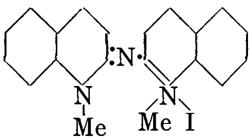
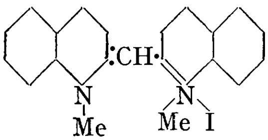
186. *Azacyanines.*

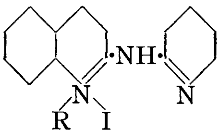
By Nellie I. Fisher and Frances M. Hamer.

Although many varieties of cyanine dyes are known, there have only been two scientific publications giving preparative details of those related compounds in which one or more of the methenyl groups, which form the chain linking the heterocyclic nuclei, are replaced by one or more nitrogen atoms (Hamer, J., 1924, **125**, 1348; Fuchs and Grauaug, *Ber.*, 1928, **61**, 57). Patents making comprehensive claims with regard to substances of this type have recently appeared (Kendall, B.P. 447,038 and 447,109/1936; cf. *Proc. Ninth Int. Congr. Phot.*, 1936, 227), so that it seems desirable to place on record an account of independent work, in which certain compounds of this kind have been studied from a different angle.

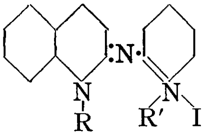
Whereas the synthesis of 1 : 1′-dimethyl-2 : 2′-azacyanine * iodide (I) was a five-stage process, starting from 2-chloroquinoline and 2-aminoquinoline (Hamer, *loc. cit.*), the 2 : 2′-cyanine (II) was more simply prepared, by condensation of 2-iodoquinoline methiodide with quinaldine methiodide (Fischer and Scheibe, *J. pr. Chem.*, 1920, **100**, 86), and this method proved capable of extension to the preparation of other types of 2′-cyanines (Hamer, J., 1928, 206; 1930, 995; Hamer and Kelly, J., 1931, 777; Fisher and Hamer, J., 1934, 1905; Brooker and Keyes, *J. Amer. Chem. Soc.*, 1935, **57**, 2488; Brooker, Keyes, and White, *ibid.*, p. 2492; Brooker, *ibid.*, 1936, **58**, 662).

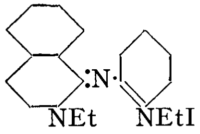

(I.)


(II.)


(III.)

The preparation of azacyanines has now been simplified, so that it has proved possible to prepare various types, for comparison with the appropriate 2′-cyanines. For instance, 2-iodoquinoline alkiodide was condensed with 2-aminopyridine to give 2-2′-*pyridylamino-quinoline alkiodide* (III). Removal of hydriodic acid, and treatment of the product with alkyl iodide, resulted in a 2-*pyrido*-2′-*azacyanine* (IV), three of which were prepared.


(IV.)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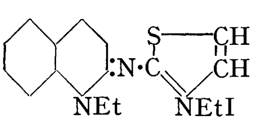
(VI.)

From 1-iodo*iso*quinoline ethiodide (Fisher and Hamer, J., 1934, 1905) and 2-amino-pyridine, a 2-*pyrido*-1′-*azacyanine* (V) was synthesised, and, from 2-iodoquinoline ethiodide and 2-aminothiazole, a *thiazolo*-2′-*azacyanine* (VI).

The absorption curve of a methyl-alcoholic solution of an azacyanine of each type was plotted, the diethyl compound being chosen in each instance. The maximum of the 2-pyrido-2′-azacyanine (IV; R = R′ = Et) lies 80 A. to the short wave-length side of that of the closely related 2-pyrido-1′-azacyanine (V). It has already been recorded that the principal absorption maximum of the 2 : 2′-azacyanine (I) lies 990 A. nearer to the region

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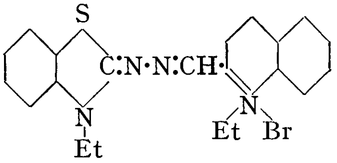
* Preferable to the original term "azocyanine."

