QUARTERLY REVIEWS

THE CYANINE DYES

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Early Work.—In 1856 C. G. Williams obtained the blue dye, cyanine, by the action of caustic alkali on a quaternary quinolinium salt.[1] Years later, it was recognised that this quinoline contained its 4-methyl homologue, lepidine,[2] and shown [3, 4] that it was the mixture of ethiodides that gave rise to cyanine, according to the equation:

$$C_9H_7N,C_2H_5I + C_{10}H_9N,C_2H_5I = C_{23}H_{23}N_2I + H_2 + HI$$

A mixture of the ethiodides of quinoline and its 2-methyl homologue, quinaldine, gave the redder *iso*cyanine.[4,5] The structures of the molecules were considered [5–7] and it was proved that in *iso*cyanine formation the 2-methyl group of quinaldine [8] and the 4-position of quinoline [9] are involved. The present-day structures (III and II) for cyanine and *iso*cyanine were suggested as a possibility in 1906,[10] though open-chain formulæ were regarded as more probable.[11]

Practical Applications.—Cyanine has no value for dyeing fabrics, because of its instability to light, but in 1873 H. W. Vogel discovered the phenomenon of photographic sensitisation by dyes,[12] amongst them cyanine,[13] and all the modern achievements of photography are its outcome. It is remarkable that, except for erythrosin, sensitisers of value are drawn only from the cyanine and related groups, out of the myriad known dyes.

A gelatino silver chloride photographic emulsion, such as is used for papers, is sensitive, according to its wedge spectrogram, only from 3500 to 4500 A. (Plate 1*A*); a bromide emulsion, such as is used for films and plates, is sensitive only from 3500 to 5300 A. (Plate 1*B*), but bathing it in a solution of cyanine conferred sensitivity to green light (Plate 1*C*). As cyanine also fogged emulsions, it appeared of solely academic interest until 1903, when

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[1] *Trans. Roy. Soc. Edinburgh*, 1856, **21**, 377; *Chem. News*, 1859, **1**, 15; 1860, **2**, 219.

[2] A. W. Hofmann, *Proc. Roy. Soc.*, 1863, **12**, 410.

[3] S. Hoogewerff and W. A. van Dorp, *Rec. Trav. chim.*, 1883, **2**, 28, 41.

[4] *Idem, ibid.*, p. 317, and 1884, **3**, 337.

[5] W. Spalteholz, *Ber.*, 1883, **16**, 1847.

[6] H. Decker, *ibid.*, 1891, **24**, 690.

[7] A. Miethe and G. Book, *ibid.*, 1904, **37**, 2008.

[8] E. Vongerichten and C. Höfchen, *ibid.*, 1908, **41**, 3054.

[9] A. Kaufmann and E. Vonderwahl, *ibid.*, 1912, **45**, 1404.

[10] W. König, *J. pr. Chem.*, 1906, [ii], **73**, 100.

[11] *Idem, ibid.*, 1912, [ii], **86**, 166.

[12] *Ber.*, 1873, **6**, 1302.

[13] *Ibid.*, 1875, **8**, 1635.

*iso*cyanines (Plate 1*D*) were observed to sensitise without fogging.[14] On this followed German patents, largely the work of E. König ; they covered *iso*cyanines into which substituents had been introduced in order to improve sensitising, or in which the acid radical had been altered so as to increase the solubility.[15] By carrying out an *iso*cyanine condensation in the presence of formaldehyde, there resulted pinacyanol,[16] the first sensitiser to red light (Plate 1*E*).

As observed by H. W. Vogel,[17] the sensitising maximum of a dye approximates to the absorption maximum of its solution but lies at a somewhat longer wave-length ; it has recently been explained that the sensitising maximum is the same as the absorption maximum of dyed silver bromide,[18] and close correspondence between the sensitising curve and this absorption curve has been established.[19]

By means of sensitising dyes, in conjunction with light filters, plates can now be made having the same sensitivity as the eye, can be made equally sensitive to the whole visible spectrum, can be sensitised to any desired part of it, which fact is utilised in colour photography, or may even be sensitised to the near infra-red. In distance photography, as in taking photographs from aeroplanes, sensitisation to red or infra-red light is essential, because the atmosphere scatters badly light of shorter wave-length. At the outbreak of the first World War, however, all sensitisers were made in Germany ; through submission of the problem to Sir William Pope, those required by the Allies were prepared in the University of Cambridge and the chemistry of the cyanines was placed on a scientific basis by the work of W. H. Mills and his pupils.

Scientific Foundation.—On the scientific foundation, laid in the decade beginning with 1920, a worthy superstructure was built in the following twenty years. By oxidative breakdown, the constitution of *iso*cyanine had been established as (II),[20] and received confirmation,[21, 22] the open-chain formula being disproved ; [23] it followed that the closely related cyanine must be represented by (III).[20] Unlike the 2 : 4′- and 4 : 4′-cyanines (II and III) which had so long been known, the first 2 : 2′-cyanine (I ; R = Me) was only prepared in 1920, by condensing quinaldine methiodide with 2-iodoquinoline methiodide ; [24] the reaction was subsequently extended, this type also being found to comprise photographic sensitisers.[22] The constitution (IV) suggested for pinacyanol [25] was established by oxidative

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[14] A. Miethe and A. Traube, G.P. 142,926/1902.

[15] Farbenfabr. vorm. F. Bayer and Co., G.P. 158,078 ; 170,048—9/1903 ; Farbw. vorm. Meister, Lucius, and Brüning, G.P. 167,159 ; 167,770/1903.

[16] Farbw. vorm. Meister, Lucius, and Brüning, G.P. 172,118/1905.

[17] *Ber.*, 1874, **7**, 976.

[18] S. V. Natanson, *Nature*, 1937, **140**, 197 ; *J. Phys. Chem. Russia*, 1938, **11**, 157.

[19] J. A. Leermakers, *J. Chem. Physics*, 1937, **5**, 889.

[20] W. H. Mills and R. S. Wishart, *J.*, 1920, **117**, 579.

[21] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2389.

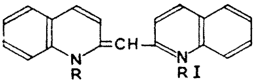
[22] F. M. Hamer, *J.*, 1928, 206.

[23] W. H. Mills and P. E. Evans, *J.*, 1920, **117**, 1035.

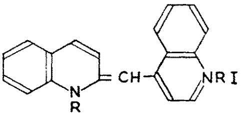
[24] O. Fischer and G. Scheibe, *J. pr. Chem.*, 1920, [ii], **100**, 86.

[25] W. H. Mills and W. J. Pope, *Phot. J.*, 1920, **60**, 253.

breakdown;[26] it was confirmed by the relationship of pinacyanol to methylenediquinaldine (1 : 3-di-2′-quinolylpropane) diethiodide[27] and, by its synthesis from quinaldine ethiodide and ethyl orthoformate.[28] The unknown 2 : 4′- and 4 : 4′-isomerides, (V) and (VI), were predicted.[26] Later, (VI) was synthesised by the action on lepidine ethonitrate in pyridine of the disulphide (VII), one function of which is to provide the central methin group (·CH:) of the trimethin chain;[29] and (V) was similarly synthesised from the ethonitrates of lepidine and quinaldine.[30] (VI) was identified with "kryptocyanine",[29] which had been made by the action of alkali, with formaldehyde or chloroform, on a lepidinium quaternary salt[31] and had proved a valuable sensitiser to infra-red light. Of "dicyanines" similarly made from 2 : 4-dimethylquinolinium salts and described as infra-red sensitisers, a commercial sample was shown to be spectroscopically similar to (V).[30]



(I.)



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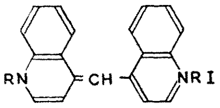

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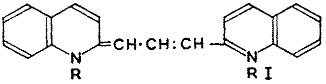

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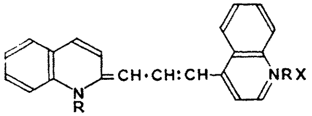

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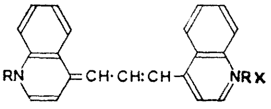

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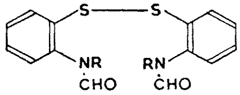

(VII.)

A purple dye, first prepared in 1887 by the action of ammonia on the alkiodides of benzthiazole and 2-methylbenzthiazole,[32] was obtained by W. H. Mills in better yield by use of pyridine and was accompanied by a yellow product, both dyes possessing sensitising properties. Mills established

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[26] W. H. Mills and F. M. Hamer, *J.*, 1920, **117**, 1550.

[27] F. M. Hamer, *J.*, 1923, **123**, 246; 1925, **127**, 211.

[28] W. König, *Ber.*, 1922, **55**, 3293.

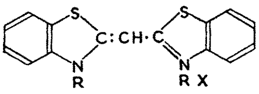
[29] W. H. Mills and W. T. K. Braunholtz, *J.*, 1923, **123**, 2804.

[30] W. H. Mills and R. C. Odams, *J.*, 1924, **125**, 1913.

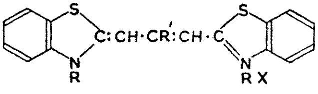
[31] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661.

[32] A. W. Hofmann, *Ber.*, 1887, **20**, 2251.

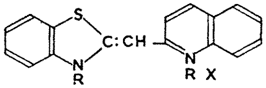
that the yellow substance was the methincyanine (VIII), and the purple dye the trimethincyanine (IX; $R' = H$).[33] The latter was also prepared from 2-methylbenzthiazole ethiodide and (VII) in pyridine; besides providing a methin group, (VII) had a second function in providing a benzthiazole nucleus, which united with the quaternary salt present, so that (IX; $R' = H$) was accompanied by (VIII).[29] Similarly, by the method involving (VII), (IV) was accompanied by (X), whilst (VI) was accompanied by (XI);[29] representatives of type (XI) were also prepared by the action of alkali on a mixture of quaternary salts of 2-methylbenzthiazole and of quinoline and were found to be sensitisers.[34] The ethyl orthoformate method[28] was applied to the synthesis of (IX; $R' = H$),[35] (XII; $Y = O$),[35] and (XII; $Y = CMe_2$).[36] By introduction of pyridine as condensing agent, this became the best practical route to trimethincyanines,[37] and was applied to the preparation of (XII; $Y = Se$)[38] and, by use of ethyl orthoacetate, to that of (IX; $R' = Me$).[39] All these proved to be sensitisers.[37–39] So far, the methincyanines comprised both symmetrical members, such as (I), (III), and (VIII), in each of which there are two similar nuclei, similarly linked, and unsymmetrical members such as (II), (X), and (XI), but the trimethincyanines were all of the symmetrical type, with the exception of (V), where two similar nuclei are differently linked. By 1929 intermediate compounds had been prepared, leading to unsymmetrical trimethincyanines, which comprised photographic sensitisers.[40] A wide field now lay open and one problem, in a review such as this, is to separate the grain from the chaff.



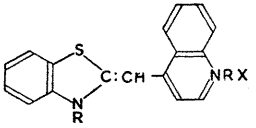
(VIII)



(IX)



(X)



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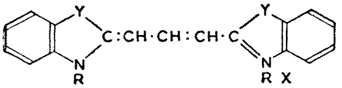
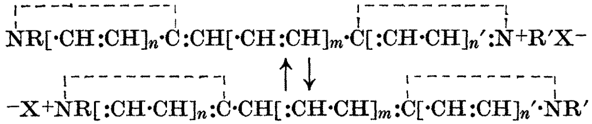


(XII)

Definition and Nomenclature.—



$$\mathrm{NR[\cdot CH{:}CH]_{n}\cdot C{:}CH[\cdot CH{:}CH]_{m}\cdot C[{:}CH\cdot CH]_{n'}{:}N^{+}R'X^{-}}$$

$$\uparrow\downarrow$$

$$\mathrm{{}^{-}X^{+}NR[{:}CH\cdot CH]_{n}{:}C\cdot CH[{:}CH\cdot CH]_{m}{:}C[\cdot CH{:}CH]_{n'}\cdot NR'}$$

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[33] *J.*, 1922, **121**, 455. [34] W. T. K. Braunholtz and W. H. Mills, *ibid.*, p. 2004.
[35] W. König and W. Meier, *J. pr. Chem.*, 1925, [ii], **109**, 324.
[36] W. König, *Ber.*, 1924, **57**, 685. [37] F. M. Hamer, *J.*, 1927, 2796.
[38] L. M. Clark, *J.*, 1928, 2313. [39] F. M. Hamer, *ibid.*, p. 3160.
[40] H A. Piggott, E. H. Rodd, and I.C.I. Ltd., B.P. 344,409/1929; 354,898/1930.

