tate (4.1 g., 1 mol.) in acetic anhydride (25 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish-yellow product (12.2 g., 69%) had m.p. 194–196°. It was used without further purification.

4-(3-Acetanilidoallylidene)-3-phenyl-5(4H)-isoxazolone (R5).—3-Phenyl-5(4H)-isoxazolone (8 g., 1 mol.), β-anilinoacrolein anil hydrochloride (12.9 g., 1 mol.) and sodium acetate (8.2 g., 2 mols.) in acetic anhydride (30 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish product (7.5 g., 90%) had m.p. 160–165°. It was used without further purification.

4-(6-Acetanilido-2,4-pentadienylidene)-3-phenyl-5(4H)-isoxazolone (R6).—3-Phenyl-5(4H)-isoxazolone (8 g., 1 mol.), glutaconaldehyde dianilide hydrochloride (14.2 g., 1 mol.) and sodium acetate (4.1 g., 1 mol.) in acetic anhydride (30 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish product (9 g., 50%) had m.p. 198–200°. It was used without further purification.

4-Acetanilidomethylene-3-phenyl-5(4H)-isoxazolone (R7).—4-Anilinomethylene-3-phenyl-5(4H)-isoxazolone (44.5 g., 1 mol.) in acetic anhydride (60 ml.) and triethylamine (8.5 g., 1 mol.) were heated to the boiling point and cooled. After filtering and washing with methyl alcohol, the yield was 31.6 g. (64%). Recrystallization from methyl alcohol gave nearly colorless crystals, m.p. 142–144°. The product was used without further purification.

5-Anilinomethylene-3-ethyl-2-thio-2,4-oxazolidenedione.—3-Ethyl-2-thio-2,4-oxazolidenedione (52.2 g., 1 mol.) and diphenylformamidine (70.2 g., 1 mol.) in kerosene (270 ml.) were heated for 1 hour at 120–125°. Filtration and washing with methyl alcohol gave 41.2 g. (48%) of yellow crystals. After recrystallization from methyl alcohol, the product had m.p. 237–239° without decomposition. The product was used without further purification.

5-Acetanilidomethylene-3-ethyl-2-thio-2,4-oxazolidenedione (R12).—5-Anilinomethylene-3-ethyl-2-thio-2,4-oxazolidenedione (41.2 g., 1 mol.) was heated for 10 minutes at 100° in acetic anhydride (150 ml.) with triethylamine (17.5 g., 1 mol.). After cooling and filtering, the yield was 42 g. (84%) of nearly colorless crystals. After recrystallization from methyl alcohol, the product had m.p. 158–160° without decomposition.

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: N, 9.66. Found: N, 9.43.

Details of the preparation of new dyes are given in Table I. These include merocyanines (designated by M; the numbers are continued from those in the previous paper[6]), *p*-dimethylaminobenzylidene derivatives (B), *p*-dimethylaminostyryl dyes (S), oxonols (O), symmetrical cyanines (C) and one unsymmetrical cyanine (U). The names of the dyes are given in Tables II, III, IV and V. In the syntheses, the reactants were heated together in the specified medium for the period indicated. Triethylamine (in 5% excess) was used as the condensing agent except where otherwise stated. Dyes of categories M, B and S and some of category C separated either spontaneously or on cooling. Oxonols were isolated by one of two methods; addition of a large volume of ether to the reaction mixture precipitated either the triethylamine or the pyridine salt of the dye, which was then purified as such, or acidification with hydrochloric acid precipitated the free oxonol. If a cyanine did not separate from its reaction mixture it was precipitated as a more sparingly soluble salt. The yield of washed dye is given, followed by the yield after two recrystallizations from the solvent indicated.

Absorption data for structurally unsymmetrical dyes in methyl alcohol are given in Table II and for symmetrical dyes in Table III. Data for absorptions in solvents other than methyl alcohol are given in Table IV and data required for Fig. 9 in Table V.

Rochester 4, New York Received April 11, 1951

[Communication No. 1398 from the Kodak Research Laboratories]

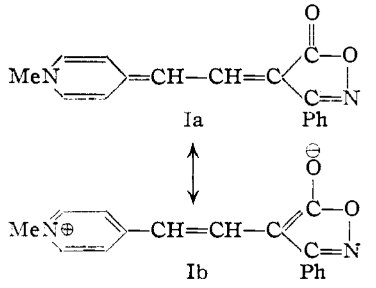
Color and Constitution. XI.[1] Anhydronium Bases of *p*-Hydroxystyryl Dyes as Solvent Polarity Indicators

By L. G. S. Brooker, G. H. Keyes and D. W. Heseltine

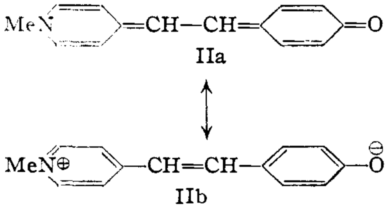
Two exceedingly polar merocyanines, for which the dipolar structures dominate even in pure pyridine solution, show such large shifts of $\lambda_{max.}$ to shorter wave lengths on increasing the polarity of the solvent (by adding water), that they could be used for the colorimetric determination of water in pyridine, or *vice versa*. For each of a number of somewhat less polar merocyanines, a characteristic change of direction in the absorption maximum–solvent composition curve (of pyridine-water mixtures) occurs at a point where the extreme resonance structures are thought to be energetically equivalent. On one side of this point the uncharged structure dominates, whereas the dipolar structure dominates on the other.

From a consideration of strongly polar nonionic dyes such as I[1] it could be predicted that the merocyanine II would also be strongly polar, for each of its rings acquires very considerable additional stabilization in the dipolar structure, IIb, relative to IIa; in IIa the rings are both *p*-quinonoidal, whereas in IIb they are benzenoidal. The polar atoms of II are also relatively exposed, consequently II might be expected to exhibit a particularly pronounced inversion of the normal behavior of un-ionized dyes toward change in the polarity of the solvent, and show a marked shift of $\lambda_{max.}$ to *shorter* wave lengths with increasing polarity of the solvent.

