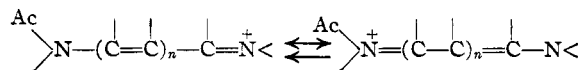


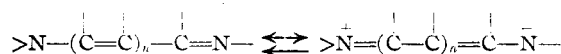
type, *i. e.*, their cations conform to the general formula $>N-(C=C)_n-C=N^+$, both the nitrogens being strongly basic. In these three series, increasing the length of the conjugated chain produces a shift of absorption toward the longer waves of roughly 1000 Å. for each added vinylenes, this amount of shift not diminishing as the series is ascended. Such large vinylenes shifts are characteristic of the symmetrical cyanines and the members of the present series are similarly thought to be highly degenerate. This is confirmed by the fact that, with an exception that is noted, individual members give values of λ_{max} which agree tolerably well with those calculated as the arithmetic means of the values of λ_{max} of the parent symmetrical dyes.

The fourth series is of a modified amidinium salt type, an acetyl group being attached to one of the nitrogen atoms. These compounds have values of λ_{max} of much shorter wave length than the corresponding unacetylated compounds, a result which is ascribed to lack of degeneracy of the resonance configurations, as indicated by the single-headed arrow



due to the greatly reduced basicity of the nitrogen atom to which the acetyl group is attached. As this series is ascended the vinylenes shifts become progressively less.

The fifth series consists of amidine bases conforming to the resonance scheme



In general, these bases absorb at markedly shorter wave length than their hydr- or ethiodides (these latter constituting two of the strongly degenerate series referred to above), and, furthermore, their vinylenes shifts decrease markedly as the series is ascended. This is correlated with inhibition of degeneracy, as indicated by the single-headed arrow, due to the fact that the imino nitrogen in the bases is not very electronegative so that $-N^-$ in the dipolar configuration is relatively unstable.

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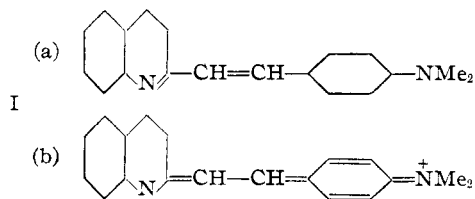
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[COMMUNICATION NO. 819 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. III.¹ Absorption of 2-*p*-Dimethylaminostyrylquinoline and Its Salts. The Effect on Absorption of a Benzene Ring in the Chromophoric Chain of Dyes²

BY L. G. S. BROOKER AND R. H. SPRAGUE

The base 2-*p*-dimethylaminostyrylquinoline (I)³ dissolves in basic or in neutral solvents with a yellow



low color but exhibits halochromism in that on acidification or on treatment with methyl iodide the color is deepened to wine red. This has at-

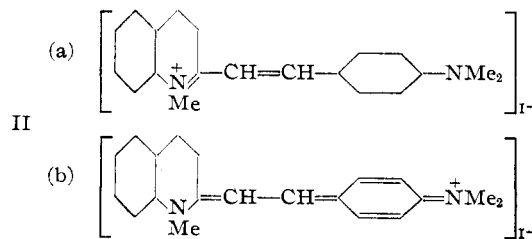
(1) Part II. THIS JOURNAL, 63, 3192 (1941).

(2) Presented in part before the Organic Section of the American Chemical Society at the April, 1941, meeting at St. Louis, Mo.

(3) More strictly Ia \leftrightarrow Ib. For the sake of simplicity, compounds are referred to throughout this paper by simple Roman numerals although their representation from the resonance standpoint may require more than one formula. In the formulas, benzenoid rings are shown without the double bonds of one of the Kekulé configurations.

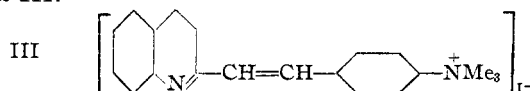
tracted the attention of several groups of workers,⁴ although no satisfactory explanation of the phenomenon has thus far been proposed.

Rupe, Hagenbach and Collin⁴ have shown that the base gives rise to two mono-methiodides, one of which is the wine red salt referred to above, the other being almost colorless. The red isomer is also formed when quinaldine methiodide is con-



(4) For references see Rupe, Hagenbach and Collin, *Helv. Chim. Acta*, 18, 1395 (1935).

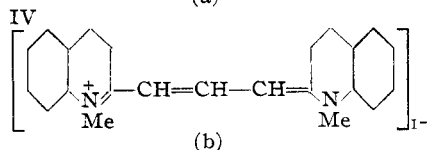
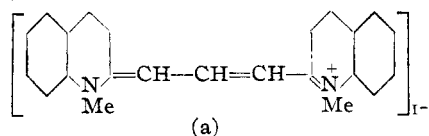
densed with *p*-dimethylaminobenzaldehyde⁵ and must therefore be represented by II. The colorless compound was obtained by condensing the methiodide of *p*-dimethylaminobenzaldehyde with quinaldine so that the three methyl groups must be attached to the same nitrogen atom as shown in III.



It is now seen that the resonance theory offers a very simple explanation for the difference in color of II and III, for, whereas it is possible to write the two alternative resonance formulas IIa and IIb for II, the ionic charge being associated first with one nitrogen and then with the other, it is not possible to devise a plausible second formula for III in which the ionic charge is associated with the quinoline nitrogen atom. Thus in II there are two resonating structures, and this fact, considered together with the long conjugated chain present in the compound, is in agreement with its relatively deep color. On the other hand, III is not a strongly resonating compound and therefore has no absorption in the visible part of the spectrum.

The resonance scheme Ia \longleftrightarrow Ib is suggested to account for the yellow color of the base itself. Of the two configurations involved, Ib with its negatively charged quinoline nitrogen will be considerably less stable than Ia,⁶ and the degeneracy of the system Ia \longleftrightarrow Ib will be correspondingly low.

Now 2-*p*-dimethylaminostyrylquinoline methiodide (II) is an unsymmetrical dye which may be regarded as the structural cross between the two symmetrical dyes 1,1'-dimethyl-2,2'-carbocyanine iodide (IV)⁷ and the acidified form of Michler's



hydrol (V). Both of these compounds are blue in color and their absorptions in nitromethane lie

(5) König and Treichel, *J. prakt. Chem.*, **102**, 63 (1921).

(6) Compare similar arguments concerning anhydronium bases in Parts I and II of this series.

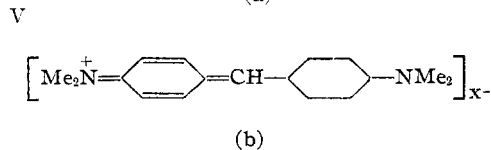
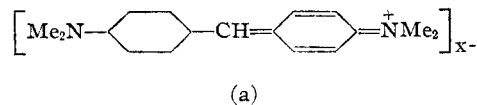
(7) Preparable by the method of Hamer, *J. Chem. Soc.*, 2798 (1927).

very close together (Fig. 1), nitromethane being used because salts of Michler's hydrol (the perchlorate, V, X = ClO₄, was chosen) are stable in this solvent but are readily hydrolyzed in hydroxylic solvents. The optical data for these dyes and others dealt with in this paper are given in Table I.