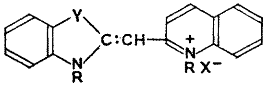
A cyanine is a monoacid salt in which two heterocyclic nitrogen-containing nuclei are linked by an odd-numbered methin chain as above (where $m = 0, 1, 2$, or 3, and n and $n' = 0$ or 1). Although one nitrogen atom is tertiary and the other quaternary, it was realised years ago that the acid radical cannot be regarded as attached to one nitrogen atom rather than to the other.[41] Each cyanine is regarded as a resonance hybrid of two canonical structures ; although no one single formula is a complete representation, in the following pages, for brevity, only one is given.

The nomenclature in the early days was comparatively simple, and trivial names such as thia-2′-cyanine for (X) and thia-4′-cyanine for (XI) still retain a certain usefulness. Cyanines in which the nuclei were linked by a trimethin chain were conveniently named " carbocyanines ",[25] whence followed the term " dicarbocyanines " for those with a pentamethin chain,[82] and " tricarbocyanines " for those with a heptamethin chain.[90] As an example, (IX ; $R = R' = Et$; $X = I$) was described as 3 : 3′ : 9-triethylthiacarbocyanine iodide. As the subject developed, however, this type of nomenclature came to involve the interpretation of a whole host of trivial names, besides the difficulties of naming simpler dyes such as (XV), very complex ones such as (LXXVI), and cyanines with anomalous chain-lengths, such as (XXXIX). There was thus built up a systematic nomenclature in which, only a knowledge of the fundamental structure of a cyanine being presupposed, each name specified the nature of the nuclei, their positions of linking, and the length of the chain joining them. According to this, (IX ; $R = R' = Et$; $X = I$) is described as bis-2-(3-ethylbenzthiazole)-β-ethyltrimethincyanine iodide. Other examples of both types of nomenclature as applied to fairly simple types of cyanine are to be found elsewhere.[234] Trinuclear cyanines have been named as substituted dinuclear cyanines.[205, 206]

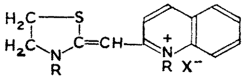
Methincyanines.—According to the historic method, a quaternary salt of lepidine or quinaldine was condensed with one of quinoline, in alcoholic solution, to give (III) [3, 4] or (II),[4, 5] respectively, according to the equation on p. 327, the liberated acid being taken up by the caustic alkali and the two hydrogen atoms by the customary excess [9, 42–44] of quinolinium salt. An 82% yield of 2 : 4′-cyanine [45] and a 63% of thia-4′-cyanine (XI) [46] were attained. 4′-Cyanines containing a simple thiazole [47, 48] or a Δ^2-thiazoline [49] nucleus were also made, and, in general, any heterocyclic quaternary ammonium salt having a 2- or a 4-methyl group can condense through it with a quinolinium salt at the 4-position. If the 4-position is blocked, condensation may occur at the 2-position, as in the preparation of 2 : 4′-cyanines by the action of alkali on lepidine alkiodides.[21]

[41] W. H. Mills and W. T. K. Braunholtz, *J.*, 1922, **121,** 1489.
[42] W. H. Mills and W. J. Pope, *Phot. J.*, 1920, **60,** 183.
[43] H. Barbier, *Bull. Soc. chim.*, 1920, **27,** 427.
[44] F. M. Hamer, *J.*, 1921, **119,** 1432 ; *Phot. J.*, 1922, **62,** 8.
[45] *Idem, J.*, 1939, 1008.
[46] G. H. Keyes and L. G. S. Brooker, *J. Amer. Chem. Soc.*, 1937, **59,** 74.
[47] W. H. Mills and J. L. B. Smith, *J.*, 1922, **121,** 2004.
[48] I.G. Farbenind. A.-G., B.P. 386,903/1931.
[49] L. G. S. Brooker, *J. Amer. Chem. Soc.*, 1936, **58,** 662.

A second method consists in condensing a heterocyclic quaternary ammonium salt, having a 2- or 4-methyl group, with a similar reactive iodo-salt, in the presence of absolute alcohol, two molecules of acid being removed by the added alkali. Thus from 2-iodoquinoline alkiodide there was first prepared type (I),[24] and subsequently (II), (X), (XIII ; Y = CMe_2),[22] and (XIV).[49] Up to a point, the other reactant also could be varied, alkiodides used being those of 2-iodopyridine and 2-iodo-β-naphthoquinoline (2-iodo-5 : 6-benzquinoline).[50] Both non-ionic iodine atoms of 2 : 4-di-iodoquinoline ethiodide can take part in this type of reaction.[51] The observation that increased yields are obtainable by using a strong organic base, such as triethylamine, as condensing agent, made practicable the preparation of (XIII ; Y = O), (XV),[52] and (XVI ; Y = O, S, or Se).[53] A limitation of the general method is that it is inoperative with 2-iodo-salts which have more than one hetero-atom in the ring carrying the iodine atom, *e.g.*, with 2-iodobenzthiazole alkiodides.



(XIII)



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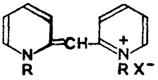
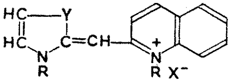
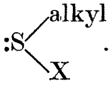


(XV)



(XVI)

A third method was on the one hand described as consisting in reaction of a heterocyclic quaternary ammonium salt, having a 2- or a 4-methyl group, with a heterocyclic base, having in the 2- or the 4-position a group such as  $:\mathrm{S}{<}^{\text{alkyl}}_{\mathrm{X}}$.[54] On the other hand, the second reactant was regarded as a quaternary heterocyclic ammonium salt having a 2- or a 4-alkylthio-group.[55] A recommended procedure consisted in heating together a base having a 2- or a 4-alkylthio-group, one having a 2- or a 4-methyl group, and an alkyl toluene-*p*-sulphonate.[55, 56] One molecule of acid and one of alkanethiol were eliminated. By means of alkylthio-compounds, five- and six-membered diazole nuclei were introduced into methincyanine molecules.[57] In such syntheses, the alkyl of the alkylthio-group should be identical with that of the ester used for salt-formation,[58] since a rearrangement of alkyl

[50] F. M. Hamer and M. I. Kelly, *J.*, 1931, 777.

[51] L. G. S. Brooker and L. A. Smith, *J. Amer. Chem. Soc.*, 1937, **59**, 67.

[52] L. G. S. Brooker and G. H. Keyes, *ibid.*, 1935, **57**, 2488.

[53] L. G. S. Brooker, G. H. Keyes, and F. L. White, *ibid.*, p. 2492.

[54] I.G. Farbenind. A.-G., B.P. 423,792/1932.

[55] J. D. Kendall, B.P. 424,559/1933 ; 438,420/1934.

[56] J. D. Kendall and H. G. Suggate, *J.*, 1949, 1503.

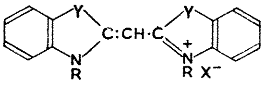
[57] J. D. Kendall, B.P. 425,609/1933.

[58] F. M. Hamer, *J.*, 1940, 799.

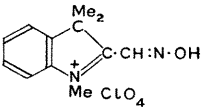
groups occurred when ethyl iodide acted on 2-methylthioquinoline[59] or on 2-methylthiobenzthiazole.[60] Reaction of a 4-arylthiopyridinium salt, a 4-methylpyridinium salt, and a strong base yielded the 4 : 4′-isomer[61] of (XV).

A fourth method, leading solely to symmetrical methincyanines, consisted in heating the alkotoluene-*p*-sulphonate of a heterocyclic base, having a 2-alkylthio-group, with malonic acid and pyridine.[62]

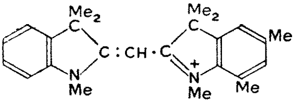
A rather curious fifth method of preparing methincyanines consisted in heating a heterocyclic quaternary ammonium salt, having a reactive methyl group, with amyl nitrite and acetic anhydride; the original patent[63] covered 2 : 3 : 3-trimethylindoleninium salts, but the products were formulated as β-azatrimethincyanines! In applying the method to 2-methylbenzthiazolium salts, the products were established as (VIII);[64] in its day, this was the best method for their preparation, but it has been superseded by the alkylthio-method. It was applied to the preparation, of (XVII; $Y = O$), which were interesting as being the first colourless cyanines,[65] and of (XVII; $Y = Se$).[66] The dyes from indoleninium salts were also established as (XVII; $Y = CMe_2$) and in this series there was isolated an intermediate compound (XVIII) and hence the unsymmetrical (XIX).[67]



(XVII.)



(XVIII.)



(XIX.)

Sixthly, the synthesis of (VIII; $R = Et$) from ethyl malonate and *o*-aminothiophenol, through di-2-benzthiazolylmethane, its ethiodide, and the base formed by elimination of acid,[33] though not a recommended preparative method, is a classic, without which any account of methincyanines would be incomplete. In this connection, an attempted synthesis through methanes substituted by two heterocyclic nuclei, of which at least one was a substituted quinoxaline, *e.g.* (XX), is interesting, as is also its failure because of the resistance of such methanes to quaternary salt formation.

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[59] B. Beilenson and F. M. Hamer, *J.*, 1939, 143.

[60] W. A. Sexton, *ibid.*, p. 470.

[61] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 2,202,827/1940; 2,231,657/1941.

[62] J. D. Kendall, B.P. 431,141/1933.

[63] I.G. Farbenind. A.-G., B.P. 291,888/1927.

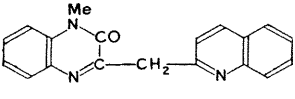
[64] N. I. Fisher and F. M. Hamer, *J.*, 1930, 2502.

[65] *Idem*, *J.*, 1934, 962.

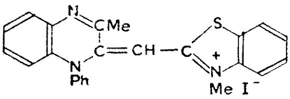
[66] I.G. Farbenind. A.-G., B.P. 380,702/1931.

[67] R. Kuhn, A. Winterstein, and G. Balser, *Ber.*, 1930, **63**, 3176.

However, two methincyanines, *e.g.* (XXI), each containing one quinoxaline nucleus, were obtained by the alkylthio-method.[68]



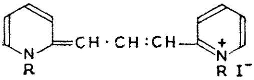
(XX)



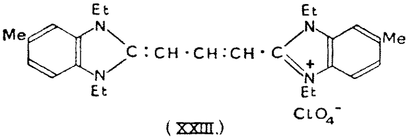
(XXI.)

Symmetrical Trimethincyanines.—The method of preparing symmetrical trimethincyanines by the action of alkali on an alcoholic solution of quinaldine alkiodide and quinoline alkiodide in the presence of formaldehyde [16] was the standard procedure of thirty years ago [25, 69–71] and is now obsolete. The quinolinium salt did not enter into the dye molecule [69] and its function may have been to take up two hydrogen atoms, which, in addition to water and acid, were eliminated; its usefulness has, however, been denied.[72]

A second early method was based on the use of a trihalogenomethane [73] to provide the central unit of the chain. It is recorded that treatment of an alcoholic solution of the appropriate picolinium iodide with potassium hydroxide and chloroform did lead to (XXII) and its 4 : 4′-analogue,[74] whereas (XXII) could not be obtained by the ethyl orthoformate method.[37, 74] Until recently, use of a trihalogenomethane, in the presence of alkali alkoxide,[75] was the only known way of preparing trimethincyanines of the benziminazole series, such as (XXIII).



(XXII.)



(XXIII.)

That method in which the central carbon atom of the chain was supplied by a disulphide (VII) was invaluable in establishing the constitution of (V), (VI), and (IX ; R′ = H) [29, 30] but is not a convenient preparative one.