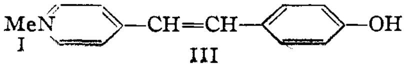
These expectations have been fully realized. The compound II was obtained as reddish crystals by the action of ammonia on 4-*p*-hydroxystyrylpyridine methiodide (III), obtained by the condensation of *p*-hydroxybenzaldehyde with γ-picoline methiodide.[2] So obtained, II is a dye which



Ia Ib



IIa IIb



III

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[1] Part X, This Journal, 73, 5332 (1951).

[2] A. P. Phillips, *J. Org. Chem.*, 14, 302 (1949).

dissolves in relatively weakly polar anhydrous pyridine to give an intensely colored blue solution with $\lambda_{max.}$ 6050 Å. and $\epsilon_{max.}$ 15.4 × 10^4, but dilution with water progressively shifts the maximum to lower extinctions and shorter wave lengths, until in pure water the solution is amber colored with $\lambda_{max.}$ 4440 Å. and $\epsilon_{max.}$ 5.4 × 10^4. The absorption maxima in the pure solvents and in mixtures of the two are given in Fig. 1.

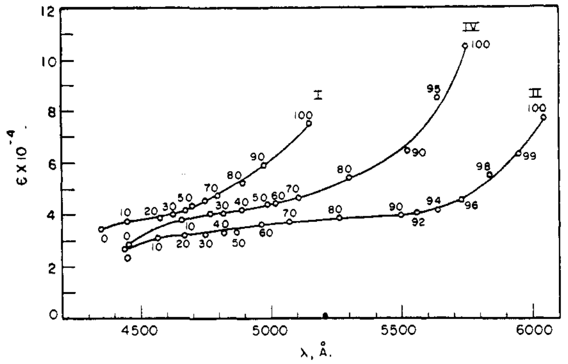
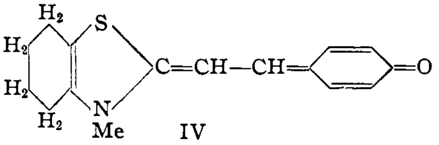


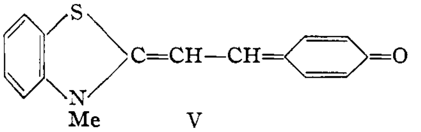
Fig. 1.—Values of $\lambda_{max.}$ and $\epsilon_{max.}$ for I, II and IV in pure pyridine and water, and in mixtures of the two. The numbers against the points on the curves denote volumes of pyridine per 100 volumes of solvent.

The hypsochromic shift of 1610 Å. shown by II in passing from pyridine to water is extremely great and exceeds that of any other dimethine merocyanine so far described;[1] it is slightly more than twice that of I (800 Å.),[1] the corresponding curve for which is included in Fig. 1 for comparison.

The dyes IV and V were also prepared in similar fashion to II. The tetrahydrobenzothiazole nucleus in IV is very strongly basic,[3] though less so than the 4-pyridine nucleus in II, consequently the intrinsic polarity of IV is less than that of II, and although the shift from $\lambda_{max.}$ pyridine to $\lambda_{max.}$ water is consequently less at 1290 Å. for IV than for II, it is nevertheless still very great (Fig. 1).



IV



V

In V the benzothiazole nucleus is of still lower basicity and the hypsochromic shift, pyridine → water, would be expected to be smaller than that for IV. This is true, the value being 760 Å., but the absorption maximum–solvent composition curve for V is further distinguished in that it shows an extraordinary reversal of direction, or "hook," in its upper part (Fig. 2,A). Unlike II and IV, which give the highest values of ϵ_{max} (and also $\lambda_{max.}$) in pure pyridine, the effect of adding a small quantity of water to the pure pyridine solution of V is to *raise* $\epsilon_{max.}$ very sharply, with an almost imperceptible movement of $\lambda_{max.}$ to longer wave lengths, until at 92.5% pyridine the curve abruptly changes direction, $\epsilon_{max.}$ thereafter falling very sharply, as in the curves for II and IV, with an increasing shift of $\lambda_{max.}$ to shorter wave lengths. The curve obtained with V but using the presumably somewhat less polar α-picoline in place of pyridine is very similar in shape (Fig. 2,B), but the extinctions at the nonpolar end of the curve are somewhat lower and the hook is rather more pronounced.

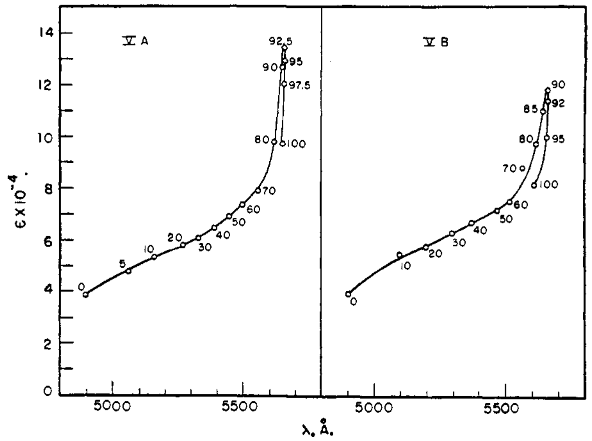


Fig. 2.—Absorption maxima of V ($\lambda_{max.}$ and $\epsilon_{max.}$) A, in pyridine and water and mixtures of the two; and B, in α-picoline and water, and mixtures of the two. The numbers against the points denote volumes of pyridine (or α-picoline) per 100 volumes of solvent.

It seems reasonable to assume that the highest points in the curves for V correspond to exact energetic equivalence of the extreme structures of the dye (conveniently called the "isoenergetic" point), although this assumption cannot at present be regarded as finally established. But if this explanation is tentatively accepted, it follows that the most conspicuous result of disturbing the equivalence of the structures by either increasing or decreasing the polarity of the pyridine–water or (α-picoline–water) mixture at the apex, is a sharp drop in $\epsilon_{max.}$, with simultaneously a less pronounced shift of $\lambda_{max.}$, the latter shift being smaller on the decreasingly polar arm of the curve than on the other.

