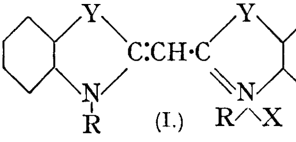
200. *Oxacyanines.*

By N. I. Fisher and F. M. Hamer.

A general method for preparing thiacyanines (I; Y = S) from benzthiazolium salts containing a reactive methyl group, by the action of amyl nitrite and acetic anhydride, has already been described (Fisher and Hamer, J., 1930, 2502). We selected chlorides, rather than iodides, for the reason that nitrous acid does not liberate halogen from them. Simultaneously Kuhn, Winterstein, and Balser elucidated the preparation of indocyanines (I; Y = CMe$_2$) from 2 : 3 : 3-trimethylindolenine salts, or the corresponding methylene base, by a method analogous to ours, and they further succeeded in isolating an intermediate; the salts which they chose as starting points were perchlorates (*Ber.*, 1930, **63**, 176). The selenacyanines (I; Y = Se) are the subject of a patent specification by I. G. Farbenindustrie; in the only example quoted, the benzselenazolium salt which is treated with amyl nitrite and acetic anhydride is an iodide, though a general claim covering various acid radicals is made (B.P. 380,702, 1931). We must now record the remarkable fact that, contrary to expectation, the use of iodides instead of chlorides is a definite improvement in certain instances, since it allows the preparation of specific dyes not otherwise accessible.

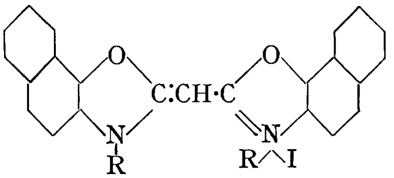


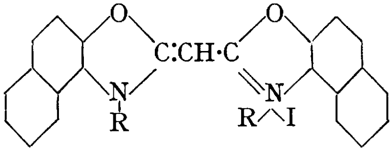
(I.)

By treating 1-methylbenzoxazole alkiodides with amyl nitrite and acetic anhydride, we have prepared *oxacyanines* (I; Y = O), which are cyanines of a new type. The use of iodides as starting-points leads to contamination of the product by periodide, whence treatment with sulphur dioxide is desirable.

The oxacyanines are of special scientific interest, in that their absorption lies further into the more refrangible region of the spectrum than that of any known kind of cyanine dye. The simplest oxacyanines are pale yellow substances, which give colourless alcoholic solutions.

(II.)





(III.)

1-Methyl-α-naphthoxazole and 2-methyl-β-naphthoxazole were prepared. To obtain the former, α-naphthol was converted, by the method of Hodgson and Kilner (J., 1924, **125**, 807), into 2-nitro-1-naphthol, reduction of which by a modification of known methods (Liebermann and Dittler, *Ber.*, 1874, **7**, 240; Liebermann, *Annalen*, 1876, **183**, 225; Liebermann and Jacobsen, *Annalen*, 1882, **211**, 36; Grandmougin and Michel, *Ber.*, 1892, **25**, 972) gave 2-amino-1-naphthol hydrochloride. Contrary to a statement that this salt undergoes no smooth reactions (Grandmougin and Michel, *loc. cit.*), a 52% yield of 1-*methyl-α-naphthoxazole* has been obtained from it. The same synthesis of the base has been outlined by Brooker (U.S.P. 1,939,201, 1932). Both it and also 2-methyl-β-naphthoxazole, which is described in the literature as a liquid, have now been obtained in the solid state. Their *methiodides* and *ethiodides* were prepared. Just as the quaternary salts of 1-methyl-α-naphthathiazole are more readily formed than those of 2-methyl-β-naphthathiazole (Hamer, J., 1929, 2598), so, similarly, those of 1-methyl-α-naphthoxazole are produced more readily than those of 2-methyl-β-naphthoxazole. From these alkiodides the *dibenzoxacyanines* (II and III) were prepared.

