line which, however, does not pass through the origin. This type of relation was found before for dissolution rates in experiments with metal and other cylinders rotating at a higher speed in appropriate reagents.[2] Explanations of this extrapolation to a finite rate constant at zero diffusion coefficient are unsatisfactory, and as shown elsewhere[9] it is more probable that the true relation is of an exponential type

$$k = \alpha D^x$$

being nearly linear over the range of values plotted in Fig. 3. This exponential relation is consistent with a diffusion layer whose thickness increases with increasing diffusion coefficient, as is necessary from a consideration of turbulence in the solution near the metal surface.[2] Such a relation is also predicted from the expressions of Colburn[10] and Chilton and Colburn[11] derived to correlate heat and mass transfer in gas–liquid and gas–solid systems. The exponent x is given as $^2/_3$ by these authors.

From a log–log plot of k *vs.* D, the best value of x for these data is found to be approximately 0.70. In Fig. 4, values of k are plotted *vs.* $D^{0.70}$; the linear relation is at least as good as that of Fig. 3. The straight line is represented by the equation

$$k = 0.36D^{0.70}$$

A similar exponential relation holds for the data of ref. 2 and also of ref. 9. In the latter case, values for heat transfer are represented by the same equation as values for dissolution rates.

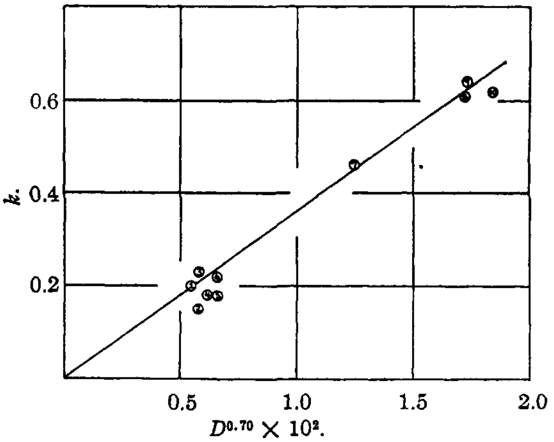

Fig. 4.—Dissolution rate constants *vs.* diffusion coefficients to the 0.70 power. Acids: numbered as in Fig. 3.

Summary

The diffusion coefficients of twelve acids have been measured in the porous glass disk type of diffusion cell, alone and in the presence of their magnesium salts when possible, otherwise with other salts present.

The dissolution rate of magnesium from cylinders rotating with a peripheral speed of 2000 cm./min. has been measured in the same acids in the presence of the same salts.

A comparison of diffusion coefficients and dissolution rate constants shows that they can be correlated fairly satisfactorily. The correlation is in agreement with a modification of the Nernst theory for such dissolution rates, and also with the Chilton–Colburn relations for heat and mass transfer at a phase boundary.

NEW YORK, N. Y. RECEIVED SEPTEMBER 9, 1936

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[9] King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937).

[10] Colburn, *Trans. Am. Inst. Chem. Engrs.*, **29**, 174 (1933).

[11] Chilton and Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).

[CONTRIBUTION NO. 581 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. VII. New Dyes Containing Three Heterocyclic Nuclei

BY L. G. S. BROOKER AND L. A. SMITH

Cyanine dyes have been described in which a quinoline nucleus is linked through either the 2- or 4-position to a second heterocyclic nucleus. In the present paper, dyes of a new type are described in which a quinoline nucleus is linked through both of these positions to two other nuclei. These dyes differ from the previously known trinuclear dyes of the neocyanine type[1] since in the latter two nuclei are linked together by a three-carbon chain, the third nucleus forming part of a group attached to one of the carbon atoms of this chain.[2-5]

If 2,4-dimethylquinoline ethiodide (I) is treated with an excess of 2-iodoquinoline ethiodide in the presence of triethylamine, both methyl groups take part in the reaction, and a

