoline (50 g.; 1 mol.) and ethyl *p*-toluenesulphonate (55.9 g.; 1 mol.) were heated together at 140–150° for 5 hours. The  $\beta$ -naphthaquinoline etho-*p*-toluenesulphonate was oxidised as in the case of the corresponding methyl compound, and the *quinolone* (50.4 g.) recrystallised from spirit (100 c.c.) and dried in a vacuum desiccator (yield, 68%); m. p. 138° (Found: N, 6.3.  $C_{15}H_{13}ON$  requires N, 6.3%).

2-*Chloro- $\beta$ -naphthaquinoline*.—A mixture of 1-methyl- $\beta$ -naphtha-2-*quinolone* (60 g.), phosphorus pentachloride (72 g.), and phosphorus oxychloride (100 c.c.) was heated for 11 hours at 150–160° with frequent shaking. The oxychloride was distilled off, and the residue was broken up, treated with ice and excess of sodium hydroxide, and ground repeatedly with benzene. The extract was washed with water, treated with concentrated hydrochloric acid, and left for 2 days in order that the hydrochloride of 2-chloro- $\beta$ -naphthaquinoline might crystallise. The crystals and the aqueous solution were treated hot with excess of aqueous ammonia. The liberated base was washed with water (51.5 g. obtained; 84% yield), recrystallised (yield, 69%) from spirit (20 c.c. per g.), and dried in a vacuum at 60–80°; m. p. 114° (Fischer, *loc. cit.*, gives m. p. 118°) (Found: Cl, 16.5. Calc. for  $C_{13}H_8NCl$ : Cl, 16.6%).

2-*Iodo- $\beta$ -naphthaquinoline Methiodide*.—2-Chloro- $\beta$ -naphthaquinoline (6 g.) and methyl iodide (5.3 c.c.) were heated in a sealed tube at 100° for 48 hours. The product was washed with ether (yield 11.4 g.; 90%) and dried in a vacuum at 60–80° (Found: I, 56.8.  $C_{14}H_{11}NI_2$  requires I, 56.8%). The bright yellow substance is very sparingly soluble in hot spirit (1 g. per l.). M. p. 202–211° (decomp.), according to the rate of heating.

2-*Iodo- $\beta$ -naphthaquinoline Ethiodide*.—2-Chloro- $\beta$ -naphthaquinoline (1.9 g.) and ethyl iodide (1.6 c.c.) were heated in a sealed tube at 100° for 24 hours; after ether-extraction, the yield was 34%. The product was recrystallised from spirit (300 c.c. per g.) and dried in a vacuum at 60–80° (Found: I, 55.1.  $C_{15}H_{13}NI_2$  requires I, 55.1%). It is yellow, and melts at 202–210° (decomp.), the exact

point depending upon the rate of heating. In another case the base (15 g.) and ethyl iodide (23 c.c.) were heated under reflux for 6 days and the product was extracted with ether: the undissolved 2-iodoquinoline ethiodide (13.4 g.) amounted to a 41% yield, and 35% of 2-chloro- $\beta$ -naphthaquinoline (5.25 g.) was recovered from the ethereal extract.

1 : 1'-*Dimethyl-5 : 6 : 5' : 6'-dibenz- $\psi$ -cyanine Iodide*.— $\beta$ -Naphthaquinaldine methiodide (2.5 g.; 1 mol.) and 2-iodo- $\beta$ -naphthaquinoline methiodide (3.35 g.; 1 mol.) were stirred in boiling absolute alcohol (80 c.c.), treated with potassium hydroxide (1.03 g.) in absolute-alcoholic solution (30 c.c.), and boiled for an hour. The product was washed with water and extracted with ether. The residue (3.01 g.) was taken up in hot methyl alcohol (4 l.), and the solution concentrated to 1/3 volume; the dull green powder obtained (yield, 0.82 g.; 21%) was dried in a vacuum at 120–130° (Found: I, 24.1.  $C_{29}H_{23}N_2I$  requires I, 24.1%). M. p. 286° (decomp. from 240°).