Solutions of the dibenzoxacyanines are very pale yellow; comparison with the parent oxacyanines (I; Y = O) shows that the replacement of two benzoxazole by two naphthoxazole nuclei has the effect of shifting the absorption maximum 25—40 μμ towards the region of longer wave-length. The absorption maxima recorded are those of methyl-alcoholic solutions; we are indebted for the measurements to Messrs. L. A. Jones and E. E. Richardson, of the Eastman Kodak Company.

The simplest oxacyanines have a practically negligible photographic effect, producing only in gelatino-chloride emulsions an extremely slight shift of the sensitising maximum towards the region of longer wave-length. The dibenzoxacyanines, on the other hand, are very powerful sensitisers for such emulsions, thus bringing the oxacyanines into line with other classes of cyanines, all groups of which contain photographic sensitisers. The sensitising maximum is shifted from λ 395 $\mu\mu$ to λ 423—433 $\mu\mu$. This difference in behaviour of the simplest and the more complex oxacyanines is correlated with the fact that the absorption maxima of the former fall within, and those of the latter beyond, the spectral region of absorption of the untreated emulsion.

For the six oxacyanines described in the present paper, the yields of recrystallised product vary from 14—26%. The yields are lowest in the case of the oxacyanines from 2-methyl-β-naphthoxazole alkiodides; this tallies with the thia-series, where (Hamer, J., 1929, 2598; Fisher and Hamer, J., 1930, 2502) the yields of dyes from quaternary salts of 2-methyl-β-naphthathiazole are, as a rule, lower than those from the corresponding salts of 1-methyl-α-naphthathiazole. The oxacyanines, especially the pair containing α-naphthoxazole nuclei, are characterised by possessing high decomposition points.

EXPERIMENTAL.

2-*Nitro*-1-*naphthol from α-Naphthol*.—To obtain the mixture of 2- and 4-nitroso-1-naphthol, α-naphthol (50 g.), dissolved in sodium hydroxide solution, was treated with nitrous acid according to the method of Hodgson and Kilner (*loc. cit.*). The total yield of purified mixture obtained from 3 or 4 such preparations was 80%. When a paste of the mixed nitrosonaphthols (100 g.) is oxidised, on ten times their scale, with hydrogen peroxide in the presence of ferrous sulphate, such a violent reaction occurs at one point during the addition of sodium hydroxide that it is advisable to use a 2-gallon earthenware pot, but without external cooling. 2-Nitro-1-naphthol (yield, 38%) was isolated by distillation with superheated steam; the yield obtained from the distillate was slightly increased by acidification with hydrochloric acid.

2-*Amino*-1-*naphthol Hydrochloride*.—An intimate mixture of 2-nitro-1-naphthol (20 g.) and fine tin powder (60 g.) was heated with concentrated hydrochloric acid (160 c.c.), carefully until decoloration was nearly complete, and then strongly for ½ hour. The tin double salt of 2-amino-1-naphthol hydrochloride, which separated on cooling, was collected and dissolved in boiling water, the filtered solution treated with hydrogen sulphide, tin sulphide removed, and the filtrate concentrated in an open dish, hydrogen sulphide being passed in continuously. A dark solid separated, but the solution itself did not darken appreciably. It was filtered, cooled, and treated with concentrated hydrochloric acid until no more solid separated. The almost white hydrochloride was filtered off and dried; it showed no sign of decomposition when kept for several weeks in a stoppered bottle. The yield was 56%.

1-*Methyl-α-naphthoxazole*.—2-Amino-1-naphthol hydrochloride (57 g.; 1 mol.) and anhydrous sodium acetate (24 g.; 1 mol.) were ground together, and then heated with acetic anhydride (55 c.c.) at 150—160° for 8 hours. The excess of acetic anhydride was distilled off, and the residue treated with water and neutralised with crystalline sodium carbonate. The base obtained from two such preparations was extracted and dried (anhydrous sodium sulphate) in ether, recovered, and distilled in a vacuum, 1-*methyl-α-naphthoxazole* being obtained in 56% yield, b. p. 178—201°/18—20 mm.; a higher-boiling fraction was rejected. The yield was considerably lower when acetic acid was used in conjunction with the acetic anhydride and sodium acetate. The base crystallised to a white solid, m. p. 36—37°, with softening from 33° (Found: N, 7·6. $C_{12}H_9ON$ requires N, 7·65%). The molten base shows the phenomenon of super-cooling, and crystallisation is accompanied by evolution of heat.