At this point our attention was drawn to articles by Kiprianov and Petrun'kin[4a,b] that had hitherto escaped our attention. These authors had prepared several dyes of the type of IV and V (though not exactly the same compounds) and noted that they absorbed at much shorter wave lengths in water than in pyridine or chloroform. They suggested that these hybrid molecules approached the dipolar resonance structure in a polar solvent and the uncharged structure in a non-polar solvent,[4b] but this statement is clearly only a very rough approximation, and considerably more has been learned about the polarity of such dyes through the use of pyridine–water mixtures. In a later paper

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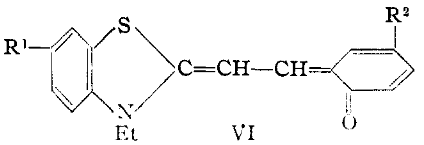
(3) Part VII, *J. Org. Chem.*, **67**, 1875 (1945). The nuclei present in II, IV, V and IX have N-methyl groups. The basicities worked out by the deviation procedure were actually for the corresponding N-ethyl nuclei, but the same order undoubtedly holds for the N-methyl nuclei.

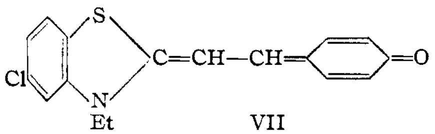
(4) (a) Kiprianov and Petrun'kin, *J. Gen. Chem.* (*U. S. S. R.*) ,**10**, 600 (1940); (b) *ibid.*, **10**, 613 (1940); (c) Kiprianov and Timoshenko, *ibid.*, **17**, 1468 (1947).

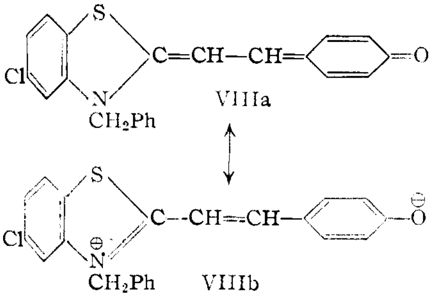
dealing with compounds of the type of VI, Kiprianov and Timoshenko clearly recognized the signifi-


VI

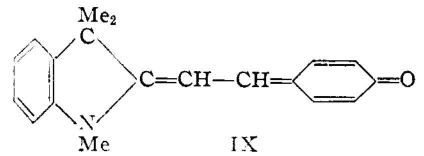
cance of the basicity of the nitrogen-containing nucleus (and the acidity of the second nucleus) in determining the non-polar solvent → polar solvent shift, although their expectations were not supported unequivocally by their results.[4c] Here, too, they worked with pure solvents, and their data did not permit them to recognize whether, in a given solution, they were at the isoenergetic point of the dye, or on one side of it or the other.

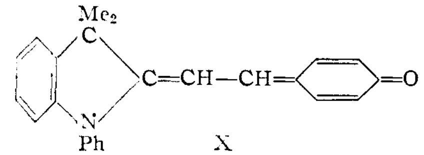
In order to examine this situation further, the dyes VII–X were prepared, the basicity of the nitrogen-containing ring being progressively reduced in the order VII > VIII > IX > X, as known partly from previous work,[3] and partly from deviation results on *p*-dimethylaminostyryl dyes given in the experimental section.


VII


VIIIa

VIIIb


IX


X

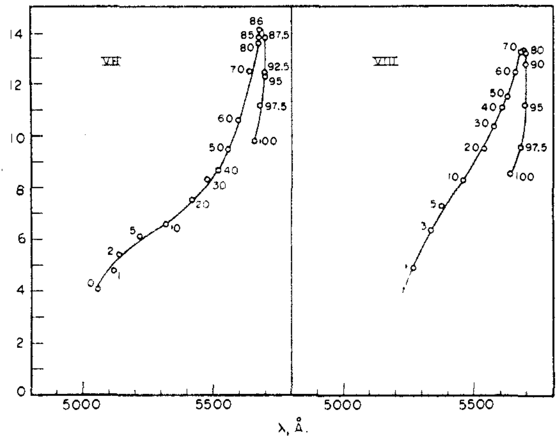


Fig. 3.—Absorption maxima of VII and VIII ($\lambda_{max.}$ and $\epsilon_{max.}$) in pyridine and water and mixtures of the two. The numbers denote volumes of pyridine per 100 volumes of solvent.

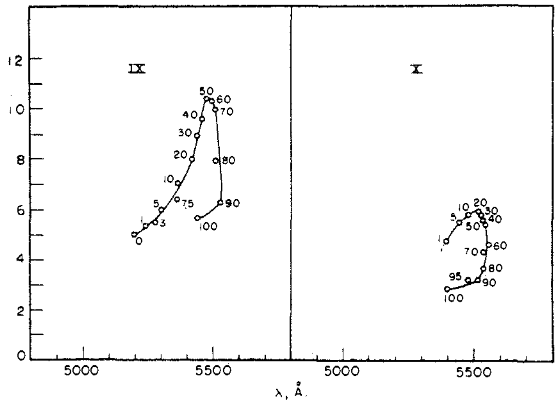


Fig. 4.—Absorption maxima of IX and X ($\lambda_{max.}$ and $\epsilon_{max.}$) in pyridine and water and mixtures of the two. The numbers denote volumes of pyridine per 100 volumes of solvent.

The absorption maximum–solvent composition curves for VII and VIII are given in Fig. 3 and for IX and X in Fig. 4.