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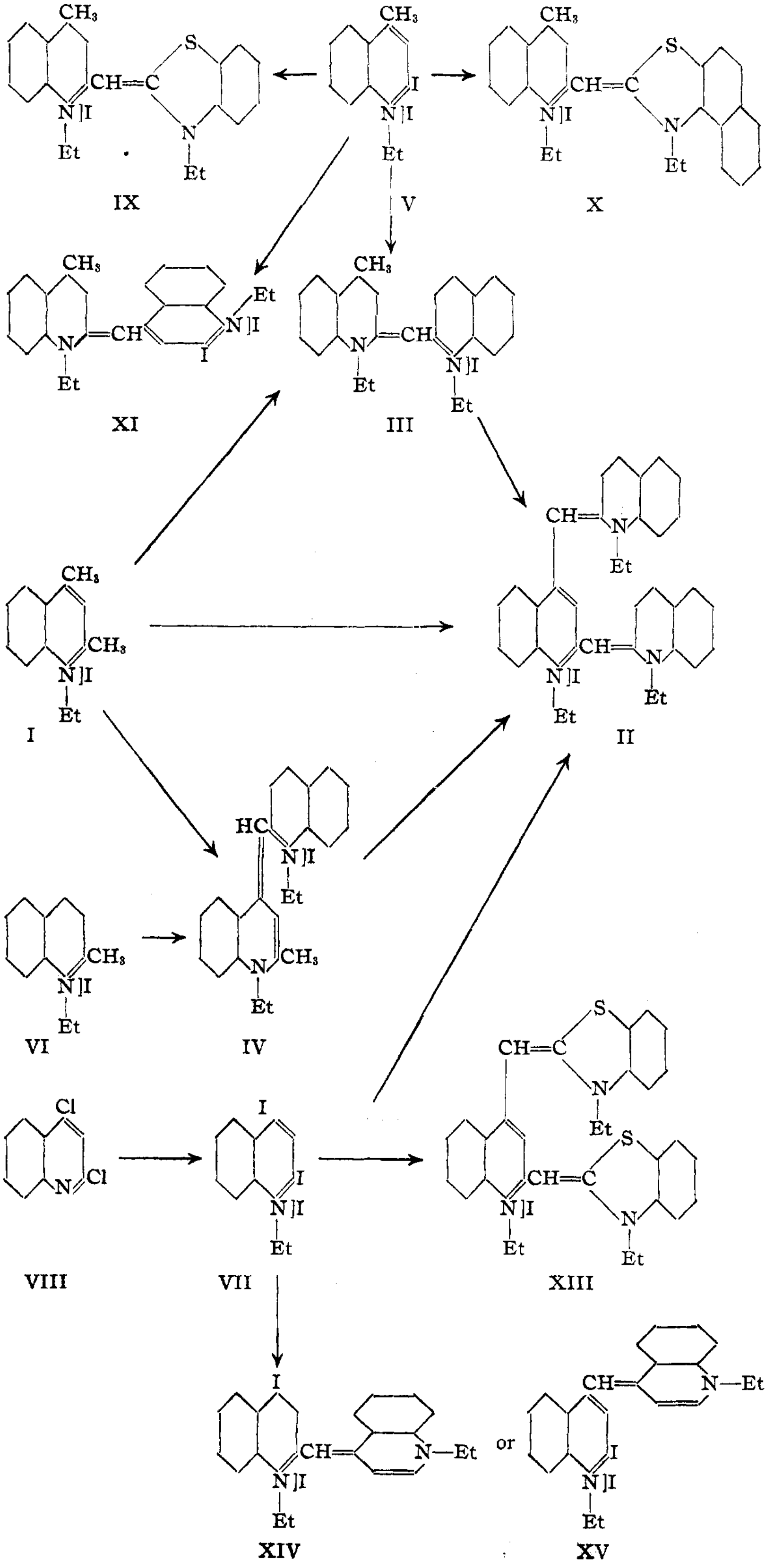
[1] Dundon, Schoen and Briggs, *J. Opt. Soc. Am.*, **12**, 397 (1926).

[2] Hamer, *J. Chem. Soc.*, 1472 (1928).

[3] Brooker, Hamer and Mees, *J. Opt. Soc. Am.*, **23**, 216 (1933).

[4] König, *Z. wiss. Phot.*, **34**, 15 (1935).

[5] Hamer, *J. Soc. Chem. Ind.*, **54**, 640 (1935).



new cyanine dye, 2,4-di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline ethiodide (II) is formed. With equimolecular proportions of the two quaternary salts, however, a mixture of dyes is produced, the less soluble component of which, isolated as the perchlorate, was found to be identical with the perchlorate corresponding to 1,1′-diethyl-4-methyl-2,2′-cyanine iodide (III) made by condensing 2-iodolepidine ethiodide (V) with quinaldine ethiodide (VI). The second component of the mixture was not isolated in a pure state, but was without doubt the isomeric 1,1′-diethyl-2′-methyl-2,4′-cyanine iodide (IV). The absorption curve of the mixture of dyes was in complete agreement with this assumption, there being present distinct maxima corresponding to III and IV. The latter has been prepared by the action of potassium hydroxide on quinaldine ethiodide.[6]

It is reasonable to ascribe a certain reactivity to the methyl groups in III and IV and to regard these dyes as intermediate steps in the synthesis of II from I. This is substantiated by the fact that II was prepared from IV by interaction with a further proportion of 2-iodoquinoline ethiodide. In an attempted preparation of II from III, not enough of the desired dye was obtained for analysis, but there was sufficient to give the characteristically colored solution of II (see below).

A further preparation of II was carried out as follows:

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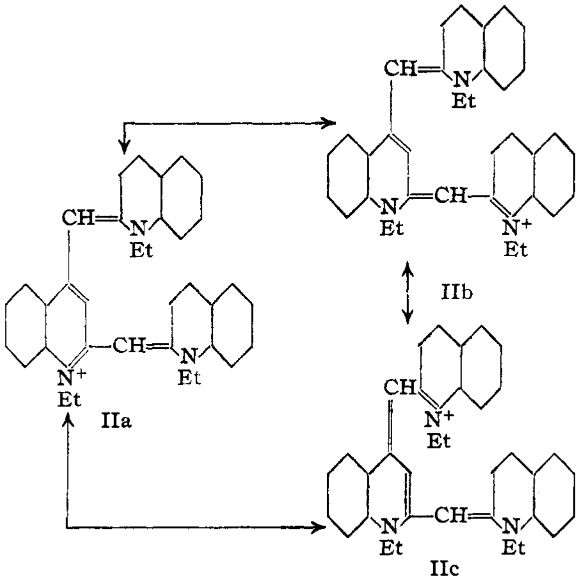
(6) Kaufmann and Vonderwahl, *Ber.*, **45**, 1413 (1912).

2,4-diiodoquinoline ethiodide (VII) was prepared from 2,4-dichloroquinoline (VIII) by heating the latter with an excess of ethyl iodide in a sealed tube at 100°. In VII the iodine atoms in positions 2 and 4 were both found to be reactive, since II was prepared by condensing it with VI, using triethylamine, it being best to use an excess of VI.

