dienes have similar donor–acceptor properties being close to methyl methacrylate and methyl acrylate in the donor–acceptor series.

2-Chlorobutadiene is 3–16 times as reactive as butadiene, depending on the reference radical. 2,3-Dichlorobutadiene is 1.1–1.3 times as reactive as 2-chlorobutadiene. The chlorovinyl group in 2-chlorobutadiene appears to be more reactive than those in 2,3-dichlorobutadiene.

1,1-Diphenylethylene is only 2.0–2.5 times as reactive as styrene. The second phenyl group presumably offers some steric hindrance, either to resonance in the transition state, or to approach of the attacking radical. Substitution of chlorines in the para-positions increases the reactivity 10–20%; para-methoxy groups double the reactivity toward methyl acrylate or acrylonitrile radicals.

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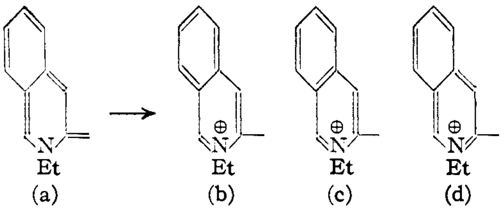
Color and Constitution. IX.[1] Absorption of Cyanines Derived from 3-Methylisoquinoline; a Rule Relating Basicity and Absorption in Symmetrical Cyanines

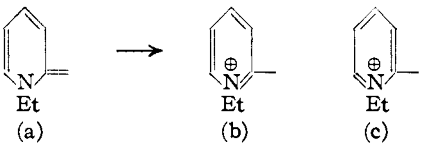
BY L. G. S. BROOKER, F. L. WHITE AND R. H. SPRAGUE

The absorption spectra of the cyanines derived from 3-methylisoquinoline[2] show several features of special interest. The basicity of the ring would be expected to be very high, for although it is possible to write only one structure of the Kekulé type (Ia) for the uncharged form of the ring, three may be written for the positively charged form (Ib, c and d). The gain in resonance stabilization on acquiring a positive charge is therefore very great indeed, greater even than for 2-linked pyridine, where the uncharged form of the ring may be written in one way (IIa) and the positively charged form in two (IIb and c).

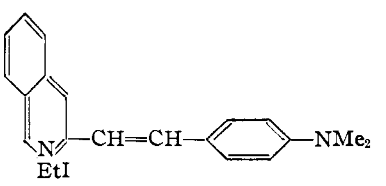
I



II

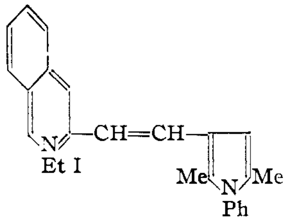


Such high basicity of the 3-linked isoquinoline ring (more precisely the high "N^{IV} minus N^{III} stabilization")[3] would be expected to result in an exceptionally high "deviation" in $\lambda_{\max.}$ for both the styryl dye III and for the unsymmetrical 3-isoquino-3′-pyrrolocarbocyanine IV. These predictions actually hold. With $\lambda_{\max.}$ 4250 Å. in nitromethane, III shows a deviation of 1455 Å., while IV shows one of 1005 Å. as calculated in the usual way.[3] These values are higher than any deviations previously reported in the two series of dyes to which III and IV belong.[3] Until now the highest deviations were shown by the 1,3-diethylbenzimidazole nucleus and were 1405 and 920 Å. for the dyes corresponding to III and IV, respectively.[3] The 2-ethyl-3-isoquinoline nucleus is thus the most strongly basic ring so far encountered in work on the cyanine dyes.



III

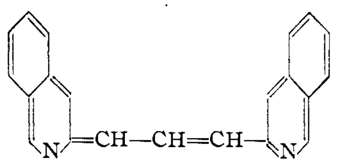
$\lambda_{\max.}$ 4220 Å., $\epsilon_{\max.}$ 3.1×10^4 in MeOH
$\lambda_{\max.}$ 4250 Å., $\epsilon_{\max.}$ 3.2×10^4 in MeNO$_2$



IV

$\lambda_{\max.}$ 3890 Å., $\epsilon_{\max.}$ 2.6×10^4 in MeOH

V



$\lambda_{\max.}$ 5300 Å., $\epsilon_{\max.}$ 1.3×10^4 in MeOH
$\lambda_{\max.}$ 5310 Å., $\epsilon_{\max.}$ 1.2×10^4 in MeNO$_2$

The "proportional deviations" of dyes III and IV, 103.5 and 109 units, respectively, are indicated in Fig. 1 together with those of a selection of the more basic nuclei of the group previously studied.[3]

Another feature of considerable interest is the fact that the 3-isoquinocarbocyanine V absorbs at markedly shorter wave lengths than the isomeric dye VI (pinacyanol) and even than the 2,2′-pyridocarbocyanine VII. In fact, V provides the first recorded example of a carbocyanine derived from a simpler carbocyanine (VII) by the addition of ben-

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[1] Presented in part before the Organic Section of the American Chemical Society, April 11, 1946, at Atlantic City, New Jersey. Part VIII, see THIS JOURNAL, **67**, 1889 (1945).