TABLE I

Compound	Curve	Solvent	$\lambda_{\max.}$, Å.	$\epsilon_{\max.}$, $\times 10^{-4}$
I	Fig. 1, D'	MeOH	3960	4.02
II	Fig. 1, A	MeNO ₂	5260	5.9
II	Fig. 1, A'	MeOH	5220	5.78
IV	Fig. 1, B	MeNO ₂	6070	13.3
IV	..	MeOH	6040	18.5
V	Fig. 1, C	MeNO ₂	6100	13.1
VI(—NR ¹ R ² = —NHPh)	..	MeOH	5285	9.50
VI(—NR ¹ R ² = —NMePh)	..	MeOH	5150	9.9
VII(—NR ¹ R ² = —NHPh)	..	MeOH	4850	6.5
VII(—NR ¹ R ² = —NMePh)	..	MeOH	4490	8.1
VIII	Fig. 1, E'	MeOH	4110	4.0
IX	Fig. 1, F'	MeOH	5380	4.9
X	Fig. 2, D'	MeOH	4000	2.8
XI	Fig. 2, A	MeNO ₂	5280	6.3
XI	Fig. 2, A'	MeOH	5240	6.5
XII	..	MeOH	5780	13.6
XIII	Fig. 3, B	MeNO ₂	5530	4.35
XIV	Fig. 3, A	MeNO ₂	4900	5.3
3,3'-Diethylthiacarbocyanine iodide	Fig. 2, B	MeNO ₂	5565	13.1

Since deep colors are associated with dyes the structures of which, on the whole, have a high degree of degeneracy, it seems reasonable to suppose that lessening the degeneracy of the structures in a dye by increasing the asymmetry should be accompanied by absorption at shorter wave lengths. This makes possible the prediction that if the nuclei in an unsymmetrical cyanine are of the same basicity, or, otherwise expressed, if the two resonance configurations have the same energy, then absorption should occur at a point midway between the absorptions of the parent symmetrical dyes, but if the configurations do not have the



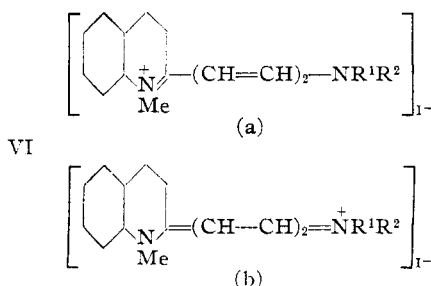
same energy, then absorption should occur at some wave length shorter than this intermediate position.

It was found by Dr. Hamer and her colleagues that most unsymmetrical cyanines have absorption maxima which agree fairly well with the

calculated mean values of the parent dyes,⁸ from which it has been concluded that the energies of the two extreme resonance configurations of such unsymmetrical cyanines are very nearly the same.⁹ In the present case, however, the unsymmetrical dye II (λ_{\max} in nitromethane 5260 Å.) absorbs at markedly shorter wave length than the harmonic¹⁰ mean of the maxima of IV and V (the harmonic mean of 6070 and 6100 Å. is 6085 Å.) the difference between the observed and calculated values (hereafter referred to as the "deviation") being no less than 825 Å.

In accordance with the above prediction, it has been shown that if the two auxochromic nitrogen atoms of an unsymmetrical dye are of markedly different basicity, then the absorption occurs at shorter wave length than that calculated from the parent dyes,⁹ but in the two cases reported the deviations were not as great as that in the present case. Furthermore, whereas these "nitrogen unbalanced" cyanines contained the feebly basic indole ring as one nucleus, in II both the nitrogen atoms would be expected to be quite strongly basic, one being in a quinoline ring and the other in the dimethylaniline residue, so that it seems unlikely that the considerable deviation can be ascribed primarily to a very marked difference of basicity between the two nitrogen atoms.

In support of this argument we have examined the absorptions of the two unsymmetrical polymethine dyes VI in which the quinoline nitrogen is linked through a conjugated chain with the



(8) Beilenson, Fisher and Hamer, *Proc. Roy. Soc. (London)*, **A163**, 138 (1937).

(9) Brooker, Sprague, Smyth and Lewis, *THIS JOURNAL*, **62**, 1116 (1940).

(10) On an energy basis, it would seem preferable to use the harmonic mean of the wave lengths rather than the arithmetic mean, the harmonic mean corresponding to the arithmetic mean of the wave numbers.

nitrogen of an aniline ($R^1 = \text{H}$; $R^2 = \text{Ph}$) or of a methylaniline residue ($R^1 = \text{Me}$, $R^2 = \text{Ph}$), the second of which might perhaps be considered closer in basicity to the nitrogen of the *p*-dimethylaminostyryl group.

The absorption maxima of these dyes were compared with those calculated from the parent sym-

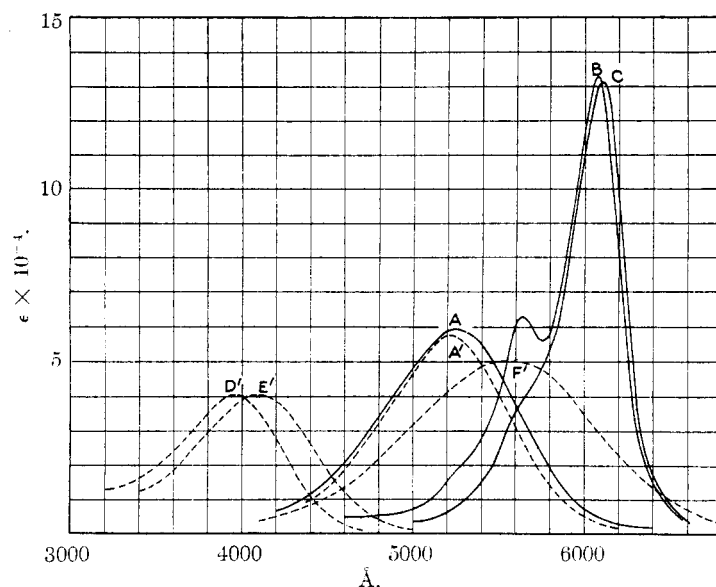
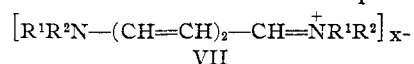


Fig. 1.—Absorption spectra: A, B, C = II, IV, V, respectively, in nitromethane; A', D', E', F' = II, I, VIII, IX, respectively, in methyl alcohol.

metrical dyes, these being the 2,2'-carbocyanine (IV) and the polymethine dyes VII.