As obtained by any of the methods given, II consists of rather dark bronze crystals which dissolve in methyl alcohol to give a solution which is dull greenish-blue when sufficiently dilute but which develops a reddish color as the concentration is increased. The absorption curve of the dye (Fig. 1, A) is remarkable and differs in character from that ever previously described for a cyanine dye. There are two principal bands with maxima at 4800 and 6150 Å., respectively, that at the shorter wave length being narrower and somewhat stronger than the other. Between these bands there is a region of almost complete transmission with minimum absorption at about 5150 Å. In addition to the two principal bands, there is a weaker band with a distinct maximum at 4550 Å. The general appearance of the absorption curve is reminiscent of that of a mixture of two distinct cyanine dyes, the individual absorption curves of which overlap but very slightly.



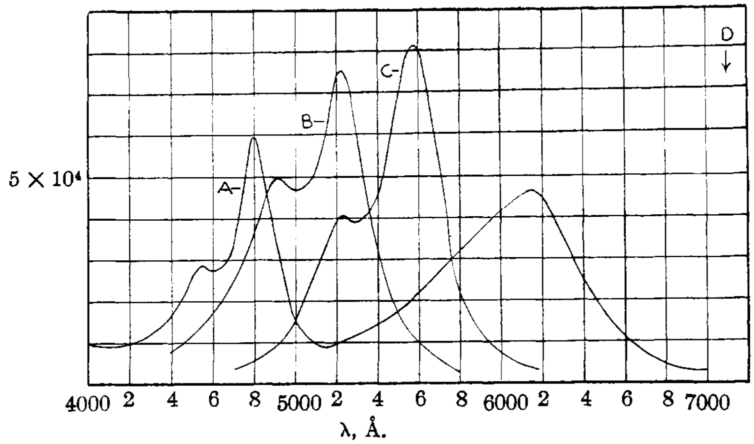
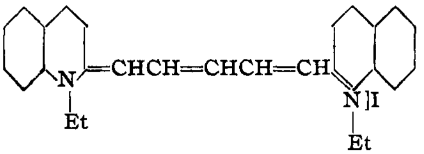


Fig. 1.—Absorption curves. A = 2,4-di[(1-ethyl-2(1)quinolylidene)methyl] quinoline ethiodide (II); B = 1,1′-diethyl-2,2′-cyanine iodide; C = 1,1′-diethyl-2,4′-cyanine iodide; D indicates maximum absorption of 1,1′-diethyl-2,2′-dicarbocyanine iodide (XII).

There is much direct and indirect evidence for the tautomerism of the cyanine dyes[7–9] and furthermore, it is plausible to assume that the color of these dyes is due to this tautomerism or, more precisely, to resonance within the conjugated chain (or chains) connecting the nitrogen atoms.[10] In the case of II this resonance may be represented as shown.

Now, the modes of resonance involved in IIa ↔ IIb and IIa ↔ IIc are those which are characteristic of 2,2′-cyanines and 2,4′-cyanines, respectively, while that of IIb ↔ IIc resembles that characteristic of 1,1′-diethyl-2,2′-dicarbocyanine iodide (XII),[11] but there is this difference, that whereas in XII the two nuclei are linked together by a simple pentamethenyl chain, in II a portion of the 5-carbon chain linking the two quinoline nuclei forms a part of the third quinoline nucleus.



XII

For purposes of comparison the absorption curves of 1,1′-diethyl-2,2′-cyanine iodide (Fig. 1, B) and of 1,1′-diethyl-2,4′-cyanine iodide (Fig. 1, C) are shown, these being the simple dyes the

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[7] Mills and Braunholtz, *J. Chem. Soc.*, **121**, 1489 (1922).

[8] Hamer, *ibid.*, 206 (1928).

[9] Brooker and Keyes, THIS JOURNAL, **57**, 2488 (1935).

[10] Compare Bury, *ibid.*, **57**, 2115 (1935).

[11] Fisher and Hamer, *Proc. Roy. Soc.* (London), **A154**, 703 1936).

characteristic linkages of which are simultaneously present in II. The absorption maximum of XII at 7080 Å., is indicated by the arrow (Fig. 1, D). The dye has a secondary maximum at 6510 Å.

It is reasonable to ascribe the unusual absorption of II to its unusual structure and specifically to the presence in the molecule of linkages characteristic of several distinct cyanine dye types. A point to be considered, however, is that whereas in a simple 2,2′-cyanine the conjugation between the two nitrogen atoms is complete in both the resonance formulas, in II the conjugation between the two nitrogen atoms of the 2,2′-cyanine linkage is interrupted in IIc. Similarly, the conjugation of the 2,4′-cyanine linkage is interrupted in IIb while the 2,2′-dicarbocyanine linkage is interrupted in IIa. Thus, although II contains conjugated linkages characteristic of three distinct cyanine dye types, in each of the three cases there is a further way of writing the formula of the dye in which the conjugation of these linkages is broken.

In the case of the meriquinoid dye Michler's Hydrol, it has been found that introducing a substituent (NH_2 or OH) in such a position that the molecule is no longer permanently quinonoid (giving Auramine or Michler's ketone, respectively) markedly lightens the color.[12] In the present case if it be assumed that that portion of the absorption curve of II which has its maximum at 6150 Å. is related to the modified dicarbocyanine system represented by IIb ⟷ IIc, it follows that the effect of incorporating part of the polymethine chain of XII in a third quinoline nucleus, giving II, is to shift the absorption maximum 930 Å. toward the blue, and this marked hypsochromic effect may be due, in part at least, to the breaking of the conjugated dicarbocyanine system in IIa.