The absorption spectrum has two bands at  $\lambda$  5150 Å. and  $\lambda$  5300 Å., of which the latter is the stronger. The band of extra-sensitivity extends to  $\lambda$  6300 Å. for moderate exposures. It is almost uniform, but shows one maximum at  $\lambda$  5900 Å. and a weaker one at  $\lambda$  5200 Å.

1 (or 1')-*Methyl-1' (or 1)-ethyl-5 : 6 : 5' : 6'-dibenz- $\psi$ -cyanine Iodide*.—This was prepared from  $\beta$ -naphthaquinaldine ethiodide (2.6 g.) and 2-iodo- $\beta$ -naphthaquinoline methiodide, and the product (2.09 g.) undissolved by water and ether was dissolved in hot methyl alcohol (2½ l.); from this solution, on concentration to 1/3 volume, a purplish powder was obtained in 28% yield (1.11 g.), which was dried in a vacuum at 120–130° (Found: I, 23.7.  $C_{30}H_{25}N_2I$  requires I, 23.5%). M. p. 300° (decomp.).

The absorption maxima lie at  $\lambda$  5100 Å. and  $\lambda$  5450 Å., the latter being the principal one. The dye is a powerful sensitiser, with maxima at  $\lambda$  5900 Å., and  $\lambda$  5200 Å., its action extending to  $\lambda$  6400 Å., but a trace of impurity is revealed by a very feeble extension of the sensitisation, the maximum effect being at  $\lambda$  6750 Å.

1 : 1'-*Diethyl-5 : 6 : 5' : 6'-dibenz- $\psi$ -cyanine Iodide*.—This was similarly prepared from  $\beta$ -naphthaquinaldine ethiodide (2.6 g.) and 2-iodo- $\beta$ -naphthaquinoline ethiodide. The washed product (1.90 g.) was dissolved in methyl alcohol (3 l.), and the solution concentrated to 1/3 volume, giving a 25% yield (1.03 g.) of green and gold crystals, which were dried in a vacuum at 120–130° (Found: I, 22.7.  $C_{31}H_{27}N_2I$  requires I, 22.9%). M. p. 310° (decomp.).

The absorption bands lie at  $\lambda$  5100 Å. and  $\lambda$  5500 Å., the latter being the stronger. The extra-sensitivity extends to  $\lambda$  6300 Å. for moderate exposures, and there is a well-marked maximum at



$\lambda$  5700 Å. Extremely feeble sensitisation at  $\lambda$  6700 Å. doubtless indicates the presence of a trace of impurity.

1 : 1'-*Dimethyl-5 : 6* (or 5' : 6')-*benz- $\psi$ -cyanine Iodide*.—This dye was prepared from quinaldine methiodide (3.5 g.) and 2-iodo- $\beta$ -naphthaquinoline methiodide (5.54 g.). The washed product (2.05 g.) was fractionally crystallised from five lots of methyl alcohol (15 c.c., 25 c.c., 40 c.c., 100 c.c., 125 c.c.). The crystals (0.44 g.; 8% yield) from fraction (4) gave a crimson solution, those from (1) (0.06 g.) a pink solution, and those from (2) and (3) (total, 0.40 g.) were intermediate in colour. The product (0.22 g.) obtained from (5) on concentration gave a bluer solution than did (4). The dye from (4) was dried in a vacuum at 115—125° [Found : I, 26.4. Calc. for  $C_{25}H_{21}N_2I$  : I, 26.65%. Found for fraction (3) : I, 26.6%].

The sensitising action was identical with that of the dye prepared by condensing  $\beta$ -naphthaquinaldine methiodide with 2-iodoquinoline methiodide in aqueous solution (Hamer, J., 1928, 206), and their melting points, and mixed melting point, were also identical.