The standard method of preparing symmetrical trimethincyanines is by use of ethyl orthoformate and pyridine.[28, 35–38]

A fifth way differs from the others in that the whole trimethin chain is furnished by glutaconic acid, or by crotonic anhydride, which is condensed, in the presence of pyridine, with two moles of the alkotoluene-*p*-sulphonate of a heterocyclic base having a reactive alkylthio-group.[62, 76]

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[68] A. H. Cook and R. F. Naylor, *J.*, 1943, 397.

[69] O. Fischer, *J. pr. Chem.*, 1918, [ii], **98,** 204.

[70] L. E. Wise, E. Q. Adams, J. K. Stewart, and C. H. Lund, *Ind. Eng. Chem.*, 1919, **11,** 460.

[71] W. T. K. Braunholtz, *J.*, 1922, **121,** 169.

[72] K. Lauer and M. Horio, *J. pr. Chem.*, 1935, [ii], **143,** 305.

[73] Farbw. vorm. Meister, Lucius, and Brüning, G.P. 200,207/1907.

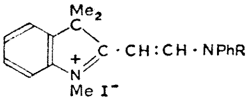
[74] E. Rosenhauer and F. Barlet, *Ber.*, 1929, **62,** 2724.

[75] I.G. Farbenind. A.-G., B.P. 521,165/1937 ; cf. A. van Dormael with J. Libeer, *Sci. et Ind. Phot.*, 1949, [2], **20,** 451.

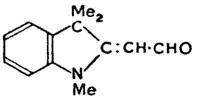
[76] J. D. Kendall, B.P. 431,186/1933.

Unsymmetrical Trimethincyanines.—Historically it is interesting that (VII) was used in synthesising the unsymmetrical (V) from a mixture of quaternary salts,[30] and that similar dyes were made commercially from 2 : 4-dimethylquinolinium salts, where both methyl groups are reactive. In general, however, the use of a mixture of salts is undesirable, because the unsymmetrical dye is liable to be contaminated by two symmetrical ones.

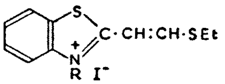
The first practical preparation of trimethincyanines having two different nuclei is an instance of valuable work which has been published only in the form of patents.[40] Diarylformamidines, ArNH•CH:NAr, were used, either to give symmetrical trimethincyanines, by condensation with two moles of heterocyclic quaternary ammonium salt having a reactive methyl group, or to give intermediate compounds by condensation of equimolecular proportions. If obtained by simple fusion, the intermediate was of the anilinovinyl type, *e.g.* (XXIV ; R = H), but, if prepared in the presence of acetic anhydride, it was an acetanilidovinyl compound, *e.g.* (XXIV ; R = Ac). By its condensation with a molecule of a different salt, having a reactive methyl group, unsymmetrical trimethincyanines were produced. It was recognised [77] that better yields result from the acetanilido- than from the anilino-type of intermediate, when the medium is other than acetic anhydride. The use of ethyl *N*-phenylformimidate (ethyl*iso*formanilide), PhN:CH•OEt, as a substitute for diphenylformamidine, was an improvement in giving higher yields of the β-anilinovinyl intermediate compounds.[78]



(XXIV.)



(XXV.)



(XXVI.)

Other intermediate compounds claimed were the semicarbazone, etc., of aldehydes, *e.g.* (XXV), which was obtained by hydrolysis of (XXIV ; R = Me) ; [79] also (XXVI), prepared either by use of ethyl trithio-orthoformate [80] or from an aldehyde and phosphorus pentasulphide, followed by an ester.[81]

Symmetrical and Unsymmetrical Pentamethincyanines.—The first pentamethincyanines were *meso*-substituted, *e.g.* (XXVII ; Y = Cl, Br, or NO_2). They were prepared [82] by condensing one mole of α-chloro-β-anilinoacraldehyde anil, NHPh•CH:CCl•CH:NPh, or the corresponding α-bromo- or α-nitro-compound, with two moles of a quaternary salt, having a reactive methyl group. Sometimes the acid salts of these anils were used, some

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[77] T. Ogata, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13,** 549 ; *Proc. Imp. Acad. Japan*, 1937, **13,** 325.

[78] E. B. Knott, *J.*, 1946, 120.

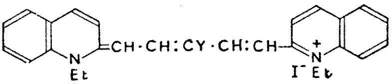
[79] I.G. Farbenind. A.-G., B.P. 486,780/1936 ; 510,242/1938.

[80] J. D. Kendall and J. R. Majer, *J.*, 1948, 687.

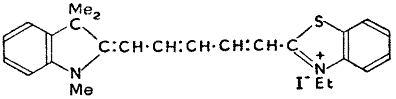
[81] K. Kumetat and O. Riester, vested in Alien Property Custodian, U.S.P. 2,349,179/1944.

[82] S. Beattie, I. M. Heilbron, and F. Irving, *J.*, 1932, 260.

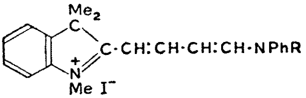
reactions being effected by piperidine in pyridine and others by potassium acetate in acetic anhydride. The unsubstituted β-anilinoacraldehyde anil hydrochloride gave dyes such as (XXVII ; Y = H) but also, by reaction with the usual 2- or 4-methyl salts, in the presence of acetic anhydride, intermediate compounds such as (XXVIII ; R = Ac), whence unsymmetrical dyes, *e.g.* (XXIX), could be obtained.[83] Non-acetylated intermediate compounds, *e.g.* (XXVIII ; R = H), were best prepared by using a strong organic base as condensing agent, with alcohol as medium ; unlike their lower vinylene homologues, where the acetylated were more useful than the non-acetylated compounds, in this series the non-acetylated salts were applied to the preparation of unsymmetrical pentamethincyanines, for use as photographic sensitisers for the deep red and infra-red.[84]



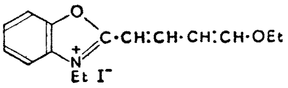
(XXVII.)



(XXIX.)



(XXVIII.)



(XXX.)

By condensing quaternary salts, having a reactive methyl group, with β-ethoxyacraldehyde diethyl acetal in the presence of acetic acid it was possible to make ethoxy-compounds such as (XXX), which could be used in preparing unsymmetrical pentamethincyanines.[85] The ethoxy-compounds were found useful, in the crude state, as a source of the pure anilinobutadienyl type of intermediate.[86] It is recorded that β-alkylthioacraldehyde acetal or dithioacetal may also be used.[87]

A method proposed for symmetrical pentamethincyanines and consisting in the condensation of a quaternary salt, having a 2-β-acetanilidovinyl group, with malonic acid [88] proved useful specifically for those having two benzoxazole nuclei.[89]

For symmetrical pentamethincyanines, a suggested method resembles the fifth for symmetrical trimethincyanines (*q.v.*), in that the whole chain is provided as a unit, in this instance by sorbic anhydride.[76]

Symmetrical and Unsymmetrical Heptamethincyanines.—Just as tri- and

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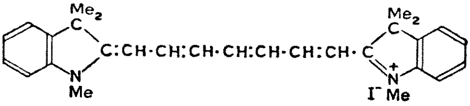
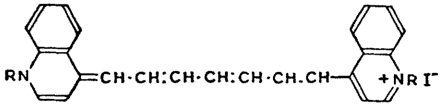
[83] H. A. Piggott, E. H. Rodd, and I.C.I. Ltd., B.P. 355,393/1930.
[84] I.G. Farbenind. A.-G., B.P. 434,234—5/1933.
[85] R. H. Sprague and Eastman Kodak Co., U.S.P. 2,269,234/1942.
[86] F. M. Hamer, *J.*, 1949, 32.
[87] J. D. Kendall and H. D. Edwards, B.P. 562,565—8/1933.
[88] T. Ogata, *Bull. Inst. Phys. Chem. Res. Japan*, 1937, **16**, 631.
[89] F. M. Hamer and R. J. Rathbone, *J.*, 1945, 595.

penta-methincyanines were prepared by use of diphenylformamidine and β-anilinoacraldehyde anil hydrochloride, respectively, so symmetrical hepta-methincyanines were prepared by condensing " glutaconaldehyde dianilide " (PhNH·CH:CH·CH:CH·CH:NPh) hydrochloride with various quaternary salts, having a reactive methyl group ; those made had two 2-linked quinoline, benzthiazole, naphtho(1′ : 2′-4 : 5)thiazole, benzselenazole, Δ^2-thiazoline, or 3 : 3-dimethylindolenine nuclei ; the condensing agent was usually caustic alkali in alcohol, but for (XXXI) was sodium acetate in acetic anhydride.[90] Dyes of this last type were also made by two other sets of workers,[91, 92] all three recording that they sensitise to infra-red light. Spectrograms showing the sensitisation were published [93, 94] and it was pointed out [94] that penta- and hepta-methincyanines had been independently discovered in Germany, chiefly by W. König, and put into commercial use. Use of triethylamine as condensing agent, at a low temperature, made it possible to prepare the symmetrical heptamethincyanines containing



(XXXI.)



(XXXII.)

simple thiazole and 4-linked quinoline nuclei.[95] The latter, (XXXII), has been used for infra-red photography, *e.g.*, of arc spectra in the region 9000—10,000 A.[96]

A scientifically interesting method of preparing heptamethincyanines consisted in treating the quaternary salt, having a reactive methyl group, with alkali and 2 : 4-dinitrophenylpyridinium chloride in the presence of alcohol,[90, 91] whereupon the pyridinium ring opened to give glutaconaldehyde,[97] which condensed with the salt.

The first intermediate compound of this series (XXXIII ; R′ = Me ; Y = CMe_2) was prepared in acetic anhydride.[91] Later, as with the next lower vinylene homologues, an alkaline medium was recommended for making (XXXIII ; R′ = H ; Y = ·CH:CH·, S, or Se).[98] Use of a strong organic base as condensing agent made available intermediate compounds of even

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[90] N. I. Fisher and F. M. Hamer, *J.*, 1933, 189.

[91] O. Wahl and I.G. Farbenind. A.-G., G.P. 499,967/1928.

[92] H. A. Piggott, E. H. Rodd, and I.C.I. Ltd., B.P. 355,693/1930.

[93] L. G. S. Brooker, F. M. Hamer, and C. E. K. Mees, *Phot. J.*, 1933, **73**, 258.

[94] W. Dieterle, H. Dürr, and W. Zeh, *Z. wiss. Phot.*, 1933, **32**, 145.

[95] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 2,095,856/1937 ; 2,165,337/1939.

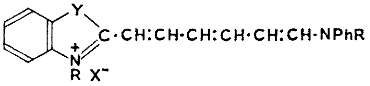
[96] W. F. Meggers and C. C. Kiess, *Bur. Stand. J. Res.*, 1932, **9**, 309.

[97] T. Zincke, *Annalen*, 1904, **330**, 361.