In no case, however, did the deviation of one of these dyes approach in magnitude that of II. Thus, for the anilino compound (VI, $R^1 = \text{H}$; $R^2 = \text{Ph}$), the observed value of λ_{\max} is 5285 Å. while that calculated is 5380 Å. (the harmonic mean of 6040 and 4850 Å.) so that the deviation is 95 Å. For the methylanilino compound (VI, $R^1 = \text{Me}$; $R^2 = \text{Ph}$) λ_{\max} obsd. is 5150 Å. as is also λ_{\max} calcd. (the harmonic mean of 6040 and 4490 Å.) so that there is no deviation. While the first deviation is not negligible, it is nevertheless much lower than that of 825 Å. found in the case of II so that it seems quite certain that only a small part of this latter deviation can possibly be ascribed to a difference of basicity between the two nitrogen atoms.

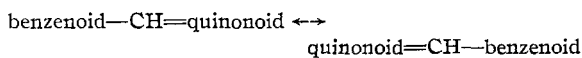
The color of a dye is not, however, a function of the auxochromic atoms alone, but also of the chromophoric chain, as well as of other parts of

the molecule, and a likely explanation of the abnormal absorption of II and one that enables a sharp distinction to be drawn between it and the compounds VI, is based on the fact that II contains a single benzene ring in the chromophoric chain, whereas the polymethines VI do not. This benzene ring is benzenoid in IIa, whereas it is quinonoid in IIb and these will not have the same stability, since the stabilizing effect of resonance between the Kekulé and other configurations tends strongly to favor the benzenoid configuration rather than the quinonoid and hence the actual state of the compound will tend toward IIa. The compound will therefore lose, in corresponding measure, its nature as a resonance hybrid and its color will be lighter in consequence. Another result is that the cationic charge will be predominantly taken by the quinoline nitrogen rather than by the nitrogen of the NMe_2 group.

In spite of the fact, then, that II has an ionic charge available for resonance, and even though the two nitrogen atoms concerned are both strongly basic, when considered separately, it is not considered that the degeneracy of II is as complete as in IV or V, although it is held to be more so than in I.

In the polymethines VI, on the other hand, there is no such disturbing influence, and the chromophoric chain linking the nitrogen atoms in VIa will have very nearly the same energy as that in VIb, hence dyes of this type, provided that the nitrogen atoms are nearly enough balanced as regards basicity, conform more or less closely to the linear relationship.

It is interesting to compare II with V, for, although there is of course the relatively unstable quinonoid arrangement in Va, this is linked to a benzenoid ring in such a way that the two nuclei can freely exchange their rôles (in Vb), thus creating the perfectly balanced system



the two sides of which are therefore completely degenerate, and hence this system can confer deep color.

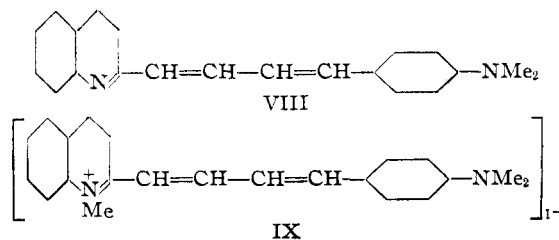
It has been remarked that I is still lighter in color than II, I having λ_{max} 3960 Å. in methyl alcohol (Fig. 1, D'), while II has λ_{max} 5220 Å. in the same solvent¹¹ (Fig. 1, A'). The degeneracy-

(11) The base I gives a red color in nitromethane corresponding to the acidified form, hence the necessity here of using a neutral (or basic) solvent for the comparison.

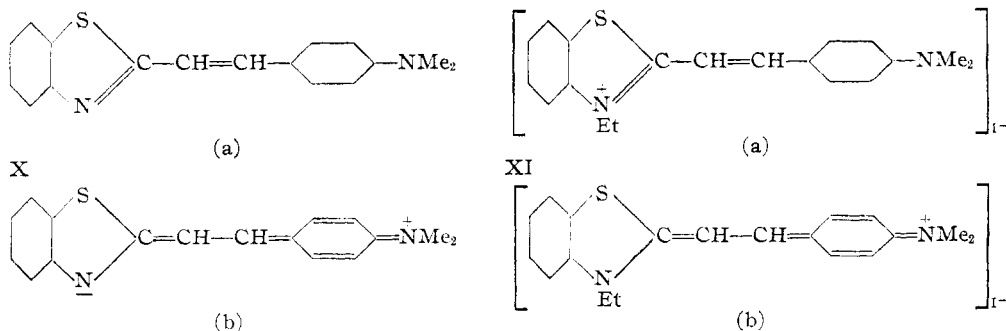
inhibiting effect of the benzene ring operates in I also, and thus Ib is less stable than Ia, not only because of the instability of $>\text{N}^-$ in the strongly basic quinoline nucleus and because Ib is a dipole, but also because in Ib the benzene ring is in the less stable quinonoid condition. These three factors therefore augment each other and there is a correspondingly strong tendency toward the uncharged state represented by Ia and in fact the observed dipole moment 3.12 is not much higher than the value of 2.6 calculated for Ia, this being in agreement with the supposition that the dipolar configuration Ib can only participate to a relatively small extent.

Judging by their absorptions, it therefore appears that these compounds fall into three distinct categories. First there is the base I, relatively light in color because three distinct factors cooperate to reduce the degeneracy of the configurations. Then there is the methiodide II which is moderately deep in color. The degeneracy of the structures of this compound is higher than in I because only one of the three degeneracy-inhibiting factors present in I is operating. Finally, there are the symmetrical dyes IV and V. In these the degeneracy of the structures is complete because of their identity. These compounds are very deeply colored.

In those vinylenes homologous series of compounds that have been studied and in which degeneracy of the structures is considered to be inhibited to a considerable extent (*e. g.*, the anhydronium bases related to the thiocyanine dyes; the acetanilido compounds, II, and the anils, V, of Part II of this series),¹ it has been found that the vinylenes shift on passing from one member of the series to the next higher is considerably less than that found in dyes such as the symmetrical cyanines in which the degeneracy of the structures is complete. We have accordingly prepared the next higher vinylenes homologs of I and II and find that the above rule holds here also. The base VIII was prepared by condensing *p*-dimethyl-



aminocinnamaldehyde with quinaldine in the



presence of concentrated hydrochloric acid. The methiodide (IX) was obtained by condensing the aldehyde with quinaldine methiodide in acetic anhydride solution. The absorptions of these two are also shown in Fig. 1 (Curves E' and F' for VIII and IX, respectively). The vinylene shift between the maxima of the bases (Curves D' and E' in Fig. 1) is only 150 Å., whereas that between the maxima of their methiodides is the higher value of 360 Å. (Curves A' and F' in Fig. 1), although even this difference is much less than the average vinylene shift of about 1000 Å. in completely degenerate series. These figures therefore support the conclusion that the degree of degeneracy of the structures of a base (I or VIII) is less than that of the corresponding methiodide, but that the degree of degeneracy of the latter falls far short of the complete degeneracy of the resonance structures in symmetrical dyes.