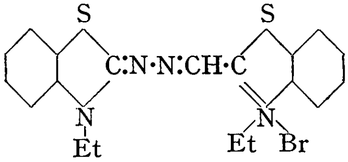
of short wave-length than does that of the 2 : 2′-cyanine (II) (Hamer, J., 1924, **125**, 1348). Two more values, 1020 A. and 700 A., respectively, are now obtained for the shift towards the blue caused by replacing by :N· the :CH· group, which links the nuclei in a 2′-cyanine : the former value by comparison of (IV) with 1 : 1′-diethyl-2-pyrido-2′-cyanine iodide, prepared from 2-iodopyridine ethiodide and quinaldine ethiodide by Hamer and Kelly (*loc. cit.*), the latter by comparison of (VI) with 3 : 1′-diethylthiazolo-2′-cyanine iodide, as recorded by Brooker, Keyes, and White (*loc. cit.*).

It should have been specified that the observation of one of us that the 2 : 2′-azacyanine (I) has no action on a photographic plate (Hamer, *loc. cit.*) was in fact confined to a gelatino-bromide plate; towards a gelatino-chloride plate it acts as a sensitiser, as noted by Kendall (*loc. cit.*). Of the three compounds represented by (IV), one confers a certain extra-sensitivity upon a gelatino-chloride photographic emulsion, but the other two extend the sensitivity so slightly that no maximum can be recorded. The 2-pyrido-1′-azacyanine (V) is without sensitising action, and the thiazolo-2′-azacyanine (VI) confers extra-sensitivity.

The method of Fuchs and Grauaug (*loc. cit.*) for preparing dyes, in which the two heterocyclic nuclei are linked by a three-membered chain :N·N:CH· (or ·N:N·CH:, since virtual tautomerism doubtless occurs in this series, as in the cyanines), consisted in condensing 2-ethylbenzthiazolonehydrazone, etc., with the aldehyde of the quaternary salt of a heterocyclic base, liberated from the corresponding *p*-dialkylaminoanil by the method of Kaufmann and Vallette (*Ber.*, 1912, **45**, 1736). The same method was followed in preparing three new compounds (VII—IX) of this kind. By an extension of the nomenclature which has already been used, these compounds are designated as diazacarbocyanines. The positions of the nitrogen atoms in the three-membered chain are counted from that nucleus which is mentioned first. Thus (VII) represents an *αβ-diazathia-2′-carbocyanine*, (VIII) an *αβ-diazadithiacarbocyanine*, and (IX) a *βγ-diazaselenathiacarbocyanine*.

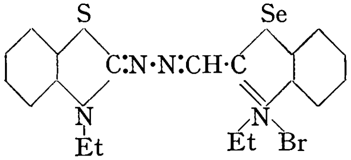
(VII.)

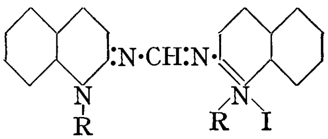




(VIII.)

(IX.)





(X.)

In (X), the three individual units of the chain joining the nuclei are the same as in (VII—IX), but they are arranged in a different order, :N·CH:N·. Two of these *αγ-diaza-2 : 2′-carbocyanines* have been prepared, by the action of ethyl orthoformate, in the presence of pyridine, on 2-aminoquinoline alkiodide, but the yields are much lower than those of the 2 : 2′-carbocyanines, obtained by reaction of ethyl orthoformate and pyridine with quinaldine alkiodide (Hamer, J., 1927, 2796).