The relationship of the remainder of the absorption curve of II to the 3- and 5-carbon nitrogen–nitrogen linkages present in the dye remains obscure, although it is again noteworthy that the band at 4800 Å. lies at shorter wave length even than the absorption of the simple 2,2′-cyanine.

Two dyes closely related to II have also been prepared, these being 2,4-di-[(1-methyl-2(1)-quinolylidene)-methyl]-quinoline methiodide and 2,4-di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline methiodide. The absorption curves of these dyes are very similar to that of II, but the three differ considerably in their sensitizing action, that containing the three methyl groups being by far the strongest, although it is weaker than some of the cyanine dyes discovered in recent times. This dye sensitizes a bromide emulsion out to about 6700 Å. for a moderate exposure, with its maximum effect at 5550 Å., there being a weaker band with its head at about 6200 Å. The other two dyes sensitize over approximately the same range, but are weaker and show some desensitization.

It has long been known that IV is greatly inferior to 1,1′-diethyl-2,4′-cyanine iodide (Ethyl Red) as a sensitizer,[13] and Mills and Pope suggested that the presence of the substituent group in the chain of ethylenic linkages joining the two nitrogen atoms decreased the ability of the system to interact with light waves.[14] However, III is similarly greatly inferior as a sensitizer to 1,1′-diethyl-2,2′-cyanine iodide, although in this case the methyl substituent does not lie on the shortest chain connecting the two nitrogen atoms. That the depressant effect of a methyl group in the 4-(or 4-′)-position varies within wide limits, however, is demonstrated by the fact that 1′,2-diethyl-4′-methylthia-2′-cyanine iodide (IX), prepared from V, is inferior to 1′,2-diethylthia-2′-cyanine iodide to a much smaller extent, whilst 1′,2-diethyl-4′-methyl-3,4-benzothia-2′-cyanine iodide (X) is only very slightly weaker than the related unsubstituted dye.[15,16]

The absorption curves of the three dyes derived from 2-iodolepidine ethiodide were similar to those of the corresponding unsubstituted dyes, introduction of the 4′-methyl group either not affecting the position of the maximum (X) or else shifting it somewhat toward the blue (IX, 50 Å.) (III, 25 Å.).

The formation of a bluish-red impurity was observed in the preparation from V of III, IX and X, and was difficult to remove in the case of III. This impurity is doubtless due to the condensation of two molecules of V giving 1,1′-diethyl-2′-iodo-4-methyl-2,4′-cyanine iodide (XI) and a bluish-red dye, the composition of which corresponded to XI was obtained by the action of tri-

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(12) Watson, "Colour in Relation to Chemical Constitution," Longmans, Green and Co., New York, 1918, p. 108.

(13) Miethe and Book, *Ber.*, **37**, 2008 (1904).

(14) Mills and Pope, *Phot. J.*, **60**, 183 (1920).

(15) Hamer, *J. Chem. Soc.*, 2598 (1929).

(16) Brooker, U. S. Patents 1,861,836, 1,969,444.

ethylamine on V alone. The combined action of the two substituents in XI on the absorption is very slight, the maxima coinciding with those of the unsubstituted dye within the limits of error, but their effect on the sensitizing action is profound, XI giving no trace of a sensitizing band for ordinary exposures.

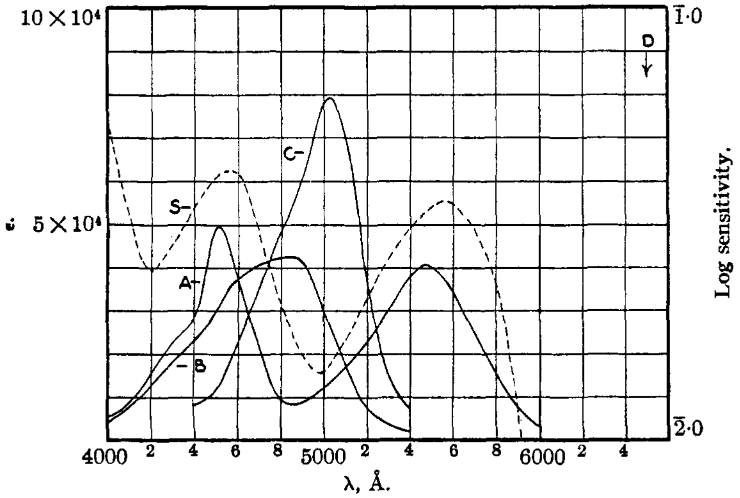
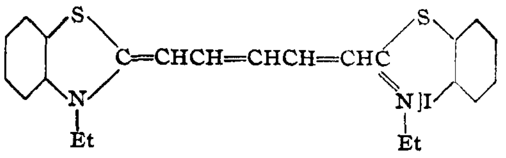


Fig. 2.—Absorption curves: A = 2,4-di[(2-ethyl-1(2)benzothiazolylidene)methyl]quinoline ethiodide (XIII); B = 1′,2-diethylthia-2′-cyanine iodide; C = 1′,2-diethylthia-4′-cyanine iodide; D indicates maximum absorption of 2,2′-diethylthiadicarbocyanine iodide (XVI). S = sensitizing curve of XIII in a chloride emulsion.