Similar compounds to those dealt with in the foregoing have also been prepared in the benzothiazole series. In this series the base 2-*p*-dimethylaminostyrylbenzothiazole (X) absorbs at much shorter wave length than its ethiodide (XI)¹² when compared in methyl alcoholic solutions (Fig. 2, Curves D' and A' with λ_{\max} . 4000 and 5240 Å., respectively). The ethiodide, in turn, absorbs at very much shorter wave length than the harmonic mean of the absorptions of the parent symmetrical dyes, 3,3'-diethylthiacarbocyanine iodide (Formula III, $n = 1$, in Part II of this series¹) and Michler's hydrol blue (V), when compared in nitromethane solution (Fig. 2). In this solvent, XI has λ_{\max} . 5280 Å., whereas the calculated mean is 5820 Å. (the harmonic mean of 5565 and 6100 Å.), so that

(12) Bloch and Hamer, *Phot. Journ.*, **70**, 380 (1930).

the deviation of 540 Å., while still considerable, is markedly less than in the case of II.

Similar arguments to those used in dealing with the quinoline compounds may be applied to these benzothiazole derivatives. Here also three categories of absorption and hence of degeneracy may be distinguished, there being the light-colored and relatively feebly degenerate base X, the deeper colored and moderately degenerate ethiodide XI and the deeply colored and completely degenerate symmetrical dyes (Curves B and C, Fig. 2).

In addition to these considerations, however,

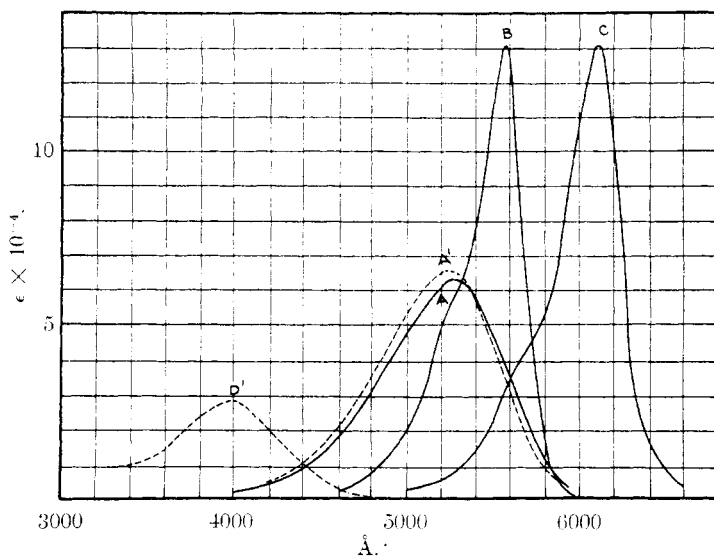


Fig. 2.—Absorption spectra: A = XI, B = 3,3'-diethylthiacarbocyanine iodide, C = V, all in nitromethane; A' = XI, D' = X, both in methyl alcohol.

there is an interesting relationship that is brought out in these absorptions.

In the cyanine dyes that have been studied in the past, the various heterocyclic nuclei that have been employed fall, as a general rule, into a definite order with respect to absorption. Thus, the existing data¹³ show that if the benzoxazole nuclei

(13) Fisher and Hamer, *Proc. Roy. Soc. (London)*, **A154**, 703 (1936).

of a symmetrical cyanine are replaced by benzothiazole, the color is always deepened, and if these are replaced, in turn, by 2-quinoline, the color is still further deepened. Thus, it is seen in the present work that the symmetrical carbocyanine derived from 2-quinoline (Fig. 1, B) absorbs at markedly longer wave length than that derived from benzothiazole (Fig. 2, B).¹⁴ Owing to the further fact that the majority of unsymmetrical cyanines absorb very close to the mean of the absorptions of the related symmetrical dyes,⁸ it follows that the above typical relationship between the three nuclei named also holds in unsymmetrical cyanines containing them. It therefore seems surprising that in the present styryl series the benzothiazole styryl dye (XI) should absorb at almost the same wave length as the corresponding quinoline derivative (II).¹⁵ Furthermore, the benzothiazole styryl base (X) is actually slightly deeper in color than the corresponding 2-quinoline base (I), so that the order in which the two nuclei stand in the cyanine dyes is here reversed.

A treatment of these apparent anomalies is suggested as follows.

From a comparison of the extreme resonance configurations IIa and IIb of the styryl dye, it is seen that IIb will be the more favored the lower the basicity of the quinoline nitrogen relative to that of the NMe₂ group, for in IIb the NMe₂ nitrogen is in the quaternary state, and the less basic the quinoline nitrogen, the less it will compete for the quaternary charge. Configuration IIb, however, is the less stable of the two so far as the benzene ring of the styryl group is concerned, this preferring the benzenoid arrangement in IIa. It follows that a reduction in the basicity of the quinoline nitrogen in II will favor IIb, and will thus tend to neutralize the degeneracy-inhibiting effect of the benzene ring which favors Ia.

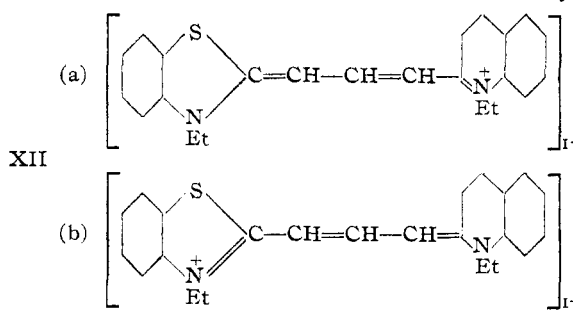
Replacement of the quinoline nucleus in II by the less strongly basic benzothiazole nucleus to give XI, would appear to be one way in which to bring about this change, and the replacement apparently is effective in increasing the net degeneracy of the structures in XI, compared with II, for

(14) It is true that the N-alkyl groups differ in these two dyes, but the effect of this is relatively slight and may be neglected in the present argument.

(15) The maximum absorption of XI, an ethiodide, actually lies at slightly longer wave length than that of II, a methiodide, in both methyl alcohol and nitromethane, but the ethiodide corresponding to II absorbs at slightly longer wave length in methyl alcohol (λ_{\max} . 5250 Å.) than XI.

the deviation is reduced from 825 to 540 Å., with the incidental result that XI absorbs at about the same wave length as II, due to the opposition between the above effect and the normal effect of replacing a quinoline nucleus by benzothiazole.

However, from a study of the absorption of 1',3'-diethylthia-2'-carbocyanine iodide (XII) it might have been argued that the benzothiazole and 2-quinoline rings in this dye are almost exactly equivalent in basicity rather than that the latter is the more basic nucleus for XI absorbs in methyl



alcohol with λ_{\max} . 5780 Å.,¹⁶ which agrees well with the mean of the absorptions of the parent symmetrical dyes (the harmonic mean of 5575 and 6040 Å. is 5795 Å.) indicating that XIIa and XIIb are almost if not quite equivalent in stability and hence that the two nitrogens are of approximately equal basicity.