With each of the three new dyes containing the chain :N·N:CH·, the principal absorption band of a methyl-alcoholic solution lies nearer to the region of short wave-length than does a secondary, ill-defined, band, whereas in true cyanines possessing a secondary absorption band, the reverse is usual (cf. Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703). To determine the effect of replacing the carbocyanine chain, :CH·CH:CH·, by the chain :N·N:CH·, the positions of the maxima of the principal absorption bands were compared. Thus that of (VII) was compared with that of the thia-2′-carbocyanine, which has already been described by Ogata (*Bull. Inst. Phys. Chem. Res.*, 1934, **13**, 556), and which we prepared by a different modification of the original method of I.C.I. Ltd., Piggott, and Rodd (B.P. 344,409/1929; B.P. 354,898/1930); the principal absorption maximum of (VIII) was compared with that which we have recorded for 2 : 2′-diethylthiacarbocyanine iodide (Fisher and Hamer, *loc. cit.*), and the maximum of (IX) with that of the selenathiacarbocyanine, which we made for this purpose. With all three pairs, the compound with the chain :N·N:CH· was found to have its principal absorption maximum at a shorter wave-length than that of the compound with the chain :CH·CH:CH·, the values of the differences being 800, 770, and 820 A., respectively.

All the five original compounds of this αβ (or βγ)-diazacarbocyanine type were described by Fuchs and Grauaug as powerful photographic desensitisers. Of our new substances, (IX) is a powerful desensitiser, whilst (VII) and (VIII) considerably depress the original blue-sensitivity of a gelatino-bromide photographic emulsion, but at the same time confer a weak extra-sensitivity to green light. When the chain :N·N:CH· of (VII—IX) is replaced by :CH·CH:CH·, the resultant carbocyanines are, on the contrary, powerful sensitisers.

When the absorption maximum of compound (X) is compared with that which we have recorded for 1 : 1′-diethyl-2 : 2′-carbocyanine iodide, containing the chain :CH·CH:CH· (Fisher and Hamer, *loc. cit.*), the former is found to lie at a shorter wave-length, by 2620 A., than the latter. Thus in replacing the chain :CH·CH:CH·, the αγ-diazacarbocyanine chain has a much more powerful hypsochromic effect than has the αβ(or βγ)-diazacarbocyanine chain.

The diethyl compound (X; R = Et) depresses the blue sensitivity of a gelatino-bromide photographic emulsion, and weakly sensitises a chloride emulsion, whilst the dimethyl compound (X; R = Me) is photographically inert.

We have adopted a suggestion by Dr. F. Richter as to the desirability of inserting the systematic name of each cyanine described, as in the 1936 edition of Beilstein's " Handbuch der organischen Chemie." We are very grateful to Dr. Clarence Smith for his helpful consideration of, and discussion of, the nomenclature.

EXPERIMENTAL.

2-2′-*Pyridylaminoquinoline Ethiodide* (III; R = Et).—2-Iodoquinoline ethiodide (11 g.; 1 mol.) and excess of 2-aminopyridine (5 g.; 2 mols.) were boiled and stirred with absolute alcohol (50 c.c.) for 15 minutes, during which time solution occurred. The yellow crystalline product was ground with water and obtained in 46% yield (4·69 g.). After recrystallisation from water (200 c.c.) the yield was 38% (3·88 g.). A sample was dried in a vacuum at 80—100° and analysed by the method of Carius, which method of analysis was used throughout this work, except where otherwise stated (Found: I, 33·6. $C_{16}H_{16}N_3I$ requires I, 33·7%). M. p. 216°.

2-2′-*Pyridylaminoquinoline methiodide* (III; R = Me) was similarly prepared (64% yield) from 2-iodoquinoline methiodide and 2-aminopyridine; after extraction with ether, the residue was twice recrystallised from water (10 c.c. per g.) and obtained in 30% yield (Found in material dried at 80—100°: I, 34·9. $C_{15}H_{14}N_3I$ requires I, 34·95%). M. p. 206°, with softening from 202°.