[2] *Ibid.*, **73**, 1094 (1951).

[3] Part VII, *ibid.*, **67**, 1881 (1945).

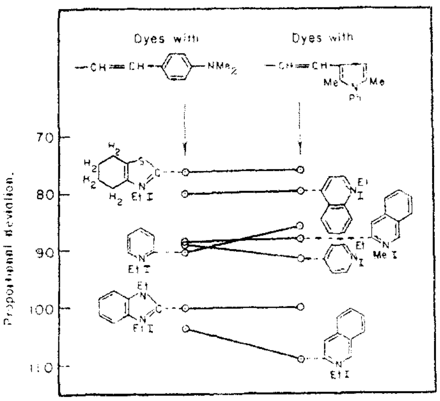
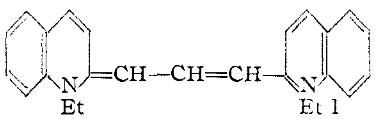


Fig. 1.—Proportional deviations of highly unsymmetrical dyes including III and IV.

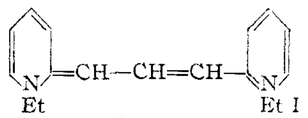
zene residues, but absorbing at shorter wave lengths than that simpler dye.

VI



$\lambda_{max.}$ 6040 Å. in MeOH

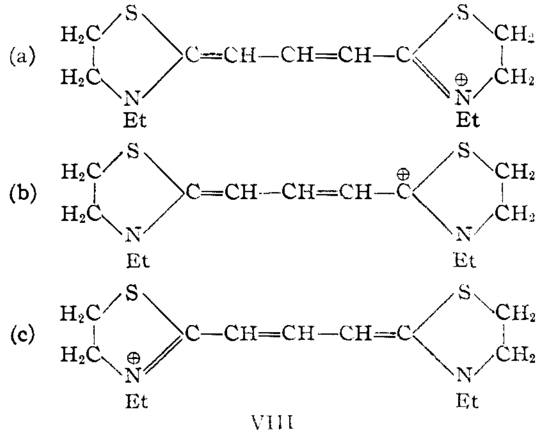
VII



$\lambda_{max.}$ 5620 Å. in MeOH

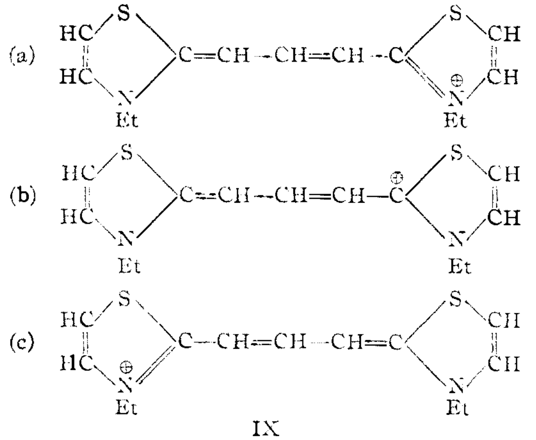
Very little has been published concerning the relative absorptions of closely related symmetrical cyanines, but Brooker and Sklar have suggested that of two symmetrical cyanines, that which contains the more basic nuclei will have the deeper color, other things being kept as nearly equal as possible.[4] Their generalization was illustrated by a comparison of the thiazolinocarbocyanine (VIII) and the thiazolocarbocyanine (IX); the cations are shown.

The argument from which this conclusion was drawn was based on Pauling's suggestion that the more probable intermediate structures for dyes of this type were those with positively charged carbon atoms, such as VIIIb and IXb.[5] (Only one intermediate structure is shown for each dye cation, but others may be imagined in which the positive charge passes along the chain of carbon atoms until it arrives at the second nitrogen atom, in the second pair of extreme structures VIIIc and IXc.) In deriving an intermediate structure of this type from an extreme structure, there will be an increase in energy since the positive charge is transferred from nitrogen to less electropositive carbon. This term may be taken as roughly constant in each of the dyes of the comparison, but in addition to this gain in energy a double bond is lost from the positively charged heterocyclic ring in each dye. This will result in a loss in resonance stabilization, but that loss is greater for the more unsaturated thiazole derivative IX, where the ring with $=^{\oplus}N<$ is stabilized by two conjugated double bonds, than in the thiazoline derivative VIII, where the corresponding ring is stabilized by only one double bond. It follows that the intermediate structures with $C^{\oplus}$ lie nearer in energy to the levels of the extreme structures in VIII than in IX, as shown qualitatively in Fig. 2, and with these conditions it follows from simple quantum mechanical considerations that the resonance interaction between the levels of the extreme structures in VIII will be greater than in IX. This means that the transition frequency will be greater for VIII and that the dye will absorb at shorter wave lengths than IX, as is actually the case experimentally.