These results clearly appear to be contradictory. On the one hand, replacement of a 2-quinoline nucleus in 1,1'-diethyl-2,2'-carbocyanine (IV, but Et groups in place of Me) by benzothiazole, giving XII, apparently does not noticeably diminish the complete degeneracy of the dye, as far as the absorption indicates. On the other hand, it is seen that the relationship between the absorptions of II and XI may be accounted for by assuming that the degeneracy of II is markedly altered (increased) by carrying out precisely the same change as before, namely, replacing the 2-quinoline nucleus by benzothiazole.

A reconciliation of these apparently divergent results is brought about by applying what appears to be a general rule, further examples of which will

(16) Other figures than this have appeared in the literature. Ogata, *Bull. Inst. Phys. and Chem. Research, Tokyo*, **13**, 557 (1934), gives 5600 Å. in ethyl alcohol, and Beilenson, Fisher and Hamer⁹ give the same figure in methyl alcohol. It was found necessary to use special methods to prepare the dye in a pure state, however, otherwise there was contamination with 3,3'-diethylthiacarbocyanine iodide which it was not found possible to remove, and it is felt that this accounts for these low figures. On the other hand, Yoshimura and Sakurai, *Bull. Inst. Phys. and Chem. Research, Tokyo*, **16**, 1295 (1937), give 5900 Å.

TABLE II

Mole fractions (C_2), dielectric constants (D), densities of solutions in benzene (d), polarizations at 25° (P_2), molar refractions (MR_D), polarizations at 25° (P_∞), observed moment (μ) and calculated moment (μ calcd.)

Compound	C_2	D	d	P_2	MR_D	$P_\infty(25^\circ)$	$\mu (\times 10^{18})$	μ calcd. ($\times 10^{18}$)
I	0.000000	2.2760	0.87334	$(P_1 = 26.668)$	88	290	3.12	2.6
	.000939	2.2899	.87395					
	.002147	2.3065	.87454					
	.002770	2.3152	.87482					
X	0.000000	2.2760	0.87334	$(P_1 = 26.668)$	86	353	3.59	2.2
	.001017	2.2966	.87458					
	.001622	2.3085	.87530					
	.002434	2.3248	.87620					

be provided in later papers of this series. This rule is: *a change in chemical structure of such a nature that it produces little or no effect on the deviation of a compound represented by two (or more) extreme resonance configurations of equal or nearly equal stability,¹⁷ will produce a greater effect on the deviation of a compound represented by two (or more) extreme resonance configurations that differ widely in stability. In the latter case, the effect on the deviation is greater the lower the degeneracy of the compound undergoing the change.*

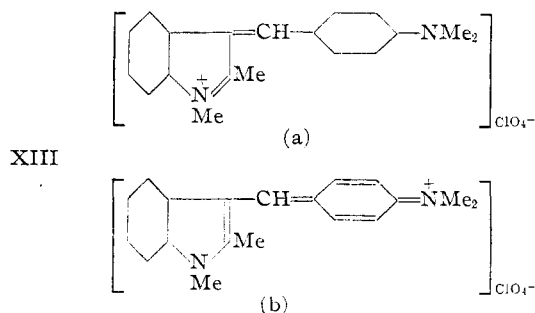
Thus the replacement of one of the 2-quinoline nuclei in the 2,2'-carbocyanine by benzothiazole is a change made in a dye the structures of which are completely degenerate, and this change is insufficient to produce any appreciable deviation, but when the 2-quinoline nucleus of II is replaced by benzothiazole, the change is being made in a dye the resonance structures of which are not of equal stability, as is demonstrated by the considerable deviation shown by II, and this deviation is markedly affected.

It has been mentioned above that in the styryl bases I and X the order in which the heterocyclic nuclei stand in the symmetrical cyanines is reversed, the benzothiazole derivative (X) having the higher value of λ_{\max} . It seems reasonable to suppose that the lower basicity of benzothiazole compared with 2-quinoline will go hand in hand with higher acidity of the former compared with the latter and therefore $>N^-$ will be more stable in Xb than in Ib. The degeneracy of X will accordingly be higher than that of I, so much so that the greater depth of color presumably conferred by the quinoline nucleus as such is slightly more than compensated for. The greater contribution of the dipolar configuration Xb compared with Ib is confirmed by the fact that the observed dipole moment of X (3.59 compared with 2.2 calculated from the uncharged configuration Xa) is appreci-

(17) A symmetrical dye may be considered to have zero deviation.

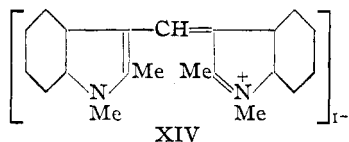
ably higher than that of I (3.12 compared with 2.6 calculated from Ia). These results are given in Table II.

From the foregoing comparison of the absorptions of II and XI, it follows that rendering the heterocyclic nitrogen in XI still less basic would neutralize the degeneracy-inhibiting effect of the benzene ring to a correspondingly greater extent, and this effect could be measured in terms of the reduction in deviation. When the effect due to N-N imbalance exactly neutralized the effect due to the benzene ring, the deviation would fall to zero, but beyond this point further reduction in the basicity of the heterocyclic nitrogen would make the N-N imbalance factor predominant, and a deviation would again appear. This latter state has not so far been reached but the first has been by selecting the unquestionably feebly basic indole ring as the heterocyclic nucleus. The dye 3-*p*-dimethylaminobenzylidene-2-methylindolenine methoperchlorate (XIII) was prepared



by condensing 1,2-dimethylindole with *p*-dimethylaminobenzaldehyde in the presence of perchloric acid. In this compound the dimethylamino nitrogen must be so much the more strongly basic of the two that configuration XIIIb will be that which is strongly favored from a consideration of the nitrogen atoms alone, while the chromophoric benzene ring strongly favors the disposition shown in XIIIa. The observed value of λ_{\max} for

this dye is 5530 Å. and that calculated as the harmonic mean of the absorptions of XIV⁹ and V (λ_{max} in nitromethane 4900 and 6100 Å., respectively) is 5435 Å., so that the deviation is -95 Å., *i. e.*, in the opposite direction to that anticipated.