1 (or 1')-*Methyl-1'* (or 1)-*ethyl-5 : 6* (or 5' : 6')-*benz- $\psi$ -cyanine iodide* was similarly prepared from 2-iodo- $\beta$ -naphthaquinoline methiodide (6 g.) and quinaldine ethiodide. After being washed with water and with ether, the product (0.84 g.) was boiled out with three successive quantities of methyl alcohol (10 c.c., 50 c.c.  $\times$  2); the extracts all gave identical brownish crystals (0.30 g.; 5% yield), which were dried in a vacuum at 115—125° (Found : I, 25.85.  $C_{26}H_{23}N_2I$  requires I, 25.9%). M. p. 275—276° (decomp.). The chief absorption band lies at  $\lambda$  5300 Å. and a weaker one at  $\lambda$  5000 Å. The substance is a powerful sensitiser, the action extending to  $\lambda$  6150 Å., with a well-marked maximum at  $\lambda$  5700 Å.

1 (or 1')-*Methyl-1'* (or 1)-*ethyl-5' : 6'* (or 5 : 6)-*benz- $\psi$ -cyanine iodide* was prepared from 2-iodo- $\beta$ -naphthaquinoline ethiodide (6.5 g.) and quinaldine methiodide. The product was washed with water and ether, and the residue (2.27 g.) boiled out with four successive lots of methyl alcohol (25 c.c., 50 c.c.  $\times$  2, 75 c.c.). The products from the last three fractions (total 1.15 g.; 17% yield) all gave cherry-red solutions; after being crystallised (75 c.c. of methyl alcohol for 0.9 g.; 0.5 g. obtained), the brownish crystals were dried in a vacuum at 115—125° (Found : I, 25.8.  $C_{26}H_{23}N_2I$  requires I, 25.9%). M. p. 277—278° (decomp.). The chief absorption maximum lies at  $\lambda$  5300 Å., and a weaker one at  $\lambda$  5000 Å. The dye is a powerful sensitiser, the action extending to  $\lambda$  6200 Å., with a well-marked maximum at  $\lambda$  5750 Å.

2-*Methyl-1'-ethyl-5' : 6'-benzthio- $\psi$ -cyanine Iodide*.—1-Methylbenzthiazole methiodide (2 g.; 1 mol.) and 2-iodo- $\beta$ -naphthaquinoline

ethiodide (3.17 g.; 1 mol.), in hot absolute alcohol (200 c.c.), were treated with potassium hydroxide (2.2 mols., 90%), dissolved in absolute alcohol (15 c.c.), and the mixture was boiled for an hour, with mechanical stirring. The product (0.85 g.) was extracted with ether and the residue (0.82 g.) was recrystallised from methyl alcohol (400 c.c.), which gave an 18% yield (0.61 g.). It was dried in a vacuum at 100—120° (Found: I, 25.4.  $C_{24}H_{21}N_2IS$  requires I, 25.6%). The minute scarlet crystals soften at 279°; m. p. 282° (decomp.). The broad absorption band has its maximum at  $\lambda$  4850 Å. The extra-sensitivity extends to  $\lambda$  6000 Å. and has its maximum at  $\lambda$  5350 Å.

1' : 2-Dimethyl-5' : 6'-benzthio- $\psi$ -cyanine iodide was similarly prepared from 1-methylbenzthiazole methiodide (2 g.) and 2-iodo- $\beta$ -naphthaquinoline methiodide. The washed product (0.87 g.), after recrystallisation from methyl alcohol (400 c.c.), obtained in 20% yield (0.67 g.) as small red crystals, was dried in a vacuum at 100—110° (Found: I, 26.1.  $C_{23}H_{19}N_2IS$  requires I, 26.3%). M. p. 275° (decomp.). The absorption maximum is at  $\lambda$  4900 Å. The extra-sensitivity extends to  $\lambda$  6000 Å. and the maximum effect is at  $\lambda$  5300 Å.

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