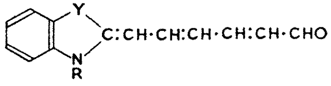
[98] I.G. Farbenind. A.-G., B.P. 438,449—50 ; 438,484/1933.

the benzoxazole series and hence heptamethincyanines with benz- or naphthoxazole nuclei.[99]

Another method of preparing unsymmetrical heptamethincyanines consisted in condensing the usual quaternary salts, having a reactive methyl group, with heterocyclic pentamethin aldehydes (XXXIV ; Y = •CH:CH•, S, or Se) obtained by the action of alkali on the corresponding *N*-substituted hexamethin salts (XXXIII).[100]



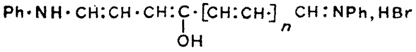
(XXXIII)



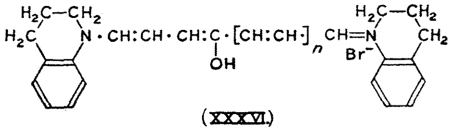
(XXXIV)

Polymethincyanines.—Much as the pyridinium nucleus had been ruptured, giving the hydrochloride of glutaconaldehyde dianilide, so rupture of the furfuraldehyde nucleus gave, *e.g.*, (XXXV ; $n = 0$), and of 2-β-furylacraldehyde gave, *e.g.*, (XXXV ; $n = 1$) and (XXXVI ; $n = 1$) * ; [101] subsequently dyes such as (XXXVI ; $n = 2$ and 3) were prepared by rupture of

(XXXV)

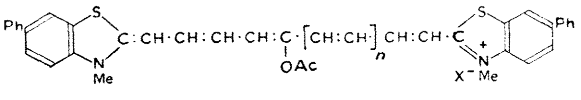


$$\mathrm{Ph{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}\underset{\displaystyle OH}{\underset{|}{C}}{\cdot}[CH{:}CH{\cdot}]_n\,CH{:}NPh,HBr}$$



(XXXVI)

the nuclei of 5-furylpenta-2 : 4-dien-1-al and 7-furylhepta-2 : 4 : 6-trien-1-al, respectively, but the instability increased as the chain was lengthened. By acyl chlorides or anhydrides, in the presence of pyridine, the hydroxyl group could be acylated, giving more stable compounds.[102] These could be condensed with various quaternary salts, having a reactive methyl group, to



(XXXVII)

give cyanines having a chain of at least seven carbon atoms, with acyloxy as substituent. Examples in a patent [103] include hepta, ennea-, and hendeca-methincyanines, *e.g.*, (XXXVII ; $n = 0$, 1, or 2), but it would seem

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[99] G. H. Keyes and Eastman Kodak Co., U.S.P. 2,251,286/1941.

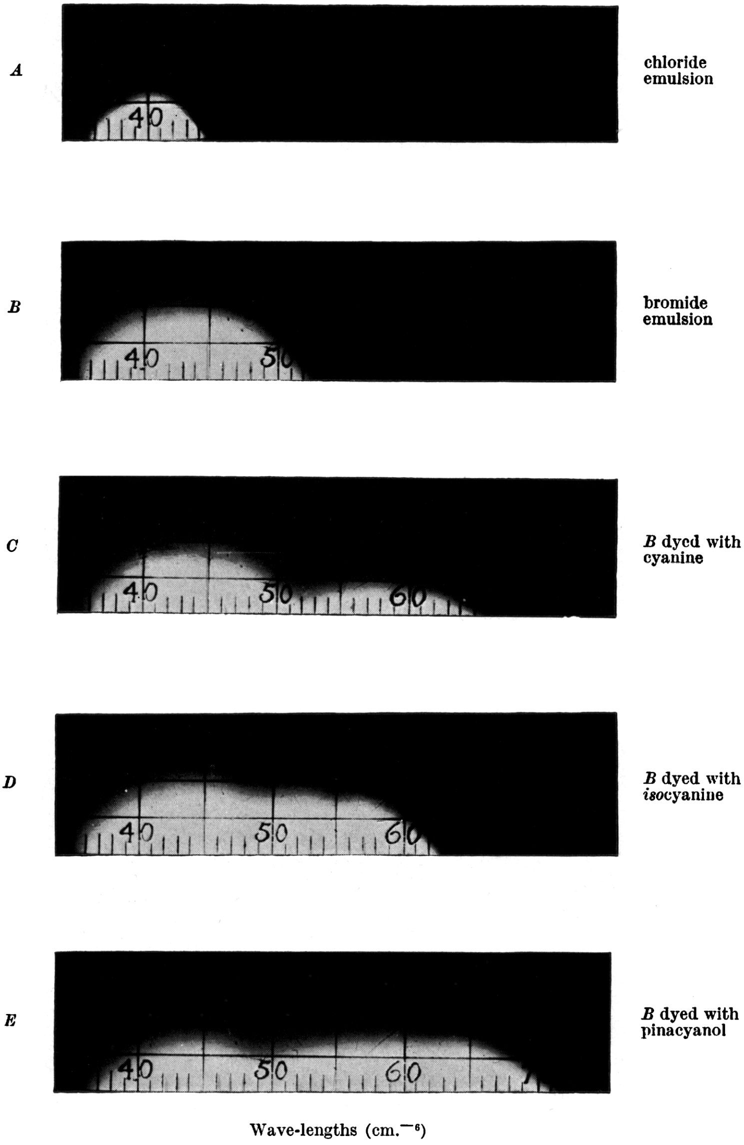
[100] I.G. Farbenind. A.-G., B.P. 499,318 ; 501,005/1936.

[101] W. König, *J. pr. Chem.*, 1905, [ii], **72**, 555 ; 1913, [ii], **88**, 193.

[102] W. König, with K. Hey, F. Schulze, F. Silberkweit, and K. Trautmann, *Ber.*, 1934, **67**, 1274.

[103] I.G. Farbenind. A.-G., B.P. 441,624/1933.

* In formula (XXXVI) a positive charge has inadvertently been omitted from the right-hand nitrogen atom.



A chloride emulsion

B bromide emulsion

C *B* dyed with cyanine

D *B* dyed with *iso*cyanine

E *B* dyed with pinacyanol

PLATE 1

Wedge spectrograms.

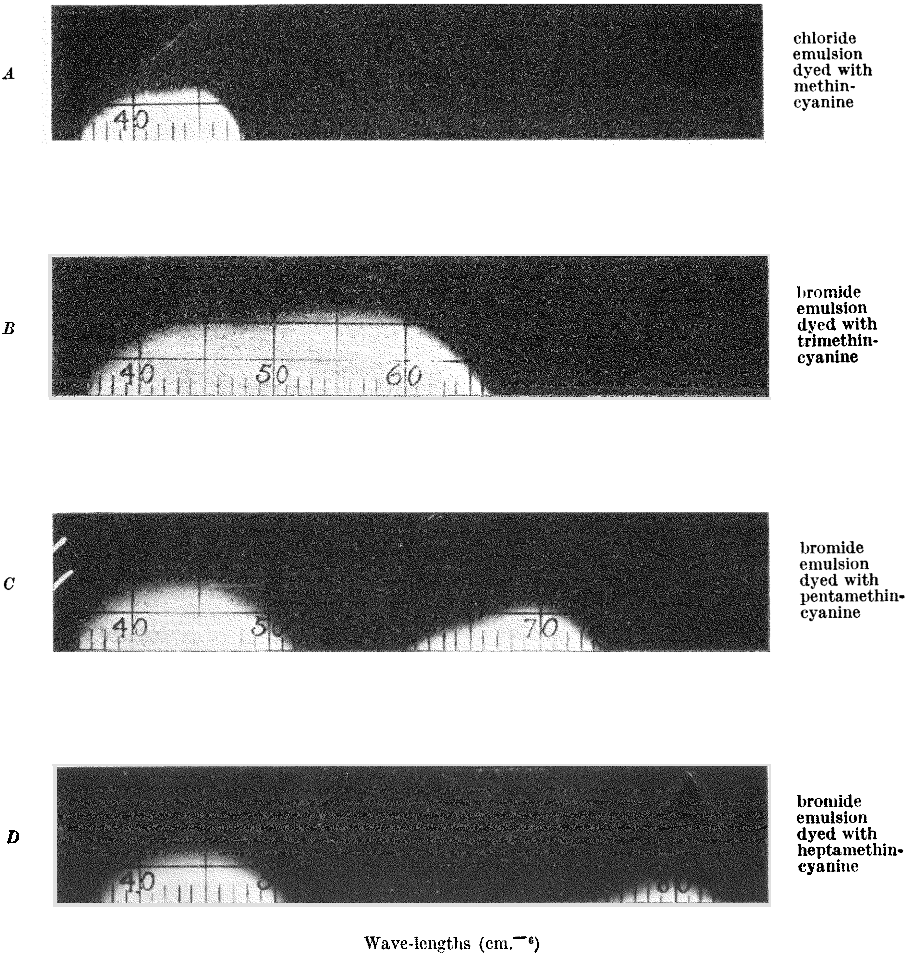


PLATE 2

Wedge spectrograms of sensitising by cyanines having two benzthiazole nuclei.

that this eleven-membered chain is the longest reached, no cyanine prepared from (XXXVI; $n = 3$) having been recorded.

A limiting factor to the infra-red sensitising properties of the polymethincyanines [104, 105] is the instability of the dyes. Thus the keeping properties of infra-red sensitised plates are poor and the sensitivity decreases with increasing wave-length,[106] so that for plates sensitised to 8500, 9500, and 10,500 A., respectively, the attainable sensitivities are as 100 : 10 : 1.[107]

It has been stated that both symmetrical and unsymmetrical enneamethincyanines, having an unsubstituted chain, are obtainable by condensing (XXXVIII; $n = 3$) with quaternary salts having a reactive methyl group; the preparation and infra-red sensitising properties of four symmetrical dyes, of the benzthiazole or benzselenazole series, have been described;[108] a symmetrical hendecamethincyanine, of the benzthiazole series, similarly obtainable from (XXXVIII; $n = 4$) is recorded as sensitising three times as strongly as its chain-substituted acetoxy-derivative.[109]

$$\text{(XXXVIII.)}\qquad \mathrm{RR'N{\cdot}[CH{:}CH{\cdot}]_nCH{:}\overset{+}{N}RR'}\ \overset{-}{\mathrm{X}}$$

Effects of Lengthening the Methin Chain.—In the cyanines, a chain of conjugated double bonds connects the two nitrogen atoms, of which only one is quaternary, this implying an odd-numbered chain of methin groups. For given nuclei, the length of this chain affects the position of the absorption and therefore of the sensitising maxima, which shift about 1000 A. into the region of longer wave-length for each vinylene (·CH:CH·) increment. Thus, for example, a methincyanine having two benzthiazole nuclei gives an alcoholic solution with its absorption maximum at 4220 A. and may be used for sensitising gelatino chloride photographic plates (Plate 2*A*). Passing the trimethincyanine with its sensitising maximum in the green (Plate 2*B*) and the pentamethincyanine, sensitising in the deep red and near infra-red (Plate 2*C*), the heptamethincyanine gives a solution with its absorption maximum at 7620 A. and sensitises to infra-red light (maximum at 7950 A.) (Plate 2*D*), the ennea- and hendeca-methincyanines sensitising still further into the infra-red. The effects of chain length on absorption and sensitising have been studied by chemists throughout the world,[110–114] and some interesting data recorded. The valuable work of L. G. S. Brooker and his co-workers [113] has already been discussed in *Quarterly Reviews*.[115]

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[104] L. G. S. Brooker and G. H. Keyes, *Phot. J.*, 1935, **75**, 191.

[105] W. Dieterle and W. Zeh, *Z. wiss Phot.*, 1935, **34**, 245.

[106] J. Eggert, *Chem. Z.*, 1934, **58**, 397.

[107] A. Seyewetz, *La Nature*, 1935, No. 2962, 300.

[108] I.G. Farbenind. A.-G., B.P. 485,623—4; 503,337/1936; 512,470/1937.

[109] W. Dieterle and O. Riester, *Z. wiss Phot.*, 1937, **36**, 141.

[110] N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.

[111] B. Beilenson, N. I. Fisher, and F. M. Hamer, *ibid.*, 1937, *A*, **163**, 138.

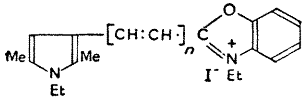
[112] T. Ogata, *Proc. Imp. Acad. Japan*, 1932, **8**, 421.

[113] L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth, and P. F. Oesper, *J. Amer. Chem. Soc.*, 1941, **63**, 3192.

[114] S. M. Soloviev, *J. Phys. Chem. Russia*, 1945, **19**, 451.

[115] A. Maccoll, *Quart. Reviews*, 1947, **1**, 16.