The absorptions of these dyes are as yet untreated mathematically, however, and it is conceivable that where the degeneracy of the structures in an unsymmetrical dye is as complete as in the parent dyes, or very nearly so, it might theoretically be possible for absorption to occur at a wave length somewhat greater than that calculated as the harmonic mean of the wave lengths of the parent

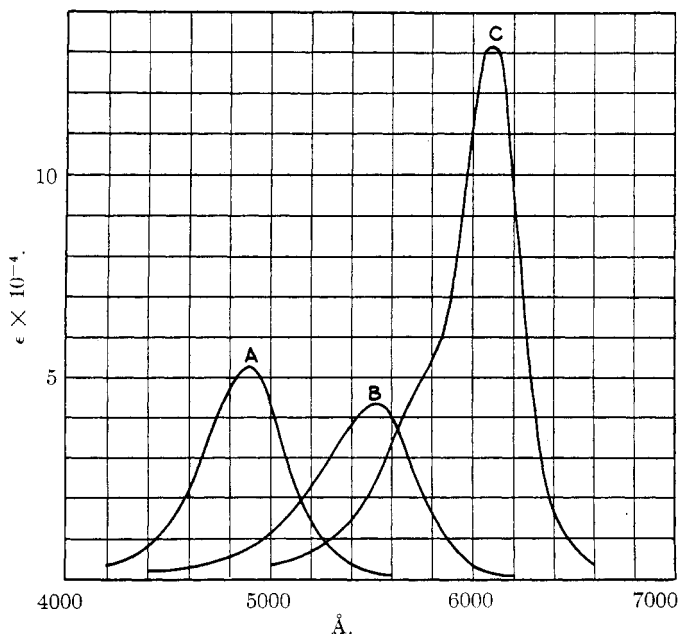


Fig. 3.—Absorptions in nitromethane: A = XIV, B = XIII, C = V.

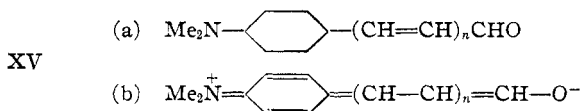
dyes. In any event, the deviation of XIII is far less than that of II or XI, so that in XIII, the influence of the benzene ring appears to be neutralized to a much greater extent than in the other two dyes. The absorptions are shown in Fig. 3.

Since the deviation is greatest in that styryl dye (II) which contains the most strongly basic heterocyclic nitrogen and least for that which contains the most weakly basic nitrogen (XIV), it follows that a comparison of the deviations in a series of *p*-dimethylaminostyryl dyes could be used to indi-

cate the relative basicities of the heterocyclic nuclei employed in these dyes, but a more detailed treatment of this subject is reserved for a later paper.

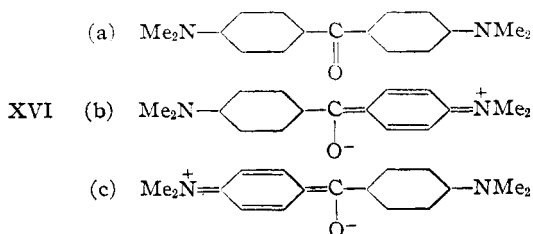
The suggestion that a single benzene ring in a chromophoric chain works to inhibit resonance along that chain (unless its influence is neutralized, as in XIII) is believed to be a principle of very wide application. A few examples are included here.

It is well known that *p*-dimethylaminobenzaldehyde and its higher vinylenes (XV,



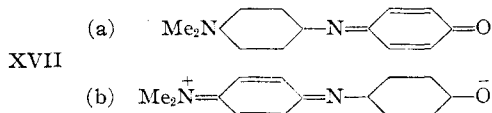
$n = 0, 1, 2$) possess well-marked aldehydic character in spite of the fact that they may be regarded as higher vinylenes homologs of dimethylformamide, $\text{Me}_2\text{NCHO} \leftrightarrow \text{Me}_2\text{N}^+=\text{CH}-\text{O}^-$, and in amides aldehydic or ketonic behavior of the carbonyl group is lacking due to resonance of the type shown. It is now suggested that amidic resonance is much reduced in XV, owing to the interposition of the benzene ring in the resonating chain, thus favoring configuration XVa and giving the $-\text{CHO}$ group more of the reactivity it would possess in benzaldehyde itself (and its higher vinylenes homologs).

The lack of color of Michler's ketone (XVI), which has long been a subject of discussion, is a related problem. In this compound it is unlikely that the resonance scheme XVIb \leftrightarrow XVIc plays a significant part in determining the absorption since this corresponds to that responsible for the deep color of V, and it is suggested that the fact that the compound may be given the formulation XVIa in which *both* benzene rings are in the stable benzenoid condition is largely responsible for the suppression of this resonance XVIb \leftrightarrow XVIc.



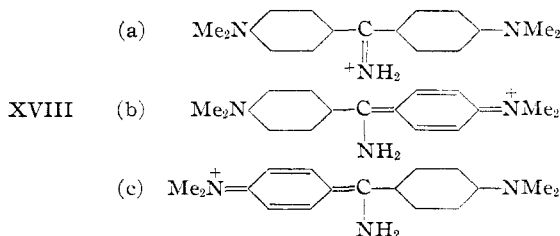
There is the further consideration that both in

XV and in XVI the configurations already considered unstable because they contain quinonoid rings also contain separated charges the energy of the separation of which will further diminish the stability of the dipolar arrangements. It seems unlikely, however, that this latter factor alone is responsible for the lack of color of XVI,¹⁸ because deeply colored compounds are known in which the carbonyl oxygen is an essential auxochromic atom. Thus, phenol blue (XVII) is very deeply colored



and this can only be ascribed to the resonance XVIIa \longleftrightarrow XVIIb. The absorption of this dye is more fully dealt with in a later paper.

The relatively light color of auramine (XVIII is the ion) is a related problem. In this dye the ionic charge may be shared between the three nitrogen atoms (XVIIIa, b and c) and aside from



any other considerations,¹⁹ it is clear that so far as the benzene rings are concerned, configuration XVIIIa will be strongly favored since it is the only one in which both rings are in the benzenoid state. This strong preference for one form satisfactorily accounts for the light color of the compound. In XVIIIa the ionic charge is carried by the amino group, but if this group is made feebly basic by acylation, there will be a much stronger tendency for the charge to be transferred to the strongly basic dimethylamino groups, thus giving greater stability to configurations corresponding to XVIIb and c (but acyl derivatives). In this case the low basicity of the acylamino group apparently forbids its sharing the ionic charge almost entirely, for such dyes are blue.²⁰

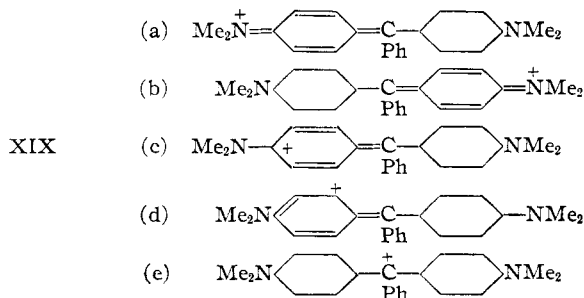
Malachite green is commonly assumed to resonate according to the scheme XIXa \longleftrightarrow XIXb,

(18) Here we differ from Taylor and Baker (Sidgwick, "Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 97) who say "Michler's ketone . . . is colorless because all possibility of resonating states is removed by the presence of the carbonyl group."

(19) Lewis and Calvin, *Chem. Rev.*, **25**, 310 (1939).