The hook already apparent in the curve of V (Fig. 2,A) becomes increasingly prominent in the curves of the sequence VII → X, until for X it constitutes the whole curve. (Dyes VIII and X were too sparingly soluble in pure water for absorption determinations; for these dyes measurements were therefore not made on solutions containing less pyridine than one volume per cent.) In the curves the composition of the solvent at the apex of the hook corresponds to 92.5, 86, 75, 50 and 20% by volume of pyridine for the dyes, V, VII, VIII, IX and X, taken in that order, *i.e.*, at the apex the polarity of the solvent mixture is higher, the lower the basicity of the nitrogen-containing ring. It is easy to see why this is so. Lowering the basicity of this ring lowers the intrinsic polarity of the dye, so that proportionately higher solvent stabilization is required for the attainment of effective energetic equivalence of the extreme structures.

For strongly polar dyes, such as IV, the absorption maximum–solvent composition curve of which exhibits no hook, the isoenergetic point must either be at the uppermost part of the curve, or, more likely, in an extrapolation of it which corresponds to rendering the pyridine solution less polar by addition of a still less polar diluent. Throughout the *whole* range of solutions of dyes II or IV in Fig. 1, the dipolar structure in the resonance has the lower energy, and this energy becomes progressively lower the higher the water content of the solution.

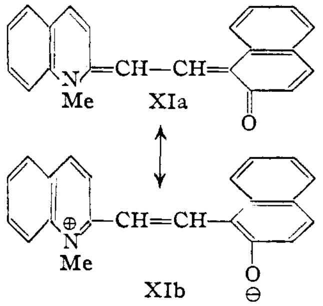
For the dyes which show a hook, such as VIIIa ↔ VIIIb, the uncharged structure, *e.g.*, VIIIa, becomes increasingly dominant over the range of solutions from the apex of the curve to the pure pyridine, while the charged structure, *e.g.*, VIIIb, becomes increasingly dominant over the range that extends from the apex of the curve to pure water.

The evidence presented here shows very clearly, if further evidence were still required, that no single structural formula can adequately account for the absorption of these dyes (and, by a logical extension, of dyes in general). Their absorptions are only intelligible in terms of the energy relationship of the contributing structures, which relationship can be varied between wide limits by changing the environment.

Since for dyes V and VII through X the absorption maximum–solvent composition curves for which show hooks, the composition of the solvent at the apex of the hook is determined by the basicity of the nitrogen-containing ring in the dye, this relationship may be made the basis of a new method for determining the basicity of additional rings of this kind, provided that such basicity is not higher than that of the benzothiazole ring in V. This new method is simpler than those already described[1,3,5] in that it requires the preparation of only one dye from a given ring. Furthermore, as an alternative to determining the solvent composition at the apex, which requires a number of absorption measurements, the data plotted in Figs. 1–4 indicate that it may be sufficient to determine the difference ($\lambda_{max.}$ pyridine minus $\lambda_{max.}$ water), that difference being greater the higher the basicity of the basic nucleus, or, if the dye is too insoluble in pure water, the difference ($\lambda_{max.}$ pyridine minus $\lambda_{max.}$ in highly aqueous pyridine of some fixed low pyridine content) may be used instead. This alternative method would have the added advantage of not being restricted to nuclei the basicity of which was not greater than that of benzothiazole. However, the detailed examination of these methods will be reserved for a later communication.[5a]

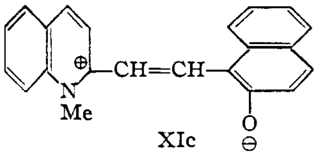
The great sensitivity shown by the absorptions of these dyes, especially II and IV, to change in polarity of a (neutral or basic) solvent mixture suggests their use for the colorimetric estimation of the composition of distillates and the like. Thus, a small amount of water, or even of an alcohol, in a base of the pyridine type could readily be estimated by the use of II or IV. Whereas II is more sensitive than IV for the detection of small amounts of water in pyridine, the curves in Fig. 1 show that the order is reversed for the estimations of small amounts of pyridine in water. As an example of usefulness in a somewhat different direction, II gives appreciably different absorptions in methyl, ethyl, *n*-propyl and isopropyl alcohols. The solution in the first of these is orange, whereas that in the fourth is bluish-red. Values of $\lambda_{max.}$ in the four alcohols are 4860, 5130, 5260 and 5460 Å. in the order given.

The behavior of the above environment-sensitive merocyanines recalls that of certain condensation products of 2-hydroxy-1-naphthaldehyde, such as XI and XII, described by Wizinger and Wenning.[6] These authors called compounds of this general type "spiraines" from their relationship to a group of heterocyclic spiranes and also to betaines. Carbenium ion formulas such as XIc were used to formulate the compounds and to account for their color.

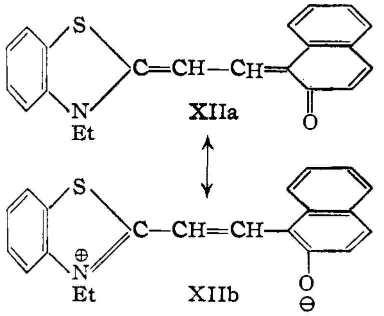


XIa

XIb



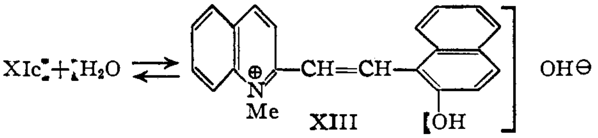
XIc



XIIa

XIIb

Wizinger and Wenning noted that the deeply colored solutions of XI and XII in solvents that are miscible with water underwent a shift of $\lambda_{max.}$ to shorter wave lengths on the addition of water. They suggested that water was taken up by the intensely colored dye, as illustrated by XI, the product being the hydroxide of the much lighter colored



XIII

cation, XIII (for which a carbenium ion formulation was used rather than XIII).

That this hypothesis is untenable and that the phenomenon is actually a true solvatochromism of the type already discussed may be shown as follows:

(1) The absorption maximum–solvent composition curves of XI and XII for solutions of the dyes in pyridine and water and mixtures of the two (Fig. 5) reveal for each dye an unbroken series of shifts of $\lambda_{max.}$ with progressive change in composition of the solvent, whereas the equilibrium in solution of two distinct molecular species with widely separated bands (*e.g.*, XI and XIII), the absorption of neither

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(5) Part V, THIS JOURNAL, **64**, 206 (1942).