2-Methyl-β-naphthoxazole has been described as a liquid by Böttcher (*Ber.*, 1883, **16**, 1933), Michel and Grandmougin (*Ber.*, 1892, **25**, 3429), and Lindemann, Könitzer, and Romanoff (*Annalen*, 1927, **456**, 284). Its preparation from 1-amino-2-naphthol hydrochloride, by a method similar to that described above for the α-compound, gave it as an almost colourless solid, m. p. 27°, with softening from 25° (Found: N, 7·75. Calc. for $C_{12}H_9ON$: N, 7·65%).

1-*Methyl-α-naphthoxazole Methiodide*.—1-Methyl-α-naphthoxazole (8·6 g.; 1 mol.) and methyl iodide (3·5 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 2 days. After ether extraction, the residual solid was ground three times with acetone (30 c.c. × 3);

after recrystallisation of the undissolved residue (13·9 g.; 87% yield) from absolute alcohol (150 c.c.), the yield was 65% (10·2 g.). A sample was dried for analysis in a vacuum at 60—80° and was analysed by the method of Carius, which methods of drying and analysis were used throughout this work, except where otherwise stated (Found: I, 39·3. $C_{13}H_{12}ONI$ requires I, 39·05%). M. p. 202° (decomp.).

1-*Methyl*-α-*naphthoxazole ethiodide* was similarly prepared. The yield was 88% after washing with acetone and 62% after recrystallisation from absolute alcohol (12 c.c. per g.). This and the two following salts were dried for analysis in a vacuum desiccator (Found: I, 37·7. $C_{14}H_{14}ONI$ requires I, 37·4%). M. p. 215° (decomp.).

2-*Methyl*-β-*naphthoxazole Methiodide.*—2-Methyl-β-naphthoxazole (10 g.; 1 mol.) was heated with methyl iodide (4 c.c.; 1·2 mols.) in a sealed tube at 100° for 2 days. After extraction with ether, the undissolved residue (17 g.) amounted to an 89% yield (Found: I, 39·2. $C_{13}H_{12}ONI$ requires I, 39·1%). Even when recrystallisation from absolute alcohol (400 c.c.) was carried out as rapidly as possible, the yield dropped to 38% (Found: I, 39·1%). M. p. 212—213° (decomp.), with softening from 209°.

2-*Methyl*-β-*naphthoxazole Ethiodide.*—When a similar preparation was carried out with ethyl iodide, the addition did not proceed to completion. The crystals were collected and extracted with ether. The undissolved residue (2·0 g.) amounted to only a 22% yield (Found: I, 37·5. $C_{14}H_{14}ONI$ requires I, 37·4%). On rapid recrystallisation from absolute alcohol (40 c.c.), the yield dropped to 11% (Found: I, 37·0%). M. p. 202—203° (decomp.). From the original filtrate and from the ethereal extract, a 33% yield of 2-methyl-β-naphthoxazole was recovered.

2 : 2′-*Dimethyloxacyanine Iodide.*—1-Methylbenzoxazole methiodide (3·5 g.) was added to boiling acetic anhydride (25 c.c.). No further heat was applied, but freshly distilled amyl nitrite (1·5 c.c.; b. p. 94—100°) was added. There was violent frothing with development of a brown colour, and all the quaternary salt dissolved. On cooling and stirring, the *oxacyanine* crystallised. It was filtered off, ground with water, and extracted with ether. The undissolved residue (0·74 g.) was suspended in spirit (10 c.c.) and, during cooling with ice, sulphur dioxide was passed in. The suspension was then boiled and stirred, and sufficient spirit for complete solution was added (100 c.c.). The solid which crystallised on cooling was almost colourless. It was obtained in 23% yield (0·59 g.). It was dried for analysis in a vacuum at 100—110° (Found: I, 31·0. $C_{17}H_{15}O_2N_2I$ requires I, 31·3%). When heated to 310°, the compound remained unmelted, though there were signs of decomposition. The methyl-alcoholic solution has a single absorption band with its maximum at λ 365 μμ.