VIII

$\lambda_{max.}$ 4450 Å. in MeOH



IX

$\lambda_{max.}$ 5425 Å. in MeOH

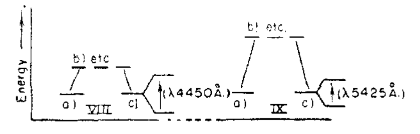


Fig. 2.—Qualitative energy-level diagram illustrating the greater separation of the levels of the ground and first excited states in VIII compared with IX.

The principle mentioned above that the resonance interaction between the two levels of the extreme structures is the greater the closer to these levels are those of the intermediate structures, follows from general resonance considerations, but appears first to have been applied to the interpretation of dye spectra by Förster,[6] who illustrated it by a comparison of the resonance possibilities of mala-

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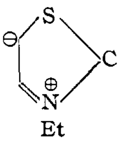
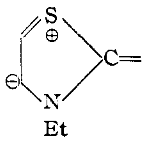
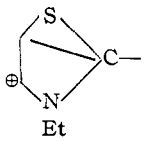
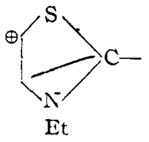
(4) Brooker, *Rev. Mod. Phys.*, **14**, 291 (1942).

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

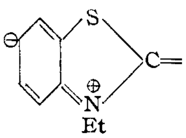
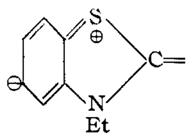
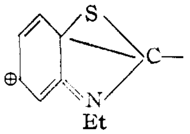
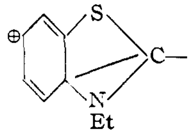
(6) Förster, *Z. Elektrochem.*, **45**, 566 (1939).

chite green and crystal violet, dyes which differed not in the nature of the terminal nuclei but rather in the nature of the connecting bridge. The general idea was also expressed again in somewhat different terms by Lewis.[7]

It has been felt for some time that the comparison of dyes VIII and IX was not convincing for the demonstration of the effect of varying the basicity of the nuclei alone, since the dyes differ in more than this respect. There is more conjugation in the nuclei in IX than in those of VIII and this will have results, aside from its influence on the basicity, which cannot be neglected. The additional conjugation in IX makes it possible to devise additional resonance structures (corresponding to the T-structures of Branch[8]) containing groupings such as

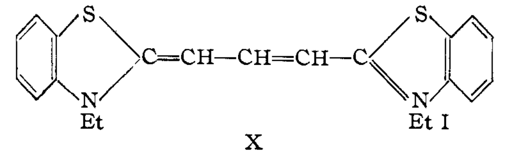
In dyes containing the thiazole nucleus, therefore, it is possible to picture at least some movement of both positive and negative charges to the peripheral carbons of the nucleus, and the consequent increase in the area over which charge may be distributed would seem very reasonably to result in some shift of the absorption to longer wave lengths, just as increasing the area over which a full ionic charge can move, by increasing the length of the conjugated connecting chain between the nitrogens, results in a strong shift in this direction. Increasing the amount of "extra-chromophoric" conjugation by proceeding from thiazole to benzothiazole will extend the area of charge distribution still further, corresponding to the possibility of writing structures such as

the result of which would be expected to be still more bathochromic.

By this reasoning it seems likely that a considerable part of the greater depth of color of IX, relative to VIII, is the result of the "extra-chromophoric" conjugation in IX, and only part is the result of the greater basicity of the nuclei in IX, though it is difficult to disentangle the two effects in this one comparison. Nevertheless, in the following additional comparisons, considered as a group, the rule appears to hold that of two symmetrical cyanines, that which has the more basic nuclei will absorb at the longer wave lengths, if allowance is made for other effects.

Thus the benzothiazole rings in the thiacarbocyanine dye X are less basic than the thiazole rings in IX as determined by the "deviation" procedure.[3] Then by the rule proposed by Brooker and Sklar, X should absorb at shorter wave lengths than IX

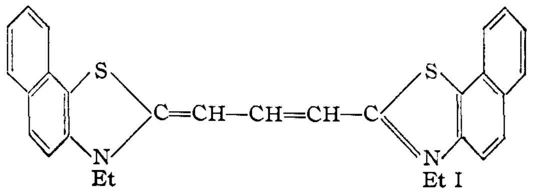


X

$\lambda_{max.}$ 5575 Å. in MeOH

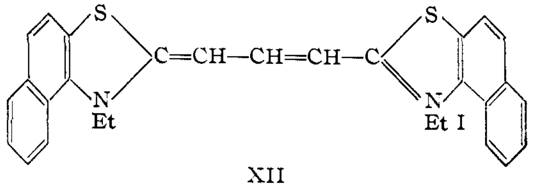
However, X has heavier nuclei than IX and, in particular, more extra-chromophoric conjugation. These factors will tend to deepen the color; hence, it is not surprising that X actually absorbs at somewhat longer wave lengths than IX rather than at the shorter wave lengths to be expected from the "higher the basicity the deeper the color" rule alone.