(5a) ADDED IN PROOF.—In those curves which have a "hook" (Figs. 2 through 5), the non-polar arm lies at longer wave lengths than the corresponding polar arm. The most significant intermediate structures for these dyes are dipolar and will respond to changes in the polarity of the solvent in similar fashion to the dipolar extreme structure. It is then easy to see, by applying the steeper-the-deeper principle [Brooker, *Rev. Mod. Phys.*, **14**, 289 (1942)], that an energetic asymmetry introduced at the isoenergetic point will give a deeper color when the energy of the dipolar extreme structure and the energies of the intermediate structures are raised by changing to a lower polarity than when these energies are lowered, by changing to a solvent of higher polarity.

(6) R. Wizinger and H. Wenning, *Helv. Chim. Acta*, **23**, 247 (1940).

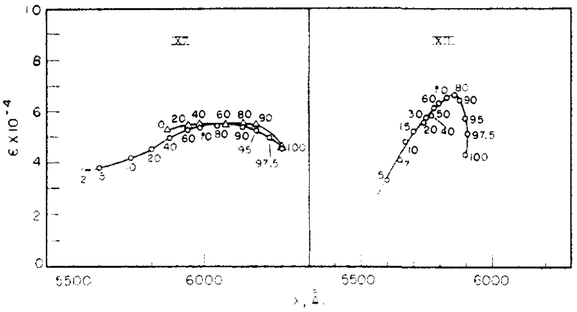
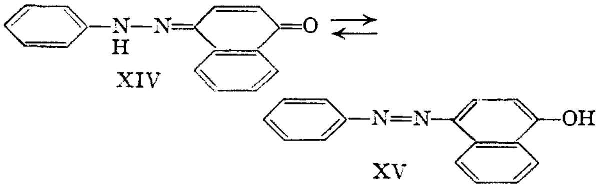


Fig. 5.—Absorption maxima for XI and XII ($\lambda_{max.}$ and $\epsilon_{max.}$) in pyridine and water and mixtures of the two; these curves are those with ⊙. The curve for XI with ⚠ gives absorption maxima for pyridine and methyl alcohol and mixtures of the two. The numbers against the points indicate volumes of pyridine per 100 volumes of solvent.

of which is especially solvent-sensitive, would be expected to give rise to two separate bands, only the relative intensities of which would vary from solvent to solvent. (An example of this kind is provided by the tautomeric system XIV ⇄ XV which was studied by Kuhn and Bär.[7] They showed that


XIV

XV

in alcohol a band at about 4100 Å. was due to XV and one at about 4700 Å. to XIV. Varying the solvent characteristically strengthened one of these bands at the expense of the other.)

(2) Quinolinium hydroxides, of which XIII is an example, are unstable as a class and tend to pass into carbinols,[8] but even supposing that XIII were a stable substance, its absorption should be identical with that of the iodide (or other salt) of the cation, just as the ammonium hydroxide corresponding to crystal violet chloride has, in the interval before it rearranges to colorless carbinol, an absorption like that of the chloride.[9] Actually an aqueous solution of the acetate corresponding to XIII (with a drop of acetic acid added to suppress formation of XI) is lemon yellow in color with $\lambda_{max.}$ 4320 Å. This solution absorbs very differently to the pinkish-mauve solutions obtained by the strong dilution with water of an alcoholic or pyridine solution of XI (Fig. 5); $\lambda_{max.}$ for these diluted solutions lies somewhere around 5540 Å. (XI is too insoluble in water alone to give a readable absorption maximum). Similar results were obtained in the series for which XII is the merocyanine. The hydroacetate of this dye gives a yellow solution in water with $\lambda_{max.}$ 4430 Å., but dilution with water of a pyridine or a methanol solution of XII produces only a pink-mauve color with $\lambda_{max.}$ between 5550 and 5600 Å. (Fig. B). (This dye is similarly insufficiently soluble in water alone for absorption determinations.) In short, highly aqueous solutions of the merocyanines, XI and XII, do not absorb as though they contained cations such as that of XIII.

(3) Wizinger and Wenning speak of taking solutions of compounds such as XI and XII which have been diluted with water so as to bring about a marked lightening of color to orange or yellow, and then of observing a return to the original blue colors on the addition of alkali. On repeating this work, we not only failed to observe changes of color as pronounced as those described by Wizinger and Wenning, as stated above, but found that addition of alkali had no noticeable effect on the pinkish-mauve highly aqueous solutions of XI (or XII).

It seems probable that in their dilution experiments, the water used by Wizinger and Wenning contained traces of acid which converted the merocyanines (*e.g.*, XI) into cations such as XIII, at least in part, with marked lightening of color. Under these circumstances alkali would liberate the merocyanine, with formation of a violet color in the case of XI, though this would still be far from the greenish-blue of a pure pyridine solution or the blue of a pure methanol solution.

(4) It is not necessary to add water to a pyridine solution of XI (or XII) to shift $\lambda_{max.}$ radically in the direction of shorter wave lengths, although water, with its low molecular weight and high polarity, is particularly effective. Thus, if a pyridine solution of XI is diluted with pure methyl alcohol rather than water, the absorption is shifted as shown in Fig. 5. Although more methyl alcohol than water must be added to a pyridine solution to produce a given shift of $\lambda_{max.}$ toward shorter wave lengths, the effects are otherwise quite comparable. In pure methyl alcohol, the absorption is almost identical with that in 40 vol. per cent. of (aqueous) pyridine.