By the interaction of VII and 1-methylbenzothiazole ethiodide (in excess) using triethylamine, there was obtained 2,4-di-[(2-ethyl-1(2)-benzothiazolylidene)-methyl]-quinoline ethiodide (XIII). The dull reddish solution of this dye gives an absorption curve of the same general shape as that of II, the maxima being at 4515 and 5475 Å. and the minimum at 4875 Å. (Fig. 2, A). There is a further band at about 4300 Å., but it is ill defined.

The absorption curves of 1′,2-diethylthia-2′-cyanine iodide (Fig. 2, B) and 1′,2-diethylthia-4′-cyanine iodide (Fig. 2, C) are included for comparison, since the linkages characteristic of these dyes are simultaneously present in XIII. The third type of linkage present in XIII is a modification of that also present in 2,2′-diethylthiadicarbocyanine iodide (XVI), the absorption maximum of which is at 6500 Å.[11] (Fig. 2, arrow at D).



XVI

On the assumption already made, the effect of incorporating part of the polyene chain of XVI in a quinoline nucleus, giving XIII, is to move the maximum of absorption 1025 Å. nearer to the blue. It will also be noticed that the disposition of the B and C curves relative to the A curves is much the same in Figs. 1 and 2.

Dye XIII is a distinctly better photographic sensitizer than II. In a chloride emulsion there are two bands with maxima at about 4575 and 5575 Å., separated by a trough with its minimum at about 4975 Å. (Fig. 2, S). There is, in fact, a remarkably close resemblance between the absorption and sensitizing curves of XIII, and although similar cases have been noted since the earliest studies of the subject,[17,18] the present illustration is particularly striking on account of the unusual character of the curves. Compared with the absorption curve, the sensitizing curve appears to have been shifted bodily toward the red, but the extent of that shift is less than in many reported instances.[19]

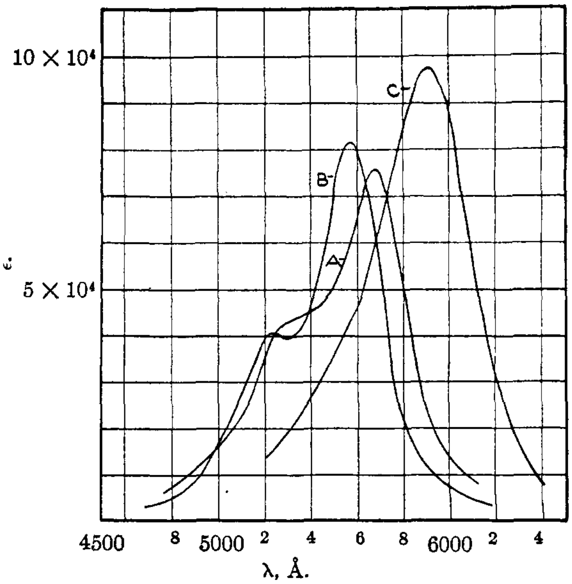


Fig. 3.—Absorption curves: A is 1,1′-diethyl-4-iodo-2,4′-cyanine iodide (XIV) or 1,1′-diethyl-2-iodo-4,4′-cyanine iodide (XV); B is 1,1′-diethyl-2,4′-cyanine iodide; C is 1,1′-diethyl-4,4′-cyanine iodide.

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(17) Vogel, *Ber.*, **6**, 1302 (1873).

(18) Becquerel, *Compt. rend.*, **79**, 185 (1874).

(19) Compare, for example, Bloch and Hamer, *Phot. J.*, **68**, 21 (1928); also Brooker and Keyes, THIS JOURNAL, **57**, 2492 (1935).

The dye similar to XIII but containing three methyl groups attached to the nitrogen atoms was also prepared. This was similar in its sensitizing action but somewhat stronger.

An attempt to prepare a dye containing three quinoline nuclei by condensing VII with two molecules of lepidine ethiodide was unsuccessful, the composition of a dye which was isolated corresponding to either 1,1′-diethyl-4-iodo-2,4′-cyanine iodide (XIV) or 1,1′-diethyl-2-iodo-4,4′-cyanine iodide (XV). The absorption curve of the dye (Fig. 3, A) has its maximum at 5675 Å. and accordingly XIV is considered to be the more likely formula since the strong hypsochromic effect that must be ascribed to the 2-iodine atom in XV, if this is held to be the correct formula, is at variance with the results observed in the case of XI, in which the 2′-iodine atom appears to counteract the, if anything, weakly hypsochromic effect of the 4-methyl group (compare III, IX and X). The sensitizing action of the dye resembles that of 1,1′-diethyl-2,4′-cyanine iodide more than it does that of 1,1′-diethyl-4,4′-cyanine iodide, but it is weaker than either of these. It gives an almost uniform extension of the spectrum to 6200 Å., with some desensitization.

The absorptions of the dyes were all determined for methyl alcoholic solutions and in the curves the molecular extinction coefficient, ϵ, is plotted against wave length. We are indebted to Dr. L. A. Jones and to Mr. E. E. Richardson for these results, to Dr. L. T. Hallett for the analyses, to Mr. G. Silberstein for the sensitizing curve, and to several other colleagues for the other photographic data.

Experimental

Intermediates

2,4-Dimethylquinoline Methiodide.[20]—The base (157 g.; 1 mol) was heated under reflux with methyl iodide (180 g.; 1.25 mols) for two days. The solid cake was ground with acetone and the yellow powder recrystallized from methyl alcohol (12 cc. per g.); yield of first crop 65%, increased to 93% by further crops. After a further recrystallization the pale yellow tables had m. p. 271–272°.