Zinc dust in pyridine, in the presence of a trace of acetic acid, reduced the mono-, tri-, penta-, and hepta-methincyanines of the indolenine series to leuco-bases ; the tri- but not the hepta-methincyanine could be regenerated by oxidation.[116] With these same dyes, chromatographic adsorption increased, step by step, on ascending the series from methin- to hepta-methin-cyanine.[117]



(XXXIX)

Certain cyanines with β-linked pyrrole nuclei, *e.g.* (XXXIX ; $n = 1$ or 2), are exceptional in having the nuclei connected by dimethin and tetramethin chains, though the chains joining the nitrogen atoms are odd-numbered.[118]

Variations connected with the Nuclei.—The nature of the nuclei has a profound influence on the position of the absorption maximum of a cyanine of given type. Thus the methincyanine with two benzoxazole nuclei absorbs in the ultra-violet, that with two benzthiazole nuclei absorbs in the blue, and cyanine itself, with two 4-linked quinoline nuclei, in the yellow. The 4-linked quinoline nucleus is the most strongly bathochromic. As discussed in an earlier review,[115] L. G. S. Brooker and his collaborators studied the absorption of unsymmetrical dyes and, using resonance as a basis of classification, arranged the various nuclei in order of basicity.[119, 120]

In the series having only one hetero-atom in the nucleus, the use of 1-iodo*iso*quinoline alkiodide gave methincyanines ; [121] subsequently not only 1- but also 3-methyl*iso*quinolinium salts were used as starting points.[122] Four dyes prepared from 9-methylphenanthridine, which is a derivative of both quinoline and *iso*quinoline, gave no sensitisation.[123] The various polycyclic nuclei may be regarded as substituted simple nuclei.

After cyanines with heterocyclic nuclei other than quinoline had been made, patenting activity followed. This literature contains, for instance, statements that improved sensitising is produced, in specified types, by the introduction of groups such as amino, alkylthio, and alkylseleno into the benzthiazole, and of 5-phenyl into the benzoxazole nucleus.[124] It is at present not possible to assign a generally beneficial influence to particular substituents. On the other hand, the generalisation that nitro-groups depress sensitisation seems acceptable, an example being the conversion of the sensitiser (IX ; $R' = H$) into a desensitiser by introduction of two 6-nitro-groups.[125] It has interested scientists to introduce a given sub-

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[116] R. Kuhn and A. Winterstein, *Ber.*, 1932, **65**, 1737.

[117] P. Ruggli and P. Jensen, *Helv. Chim. Acta*, 1935, **18**, 624.

[118] L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, 1945, **67**, 1869.

[119] L. G. S. Brooker, G. H. Keyes, and W. W. Williams, *ibid.*, 1942, **64**, 199.

[120] L. G. S. Brooker, A. L. Sklar, H. W. J. Cressman, G. H. Keyes, L. A. Smith, R. H. Sprague, E. van Lare, G. van Zandt, F. L. White, and W. W. Williams, *ibid.*, 1945, **67**, 1875.

[121] N. I. Fisher and F. M. Hamer, *J.*, 1934, 1905.

[122] F. L. White, L. G. S. Brooker, and Eastman Kodak Co., B.P. 633,873—4/1946 ; U.S.P. 2,466,523/1949.

[123] L. G. S. Brooker and G. H. Keyes, *J. Amer. Chem. Soc.*, 1936, **58**, 659.

[124] I.G. Farbenind. A.-G., B.P. 400,951/1931 ; 420,971 ; 421,015/1932 ; 494,715/1937.

[125] J. D. Kendall, B.P. 543,993/1940.

stituent into different positions in the dye molecule and observe the effect on absorption or sensitising maxima. Thus at first this was done with *iso*cyanines [42, 44] and 2 : 2′-trimethincyanines ; [25, 71] more recently, symmetrical trimethincyanines having two 4- or 5-methylbenzthiazole [126] or two 4-, 5-, 6-, or 7-methoxybenzthiazole nuclei,[127] and tri- and pentamethincyanines having two 5- or 7-phenylbenzoxazole nuclei [128] have been examined. Dyes having 6-chloro- and 6-bromo-benzthiazole nuclei were compared,[129] and into each of the 6-positions in (IX ; $R' = H$) a series of electro-positive substituents [130] and one of electro-negative substituents [131] were introduced.

With the cyanines, an effective way of introducing heavy substituents and thus, according to Nietzki's rule, shifting the absorption (and sensitising) maximum towards the region of longer wave-length is to increase the complexity of the nuclei ; *e.g.*, trimethincyanines containing two naphtho-(1′ : 2′- or 2′ : 1′-4 : 5)thiazole nuclei absorb at a longer wave-length, by 350 A., than does that containing two benzthiazole nuclei.[132] Absorption in a desired region does not, by any means, guarantee a corresponding sensitising action, but cyanines containing these naphthothiazole nuclei did comprise valuable sensitisers.[132, 133] Although patents cover the preparation of cyanines from thiazoles of still greater complexity,[134, 135] it has been denied that trimethincyanines containing two anthraceno(1′ : 2′- or 2′ : 1′-4 : 5)thiazole nuclei sensitise more strongly than does their homologue having two benzthiazole nuclei ; [136] nor do cyanines with two anthraceno(9′ : 10′-4 : 5)thiazole nuclei sensitise as strongly as those with two of the naphthothiazole nuclei mentioned above.[46] Turning to simpler nuclei, we find that quaternary salts of 2-methylthiazole were used both early [29, 47] and in later work [48, 53, 64, 121] whilst 2-methyloxazole and 2-methylselenazole salts were also used.[53] The absorption maxima of dyes from quaternary salts of 2-methyl-Δ^2-thiazoline lay at a shorter wave-length than those of dyes from salts of 2-methylthiazole.[49] Similarly the absorption maxima of cyanines having tetrahydronaphthothiazole nuclei were hypsochromic as compared with those having naphthothiazole nuclei.[137] Replacement of the Δ^2-thiazoline by the dihydro-1 : 3-thiazine nucleus produced a bathochromic shift of absorption.[138] The fact that cyanines with sulphur-

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[126] A. I. Kiprianov and E. D. Sitsch, *Trav. Inst. Chim. Charkov*, 1936, **2**, 25.

[127] I. I. Levkoev, N. N. Sveshnikov, and S. A. Kheifets, *J. Gen. Chem. Russia*, 1946, **16**, 1489.

[128] A. T. Troschtschenko, *J. Gen. Chem. Russia*, 1939, **9**, 1661.

[129] B. Beilenson and F. M. Hamer, *J.*, 1936, 1225.

[130] A. I. Kiprianov, I. K. Uschenko, and E. D. Sitsch, *J. Gen. Chem. Russia*, 1945, **15**, 200.

[131] A. I. Kiprianov and I. K. Uschenko, *ibid.*, p. 207.

[132] F. M. Hamer, *J.*, 1929, 2598.

[133] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 1,846,300—1/1932; 1,969,444/1934.

[134] I.G. Farbenind. A.-G., B.P. 396,217 ; 400,401/1931.

[135] General Aniline and Film Corp., B.P. 597,612/1944.

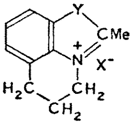
[136] I. I. Levkoev and V. V. Durmaschkina, *J. Gen. Chem. Russia*, 1945, **15**, 215.

[137] I.G. Farbenind. A.-G., B.P. 427,887/1932.

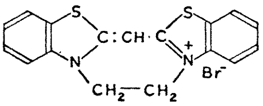
[138] F. M. Hamer and R. J. Rathbone, *J.*, 1943, 243.

containing nuclei were sometimes vastly superior to those having quinoline nuclei, in that they might combine powerful sensitising with anti-fogging action,[139–141] was doubtless a factor contributing to their thorough investigation. An attempt to obtain improved sensitisers, by the introduction of certain sulphur-containing substituents, was, however, unsuccessful.[141]

The original cyanines carried an alkyl group on each of the two cyclic nitrogen atoms but members with hydroxyalkyl [142] or aralkyl [142, 143] groups have been recommended, whilst *N*-aryl-2-methyl-Δ^2-thiazolinium salts have been synthesised, making available *N*-aryl-substituted cyanines of that series.[144] Instead of a 3-alkyl group, certain cyanines have been made with a 3 : 4-trimethylene group : this depends on the synthesis of a salt (XL ; Y = O, S, or Se).[145–147]



(XL.)

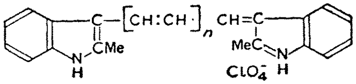


(XLI.)

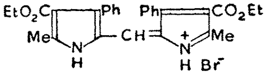
In place of *NN'*-dialkyl compounds, in the methincyanine series the corresponding *NN'*-alkylene derivatives, *e.g.* (XLI), have been synthesised.[148]

The possibility of cyanines having heterocyclic imino-, instead of *N*-alkyl, groups, was early realised in the pyrrole and indole series, and dyes such as (XLII ; *n* = 0 or 1) * were described ; [149] the sulphate corresponding

(XLII.)



(XLIII)



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[139] E. Fuchs, *Chem. Z.*, 1933, **57**, 853.

[140] M. M. Sobolev, M. V. Bondareva, and M. F. Evteeva, *J. Appl. Chem. Russia*, 1936, **9**, 335.

[141] A. I. Kiprianov, Z. P. Sitnikov, and E. D. Sitsch, *J. Gen. Chem. Russia*, 1936, **6**, 576.

[142] L. G. S. Brooker, L. A. Smith, and Eastman Kodak Co., U.S.P. 2,213,238/1940 ; 2,241,237/1941.

[143] W. Mees, M. Schouwenaars, and G. Schwarz, *Tijds. Vlaams. Ing. Vereen*, 1937, **6**, 89.

[144] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 2,441,558/1948.

[145] W. König, W. Kleist, and J. Götze, *Ber.*, 1931, **64**, 1664.

[146] G. Schwarz, M. Schouwenaars, and Gevaert Photo-Producten N.V., B.P. 625,245/1940.

[147] L. G. S. Brooker and H. W. J. Cressman, *J. Amer. Chem. Soc.*, 1945, **67**, 2046.

[148] L. G. S. Brooker, R. H. Sprague, and Eastman Kodak Co., U.S.P. 2,478,367/1949.

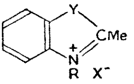
[149] W. König, *J. pr. Chem.*, 1911, [ii], **84**, 194 ; *Z. angew. Chem.*, 1925, **38**, 743.

* In formula (XLII) a positive charge has inadvertently been omitted from the right-hand nitrogen atom.

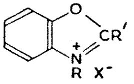
to (XLII; $n = 1$) has recently been made by another method. Methincyanines, such as (XLIII), were prepared by condensing a pyrrole, having a free α-position, with ethyl orthoformate in the presence of acid.[150]

Cyanines with Substituents on the Chain.—In the methincyanine series, 2-iodoquinoline alkiodide may be condensed with cyclic ammonium quaternary salts having a 2-ethyl or 2-benzyl instead of a 2-methyl group, giving dyes with absorption at a longer wave-length.[151, 152]

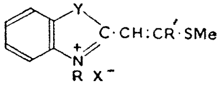
In the trimethincyanine series, the preparation, through ethyl ortho-acetate, of symmetrical *meso*-methyl dyes having two benzthiazole nuclei [39] was followed by that of others with various higher *meso*-alkyl, as well as -benzyl and -phenyl, groups and of some analogues with two benzoxazole or two benzselenazole nuclei.[153] Other groups, such as *meso*-2-thienyl [154] and -alkylthiomethyl,[141] were also introduced. The ortho-ester method is applicable to dyes with Δ^2-thiazoline,[49] Δ^2-selenazoline,[155] and thiazole [156] nuclei, but notable exceptions, whether by this or by any other method, are those containing quinoline nuclei.



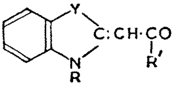
(XLIV.)



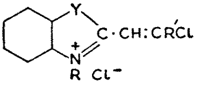
(XLV.)



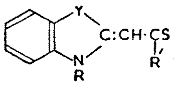
(XLVI.)



(XLVII.)



(XLVIII.)



(XLIX.)

A very intriguing reaction is that of a quaternary salt (XLIV; Y = S or Se) with a benzoxazolium salt (XLV) and sodium dissolved in alcohol, whereby the 2-R′ group of (XLV) becomes the *meso*-R′ group of the resultant symmetrical trimethincyanine [157] (IX or its selenium analogue).