In the naphthothiazole dyes XI and XII, both the α- and β-naphthothiazole rings (in XI and XII, respectively) have been shown to be more basic than the benzothiazole ring in X.[3] Both XI and XII should therefore be deeper in color than X for this reason. There is, in addition, more extra-chromophoric conjugation in XI and XII and this will further deepen the color of the naphthothiazole dyes relative to X. The effects of increased basicity and increased conjugation therefore augment each other in these comparisons (whereas they oppose each other in IX and X) and in consequence XI and XII absorb at very decidedly longer wave lengths than X.



XI

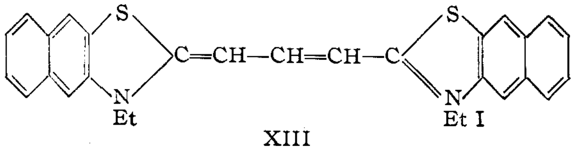
$\lambda_{max.}$ 5925 Å. in MeOH



XII

$\lambda_{max.}$ 5950 Å. in MeOH

On the other hand, the ring in the linear naphthothiazole derivative XIII has been shown to be less basic than that of benzothiazole,[3] so that if the basicity factor were alone of importance, XIII should absorb at shorter wave lengths than X. There is additional conjugation in XIII, however, which would be expected to deepen the color. The two effects therefore oppose each other, so that it is



XIII

$\lambda_{max.}$ 5695 Å. in MeOH

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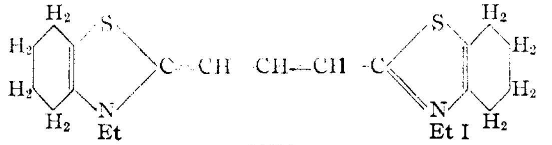
(7) Lewis, THIS JOURNAL, 67, 775 (1945).

(8) Branch, Tolbert and Lowe, *ibid.*, 67, 1693 (1945).

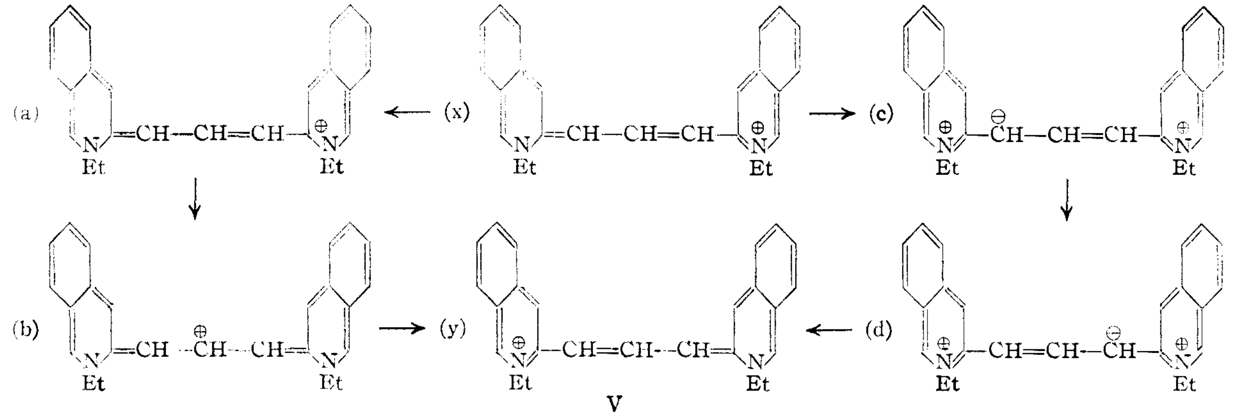
not surprising that the absorptions of X and XIII actually do not lie very far apart.

Perhaps the most convincing example of the basicity color rule is that provided by the comparison of X with XIV. The tetrahydrobenzothiazole nucleus in XIV is considerably more basic than the benzothiazole nucleus in X,[3] and although the resulting effect which would make XIV deeper than X is opposed by the greater amount of conjugation in X, the effect of the greater basicity of the nuclei in XIV clearly predominates, for this dye is decidedly the deeper of the two. In the absence of these considerations it would be very puzzling that saturating a part of each benzothiazole ring in X to give XIV should deepen the color, whereas the reverse occurs when the thiazole rings in IX are hydrogenated to give VIII. In the one comparison (X → XIV) hydrogenation increases the basicity of the nucleus, whereas in the other example (IX → VIII) hydrogenation has the opposite effect and reduces the basicity of the nucleus. When, in addition to the relationships to be expected from these relative basicities, it is realized that the effect of extra-chromophoric conjugation will increase the difference between VIII and IX but reduce the difference between X and XIV, the actual absorption relationships of the four dyes are reasonably accounted for.