Anal. Calcd. for $C_{12}H_{14}IN$: I, 42.44. Found: I, 42.52.

2,4-Dimethylquinoline ethiodide (I)[20] was prepared similarly; yield 77% before and 73% after recrystallization (two crops). After a further recrystallization, the pale yellow crystals had m. p. 231–233°.

Anal. Calcd. for $C_{13}H_{16}IN$: I, 40.55. Found: I, 40.71.

2-Iodolepidine Ethiodide (V).—2-Chlorolepidine (50 g.; 1 mol) was heated under reflux with ethyl iodide (110 g.; 1.5 mols) for eight days in darkness.[8] The product was ground with acetone and weighed 64.6 g. (54%) and had m. p. 216–218° dec. After two recrystallizations from water (200 cc. per g.) (charcoal) the minute yellow crystals had m. p. 218–219° dec.

Anal. Calcd. for $C_{12}H_{13}I_2N$: I, 59.73. Found: I, 59.75.

2,4-Dihydroxyquinoline was made by the method of Ashley, Perkin and Robinson,[21] by treating methyl acetylanthranilate with sodium in toluene. These authors do not specify the time of heating nor do they give yields. We found that by refluxing for four hours the yield of purified product varied between 28 and 31%.

Anal. Calcd. for $C_9H_7NO_2$: C, 67.04; H, 4.38. Found: C, 67.38; H, 4.30.

2,4-Dichloroquinoline (VIII) was prepared from 2,4-dihydroxyquinoline by a modification of the method of Friedländer and Weinberg.[22] Contrary to the experience of Koller,[23] we were able to carry out the preparation satisfactorily using phosphorus pentachloride. In one experiment 2,4-dihydroxyquinoline (38.4 g.; 1 mol) was heated with phosphorus pentachloride (100 g.; 2 mols) and phosphorus oxychloride (80 cc.) at 100° for two hours. The excess of phosphorus oxychloride was removed under reduced pressure and the residue poured on ice. The solid was ground with ice water and filtered after neutralizing with sodium carbonate. It was then distilled *in vacuo;* yield 35 g. (74%). After recrystallization from methyl alcohol (2.5 cc. per g.) the yield (32.7 g.) was 69% (two crops). The colorless crystals melted at 66–67°.

Anal. Calcd. for $C_9H_5NCl_2$: C, 54.54; H, 2.55. Found: C, 54.39; H, 2.56.

2,4 - Diiodoquinoline Methiodide.—2,4-Dichloroquinoline (4 g.; 1 mol) and methyl iodide (14.4 g.; 5 mols) were heated at 100° in a sealed tube for three days. The product was ground with acetone; yield 5.1 g. (49%). After two recrystallizations from nitromethane (1 liter per g.) the yellow crystals had m. p. 236–237°, dec.

Anal. Calcd. for $C_{10}H_8I_3N$: I, 72.80. Found: I, 72.45.

2,4-Diiodoquinoline ethiodide (VII) was prepared similarly by heating at 100° for three weeks; crude yield 47%. After one recrystallization from nitromethane (500 cc. per g.) the yellow crystals had m. p. 235–236°, dec.

Anal. Calcd. for $C_{11}H_{10}I_3N$: I, 70.91. Found: I, 70.80.

Dyes

In all cases methyl alcohol was used for recrystallizing the dyes.

1,1′ - Diethyl - 4 - methyl - 2,2′ - cyanine Perchlorate (cf. III).—Quinaldine ethiodide (3 g.; 1 mol), 2-iodolepidine ethiodide (4.25 g.; 1 mol) and triethylamine 2.9 cc.; 2.1 mols) were refluxed with absolute ethyl alcohol (25 cc.) for twenty minutes. Dye separated (62% yield) and after two recrystallizations was converted into the

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(20) Compare Beyer, *J. prakt. Chem.*, ii, **33**, 406 (1886).

(21) Ashley, Perkin and Robinson, *J. Chem. Soc.*, 382 (1930).

(22) Friedländer and Weinberg, *Ber.*, **15**, 2679 (1882).

(23) Koller, *ibid.*, **60**, 1108 (1927).

perchlorate by treatment with potassium perchlorate and given two further recrystallizations (500 cc. per g.). The characteristic brownish spheroidal crystal aggregates had m. p. 279–280° dec. The maximum absorption of the dye is at 5200 Å. A well-marked secondary band has its maximum at 4900 Å.

Anal. Calcd. for $C_{24}H_{25}ClN_2O_4$: C, 65.33; H, 5.72. Found: C, 65.00; H, 5.48.

When 2,4-dimethylquinoline ethiodide (3.1 g.; 1 mol) and 2-iodoquinoline ethiodide (4.1 g.; 1 mol) were similarly condensed using triethylamine (2.9 cc.; 2.1 mols) the yield of the mixed dyes was 86%. The absorption curve of the product at this stage showed two maxima of nearly equal strength at 5200 and 5550 Å. with a weaker one at 4900 Å. The mixture was converted into the perchlorates and extracted with boiling methyl alcohol (250 cc.). This removed most of the purplish-red dye (2,4′-cyanine) and after three recrystallizations the residue was identical (appearance; mixed m. p.; absorption) with the specimen obtained above. Found: C, 65.34; H, 5.64.