(5) Wizinger and Wenning cite the benzene extraction (the extract being blue) of a highly aqueous solution of a dye such as XI or XII, as evidence for an equilibrium of the type they suggested, involving XIc and XIII. This experiment, however, is in complete accordance with our view of dyes such as XI and XII as solvent-sensitive merocyanines. Because of their strong polarity, these non-ionic dyes are frequently more soluble in hydroxylic solvents than less polar merocyanines, but they may still have considerable solubility in relatively weakly polar solvents, and the benzene layer of the extraction (though saturated with water and having extracted some pyridine or methyl alcohol) is nevertheless sufficiently non-polar for the appearance of the deeper color. The ability to dissolve in two immiscible solvent layers and to impart a different color to each is, as a matter of fact, a very characteristic property of those solvent-sensitive merocyanines that we have examined.

There can, therefore, be no doubt that XI and XII exhibit true solvatochromic shifts. However, the keto-naphthalene ring in these dyes is in all probability not as strongly acidic as the keto-benzene ring in dyes II, IV and V and VII through X. This conclusion is reached by reasoning similar to that used to explain the lower *basicity* of the quinoline ring relative to pyridine,[3] and is confirmed by the following comparison of the two benzothiazole

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[7] R. Kuhn and F. Bär, *Ann.*, **516**, 143 (1935).

[8] H. Decker, *Ber.*, **25**, 443 (1892).

[9] T. W. J. Taylor and W. Baker, in Sidgwick's "Organic Chemistry of Nitrogen," 2nd Edition, Clarendon Press, New York, N. Y., 1937, p. 90.

TABLE I

DETAILS OF DYE SYNTHESES

The dyes appear as follows: II, red crystals; IV, reddish-brown crystals; V, steel-blue crystals; VII, bronze crystals; VIII, blue crystals; IX, amorphous reddish solid; X, brownish crystals.

Dye no.	Name	Yield, %	Solvent, ml./g.	M.p., °C. dec.	Formula	Analyses, % Calcd.	Analyses, % Found
II	1-Me-4-[(4-oxocyclohexadienylidene)-ethylidene]-1,4-dihydropyridine	52, 28	H_2O 50	194–196	$C_{14}H_{13}NO\cdot{}^1/_2H_2O$	C, 76.32 H, 6.40	76.2 6.7
IV	3-Me-2[(4-oxocyclohexadienylidene)-ethylidene]-4,5,6,7-tetrahydrobenzothiazoline	85, 59	H_2O 18	169–171	$C_{16}H_{17}NOS\cdot H_2O$	C, 66.39 H, 6.62 N, 4.85 S, 11.09	66.4 6.6 4.7 10.9
V	3-Me-2-[(4-oxocyclohexadienylidene)-ethylidene]-benzothiazoline	96, 35	MeOH 30	143–145	$C_{16}H_{13}NOS$	C, 71.86 H, 4.90	71.5 5.2
VII	5-Chloro-3-Et-2-[(4-oxocyclohexadienylidene)-ethylidene]-benzothiazoline	92, 17	MeOH 100	203–204	$C_{17}H_{14}ClNOS.2H_2O$	C, 57.99 H, 5.16 N, 3.98	58.0 4.5 4.1
VIII	3-Benzyl-5-chloro-2-[(4-oxocyclohexadienylidene)-ethylidene]-benzothiazoline	82, 42	MeOH 125	154–155	$C_{22}H_{16}ClNOS$	C, 69.92 H, 4.27	69.5 4.6
IX	1,3,3-TriMe-2-[(4-oxocyclohexadienylidene)-ethylidene]-indoline	21, 12	MeOH[a]	61–63	$C_{19}H_{19}NO$	C, 82.24 H, 6.91	82.3 7.6
X	3,3-DiMe-2-[(4-oxocyclohexadienylidene)-ethylidene]-1-Ph-indoline	98, 25	Ligroin, 450 b.p. 90–120°	93–95	$C_{24}H_{21}NO\cdot{}^1/_2H_2O$	C, 82.71 H, 6.37 N, 4.02	83.0 6.5 3.8

[a] Dye dissolved in MeOH and precipitated with water.

derivatives, V and XII (neglecting the fact that one of these has N-methyl and the other N-ethyl): The solvent mixture at the apex of the hook in the curve for XII in Fig. 5 (80 vol. per cent. of pyridine) is more polar than that in Fig. 2,A (92.5 vol. per cent. of pyridine), *i.e.*, higher solvent stabilization of the dipolar structure is required for attainment of equivalence of the extreme structures in XII than in V.[9a]

There is a conspicuously smaller variation in $\epsilon_{max.}$ with change in solvent for XI and XII than for the other merocyanines except X. This is especially true of XI, the apex of the curves for which (Fig. 5) is so flat that one hesitates to say that the highest point in the pyridine–water curve, at 80 vol. per cent. of pyridine, corresponds to energetic equivalence of the extreme structures. This dye, too, absorbs at appreciably longer wave lengths in pure pyridine than at the highest point, and until now it has not seemed likely that the absorption maximum of an energetically symmetrical dye would be shifted to *longer* wave lengths on introducing an asymmetry, either by a structural or an environmental change. Nevertheless, such a shift is quite conceivable[10] and we hope to examine the matter further.

Acknowledgments.—We are grateful to Mr. Don Ketchum and his collaborators for the microanalyses and to Mr. Edward Long for the absorption determinations.

Experimental

All melting points are corrected.

5,5′-Dichloro-3,3′-diethylthiacarbocyanine Bromide.[11]—5-Chloro-3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate[11] (3.84 g., 1 mol.) and ethyl orthoformate (2.22 g., 1.5 mols.) were heated under reflux with pyridine (10 ml.) for 30 minutes. The crude dye (86%) was precipitated with aqueous potassium bromide. After two recrystallizations from methyl alcohol (87 ml./g.), the dye (47%) appeared as bluish-purple needles; m.p. 289–291° dec. and $\lambda_{max.}$ in methyl alcohol at 5620 Å.

Anal. Calcd. for $C_{21}H_{19}BrCl_2N_2S_2$: C, 49.01; H, 3.72. Found: C, 48.96; H, 3.59.