2 : 2′-*Diethyloxacyanine Iodide.*—When 1-methylbenzoxazole ethiodide (3·5 g.) was added to propionic anhydride (25 c.c.) at 135°, most of the solid dissolved. Solution was complete when freshly distilled amyl nitrite (1·5 c.c.) was added. After extraction of the crystalline product with water and with ether, the undissolved residue (0·78 g.) was suspended in spirit (10 c.c.) and treated in the cold with sulphur dioxide, and more spirit (40 c.c.) was added for the recrystallisation. The yield (0·74 g.) was 28% (Found: I, 29·2. $C_{19}H_{19}O_2N_2I$ requires I, 29·2%). M. p. 301° (decomp.). The absorption maximum lies at λ 370 μμ.

2 : 2′-*Dimethyl*-5 : 6 : 5′ : 6′-*dibenzoxacyanine Iodide.*—The crude dye obtained by the action of amyl nitrite and acetic anhydride on 1-methyl-α-naphthoxazole methiodide (3·5 g.) was ground with water and extracted with ether. Although the undissolved residue (0·86 g.) was almost colourless, its methyl-alcoholic suspension (10 c.c.) was treated with sulphur dioxide, after which recrystallisation from methyl alcohol (1500 c.c.) was effected. The yield was 17% (0·47 g.) (Found: I, 25·1. $C_{25}H_{19}O_2N_2I$ requires I, 25·1%). The substance remained unmelted at 320°, though decomposition was just beginning. The crest of the absorption band is at λ 395 μμ, but it is surprising that there is another strong band at λ 240 μμ and a weaker one at λ 295 μμ.

2 : 2′-*Diethyl*-5 : 6 : 5′ : 6′-*dibenzoxacyanine Iodide.*—The crude dye from 1-methyl-α-naphthoxazole ethiodide (1·75 g.) was washed with water and with ether and the undissolved residue (0·46 g.) was suspended in spirit, treated with sulphur dioxide, and then recrystallised from spirit (550 c.c.). The crystals were obtained in 26% yield (0·35 g.) (Found: I, 21·7. $C_{27}H_{23}O_2N_2I$ requires I, 23·8%). Melting had not occurred at 315°, though there were signs of decomposition. The absorption is similar to that of the preceding compound.

2 : 2′-*Dimethyl*-3 : 4 : 3′ : 4′-*dibenzoxacyanine Iodide.*—2-Methyl-β-naphthoxazole methiodide (2·5 g.) was added to boiling acetic anhydride. On addition of amyl nitrite, the salt did not all dissolve; the mixture was therefore again brought to the boiling point and again treated with amyl nitrite. The crude product was purified by washing with water and with ether.

The undissolved residue (0·65 g.) was suspended in methyl alcohol and treated with sulphur dioxide, the dark brown solid becoming golden-yellow. More boiling methyl alcohol (490 c.c.) was added for solution. The yield of recrystallised product was 14% (0·38 g.) (Found : I, 24·8. $C_{25}H_{19}O_2N_2I$ requires I, 25·1%). M. p. 291° (decomp.). The absorption maximum is at λ 405 μμ.

2 : 2′-*Diethyl*-3 : 4 : 3′ : 4′-*dibenzoxacyanine iodide* was prepared from 2-methyl-β-naphthoxazole ethiodide (1·75 g.). The crude product (0·53 g.; 38% yield) changed from brown to yellow when its spirit suspension was treated with sulphur dioxide. After recrystallisation from spirit (200 c.c.), the yield was 14% (Found : I, 23·65. $C_{27}H_{23}O_2N_2I$ requires I, 23·8%). M. p. 283° (decomp.), with previous shrinking. The absorption maximum lies at λ 402 μμ.

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