XIV

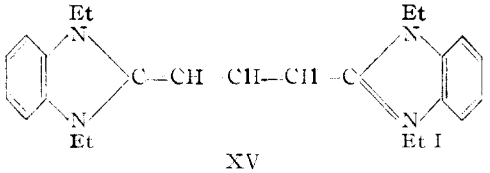
$\lambda_{max.}$ 5700 Å. in MeOH



V

Now, in view of the above findings, it is at first sight surprising that V, which contains nuclei of extremely high basicity, should absorb at extraordinarily short wave lengths. However, the explanations advanced above for the relative absorptions of dyes of the thiazole family were based on the assumption that for all of this family of dyes, the most important intermediate structures were those with $C^{\oplus}$, such as VIIIb and IXb. For V such intermediate structures would be Va and Vb, but in these structures both heterocyclic nuclei are in the extremely unstable uncharged state, with both 6-membered rings of each nucleus in an *o*-quinonoidal arrangement. Such intermediate structures are consequently of very high energy. There come into the picture, therefore, alternative tripolar intermediate structures Vc and Vd, which, though they contain the arrangement $-^{\ominus}CH-$, in itself not as stable as the $-^{\oplus}CH-$ of Va and Vb, are enormously stabilized by the circumstance that both the heterocyclic nuclei have full aromatic stabilization (though only one of the three ways of drawing this ring is shown). There can be little doubt, therefore, that for V these tripolar intermediate structures are much more stable than the monopolar structures Va and Vb, and these tripolar structures clearly become relatively lower in energy the more strongly basic the nuclei of the dye. In the case of V, the 3-linked isoquinoline nucleus is so strongly basic that it seems likely that Vc and Vd are very likely as low in energy, approximately, as the extreme structures, Vx and Vy. The resulting concentration of energy levels of extreme and intermediate structures not far apart in energy will provide exceptionally strong resonance interaction and a wide splitting of the levels of ground and first excited states, hence the absorption of the dye at short wave lengths.

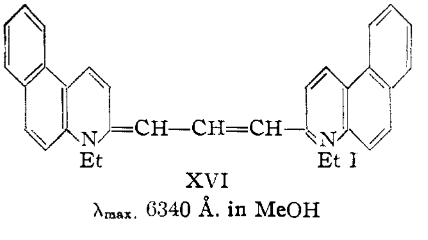
It seems unlikely that V is the only symmetrical cyanine to which the foregoing treatment will apply. The benzimidazole dye XV, of which the rings are also very strongly basic,[3] also absorbs at significantly short wave lengths, probably for a similar reason.



XV

$\lambda_{max.}$ 4955 Å. in MeOH

Again, it is interesting to compare the absorptions of dyes VII, VI and XVI. The relationship between VI and XVI is similar to that between X



XVI

$\lambda_{max.}$ 6340 Å. in MeOH

and XI. The benzo[f]quinoline nucleus in XVI is more basic than the quinoline nucleus in VI (though neither ring approaches the basicity of the rings in V or XV). There is also more conjugation in XVI, and for these two reasons, which augment each other, XVI would be expected to absorb at considerably longer wave lengths than VI, which it in fact does. However, the pyridine rings in VII are much more basic than those in VI, a factor which, by itself, might have been expected to cause VII to absorb at longer wave lengths than VI. There is, however, extra conjugation in VI which will oppose the basicity factor, and it would not have been surprising, therefore, if VI and VII had absorbed rather near together, just as IX and X do. In actual fact VII absorbs at decidedly shorter wave lengths than this expectation. It is therefore suggested that in VII the pyridine rings are already sufficiently strongly basic for the tripolar intermediate structures to be of considerable significance, so that the lightening effect on the color with high basicity is starting to be felt.

On the basis of these results and considerations, a general rule connecting basicity and absorption in symmetrical (carbo)cyanine dyes may be stated as follows: *For symmetrical cyanine dyes in which the nuclei are of weak or moderate basicity (i.e., such nuclei as show proportional deviations of up to about 85 units in Fig. 3 of the reference already cited*[8]*), increasing the basicity of the nuclei will,* ceteris paribus, *have the effect of deepening the color. For symmetrical cyanines in which the nuclei are of stronger basicity than the limit suggested, increasing the basicity of the nuclei still further will have the effect of lightening the color.*

A further point that calls for comment is an extraordinary difference in the absorptions of the diethyl dye V and the corresponding dimethyl dye. The latter, with $\lambda_{max.}$ 4960 Å., absorbs at shorter wave lengths than the diethyl dye by 340 Å. The two curves are shown in Fig. 3 where, for comparison, the curves of VI and VII are also given.

A rather small shift to shorter wave lengths is encountered as a general rule in going from an uncrowded symmetrical cyanine with ethyl groups on the nitrogens to that with methyl groups, but a shift of 340 Å. is unprecedented.

If the short wave length absorption of the dimethyl dye were ascribable to a still further increase in basicity of the N-methyl-3-isoquinoline nucleus over the N-ethyl nucleus, that increase in basicity would be expected to be reflected in the deviations of the N-methyl dyes corresponding to III and IV. However, the N-methyl dye corresponding to III has $\lambda_{max.}$ 4290 Å. in nitromethane, a figure close to that for III itself, whence its deviation comes to 1245 Å., considerably less than that of III. Similarly, the N-methyl dye corresponding to IV has $\lambda_{max.}$ 3915 Å. in methyl alcohol, a figure not very different from that of IV itself, and gives a deviation of 810 Å., which is much less than that for IV. From these figures the basicity of the N-methyl-3-isoquinoline nucleus would come out to be decidedly lower than that of the N-ethyl nucleus rather than higher.