1 : 1′-*Diethyl-2-pyrido-2′-azacyanine Iodide* (IV; R = R′ = Et), or (1-*Ethyl-2-pyridine*)(1-*ethyl-2-quinoline*)*azamethincyanine Iodide*.—2-2′-Pyridylaminoquinoline ethiodide (5 g.; 1 mol.) and powdered crystalline sodium carbonate (7·6 g.; 2 mols.) were boiled with water (50 c.c.) for 15 minutes. The brown oil which separated was extracted with ether. After removal of the solvent from the dried extract, the oily residue was heated on the water-bath with ethyl iodide (1·3 c.c.; 1·2 mols.) for an hour. The resultant solid was washed with ether (4·16 g. obtained) and recrystallised from methyl alcohol (15 c.c.). The yield (3·25 g.) was 61%. The substance was dried in a vacuum at 60—80° and this method of drying was used except where otherwise stated (Found: I, 31·4. $C_{18}H_{20}N_3I$ requires I, 31·3%). M. p. 240°. The absorption maximum of a methyl-alcoholic solution of the pale yellow crystals lay at 3930 A.

1-*Methyl*-1′-*ethyl-2-pyrido-2′-azacyanine Iodide* (IV; R = Et, R′ = Me), or (1-*Methyl-2-pyridine*)(1-*ethyl-2-quinoline*)*azamethincyanine Iodide*.—In an experiment similar to the preceding one, the oily base was heated with methyl iodide (1·2 c.c.; 1·2 mols.). After washing with ether, the pale yellow product (3·70 g.) was recrystallised from methyl alcohol (15 c.c.); the yield (3·2 g.) was then 61% (Found after a second recrystallisation: I, 32·4. $C_{17}H_{18}N_3I$ requires I, 32·5%). M. p. 232°.

1 : 1′-*Dimethyl-2-pyrido-2′-azacyanine Iodide* (IV; R = R′ = Me), or (1-*Methyl-2-pyridine*)(1-*methyl-2-quinoline*)*azamethincyanine Iodide*.—2-2′-Pyridylaminoquinoline methiodide with sodium carbonate solution gave an oil, which with methyl iodide gave a 69% yield of the *azacyanine*. After recrystallisation from methyl alcohol (10 c.c. per g.), the yield of bright yellow product was 52% (Found: I, 33·6. $C_{16}H_{16}N_3I$ requires I, 33·7%). M. p. 258°. Upon a chloride emulsion it confers weak extra-sensitivity, with a maximum at 4250 A.

1 : 2′-*Diethyl*-2-*pyrido*-1′-*azacyanine Iodide* (V), or (1-*Ethyl*-2-*pyridine*)(2-*ethyl*-1-iso*quinoline*) *azamethincyanine Iodide*.—After 1-iodo*iso*quinoline ethiodide and 2-aminopyridine had been heated together in alcohol, ether precipitated an oil, which was heated with sodium carbonate solution. The product was taken up in ether and, after removal of the solvent from the dried extract, was heated with ethyl iodide. The yield was 19% after the yellow solid had been washed with ether, and 14% after it had been recrystallised from methyl alcohol (2 c.c. per g.) (Found : I, 31·7. Found after a second recrystallisation : I, 31·3. $C_{18}H_{20}N_3I$ requires I, 31·3%). The pale yellow product, m. p. 213°, gives an absorption maximum at λ3850 A.

3 : 1′-*Diethylthiazolo*-2′-*azacyanine Iodide* (VI), or (3-*Ethyl*-2-*thiazole*)(1-*ethyl*-2-*quinoline*)*azamethincyanine Iodide*.—2-Iodoquinoline ethiodide and 2-aminothiazole were condensed, the product treated with sodium carbonate, and the base obtained from it heated with ethyl iodide. After washing with ether, crystals were obtained in 20% yield and, after recrystallisation from methyl alcohol (10 c.c. per g.), in 16% yield (Found : I, 30·85. $C_{16}H_{18}N_3IS$ requires I, 30·9%). The bright yellow substance had m. p. 239°. Its absorption maximum is at λ3950 A. and it confers upon a chloride emulsion extra-sensitivity with a maximum at 4350 A.