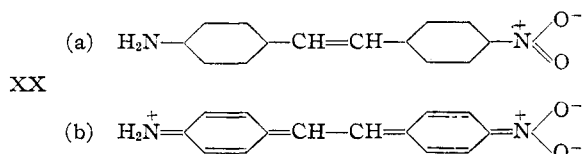
(20) Taylor and Baker in Sidgwick, "Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 96.

such intermediate steps as XIXc, d and e also participating.²¹ Of these three latter states XIXe



should be the most stable because here all three benzene rings are benzenoid, and it is suggested that it is for this same reason that when the dye is made alkaline, the central carbon atom is the one to which the hydroxyl group becomes covalently linked (in the carbinol base). The carbonium carbon atom in XIXe cannot compete strongly for the ionic charge against the much more electro-positive nitrogen atoms, however, hence the participation of even this form will be small in spite of the stable arrangement of the benzene rings.

In dyes such as V, XVII and XIX in which the chromophoric chain contains two benzene rings linked together through a group $-A=$ (e. g., $-CR=$ or $-CH=CH-CH=$ or $-N=$), resonance may reach a very high level, and it is interesting to compare these compounds with *p*-amino-*p*'-nitrostilbene (XX) in which the benzene



rings are linked through an even number of methine groups. Although the conjugated chain in this compound is very long and is provided with the necessary terminal auxochromic atoms, it nevertheless scarcely absorbs beyond the ultra-violet region (λ_{\max} , 4095 Å. in EtOH),²² which may be correlated with the fact that in the second extreme configuration of the scheme XXa \longleftrightarrow XXb, both benzene rings are quinonoid, and hence there will be an especially strong tendency toward XXa. There will be, in addition, a tendency in the same direction caused by the electrostatic attraction of charges in XXb and the combination of these forces causes the degeneracy of the con-

(21) Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939).

(22) Calvin and Buckles, *THIS JOURNAL*, **62**, 3324 (1940).

figurations to be very low, which, in turn, causes the absorption to take place at short wave length.

Acknowledgments.—We desire to express our gratitude to Professor C. P. Smyth and his colleagues for the dipole moment determinations given in Table II; to Mr. E. E. Richardson, Dr. L. A. Jones and their co-workers for the absorptions; to Dr. L. T. Hallett for the microanalyses; and to Mr. F. L. White for the preparation of 1',3-diethylthia-2'-carbocyanine iodide.

Experimental^{22a}

2-(4-Anilino-1,3-butadienyl)-quinoline methiodide (VI, R¹ = H, R² = Ph).—The acetyl derivative, 2-(4-acetanilido-1,3-butadienyl)-quinoline methiodide, was first prepared by heating equimolecular amounts of quinaldine methiodide and β -anilinoacrolein anil hydrochloride in acetic anhydride at the boiling point for fifteen minutes. The product separated on cooling and after washing with acetone followed by water was used without further purification, yield 65%. This was treated with an equimolecular amount of aniline in absolute ethyl alcohol at the boiling point for ten minutes. The yield was 80% before and 60% after recrystallization from methyl alcohol (230 cc./g.). The dye formed dark brownish needles with a blue reflex and had m. p. 231–232° dec.

Anal. Calcd. for C₂₀H₁₉IN₂: I, 30.65. Found: I, 30.66.

2-(4-Methylanilino-1,3-butadienyl)-quinoline iodide (VI, R¹ = Me, R² = Ph), was prepared from the anil 1-methyl-2-(4-phenyliminobutenylidene)-1,2-dihydroquinoline by the method previously described.¹ The anilino compound above (8.3 g.) was shaken for ten minutes at room temperature with a mixture of acetone (75 cc.) and 10% sodium hydroxide solution (50 cc.). The layers were separated and the product thrown out of the acetone layer by precipitation with water; yield 77%. After recrystallization from ligroin, yield 55%, the brownish needles with a green reflex had m. p. 101–102°.

Anal. Calcd. for C₂₀H₁₈N₂: C, 83.85; H, 6.34. Found: C, 83.65; H, 6.40.

The base readily added methyl *p*-toluenesulfonate (one hour at 100°) and after conversion to the iodide the yield was quantitative. After recrystallization from methyl alcohol (23 cc. per g., yield 77%) the dye formed dark needles with a metallic reflex and had m. p. 205–207°.

Anal. Calcd. for C₂₁H₂₁IN₂: I, 29.65. Found: I, 29.76.

2-(4-Dimethylamino-1,3-butadienyl)-quinoline methiodide (VI, R¹ = R² = Me) was prepared by heating the above acetanilido compound under reflux for one-half hour with a large excess of dimethylamine dissolved in absolute ethyl alcohol. The product separated (yield 73%) and was purified by recrystallization from methyl alcohol (130 cc. per g.; yield 55%). The almost black needles had a bluish metallic reflex and m. p. 260–261° dec.

Anal. Calcd. for C₁₆H₁₈IN₂: I, 34.67. Found: I, 34.51.

2-(4-*p*-Dimethylaminophenyl-1,3-butadienyl)-quinoline (VIII).—Quinaldine (3.6 g., 1 mol), *p*-dimethylaminocinnamaldehyde (4.4 g., 1 mol) and concd. hydrochloric acid (2 cc.) were heated at 100° for sixteen hours. The solid cake was dissolved in hot methyl alcohol, made alkaline with sodium hydroxide solution and the sticky base stirred with a little methyl alcohol when it became crystalline. It was purified by two recrystallizations from methyl alcohol and then two from propyl alcohol (23 cc. per g., final yield 9%). The orange powder had m. p. 182–184° dec.

Anal. Calcd. for C₂₁H₂₆N₂: C, 83.95; H, 6.72. Found: C, 83.43; H, 6.62.

2-(4-*p*-Dimethylaminophenyl-1,3-butadienyl)-quinoline methiodide (IX).—Quinaldine metho-*p*-toluenesulfonate (prepared by heating the base and methyl *p*-toluenesulfonate at 100° for one hour) (3.3 g., 1 mol) and *p*-dimethylaminocinnamaldehyde (1.75 g., 1 mol) were heated under reflux with acetic anhydride (30 cc.) for five minutes. The dye was precipitated by the addition of ether and converted to the iodide, using sodium iodide (crude yield 35%). The dye separated from methyl alcohol (425 cc. per g.; yield 12% after three recrystallizations) in beautiful green crystals with a greenish-bronze reflex and had m. p. 262–264° dec.

Anal. Calcd. for C₂₂H₂₃IN₂: I, 28.71. Found: I, 28.60.

2-*p*-Dimethylaminostyrylbenzothiazole (X).—2-Methylbenzothiazole (14.9 g., 1 mol), *p*-dimethylaminobenzaldehyde (14.9 g., 1 mol) and concd. hydrochloric acid (3 cc.) were heated at 100° for sixteen hours. After being made alkaline (crude yield 96%) the product was recrystallized from methyl alcohol (260 cc. per g., yield 78%). The yellow needles had m. p. 206–208° dec.