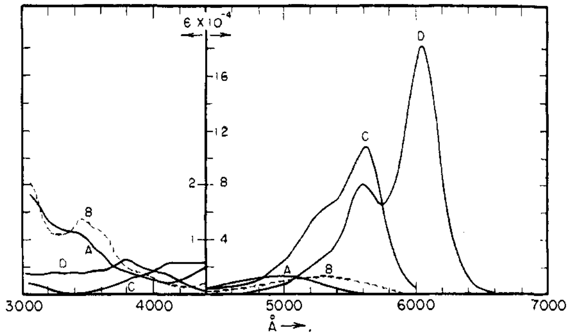


Fig. 3.—Absorption spectra in methyl alcohol: A = 2,2′-dimethyl-3,3′-isoquinocarbocyanine chloride; B = 2,2′-diethyl-3,3′-isoquinocarbocyanine iodide (V); C = 1,1′-diethyl-2,2′-pyridocarbocyanine iodide (VII); D = 1,1′-diethyl-2,2′-carbocyanine iodide (VI).

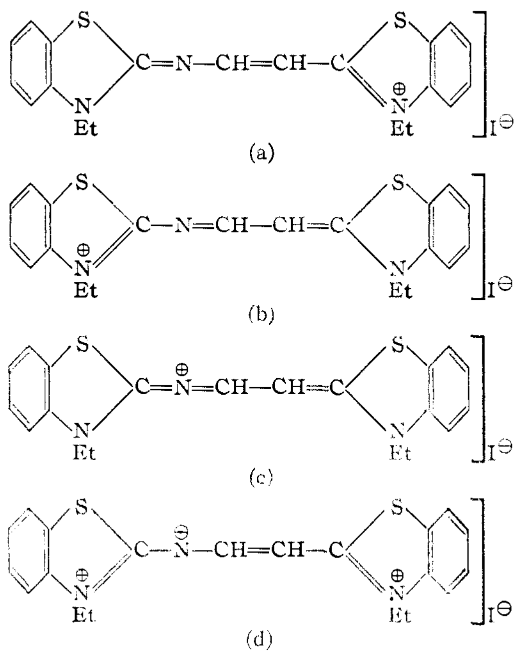
These results with the N-methyl-3-isoquinoline nucleus are plotted in Fig. 1 (the proportional deviations of the N-methyl dyes corresponding to III and IV are 88.5 and 88 units, respectively) where it is seen that the nucleus occupies about the same location as the 2- and 4-pyridine nuclei. Now, it has been seen that the high basicity assigned in Fig. 1 to the N-ethyl-3-isoquinoline nucleus is in accordance with a consideration of the relative resonance stabilizations of the net-uncharged and net-positively charged forms of the ring. The same arguments regarding stabilizations clearly apply to the N-methyl nucleus, and it seems unthinkable that the "N^{IV} minus N^{III} stabilization" of this ring should only be about the same as that of the 2- and 4-pyridine rings.

It is possible that for some reason not as yet clear, the deviation method fails to give reliable results for exceedingly strongly basic nuclei. It may be that for all the dyes, both symmetrical and unsymmetrical, which have hitherto been used in the compilation of the deviation series, the extreme structures and the low-energy intermediate structures are all of the same monopolar positively charged type, and that the success of the method is contingent upon this circumstance, whereas with the use of the 3-linked isoquinoline nucleus, tripolar structures come into consideration which somehow lead to anomalous results. It is hoped to investigate the matter further.

In order to see whether a marked difference in absorption between N,N′-dimethyl and diethyl homologs was perhaps a general feature of symmetrical carbocyanines containing strongly basic nuclei, the N,N′-dimethyl dye corresponding to VII was examined. Though that absorbs at shorter wave lengths than VI, with $\lambda_{max.}$ 5580 Å., the difference is only 40 Å. The tetramethyl dye corresponding to XV was also examined. It has $\lambda_{max.}$ 4875 Å., the difference in this case being 80 Å., which does not approach the 340 Å. difference of the isoquinoline dyes although four ethyl groups in XV have been replaced by methyl. The unusual relationship between the 2,2′-dimethyl- and diethyl-3,3′-isoquinocarbocyanines therefore remains unexplained.