2 : 1′-*Diethyl*-αβ-*diazathia*-2′-*carbocyanine Bromide* (VII), or (1-*Ethyl*-2-*quinoline*)(2-*ethyl*-1-*benzthiazole*)-αβ-*diazatrimethincyanine Bromide*.—The *p*-dimethylaminoanil of quinaldinealdehyde ethobromide (cf. Kaufmann and Vallette, *loc. cit.*) (1·99 g. ; 1 mol.) was treated with cold dilute hydrochloric acid (8 c.c. of concentrated acid + 8 c.c. of water) and into the mixture was stirred 2-ethylbenzthiazolonehydrazone (Fuchs and Grauaug, *loc. cit.*) (1 g. ; 1 mol.). The whole was boiled for 1 minute and then treated with a hot solution of sodium bromide (8 g.) in water (16 c.c.). The precipitated product was filtered off, washed with water, dried in a vacuum desiccator, powdered, and washed with ether. The undissolved residue (1·80 g. ; 79% yield) was recrystallised from dilute methyl alcohol (50% ; 4 c.c.), the yield then being 62% (1·42 g.) (Found : Br, 18·05. $C_{21}H_{21}N_4BrS$ requires Br, 18·1%). The brown crystals melted at 221° (decomp.). The principal absorption maximum of the methyl-alcoholic solution lies at λ4800, with an ill-defined weaker one at 5050 A. Whilst considerably depressing the blue sensitivity of a gelatino-bromide plate, the substance confers weak extra-sensitivity, which extends to 5800 A. for moderate exposures.

2 : 2′-*Diethyl*-αβ-*diazadithiacarbocyanine bromide* (VIII), or *bis*-(2-*ethyl*-1-*benzthiazole*)-αβ-*diazatrimethincyanine bromide*, was similarly prepared from the *p*-dimethylaminoanil of benzthiazole-1-aldehyde ethochloride (cf. Bloch and Hamer, *Phot. J.*, 1930, **70**, 374) and 2-ethylbenzthiazolonehydrazone. The washed product (67% yield) was recrystallised from dilute methyl alcohol (1·5 c.c. of methyl alcohol and 6 c.c. of water per g.), the yield then being 59%. It was recrystallised a second time before analysis (Found : Br, 17·6. $C_{19}H_{19}N_4BrS_2$ requires Br, 17·9%). M. p. 219° (decomp.), but shrinking began at *ca.* 120°. The brick-red substance has its absorption maxima in the same positions as has the preceding substance. It depresses the blue sensitivity of a photographic plate and confers weak green sensitivity, extending to 5700 A. for moderate exposures.

p-*Dimethylaminoanil of Benzselenazole*-1-*aldehyde Ethobromide*.—1-Methylbenzselenazole ethobromide (4 g. ; 1 mol.), *p*-nitrosodimethylaniline (1·97 g. ; 1 mol.), absolute alcohol (25 c.c.), and piperidine (4 drops) were boiled together for 3 hours. The product was filtered off, washed with ether, and recrystallised from methyl alcohol (22 c.c. per g.), being obtained in 26% yield (1·48 g.). Halogen in the presence of selenium was determined as described elsewhere (Hamer, *Analyst*, 1933, **58**, 26) (Found : Br, 17·6. $C_{18}H_{20}N_3BrSe,\frac{1}{2}CH_3{\cdot}OH$ requires Br, 17·6%). M. p. 225° (decomp., starting from 140°). The green crystals, when dissolved in methyl alcohol, give a broad absorption band, with its maximum at 5600 A. Like various other anils of this kind (Hamer, *Phot. J.*, 1929, **69**, 409; Bloch and Hamer, *loc. cit.*), the compound is a photographic desensitiser.

2 : 2′-*Diethyl*-βγ-*diazaselenathiacarbocyanine Bromide* (IX), or (2-*Ethyl*-1-*benzthiazole*)(2-*ethyl*-1-*benzselenazole*)-αβ-*diazatrimethincyanine Bromide*.—The washed product obtained (in 75% yield) from the above anil and 2-ethylbenzthiazolonehydrazone was recrystallised from methyl alcohol (13 c.c. per g.) and resulted in 30% yield (Found : Br, 16·15. $C_{19}H_{19}N_4BrSSe$ requires Br, 16·2%). The dull red crystals had m.p . 259° (decomp.). The principal absorption maximum is at 4800 A., with a weaker one at 5100 A. The substance possesses photographic desensitising properties.