Symmetrical trimethincyanines of three series, having in the *meso*-position an *o*-carboxyphenyl or a 2-carboxyethyl group, were prepared by condensing phthalic anhydride or succinic anhydride, respectively, with a quaternary salt of type (XLIV; Y = O, S, or Se) in pyridine.[158]

Into the *meso*-position of symmetrical trimethincyanines of two series, the alkyl or aryl group R′ could be introduced by condensing a quaternary

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[150] A. H. Cook and J. R. Majer, *J.*, 1944, 482, 486.

[151] J. Götze, *Z. angew. Chem.*, 1936, **49**, 563.

[152] J. Götze and W. Schulte, *Chem. Z.*, 1938, **62**, 458.

[153] L. G. S. Brooker and F. L. White, *J. Amer. Chem. Soc.*, 1935, **57**, 2480.

[154] I.G. Farbenind. A.-G., B.P. 403,845/1932.

[155] F. L. White and Eastman Kodak Co., U.S.P. 1,957,869/1934; 1,990,682/1935.

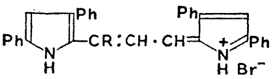
[156] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 1,973,462/1934; 1,994,563/1935.

[157] I.G. Farbenind. A.-G., B.P. 439,359; 439,807/1933.

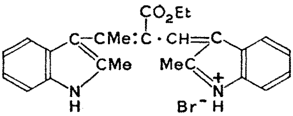
[158] L. G. S. Brooker, R. H. Sprague, and Eastman Kodak Co., U.S.P. 2,226,156/1940.

salt (XLIV ; Y = S or Se) with an alkylthio-imide, such as PhN:CR′·SMe ; intermediate compounds (XLVI ; Y = S or Se) could also be prepared.[159] By condensing quaternary salts, (XLIV ; Y = S or Se), with an acyl chloride in pyridine, intermediate compounds (XLVII) were prepared. These were convertible into halogenovinyl compounds, such as (XLVIII),* whence (XLVI ; Y = S or Se) could be obtained ; thioketones (XLIX ; Y = S or Se) could be prepared from (XLVII) or (XLVIII).[160] By use of appropriate thioketones, *meso-cyclo*alkyl groups were introduced.[161]

Trimethincyanines of the pyrrole series, such as (L), with an α-R substituent, were prepared by condensing two moles of a pyrrole carrying an imino-group and having the 2- or the 2- and the 5-position free, with one each of ethyl orthoformate and a ketone, R·COMe, in the presence of acid. Trimethincyanines of the indole series, *e.g.* (LI), with α-R and β-carbethoxy-substituents, were prepared by condensing an indole carrying an imino-group and having its 3-position free, with a β-keto-ester, followed by reaction of the product with a 2-methylindole-3-aldehyde (similarly with a pyrrole-2-aldehyde).[150]



(L.)



(LI)

In the pentamethincyanine series, derivatives with various electronegative *meso*-substituents were the earliest known and have been discussed.[82] Recently, a *meso*-cyano-group has been introduced by condensing (XXVI) with cyanoacetic acid.[162] A methyl group has been introduced into every possible position in the chain [84, 89, 163, 164] and the effect on absorption and sensitisation studied.

Hepta- and poly-methincyanines with acyloxy-substituents have been considered.[103] With the heptamethincyanines, the effect of introducing a methyl group into various positions in the chain has been studied,[98, 165] and heptamethincyanines having γ-halogeno-,[166] δ-alkoxy-,[167] and δ-cyano-substituents [162] have been made.

Certain symmetrical trimethincyanines, *e.g.* (LII) and (LIII), in which

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[159] I.G. Farbenind. A.-G., B.P. 412,309/1932.

[160] L. G. S. Brooker, F. L. White, and Eastman Kodak Co., U.S.P. 2,112,139—40/1938 ; 2,231,659 ; 2,233,509—10 ; 2,243,081/1941 ; 2,315,498/1943 ; 2,369,646—7/1945.

[161] L. G. S. Brooker, G. H. Keyes, and Eastman Kodak Co., U.S.P., 2,441,529/1948.

[162] F. P. Doyle, J. D. Kendall, and Ilford Ltd., B.P. 620,801/1947.

[163] Z. P. Sitnik and B. S. Steingardt, *J. Appl. Chem. Russia*, 1936, **9**, 1842.

[164] J. D. Kendall, H. W. Wood, and J. R. Majer, B.P. 553,143—4/1941.

[165] F. M. Hamer and R. J. Rathbone, *J.*, 1947, 960.

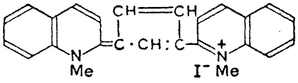
[166] A. Corbellini and R. Fusco, *Rend. Ist. Lomb. Sci. Lett.*, 1935, **68**, 961.

[167] J. D. Kendall, B.P. 526,684/1939.

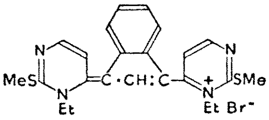
* In formula (XLVIII) the double bonds of the benzene ring have inadvertently been omitted.

the chain forms part of a homocyclic nucleus, were prepared by condensing quaternary salts, having a reactive alkylthio-group, with *cyclo*pentadiene or indene ; subsequently intermediate compounds and hence unsymmetrical trimethincyanines with the *cyclo*pentadiene nucleus were claimed.[168]

The *cyclo*hexene ring was inserted as part of the pentamethin chain, giving, *e.g.*, (LIV), by condensing a quaternary salt, having a reactive methyl group, with a *cyclo*hexane-1 : 3-dione or with a 3-alkylthio*cyclo*hex-2-enone.[169] Pentamethincyanines in which the chain formed part of a benzene nucleus, *e.g.* (LV), were prepared by eliminating acid from a diquaternary salt in which two benzthiazole nuclei were linked by $\cdot(p\text{-})CH_2\cdot C_6H_4\cdot$.[170, 171] Cyclisation of the pentamethin chain had a hypsochromic effect upon absorption.

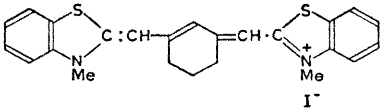


(LII.)

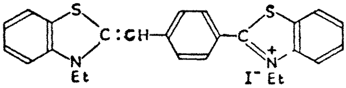


(LIII)

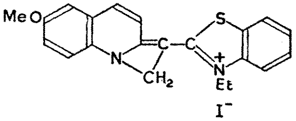
(LIV.)



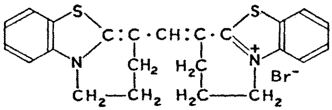
(LV.)



(LVI.)



(LVII.)



Special types of chain-substituted methin- and trimethin-cyanines, *e.g.* (LVI) and (LVII), were prepared through cyclic ammonium quaternary salts in which a 2 : 3-di-, 2 : 3-tri-, or 2 : 3-tetra-methylene group played

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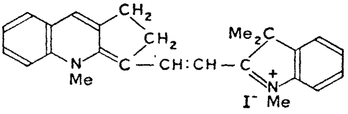
[168] *Idem*, B.P. 431,142 ; 431,187/1933 ; 526,892—3/1939.

[169] J. D. Kendall, F. P. Doyle, and Ilford Ltd., B.P. 595,783—5 ; 604,217/1945.

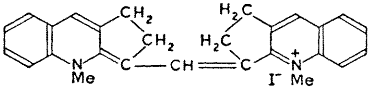
[170] L. G. S. Brooker, R. H. Sprague, and Eastman Kodak Co., U.S.P. 2,356,445/1944.

[171] A. I. Kiprianov, I. K. Uschenko, and A. L. Gerschun, *J. Gen. Chem. Russia*, 1944, **14**, 865.

the part of the 2-methyl and *N*-alkyl groups.[172, 173] Other special types of chain-substituted trimethincyanines, such as (LVIII) and (LIX), were prepared by making use of the reactive homocyclic methylene group of quaternary salts of dihydro-*β*-quinindene.[174]



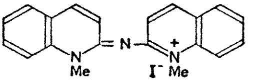
(LVIII)



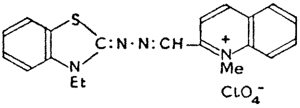
(LIX)

Azacyanines.—The possibility of preparing methincyanine analogues, with the nuclei linked by nitrogen, was realised when the first azamethincyanine (LX) was synthesised through a quaternary salt of *N*-acetyldi-2-quinolylamine. As compared with the methincyanine, its absorption was hypsochromic.[175] A general method for preparing azamethincyanines consisted in condensing a quaternary salt having an alkylthio-group either with one having an amino-group in the reactive position, or with ammonia; a base having a reactive amino-group could be used instead of a salt, giving a base of which the azacyanine was the quaternary salt.[176]

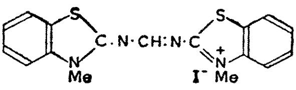
The first *αβ*-diazatrimethincyanines, *e.g.* (LXI), synthesised by condensing a nascent 2-formyl quaternary heterocyclic ammonium salt with the hydrazone of a heterocyclic ketone (such as 3-ethyl-2-benzthiazolone hydrazone), were found to have desensitising properties,[177] and the method was extended to others of this type.[178] *αα'*-Diazatrimethincyanines, *e.g.* (LXII), were synthesised from a heterocyclic base, having a 2-amino-group,



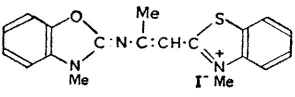
(LX)



(LXI)



(LXII)



(LXIII)

and ethyl orthoformate, *via* a di-heterocyclic-substituted formamidine, or else from a quaternary salt, having a reactive alkylthio-group, and an amidine; [176] others were prepared by the action of ethyl orthoformate and

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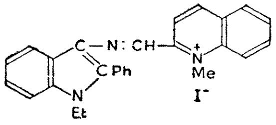
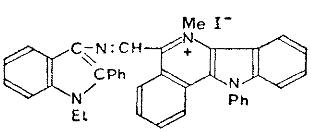
[172] G. Schwarz, *Natuurwetensch. Tijds.*, 1937, **19**, 243.
[173] P. de Smet and G. Schwarz, *ibid.*, 1939, **21**, 271.
[174] A. B. Lal and V. Petrow, *J.*, 1948, 1895.
[175] F. M. Hamer, *J.*, 1924, **125**, 1348.
[176] J. D. Kendall, B.P. 447,038; 447,109/1934; 461,668/1935.
[177] K. Fuchs and E. Grauaug, *Ber.*, 1928, **61**, 57.
[178] N. I. Fisher and F. M. Hamer, *J.*, 1937, 907.

pyridine on 2-aminoquinoline alkiodide.[178] As compared with the trimethin chain, $\alpha\beta$-diaza-groups produced a hypsochromic shift of about 800 A. but an $\alpha\alpha'$-diaza-structure caused one more than thrice as great.[178] Symmetrical and unsymmetrical *meso*-alkyl-α-azatrimethincyanines, *e.g.* (LXIII), were made by condensing a heterocyclic base, having a reactive amino-group, with an ortho-ester, and treating the quaternary salt of the product with a salt, having a reactive methyl group, and with pyridine.[179] Some aza-cyanines possessed photographic sensitising properties.[176] The generalisation was made that desensitisation occurs when the nitrogen atom of the chain is connected to one or more of the heterocyclic nitrogen atoms by an even-numbered carbon chain.[180] Several azadimethincyanines of a type subsequently prepared, *e.g.* (LXIV), having two such even-numbered carbon chains, did in fact desensitise. They were synthesised by condensing a 1 : 2-disubstituted 3-nitroso-indole with certain quaternary salts having a reactive methyl group,[181] or, alternatively, a 1 : 2-disubstituted 3-amino-indole with, *e.g.*, quinoline-2-aldehyde, followed by conversion of the base into a quaternary salt.[182] Cyclisation of 3-acylamido-1-alkyl-(or aryl-)2-phenyl-indoles gave indolo*iso*quinolines ; their methiodides had a reactive methyl group, whence azadimethincyanines, such as (LXV), were obtainable.[183]

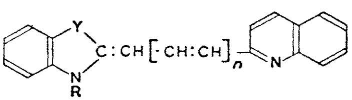


(LXIV.)