The exceedingly low values of $\epsilon_{max.}$ of the bands in the visible of the two 3,3′-isoquinocarbocyanines are very apparent in Fig. 3, though these dyes are seen to absorb more strongly in the ultraviolet than either VI or VII. These low values of

$\epsilon_{\max.}$ in the visible may be understood in a roughly qualitative way as follows. If the suggestion is accepted that for V the important (*i.e.*, low energy) intermediate structures are the tripolar structures of the type of Vc and Vd, and if, furthermore, these are accepted as not being greatly higher in energy than the extreme structures, then the conjugated chain between the nitrogens is virtually split up into shorter resonating fragments, with the $-C^{\ominus}-$ atoms behaving as new auxochromic centers. The (in effect) shorter resonating chains will account not only for the absorption of the dye at shorter wave lengths, but also for the low intensity, for, in comparable (*i.e.*, vinylogous) series of cyanines, the members with shorter chains commonly absorb with relatively low intensities.[9]



XVII

$\lambda_{\max.}$ 4660 Å. in MeOH

That the effect of dividing a long resonating chain into shorter fragments is to shift the absorption toward shorter wave lengths and to reduce the intensity is illustrated by the comparison of the carbocyanine X with the azacarbocyanine XVII, a dye of a type first disclosed by Kendall.[10] In XVII, the chain nitrogen is so placed, with uneven numbers of carbons between it and the heterocyclic nitrogens, that it can share the ionic charge, as shown in XVIIc, and can thus function as a third auxochromic atom in the dye molecule. A possible objection to XVIIc is that it requires the two heterocyclic rings to occupy planes at right angles to each other, but XVIId, which is analogous to structures Vc and Vd, is an alternative structure that is free from this objection. In either case, the chain nitrogen serves to divide the originally long conjugated chain (in X) into two shorter fragments, and XVII accordingly absorbs at much shorter wave lengths than X and with greatly diminished intensity (Fig. 4).

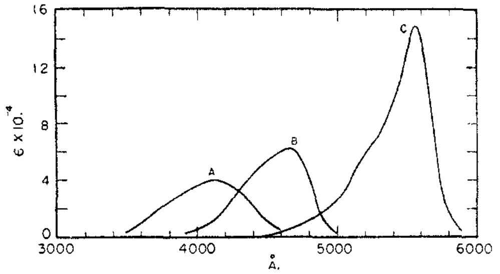
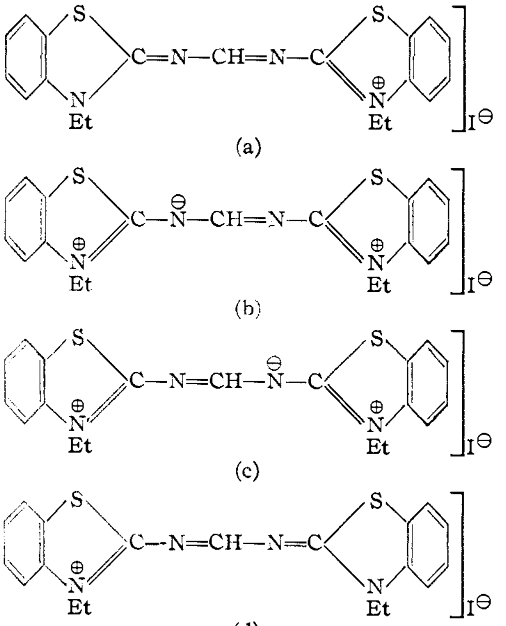


Fig. 4.—Absorption spectra in methyl alcohol: A = 3,3′-diethyl-8,10-diazathiacarbocyanine iodide (XVIII) in ethylene chloride; B = 3,3′-diethyl-8-azathiacarbocyanine iodide (XVII) in methyl alcohol; C = 3,3′-diethylthiacarbocyanine iodide (X) in methyl alcohol.

The effect is shown in a more exaggerated form by the diazacarbocyanine XVIII, a dye of a type also first disclosed by Kendall.[11] The chain nitrogens in XVIII can both serve as auxochromic centers corresponding to the possibility of writing structures XVIIIb and XVIIIc. The long chain of X is thus broken up into three fragments in XVIII, each of them very short, hence it is not surprising that XVIII absorbs at still shorter wave lengths than XVII[12] and with still lower intensity (Fig. 4).



XVIII

$\lambda_{\max.}$ 4120 Å. in ethylene chloride

Acknowledgments.—We take pleasure in acknowledging our indebtedness to Mr. Donald F. Ketchum and his department for the microanalyses and to Mr. E. E. Richardson, Mrs. Betty Colwell and Mr. Lewis L. Lincoln for the absorptions.

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[9] *Cf.* absorption of a vinylogous series of thiacyanines in Part I of this series, This Journal, **62**, 1116 (1940).

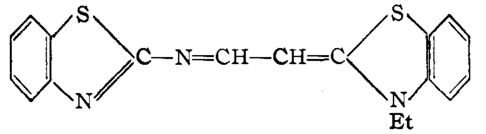
[10] Kendall, U. S. Patent 2,080,050 (1937).

[11] Kendall, U. S. Patent 2,080,049 (1937).

[12] An account of the hypsochromic effect of the chain nitrogens in dyes such as XVII and XVIII was given at the Rochester Meeting of the National Academy of Sciences in October, 1937 [Brooker, *Science*, **86**, 410 (1937)]. An essentially similar explanation of the hypsochromic effect of various substitutions in dyes of the di- and triphenylmethane series was also published by Förster [*Z. Elektrochem.*, **45**, 568 (1939)].