5-Chloro-2-*p*-dimethylaminostyryl-3-ethylbenzothiazolium Iodide.—The 5-chloro-3-ethyl-2-methylbenzothiazolium iodide (3.39 g., 1 mol.) and *p*-dimethylaminobenzaldehyde (1.49 g., 1 mol.) were dissolved in ethyl alcohol (35 ml.) and heated under reflux for two hours. The crude dye (84%), after two recrystallizations from methyl alcohol (400 ml./g.), yielded 55% of purple needles with a metallic reflex; m.p. 267–268° dec.

Anal. Calcd. for $C_{19}H_{20}ClIN_2S\cdot CH_3OH$: I, 25.25. Found: I, 25.1.

This dye absorbs in methyl alcohol with $\lambda_{max.}$ 5370 Å.; the deviation[1,3] is thus (6060 Å. + 5620 Å.)/2 − 5370 Å. = 470 Å.

3,3′-Dibenzyl-5,5′-dichlorothiacarbocyanine Bromide.—3-Benzyl-5-chloro-2-methylbenzothiazolium bromide (3.56 g., 1 mol.) (prepared by heating equimolecular portions of 5-chloro-2-methylbenzothiazole and benzyl bromide on the steam-bath for 20 hours; yield 50% after washing with ether and acetone) and diethoxymethyl acetate (1.62 g., 2 mol.) were dissolved in pyridine (20 ml.) and heated under reflux for 15 minutes. The crude dye (92%) was twice recrystallized from methyl alcohol (260 ml./g.); yield 38% of greenish-bronze crystals, m.p. 264–265° dec. and $\lambda_{max.}$ in methyl alcohol 5680 Å.

Anal. Calcd. for $C_{31}H_{23}BrCl_2N_2S_2$: Br, 12.52. Found: Br, 12.4.

3-Benzyl-5-chloro-2-*p*-dimethylaminostyrylbenzothiazolium Bromide.—3-Benzyl-5-chloro-2-methylbenzothiazolium bromide (3.56 g., 1 mol.) and *p*-dimethylaminobenzaldehyde (1.49 g., 1 mol.) were dissolved in ethyl alcohol (25 ml.) and heated under reflux for one hour. The crude dye (86%) was twice recrystallized from methyl alcohol (130 ml./g.); yield 42% of bluish crystals, m.p. 243–244° dec.

Anal. Calcd. for $C_{24}H_{22}BrClN_2S\cdot{}^1/_2CH_3OH$: Br, 15.92. Found: Br, 15.8.

This dye absorbs in methyl alcohol with $\lambda_{max.}$ 5480 Å.; the deviation[1,3] is thus (6060 Å. + 5680 Å.)/2 − 5480 Å. = 390 Å.

Merocyanines II, IV, V, VII, VIII, IX and X were made by the same general procedure. The appropriate quaternary salt containing reactive methyl was condensed with *p*-hydroxybenzaldehyde (using piperidine as a catalyst only in condensations corresponding to II and IV). The *p*-hydroxystyryl derivative was then converted into the merocyanine by treatment with concentrated aqueous ammonia. The yield of washed product (from *p*-hydroxystyryl dye) is

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[9a] ADDED IN PROOF.—Just as II, IV and V are more strongly polar substances than IX, so XI will be more polar than the corresponding indolenine derivative and have a higher dipole moment, as has recently been found by E. D. Bergmann, A. Weizmann and E. Fischer [THIS JOURNAL, **72**, 5009 (1950)].

(10) *Cf.* W. T. Simpson, *ibid.*, **73**, 5359 (1951).

(11) F. M. Hamer, R. J. Rathbone and B. S. Winton, *J. Chem. Soc.*, 957 (1947).

TABLE II

OPTICAL DATA[a]

Dye no.		Diluent	Volume of pyridine[e]													
			0[c]	5	10	20	30	40	50	60	70	80	90	95	97.5	100
II[b,e]	$\lambda_{max.}$, Å.	H_2O	4440		4570	4690	4750	4820	4870	4950	5070	5270	5500			6050
	$\epsilon_{max.} \times 10^{-4}$		2.7		3.1	3.14	3.25	3.3	3.4	3.6	3.7	3.87	3.96			7.65
IV[c]	$\lambda_{max.}$, Å.	H_2O	4460		4660	4770	4820	4890	4990	5020	5110	5300	5530	5640		5750
	$\epsilon_{max.} \times 10^{-4}$		2.7		3.8	4.05	4.05	4.20	4.40	4.46	4.68	5.4	6.46	8.5		10.5
V[d]	$\lambda_{max.}$, Å.	H_2O	4900	5060	5150	5280	5340	5380	5460	5500	5560	5620	5660	5660	5660	5650
	$\epsilon_{max.} \times 10^{-4}$		3.9	4.8	5.25	5.7	6.0	6.45	6.85	7.05	7.7	9.8	12.7	12.8	12.1	9.7
V[f]	$\lambda_{max.}$, Å.	H_2O	4900	5100	5200	5300	5370	5400	5470	5520	5570	5620	5660	5660		5610
	$\epsilon_{max.} \times 10^{-4}$		3.90	5.45	5.75	6.3	6.7	6.7	7.15	7.5	8.8	9.7	11.8	10.0		8.1
VII[g]	$\lambda_{max.}$, Å.	H_2O	5060	5220	5320	5420	5480	5520	5560	5600	5640	5670	5680	5700	5680	5660
	$\epsilon_{max.} \times 10^{-4}$		4.1	6.1	6.6	7.5	8.3	8.7	9.5	10.6	12.6	13.65	13.6	12.3	11.2	9.8
VIII	$\lambda_{max.}$, Å.	H_2O		5380	5460	5540	5580	5610	5630	5660	5680	5700	5700	5700	5690	5640
	$\epsilon_{max.} \times 10^{-4}$			7.4	8.3	9.5	10.4	11.1	11.5	12.3	13.4	13.4	12.8	11.0	9.6	8.5
IX[h]	$\lambda_{max.}$, Å.	H_2O	5200	5300	5370	5420	5440	5460	5480	5500	5510	5510	5510			5440
	$\epsilon_{max.} \times 10^{-4}$		5.0	6.0	7.0	8.0	8.9	9.6	10.4	10.3	10.0	7.9	6.1			5.7
X[i]	$\lambda_{max.}$, Å.	H_2O		5450	5480	5520	5530	5540	5540	5560	5540	5540	5520	5480		5400
	$\epsilon_{max.} \times 10^{-4}$			5.8	6.0	6.1	6.0	5.8	5.7	4.8	4.5	3.8	3.6	3.4		2.9
XI[k]	$\lambda_{max.}$, Å.	H_2O		5600	5700	5800		5870		5940	5980	6050	6150	6200	6250	6300
	$\epsilon_{max.} \times 10^{-4}$			3.82	4.16	4.49		4.97		5.22	5.36	5.46	5.32	5.29	4.97	4.56
XI[l]	$\lambda_{max.}$, Å.	MeOH	5860			5940		5980		6080		6150	6200			6300
	$\epsilon_{max.} \times 10^{-4}$		5.23			5.33		5.41		5.46		5.48	5.46			4.56
XII[m]	$\lambda_{max.}$, Å.	H_2O		5600	5670	5740	5750	5770	5780	5800	5830	5860	5880	5900	5910	5900
	$\epsilon_{max.} \times 10^{-4}$			3.3	4.8	5.6	5.7	5.8	6.1	6.3	6.5	6.6	6.4	5.7	5.1	4.3