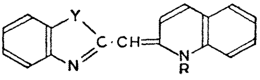


(LXV.)

Bases of which Cyanines are the Quaternary Salts.—In the synthesis of (VIII), the penultimate step was the base of which this cyanine is the quaternary salt.[33] Some years later, the base (LXVI ; Y = S ; R = Me ; $n = 0$), of which (X) is the quaternary salt, was also made.[184] A general method of preparing bases, such as (LXVI), consisted in condensing a 2- or 4-methylquinoline with a heterocyclic quaternary salt having a reactive alkylthio- or β-acetanilidovinyl group ; some of them were sensitisers.[185] The scope of the method was extended in that bases, *e.g.* (LXVII), were synthesised, having the alkyldihydro-structure in the quinoline nucleus.



(LXVI.)



(LXVII.)

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[179] J. D. Kendall and D. J. Fry, B.P. 544,646/1940.

[180] J. D. Kendall, *Proc. 9th Internat. Congr. Phot., Paris,* 1935, 227.

[181] F. G. Mann and R. C. Haworth, *J.*, 1944, 670.

[182] Huang-Hsinmin and F. G. Mann, *J.*, 1949, 2903.

[183] *Idem, ibid.*, p. 2911.

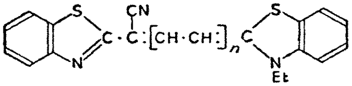
[184] L. M. Clark, *J.*, 1936, 507.

[185] J. D. Kendall, B.P. 456,362/1935 ; M. Barent and J. D. Kendall, B.P. 477,983/1936.

The absorption maxima of such bases compared with those of the related cyanines seemed erratic [58] but were usually hypsochromic.[186] The study of this subject, in connection with the theory of colour, has already been reviewed.[115] It is interesting that 2-methyl*peri*naphtho-1 : 3-thiazine resisted quaternary salt formation but, by its reaction with quaternary salts having a 2-β-acetanilidovinyl group, gave bases of trimethincyanines.[187] Similarly 2-alkylthio- and 2-methyl-4 : 5-benz-1 : 3-thiazine resisted quaternary salt formation and were used for synthesising bases of the methin- and trimethin-cyanine series.[188, 189]

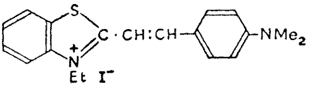
Certain symmetrical cyanines, *e.g.* (IV), (VIII), or (IX ; R′ =H), when heated with a high-boiling base such as diethylaniline, lost RX, giving the dye bases.[190]

By condensing a heterocyclic nitrogenous base, having a 2-cyanomethyl group, with a heterocyclic quaternary ammonium salt having a suitable reactive group, α-cyano-substituted bases, *e.g.* (LXVIII ; $n = 0$, 1, 2, or 3), were obtainable ; on acid hydrolysis, the cyano-group was replaced by hydrogen.[191] Similarly, methin and trimethin bases having an α-COR group were synthesised and hydrolysed.[192]

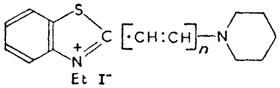


(LXVIII)

Some Salts related to Cyanines.—Quaternary heterocyclic ammonium salts having a reactive methyl group are capable of condensation with aldehydes, and the patent literature dealing with cyanines from these various salts contains numerous references to styryl compounds, some of which are sensitisers. When an aldehyde such as p-dimethylaminobenzaldehyde is used, the products, *e.g.* (LXIX), are indeed closely related to the cyanines but, because only one nitrogen atom is cyclic, are not regarded as true cyanines. Again, condensation of a quaternary heterocyclic ammonium salt having a 2-β-acetanilidovinyl group, or of either of the two higher vinylene homologues, with a primary or secondary non-aromatic



(LXIX.)



(LXX.)

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[186] L. G. S. Brooker, R. H. Sprague, C. P. Smyth, and G. L. Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116.

[187] F. M. Hamer and R. J. Rathbone, *J.*, 1943, 487.

[188] B. Beilenson and F. M. Hamer, *J.*, 1942, 98.

[189] B. Beilenson, F. M. Hamer, and R. J. Rathbone, *J.*, 1945, 222.

[190] Gevaert Photo-Producten N.V., B.P. 477,990/1935.

[191] L. G. S. Brooker, R. H. Sprague, and Eastman Kodak Co., U.S.P. 2,345,094/1944; 2,393,743/1946.

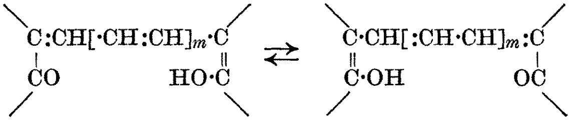
[192] A. van Dormael and J. Nys, *Bull. Soc. chim. Belg.*, 1948, **57**, 547.

amine, gave polymethin compounds, *e.g.* (LXX ; $n = 1, 2$, or 3), which comprise sensitisers and are closely related to the cyanines.[193]

***mero*Cyanines.**—

$$\mathrm{NR[{\cdot}CH{:}CH]_n{\cdot}C[{:}CH{\cdot}CH]_m{:}C{\cdot}CO{\cdot}NR'}$$

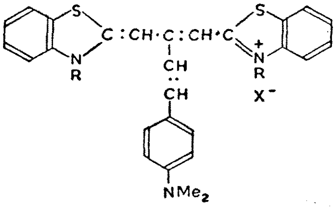
*mero*Cyanines of the above constitution ($m = 0, 1, 2$, or 3 ; $n = 0$ or 1) [194] must be considered before trinuclear cyanines can be dealt with. They are non-ionic dyes, prepared by condensing intermediate compounds, which would give cyanines, with substances having a reactive cyclic methylene group ; they comprise valuable photographic sensitisers and were discovered in two countries ; [195, 196] they are intermediate in structure between the cyanines and the oxonols, formulated below ($m = 0, 1, 2$, or 3), and have



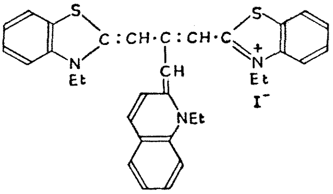
been named systematically.[194] As with cyanines, so also with *mero*-cyanines, various unusual intermediate compounds have been used and chain-substituted dyes made. Polynuclear *mero*cyanines have been built up.

Trinuclear Cyanines.—Trinuclear cyanines, prepared by taking advantage of both reactive groups in a 2 : 4-disubstituted quinoline alkiodide, have already been mentioned.[51]

A very interesting observation was that of the reactivity of the *meso*-methyl group in (IX ; R′ = Me) : *e.g.*, with *p*-dimethylaminobenzaldehyde it gave the chain-substituted trimethincyanine (LXXI).[197] Subsequently (IX ; R′ = Me) with heterocyclic quaternary ammonium salts having a reactive alkylthio-group, etc., gave trinuclear cyanines such as (LXXII).[198]



(LXXI.)



(LXXII.)

Neocyanine was announced in 1926 as sensitising more powerfully beyond 8000 A. than any dye then known ; [199] it had been made by treating

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[193] F. L. White, G. H. Keyes, and Eastman Kodak Co., U.S.P. 2,166,736/1939 ; 2,263,749/1941.

[194] F. M. Hamer and B. S. Winton, *J.*, 1949, 1126.

[195] J. D. Kendall, B.P. 426,718/1933.

[196] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 2,078,233/1937.

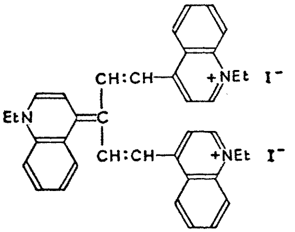
[197] T. Ogata, *Bull. Chem. Soc. Japan*, 1936, **11**, 262.

[198] L. G. S. Brooker, F. L. White, and Eastman Kodak Co., U.S.P. 2,282,115/1942.

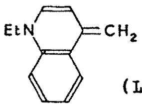
[199] M. L. Dundon, A. L. Schoen, and R. M. Briggs, *J. Opt. Soc. Amer.*, 1926, **12**, 397.

a lepidinium salt with iodoform and alkali.[200] It also arose as by-product in making a 4 : 4′-trimethincyanine by the ethyl orthoformate and pyridine method,[37] which, on modification, gave greatly improved yields of neocyanines from lepidinium salts. Analyses showed that the neocyanine molecule had been formed from three molecules of lepidine alkyl halide, with elimination of hydrogen halide, and that either one or two additional carbon atoms had entered. Based on the former supposition, the first neocyanine formula, showing it as a β-substituted 4 : 4′-trimethincyanine, was proposed.[201] This formulation was applied to other dyes, made from alkiodides of various heterocyclic bases, with orthoformic ester or diphenylformamidine, in the presence of different condensing agents,[202] but, when neocyanines of the thiazole series were described, an alternative was suggested [203] which had the advantage of explaining the stability of the neocyanines to alkali.

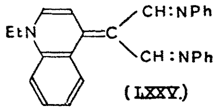
In 1935 neocyanines were formulated as having an unbranched pentamethin chain, with three similar nuclei symmetrically attached, so that two trimethin chains were also present.[204] According to the modern equivalent of this formula, the two units of positive charge of the cation are distributed over the three basic groups, the molecule being regarded as a resonance hybrid of three canonical structures, of which (LXXIII) is one. The synthesis of such trinuclear cyanines was effected, starting from various heterocyclic methylene bases, e.g. (LXXIV), or their anilomethyl derivatives, which, on heating with ethyl N-phenylformimidate and zinc chloride, gave intermediate dianilo-compounds, e.g. (LXXV), which were condensed with the usual salts, having a reactive methyl group. The synthetic dyes, having three similar heterocyclic nuclei, were, in three instances, identified with neocyanines which had arisen empirically. By condensing a dianil with a salt having a reactive methyl group but a different nucleus, there resulted trinuclear cyanines with two similar nuclei and one other, e.g. (LXXVI), the two similar ones being at the ends of the penta-



(LXXIII)



(LXXIV)



(LXXV)

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[200] H. T. Clarke and Eastman Kodak Co., U.S.P. 1,804,674/1931.

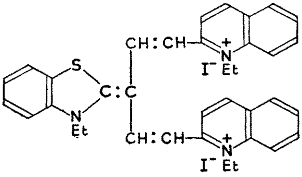
[201] F. M. Hamer, *J.*, 1928, 1472.

[202] T. Ogata, *Proc. Imp. Acad. Tokyo*, 1932, **8**, 503 ; 1933, **9**, 602 ; *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497.

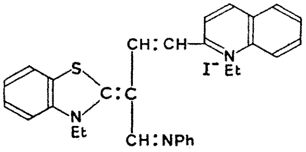
[203] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 1,969,445/1934; 1,994,562/1935.

[204] W. König, *Z. wiss. Phot.*, 1935, **34**, 15.

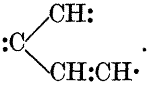
methin chain. Under milder conditions, the dianils reacted with quaternary salts to give anilomethyl intermediate compounds, such as (LXXVII),* having two nuclei; from these were prepared, first, neocyanines with two similar nuclei and one other, the two similar nuclei lying at the ends of a trimethin chain, and secondly, neocyanines with three dissimilar nuclei.

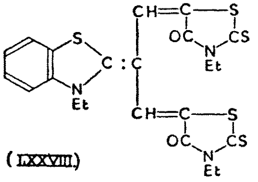


(LXXVI.)

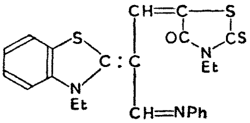


(LXXVII.)