1,1′-Diethyl-2′-methyl-2,4′-cyanine Iodide (IV).—The earlier method was modified. A boiling solution of quinaldine ethiodide (29.9 g.; 2 mols) in ethyl alcohol (150 cc.) was treated with powdered potassium hydroxide (3.1 g.; 1 mol) with constant shaking and the whole refluxed for twenty minutes; yield after washing 66%, being 31% after two recrystallizations (25 cc. per g.); m. p. 191–192°.

Anal. Calcd. for $C_{24}H_{25}IN_2$: I, 27.11. Found: I, 27.11.

This dye has its maximum absorption at 5550 Å. with a secondary maximum at about 5225 Å.

2,4-Di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline Ethiodide (II). (A) From 2,4-Dimethylquinoline Ethiodide.—This salt (3.1 g.; 1 mol), 2-iodoquinoline ethiodide (16.4 g.; 4 mols), triethylamine (8.7 cc.; 6.2 mols) and ethyl alcohol (40 cc.) were refluxed for forty minutes. Dye separated on cooling and was washed (acetone, then water). After three recrystallizations (140 cc. per g.) the yield was 0.15 g. (2%). The dye formed minute dull bronze crystals, m. p. 291–292°, dec.

Anal. Calcd. for $C_{35}H_{34}IN_3$: C, 67.39; H, 5.50; I, 20.36; N, 6.74. Found: C, 66.72; H, 5.41; I, 20.39; N, 6.84.

(B) **From 2,4-Diiodoquinoline Ethiodide.**—This salt (2.7 g.; 1 mol), quinaldine ethiodide (6 g.; 4 mols), triethylamine (4.32 cc.; 6.2 mols) and ethyl alcohol (50 cc.) were refluxed for forty minutes. Dye separated on chilling and after washing was extracted with boiling methyl alcohol (75 cc. × 2). The first extract contained much purplish-red dye and was rejected, but the second extract deposited moderately pure product; wt. 0.4 g. (13%). After a further recrystallization (6.5%) the dye was analytically pure. Found: I, 20.32.

(C) **From 1,1′-Diethyl-2′-methyl-2,4′-cyanine Iodide (IV).**—This dye (2.34 g.; 1 mol) and 2-iodoquinoline ethiodide (8.24 g.; 4 mols) were refluxed for forty minutes with ethyl alcohol (30 cc.) and triethylamine (4.2 cc.; 6.2 mols). The dye which separated was washed, extracted with hot methyl alcohol (15 cc.) and the residue twice recrystallized; yield 4.5%. Found: I, 20.35.

The specimens prepared by the three methods were identical (appearance; mixed m. p.; absorption; sensitizing).

2,4-Di-[(1-methyl-2(1)-quinolylidene)-methyl]-quinoline methiodide was prepared similarly, using method B (above). Some unused 2,4-diiodoquinoline methiodide was removed by filtration from the hot reaction mixture together with some dye which apparently consisted of 2,2′- and 2,4′-cyanine. The hot filtrate deposited the desired dye on cooling (15% yield). Dull brownish crystals from methyl alcohol (225 cc. per g.); yield 10%; m. p. above 310° dec., with shrinking from about 300°.

Anal. Calcd. for $C_{32}H_{28}IN_3$: C, 66.07; H, 4.86; I, 21.84; N, 7.23. Found: C, 65.40; H, 4.94; I, 21.64; N, 7.23.

This dye has absorption maxima at 4775 and 6050 Å. The third band is not so clearly defined in this case, but appears to be at about 4500 Å.

2,4-(Di-[(1-ethyl-2(1)-quinolylidene)-methyl]-quinoline methiodide was prepared using method A (above). Dye separated during the reaction and was filtered from the hot liquor and given three recrystallizations (700 cc. per g.); yield 6%. The minute crystals had a coppery luster; m. p. 302–303° dec.

Anal. Calcd. for $C_{34}H_{32}IN_3$: I, 20.83; N, 6.90. Found: I, 20.84; N, 7.09.

In a later experiment better results were obtained using *n*-propyl alcohol as solvent, and refluxing for forty minutes, the yields being 31% before and 15% after recrystallization. The absorption of this dye was like that of II.

2,4-Di-[(2-ethyl-1(2)-benzothiazolylidene)-methyl]-quinoline Ethiodide (XIII).—2,4-Diiodoquinoline ethiodide (1.34 g.; 1 mol), 1-methylbenzothiazole etho-*p*-toluenesulfonate (3.5 g.; 4 mols), triethylamine (2.15 cc.; 6.2 mols) and ethyl alcohol (50 cc.) were refluxed for forty minutes. Solid separated on cooling but this was not the dye sought for and was removed. Ether was added to the filtrate and the dye separated; yield 0.25 g. (15%). After two recrystallizations (50 cc. per g.) the yield was 3%. The minute brownish crystals with greenish reflex had m. p. 274–276° dec.

Anal. Calcd. for $C_{31}H_{30}IN_3S_2$: I, 19.97. Found: I, 19.88.

The sensitizing curve was determined on the monochromatic sensitometer described by Jones and Sandvik,[24] the sensitivity being the reciprocal of the exposure (in ergs/sq. cm.) necessary to produce a density of 1.0.

2,4-Di-[(2-methyl-1(2)-benzothiazolylidene)-methyl]-quinoline methiodide was prepared similarly. Dye separated in the hot reaction mixture; yield 33% (17% after two recrystallizations; 1200 cc. per g.). The dye formed a brown felt of minute crystals with a greenish reflex and had m. p. 301–302° dec.