[a] Data for I are already given.[1] [b] Additional data for II in pyridine–water solutions not given in the body of the table follow, the percentage volume of pyridine is given followed by $\lambda_{max.}$ in Å. and $\epsilon_{max.} \times 10^{-4}$: 92, 5560, 4.06; 94, 5640, 4.15; 96, 5730, 4.55; 98, 5840, 5.5; 99, 5940, 6.31. [c] Plus a trace of piperidine. [d] Additional data for V follow, the figures being given as in *b:* 92.5, 5660, 12.9. [e] The second row of data against V are for α-picoline–water solutions. [f] Values in this horizontal row are for α-picoline–water solutions. Additional data are as follows, the figures being given as in footnote *b:* 85, 5640, 11.0; 92.5, 5660, 11.4. [g] Additional values follow, the figures being given as in footnote *b;* 1, 5120, 4.8; 2, 5140, 5.4; 86, 5680, 14.1; 87.5, 5700, 13.8. [h] Additional values follow, the figures being given as in *b:* 1, 5240, 5.35; 3, 5280, 5.5; 7.5, 5360, 6.4. [i] Additional values follow, the figures being given as in *b:* 1, 5400, 4.9. [k] Additional value of $\lambda_{max.}$ for 2 volumes % of pyridine is 5540 Å. [l] Absorptions in this row were run plus a trace of triethylamine. [m] Additional values follow, the figures being given as in *b:* 7, 5650, 4.1; 15, 5700, 5.2.

given in Table I, followed by the yield after constant melting point had been attained by several recrystallizations from the solvent indicated.

Optical data are given in Table II.

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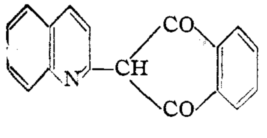
[COMMUNICATION NO. 1399 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. XII.[1] Absorption of the Phthalones

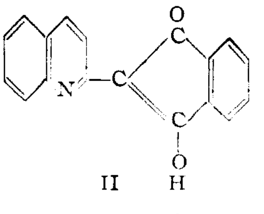
BY L. G. S. BROOKER AND G. H. KEYES

The shift of $\lambda_{max.}$ to shorter wave lengths shown by N-methylpyrophthalone (VI) in passing from chloroform as a solvent to water, which was observed by Kuhn and Bär [*Ann.*, **516**, 155 (1935)], is characteristic of strongly polar merocyanines, to which category VI belongs. The higher vinylog of VI shows a larger shift in the same direction. The corresponding quinoline dyes also show these shifts, as do pyrophthalone and quinophthalone themselves.

Many years ago formula I was suggested by Eibner[2] for the yellow dye, quinophthalone, but this was rejected by Kuhn and Bär because it showed no conjugation between the two ring systems.[3] Both II and III show such conjugation, however, and of these III was selected by Kuhn and Bär because methylation (under rigidly prescribed conditions) gave an N-methyl derivative (V) (the structure of which was established by oxidation to 1-methyl-2-quinolone) and because of the close correspondence between the absorption curves of quinophthalone and V.



I



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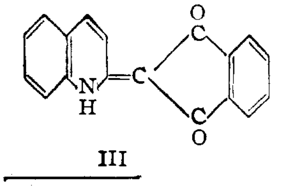
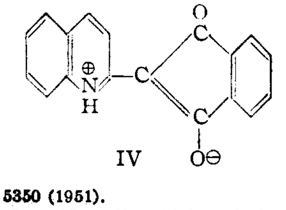


III



IV

Dye V is a merocyanine[4] which is easily prepared by the condensation of 2-phenylmercaptoquinoline metho-*p*-toluenesulfonate with 1,3-indandione. Use of 2-iodopyridine methiodide similarly furnished the N-methyl "pyrophthalone" (VI), which Kuhn and Bär had also obtained by their special methylation procedure.[3]

Kuhn and Bär commented on the considerable water-solubility of VI and also on the fact that it

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(1) Part XI, THIS JOURNAL, **73**, 5350 (1951).

(2) A. Eibner and H. Merkel, *Ber.*, **35**, 2297 (1902); **37**, 3006 (1904); A. Eibner and K. Hofmann, *ibid.*, **37**, 3011 (1904); A. Eibner, *Chem. Ztg.*, **28**, 1206 (1904).

(3) R. Kuhn and F. Bär, *Ann.*, **516**, 155 (1935).

(4) THIS JOURNAL, **73**, 5350 (1951).