By condensing one mole of a dianil with two of a substance having a reactive cyclic methylene group, there resulted dyes, *e.g.* (LXXVIII), having the trimethin chain of an oxonol and two of the chains characteristic of dimethin*mero*cyanines. They also gave intermediate compounds, *e.g.* (LXXIX), which are anilomethyl-dimethin*mero*cyanines. These could be used to give a dye of the same type as (LXXVIII) but with the three nuclei all different. On the other hand, condensation with a quaternary salt having a reactive methyl group gave dyes, *e.g.* (LXXX), characterised by the chain  $:C\begin{smallmatrix}\diagup CH: \\ \diagdown CH:CH\cdot\end{smallmatrix}$. This kind of dye, which is simultaneously a trimethincyanine, a dimethin*mero*cyanine, and a tetramethin*mero*cyanine, could also be synthesised from the other type of intermediate compound

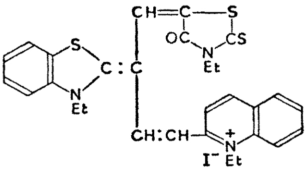


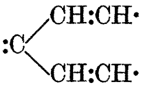
(LXXVIII.)



(LXXIX.)

(LXXX.)



(LXXVII). In each of thirty-seven instances, the absorption maximum of the neocyanine having the chain  $:C\begin{smallmatrix}\diagup CH:CH\cdot \\ \diagdown CH:CH\cdot\end{smallmatrix}$ lay at a shorter wave-length

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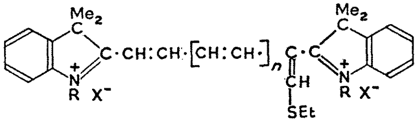
* In formula (LXXVII) a positive charge has inadvertently been omitted from the right-hand nitrogen atom.

than that of the corresponding pentamethincyanine; in forty-five of forty-seven instances, that of the neocyanine lay at a longer wave-length than that of the corresponding trimethincyanine—in the two exceptions, the Δ^2-thiazoline nucleus was concerned. As sensitisers, the neocyanines were disappointing, which is partly explained by the fact that, since the announcement of the first, the standard of infra-red sensitisers has soared, through the discovery of the penta-, hepta-, and poly-methincyanines.[205]

Another preparation of neocyanines consisted in heating a trimethincyanine with a quaternary salt, having a reactive methyl group, and ethyl trithio-orthoformate in acetic anhydride; thus (XII; Y = O) with 2-methylbenzoxazole ethiodide gave the benzoxazole analogue of (LXXIII). From unsymmetrical trimethincyanines, neocyanines with two or three different nuclei could be prepared. The predominant formation of only one neocyanine from an unsymmetrical trimethincyanine was remarkable, entailing the working out of the constitution of each product by an alternative synthesis.[206] However, the fact of there being only one product makes this method a convenient preparative one. Inclusion of acid amongst the reactants led to the production of intermediate compounds, such as (LXXXI; $n = 0$), which led to neocyanines.[207]

(LXXXI.)



Intermediate compounds, *e.g.* (LXXXI; $n = 1$), similarly prepared from pentamethincyanines, yielded, with quaternary salts having a reactive methyl group, higher vinylene homologues of neocyanines.[207]

Photographic Sensitisation.—The optimum quantity of sensitiser varies from 5 to 100 parts per million of photographic emulsion; above the optimum, desensitisation and fogging may become serious. The longer the wave-length of sensitisation, the less the amount of sensitiser required; this has been attributed [19] to the efficiency of energy-transfer from dye to silver halide at longer wave-lengths. Contrary to the theory that the sensitising process is a true photochemical reaction of a dye unstable to light, it seemed probable that the sensitiser facilitated transfer of an electron from Br^- to Ag^+, without itself undergoing decomposition.[208] A determination of the number of silver atoms formed during exposure of infra-red sensitised emulsions led to the conclusion that at wave-lengths of 7000, 8500, 9500, and 10,500 A., each sensitiser molecule acted at least 5, 90, 160, and 8 times, respectively, in causing decomposition of one silver bromide molecule.[209]

[205] F. M. Hamer, R. J. Rathbone, and B. S. Winton, *J.*, 1947, 954, 1434; *J.*, 1948, 1872; *J.*, 1949, 1113.

[206] J. D. Kendall and J. R. Majer, *J.*, 1948, 690.

[207] J. D. Kendall, F. P. Doyle, and Ilford Ltd., B.P. 638,023—4/1947.

[208] S. E. Sheppard, R. H. Lambert, and R. D. Walker, *Nature*, 1937, **140**, 1096; 1938, **142**, 478; *J. Chem. Physics*, 1939, **7**, 426.

[209] J. Eggert, W. Meidinger, and H. Arens, *Helv. Chim. Acta*, 1948, **31**, 1163.

Since the amounts of dye producing optimum sensitisation were found to be directly proportional to the silver halide surface, it was concluded that the dye molecules were adsorbed in a unimolecular layer.[210] According to another view, the first layer of dye was adsorbed through the polar nitrogen atoms, the molecules projecting upwards from the surface, whilst a second layer might be oppositely orientated.[211]

Resonance within conjugated systems results in a tendency towards planarity of the molecule. For optical sensitising, it appeared that a planar configuration of the dye molecule was necessary.[212] With one symmetrical cyanine it was found that the replacement of two imino- by two methylimino-groups necessitated a departure from planarity; this required energy, whence the observed shift of the absorption to longer wave-lengths was explained.[213] Subsequently other examples were added of such a shift of absorption, caused either by crowding of the nuclei out of a plane or by increased distortion in a molecule already non-planar. Unsymmetrical dyes behaved differently but in both groups non-planar dyes absorbed less intensely than the corresponding planar ones.[214] In certain chain-substituted trimethincyanines, the planar principal resonance structure was determined by comparison of the absorption spectra with those of simpler related dyes, which were planar.[215]

Supersensitisation.—Photographic emulsion makers know only too well the difficulties of using mixtures of sensitising dyes and, with a pair of sensitisers, to achieve sensitisation approximating to the sum of two separate sensitisations seemed, until fairly recently, as much as could be aimed at. However, it now appears that, in some instances, mixing gives a result actually superior to the sum of two separate factors, which effect is known as supersensitisation. The first recorded observation of it was in 1918,[216] in the improvement of the sensitisation of pinacyanol by addition of auramine, but this remained an isolated instance. In the earliest of the comparatively recent patents, pinacyanol or a 2 : 2′-cyanine [217] was named as sensitiser, the action of which was improved by adding, as supersensitiser, a dye having a dialkylaminostyryl group. There followed many instances in which cyanines of one specific type were used in conjunction with cyanines of another, or with dyes of a different class; later, the distinction as to which was sensitiser and which supersensitiser was not made. Moreover certain sensitising dyes could be improved by addition of supersensitisers, which themselves possessed no sensitising power. Most of the dyes which can undergo supersensitisation are those capable of producing two types

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[210] J. A. Leermakers, B. H. Carroll, and C. J. Staud, *J. Chem. Physics*, 1937, **5**, 893.

[211] S. E. Sheppard, R. H. Lambert, and R. D. Walker, *ibid.*, 1939, **7**, 265.

[212] *Idem*, *Nature*, 1940, **145**, 386.

[213] K. J. Brunings and A. H. Corwin, *J. Amer. Chem. Soc.*, 1942, **64**, 593.

[214] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, and G. van Zandt, *Chem. Reviews*, 1947, **41**, 325.

[215] P. Bruylants, A. van Dormael, and J. Nys, *Bull. Acad. Belg., Cl. Sci.*, 1948, **34**, 703.

[216] O. F. Bloch and F. F. Renwick, *Phot. J.*, 1920, **60**, 145.

[217] C. E. K. Mees and Eastman Kodak Co., U.S.P. 2,075,046—7/1937.

of sensitising, according to their existence in the molecular or in the aggregated condition.

Aggregation of Cyanine Dyes.—The first indication of aggregation in the cyanine group was the observation that Beer's law did not hold for certain members in aqueous solution.[218] Thereafter followed observations that such solutions of 2 : 2′-cyanine chloride might exhibit an intense narrow absorption band, accompanied by resonance fluorescence, and methods for inducing this condition were described.[219, 220] On the one hand it was regarded as a molecular phase, intermediate between an earlier one of true solution and a later formation of nematic aggregates of dye molecules, that phase in turn being succeeded by crystallisation.[221] As the fluorescence and narrow absorption were accompanied by abnormally high viscosity, the phenomenon was alternatively explained as due to polymerisation, following ionic dissociation.[220] From the absorption curves of pinacyanol chloride at different concentrations, the presence of mono-, di-, and poly-molecular forms was inferred ; absence of high viscosity in this instance was explained by postulating spherical particles.[222] With the 2 : 2′-methincyanine, adsorption experiments on mica led to the conclusion that the individual cations in the polymer were held parallel, with staggering of alternate units, by the inductive forces of the *p*-electrons of the nuclei and of the chain.[223] Alternatively, direct parallel apposition of the units accounted for the absence of aggregation in certain unsymmetrical cyanines, the forces postulated being intermolecular resonance linkages through hydrate water molecules ; a new type of nematic phase, consisting of plurimolecular filaments, was proposed.[224] Measurements of the decay of fluorescence were used to determine the degree of polymerisation of methincyanines.[225] The absorption curves of a 2 : 2′-cyanine and of *iso*Quinoline Red supported conclusions as to their degree of aggregation, as determined by osmotic pressure and conductivity measurements.[226]

Under suitable conditions, a cyanine may confer sensitivity in different spectral regions, corresponding with the molecular and aggregated states.[227] Thus whereas all sensitising cyanines show that type of sensitisation in which the maximum lies 250—500 A. beyond the absorption maximum of an alcoholic solution, *meso*-alkyltrimethincyanines, under conditions favouring adsorption, may show sensitisation at a longer wave-length : [228] the capacity of numerous dyes to behave thus has been examined.[229] Absorption spectra of trimethincyanines indicated the existence of molecular,

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[218] G. Scheibe with E. Rager, *Angew. Chem.*, 1936, **49**, 563.

[219] E. E. Jelley, *Nature*, 1936, **138**, 1009.

[220] G. Scheibe, L. Kandler, and H. Ecker, *Naturwiss.*, 1937, **25**, 75.

[221] E. E. Jelley, *Nature*, 1937, **139**, 631.

[222] G. Scheibe, A. Mareis, and H. Ecker, *Naturwiss.*, 1937, **25**, 474.

[223] G. Scheibe, *Angew. Chem.*, 1939, **52**, 631.

[224] S. E. Sheppard, *Science*, 1941, **93**, 42.

[225] F. Katheder, *Kolloid Z.*, 1940, **92**, 299 ; **93**, 28.

[226] H. O. Dickinson, *Trans. Faraday Soc.*, 1947, **43**, 486.

[227] J. A. Leermakers, B. H. Carroll, and C. J. Staud, *J. Chem. Physics*, 1937, **5**, 878.

[228] G. Schwarz, *Sci. et Ind. Phot.*, 1939, (2), **10**, 233.

[229] I. I. Levkoev and S. Natanson, *Acta Physiochem. Russ.*, 1946, **21**, 437.

polymeric, and aggregated states.[230] Certain cyanines were adsorbed to silver halide in two forms and sensitising data also led to the conclusion that both single and aggregated dye molecules exist.[231] In leaving the subject of aggregation, we may note claims concerning the preparation of certain polymeric cyanines as sensitisers; [232, 233] starting points were the quaternary salts of bis-heterocyclic bases, in which the two cyclic nitrogen atoms were linked by a hydrocarbon radical and there was a reactive group in the α-position to each.

In this review an attempt has been made to cover primarily the different types of cyanine dyes and the methods used in their synthesis, with special reference to their use in photography. The wide range of cyanines of various kinds offers an incomparable opportunity for developing and testing theories about colour. A probable future development is the synthesis of complex cyanines with new types of branched polymethin chains. On the applied side, progress may depend not so much on the discovery of new complex dyes as in finding how to make the best of comparatively simple ones, which end must surely be reached by fundamental work on sensitisation.

[230] S. M. Soloviev, *J. Phys. Chem. Russia*, 1945, **19**, 459.

[231] E. P. Davey, *Trans. Faraday Soc.*, 1940, **36**, 323.

[232] C. D. Wilson and E. I. du Pont de Nemours and Co., U.S.P. 2,393,351/1946; 2,425,772—4/1947; 2,465,774/1949.

[233] L. G. S. Brooker and Eastman Kodak Co., U.S.P. 2,461,137/1949.

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