Experimental

3,3′-Diethyl-8-azathiacarbocyanine iodide (XVII) was made by two procedures: (A) 2-Aminobenzothiazole (1.5 g., 1 mol.), 2-β-acetanilidovinylbenzothiazole ethiodide[13] (4.5 g., 1 mol.) and pyridine (20 ml.) were refluxed for 5 minutes. The product, 2-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-aminobenzothiazole (XIX), was precipitated by the addition of water. It separated from methyl alcohol in lustrous brown crystals with m.p. 204–206° dec.; yield 40%.

XIX 

Anal. Calcd. for $C_{18}H_{15}N_3S_2$: C, 64.0; H, 4.5; N, 12.5. Found: C, 64.0; H, 4.7; N, 12.2.

The above base (XIX) (1.69 g., 1 mol.) was quaternized by heating with ethyl sulfate (1.3 g., 1 mol. + 100% excess) at 100° for 1.5 hours. The pulverized product was washed with acetone and recrystallized from ethyl alcohol; yield 92%, being 85% after a further recrystallization. The orange crystals had m.p. 199–201° dec.

Anal. Calcd. for $C_{22}H_{25}N_3O_4S_3$: C, 53.7; H, 5.1. Found: C, 54.0; H, 5.3.

A portion of the above ethosulfate of the dye, converted into iodide (aqueous sodium iodide), had m.p. 257–258° dec., identical with that of a specimen obtained by method B. The absorptions were also identical (the dye has $\lambda_{max.}$ 4660 Å. and $\epsilon_{max.}$ 6.3×10^4 in methyl alcohol), so that XIX alkylates on the benzothiazole nitrogen and not the chain nitrogen.

(B) 2-Aminobenzothiazole ethiodide was prepared by treating ethyl alcoholic 3-ethyl-2-iminobenzothiazoline with sodium iodide in the presence of concentrated hydrochloric acid. After two recrystallizations from water the colorless crystals had m.p. 228–231° dec. and were used without further treatment. This salt (2.9 g., 1 mol.), 2-β-acetanilidovinylbenzothiazole ethiodide[13] (4.5 g., 1 mol.) and pyridine (15 ml.) were heated under reflux for 5 minutes. Dye separated on cooling and after washing corresponded to a yield of 77%. After three recrystallizations from methyl alcohol (yield 22%), the dye formed reddish-brown crystals with a golden reflex and had m.p. 257–258° dec.

Anal. Calcd. for $C_{20}H_{20}IN_3S_2$: C, 48.7; H, 4.1. Found: C, 48.8; H, 4.2.

3,3′-Diethyl-8,10-diazathiacarbocyanine iodide (XVIII).—2-Aminobenzothiazole ethiodide, prepared as described above (6.1 g., 2 mols.), ethyl orthoformate (9 g., 1 mol. + 500% excess) and pyridine (15 ml.) were heated to refluxing for 5 minutes. Dye separated on cooling; yield 53% after washing. The product separated from glacial acetic acid in yellow crystals, m.p. 232–234° dec. The dye was unstable in methyl alcoholic solution; in ethylene chloride it had $\lambda_{max.}$ 4120 Å. and $\epsilon_{max.}$ 4.0×10^4.

Anal. Calcd. for $C_{19}H_{19}IN_4S_2$: C, 46.1; H, 3.9; N, 11.3. Found: C, 45.8; H, 4.0; N, 10.8.

Summary

1. The exceptionally high basicity of the 1-ethyl-3-isoquinoline nucleus, predictable from a comparison of the resonance structures of the uncharged and positively charged forms of the ring, is confirmed by the unprecedentedly high "deviation in $\lambda_{max.}$" shown by 2-ethyl-3-p-dimethylaminostyrylisoquinolinium iodide and by a second highly unsymmetrical dye.

2. The carbocyanine derived from 3-methylisoquinoline ethiodide, 2,2′-diethyl-3,3′-isoquinocarbocyanine iodide (V), absorbs at much shorter wave lengths and with much lower $\epsilon_{max.}$ than the isomeric 1,1′-diethyl-2,2′-(quino)-carbocyanine iodide (VI). This relationship may be traced to the extremely high basicity of the 3-isoquinoline ring.

3. Comparison of the absorptions of a number of symmetrical cyanines leads to the rule: *For symmetrical cyanines in which the nuclei are weakly or moderately basic, increasing the basicity of the nuclei will deepen the color (though allowance must be made for other factors, such as the effect of more "extrachromophoric" conjugation in one dye than another). For symmetrical cyanines in which the nuclei are very strongly basic, increasing the basicity of the nuclei still further, will lighten the color.*

4. 2,2′-Dimethyl-3,3′-isoquinocarbocyanine iodide absorbs at shorter wave lengths by 340 Å. than the 2,2-diethyl dye. This relationship, unprecedented in the literature of cyanine dyes, has thus far not been explained satisfactorily.

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[13] Part II of this series, THIS JOURNAL, 63, 3192 (1941).