Anal. Calcd. for $C_{28}H_{24}IN_3S_2$: I, 21.39. Found: I, 21.42.

1,1′-Diethyl-4-iodo-2,4′-cyanine Iodide (XIV), or 1,1′-Diethyl-2(or 2′)-iodo-4,4′-cyanine Iodide (XV).—Lepidine ethiodide (3 g.; 4 mols), 2,4-diiodoquinoline ethiodide (1.34 g.; 1 mol), ethyl alcohol (40 cc.) and triethylamine (2.15 cc.; 6.2 mols) were refluxed for forty minutes. Dye (0.7 g.) separated on cooling and was purified by several

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[24] Jones and Sandvik, *J. Opt. Soc. Am.*, **12**, 401 (1926).

recrystallizations (200 cc. per g.). The dye formed beautiful prisms with a greenish-bronze reflex; m. p. above 300°, dec., with sintering from 275°.

Anal. Calcd. for $C_{23}H_{22}I_2N_2$: I, 43.76. Found: I, 43.56.

1',2 - Diethyl - 4' - methylthia - 2' - cyanine iodide (IX) was obtained from V in similar fashion to III, using 1-methylbenzothiazole etho-*p*-toluenesulfonate. The yield of crude product was 84%, and 45% after two recrystallizations (125 cc. per g.). The orange-yellow needles had m. p. 276–277.5°, dec.

Anal. Calcd. for $C_{22}H_{23}IN_2S$: I, 26.76. Found: I, 26.86.

The maximum absorption is at 4800 Å.

1',2 - Diethyl - 4 '- methyl - 3,4 - benzothia - 2' - cyanine iodide (X) was obtained similarly using 2-methyl-β-naphthothiazole etho-*p*-toluenesulfonate. The yield of product was 57% before and 42% after recrystallization (325 cc. per g.). The minute reddish-orange needles had m. p. 272–274°, dec.

Anal. Calcd. for $C_{26}H_{25}IN_2S$: I, 24.21. Found: I, 24.19.

The dye has its maximum absorption at 5000 Å. There is an indefinite secondary band with its head at about 4800 Å.

1,1' - Diethyl - 2' - iodo - 4 - methyl - 2,4' - cyanine Iodide (XI).—2-Iodolepidine ethiodide (4.25 g.; 2 mols), triethylamine (1.5 cc.; 2.1 mols) and ethyl alcohol (25 cc.) were refluxed for twenty minutes. Dye separated from the hot reaction mixture; yield 71% (44%; 140 cc. per g.). After a further recrystallization (yield 20%) the greenish-bronze crystals had m. p. 231–232°, dec.

Anal. Calcd. for $C_{24}H_{24}I_2N_2$: C, 48.49; H, 4.07; I, 42.73. Found: C, 48.65; H, 4.10; I, 42.37.

Summary

1. Both the methyl groups in 2,4-dimethylquinoline ethiodide can undergo condensation with 2-iodoquinoline ethiodide and there results a cyanine dye of a new type containing three quinoline nuclei. The same dye is formed when 2,4-diiodoquinoline ethiodide is condensed with quinaldine ethiodide and also when 1,1'-diethyl-2'-methyl-2,4'-cyanine iodide is condensed with 2-iodoquinoline ethiodide.

2. The absorption curve of the new dye is unusual. It consists of two distinct bands separated by a trough of almost complete transmission. This is probably due to the unusual structure of the dye, for the molecule contains linkages characteristic of three distinct cyanine dye types.

3. 2,4-Diiodoquinoline ethiodide condenses with 1-methylbenzothiazole etho-*p*-toluenesulfonate to give a trinuclear dye containing one quinoline and two benzothiazole nuclei. The absorption curve of this dye likewise consists of two distinct bands and bears a very close resemblance to the sensitizing curve of the dye for silver chloride, thus affording a particularly striking example of this relationship.

Rochester, N. Y. Received October 5, 1936

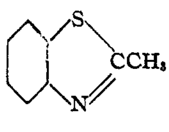
[Contribution No. 582 from the Kodak Research Laboratories]

Studies in the Cyanine Dye Series. VIII. Dyes Derived from 2-Methylphenanthro-[9,10]-thiazole

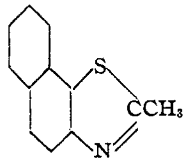
By G. H. Keyes and L. G. S. Brooker

Certain cyanine dyes derived from 1-methylbenzothiazole (I) are well known, and in the search for effective photographic sensitizers, cyanines have been prepared from the methyl-α- and β-naphthothiazoles (II and III, respectively)[1,2,3] some of which dyes proved to be of considerable value. It was accordingly felt to be of interest to attempt to prepare dyes from 2-methylphenanthro-[9,10]-thiazole (IV), since this base may be considered to bear a similar relationship to II (or III) as III (or II) bears to I.

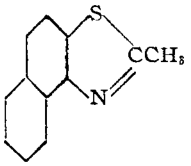
The method used for preparing IV was a modi-



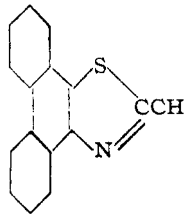
I



II



III



IV

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[1] Brooker, U. S. Patent 1,935,696; 1,969,444.

[2] Hamer, *J. Chem. Soc.*, 2598 (1929).

[3] Brooker and White, This Journal, **57**, 547, 2480 (1935).