2 : 1′-*Diethylthia*-2′-*carbocyanine Iodide*, or (1-*Ethyl*-2-*quinoline*)(2-*ethyl*-1-*benzthiazole*)*trimethincyanine Iodide*.—Ogata's method (*loc. cit.*) was to condense 2-β-anilinovinylquinoline ethiodide with 1-methylbenzthiazole ethiodide, in the presence of acetic anhydride and potassium acetate. In the present preparation, quinaldine ethiodide (4·98 g. ; 1 mol.), 1-β-acetanilidovinyl-

benzthiazole ethiodide (7·5 g.; 1 mol.), anhydrous sodium acetate (1·5 g.), and acetic anhydride (36 c.c.) were boiled together for 1 hour. The product was filtered off and ground with ether and then with water (3·86 g.; 48% yield). A fractional crystallisation from methyl alcohol (100 c.c. × 3) effected the removal of the symmetrical 2 : 2′-carbocyanine in the last fraction, and the yield of pure dye from the first two fractions was 34% (2·73 g.) (Found: I, 26·2. Calc. for $C_{23}H_{23}N_2IS$: I, 26·1%). On heating, the green crystals lost solvent and melted at 248° (decomp.). Ogata gives m. p. 277°. The absorption maximum is at 5600 A.

2 : 2′-*Diethylselenathiacarbocyanine Iodide*, or (2-*Ethyl*-1-*benzthiazole*)(2-*ethyl*-1-*benzselenazole*)-*trimethincyanine Iodide*.—This was similarly prepared from 1-β-acetanilidovinylbenzselenazole ethiodide, 1-methylbenzthiazole ethiodide, sodium acetate, and acetic anhydride. The washed product (52% yield) was recrystallised from methyl alcohol (70 c.c. per g.) and thus obtained in 34% yield (Found: I, 23·3. $C_{21}H_{21}N_2ISSe$ requires I, 23·5%). The dull green crystals have m. p. 257° (decomp.). The absorption maximum lies at 5620 A.

1 : 1′-*Diethyl*-αγ-*diaza*-2 : 2′-*carbocyanine Iodide* (X; R = Et), or *Bis*-(1-*ethyl*-2-*quinoline*)-αγ-*diazatrimethincyanine Iodide*.—2-Aminoquinoline ethiodide (3 g.; 2 mols.), ethyl orthoformate (3·6 c.c.; 4 mols.), and pyridine (15 c.c.) were boiled together under reflux for 1 hour, after which the reaction mixture was treated with hot water (30 c.c.). The product obtained on cooling was filtered off, washed with water, and dried (0·80 g.; 33% yield). After recrystallisation from water (250 c.c.), the yield (0·60 g.) was 25%. It was dried for analysis in a vacuum at 80—90° (Found: I, 26·3. $C_{23}H_{23}N_4I$ requires I, 26·3%). The orange powder has m. p. 209°, with previous softening. The absorption maximum lies at λ3430 A. Its sensitising action on a chloride emulsion is very weak, with a maximum at 5000 A.

1 : 1′-*Dimethyl*-αγ-*diaza*-2 : 2′-*carbocyanine Iodide* (X; R = Me), or *Bis*-(1-*methyl*-2-*quinoline*)-αγ-*diazatrimethincyanine Iodide*.—The washed product (36% yield) similarly obtained from 2-aminoquinoline methiodide, ethyl orthoformate, and pyridine was recrystallised from water (270 c.c. per g.), being obtained in 17% yield. It was dried for analysis as in the preceding case (Found: I, 28·3. $C_{21}H_{19}N_4I$ requires I, 28·0%). The yellow powder melts at 193°.

We are deeply indebted to our colleagues Dr. E. P. Davey, Mr. R. B. Morris, and Dr. A. S. Roy for furnishing the absorption and sensitising data recorded in this paper.

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