Anal. Calcd. for C₁₇H₁₆N₂S: C, 72.80; H, 5.76. Found: C, 72.86; H, 6.02.

1',3-Diethylthia-2'-carbocyanine iodide or [3-Ethylbenzothiazole-(2)]-[1-ethyl-quinoline-(2)]-trimethincyanine iodide.—When attempts were made to prepare this dye, using either quinaldine ethiodide and 2-(2-acetanilidovinyl)-benzothiazole ethiodide as components or 2-methylbenzothiazole ethiodide and 2-(2-acetanilidovinyl)-quinoline ethiodide, and employing a wide variety of experimental conditions, the results were unsatisfactory. The analytical figures for sulfur were consistently high, indicating contamination by 3,3'-diethylthiacarbocyanine iodide, and this it was not found possible to remove. Since the contaminating dye appeared to be that containing two benzothiazole nuclei rather than that containing two quinoline nuclei, preliminary experiments were made on the preparation of the isomeric 1'-methyl-3-*n*-propylthia-2'-carbocyanine iodide. This dye, obtained by condensing 2-(2-acetanilidovinyl)-benzothiazole *n*-propiodide with quinaldine metho-*p*-toluenesulfonate in boiling pyridine solution for fifteen minutes, proved easy to purify as had been anticipated, any 3,3'-di-*n*-propylthiacarbocyanine iodide formed as by-product being sufficiently more soluble than the desired dye to be removed with ease. After two recrystallizations from methyl alcohol (138 cc. per g., 54% yield), the dye was analytically pure. It separated in dark bluish needles with m. p. 255–257° dec. and had λ_{max} , 5790 Å. in methyl alcohol.

(22a) All melting points given are corrected.

Anal. Calcd. for $C_{23}H_{23}IN_2S$: S, 6.59. Found: S, 6.71, 6.73.

The 1',3-diethyl dye was finally obtained by the use of intermediates which are less reactive than the acetanilido-vinyl derivatives.¹ Either of the following procedures was satisfactory and may be recommended in similar cases:

(a) 2-(2-Methylanilinovinyl)-benzothiazole ethiodide¹ (2.11 g., 1 mol) and quinaldine etho-*p*-toluenesulfonate (1.72 g., 1 mol) were allowed to react in pyridine (10 cc.) at the boiling point for one-half hour. The yield was 78% before and 40% after several recrystallizations from methyl alcohol (110 cc. per g.). The lustrous green crystals had m. p. 276–277° dec.

Anal. Calcd. for $C_{28}H_{28}IN_2S$: C, 56.76; H, 4.77; S, 6.59. Found: C, 56.86; H, 4.75; S, 6.60.

(b) 2-[2-(1-Piperidyl)-vinyl]-benzothiazole ethiodide¹ (1 g., 1 mol) and quinaldine etho-*p*-toluenesulfonate (0.86 g., 1 mol) were refluxed with pyridine (10 cc.) for one-half hour. The yield was 66% before and 21% after two recrystallizations from methyl alcohol; m. p. as above.

Anal. Found: C, 56.70; H, 4.69; S, 6.44.

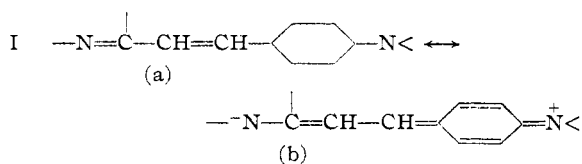
3-*p*-Dimethylaminobenzylidene-2-methylindolenine methoperchlorate (XIII).—1,2-Dimethylindole (2.9 g., 1 mol) *p*-dimethylaminobenzaldehyde (3 g., 1 mol) and 72% aqueous perchloric acid (2.8 g., 1 mol) were stirred together in 10 cc. of water at room temperature. Heat was evolved and the dye separated as a sticky blue solid which was washed several times with water and then with ether. Crystallization was induced by heating with acetone and chilling; yield 33%. The dye appeared to be unstable and was analyzed and used without further purification. The mass of minute blue crystals had m. p. 183–185° dec.

Anal. Calcd. for $C_{19}H_{21}ClN_2O_4$: C, 60.52; H, 5.62; N, 7.44. Found: C, 60.72; H, 5.62; N, 7.35.

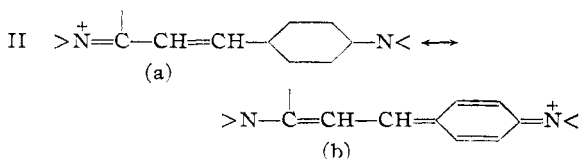
Summary

1. An explanation of the relatively short wave length absorption (λ_{\max} , 3960 Å.) of the yellow base 2-*p*-dimethylaminostyrylquinoline (I) compared with its red methiodide (II, λ_{\max} , 5220 Å.) is satisfactorily provided by the resonance theory.

2. The base resonates according to the scheme



and the methiodide thus



In II there is an ionic charge available for resonance and the system belongs to the amidinium ion type. There is, however, a considerable deviation between λ_{\max} observed and that calculated as the harmonic mean of the absorptions of the related symmetrical dyes, IV and V. This is ascribed to the presence of the single benzene ring in the chromophoric chain. The side IIa is stabilized by resonance within this benzene ring to a much greater extent than IIb and therefore IIa has lower energy and the degeneracy of the system $\text{IIa} \longleftrightarrow \text{IIb}$ is consequently reduced.

In I this "benzene" factor operates too, but Ib is unstable for two additional reasons; —N[–]— is unstable in the strongly basic quinoline ring, and the dipole is in itself unstable. The degeneracy of the system $\text{Ia} \longleftrightarrow \text{Ib}$ is therefore still lower, hence it absorbs at shorter wave length.

Compounds I and II therefore fall into distinct categories with respect to resonance and hence to absorption. In a third category are the two symmetrical dyes of which II may be considered the structural cross. The resonance structures of each of these latter dyes are completely degenerate and the dyes are very deeply colored.

In agreement with this classification are the shifts of λ_{\max} to the next higher vinylene homologs. That for the least highly degenerate compound, I, is least (150 Å.); that for the moderately degenerate methiodide, II, is next (360 Å.), but even this figure is much lower than that of around 1000 Å. characteristic of symmetrical polymethine dyes.

3. In $\text{IIa} \longleftrightarrow \text{IIb}$ the effect of the benzene ring may be neutralized to a greater or less extent by substituting a less strongly basic N for that of quinoline. If the quinoline ring in II is accordingly replaced by benzothiazole, giving XI, the deviation drops from 825 to 540 Å. If replacement is by the still less basic indole ring, the deviation falls still further.

4. In order to reconcile some of the findings in the above paragraph with certain others that are apparently contradictory, it is necessary to invoke a rule which appears to be general.

5. The effect of a benzene ring in reducing the degeneracy of conjugated systems is a principle of wide application and is illustrated by a number of examples.

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