STERIC HINDRANCE TO PLANARITY IN DYE MOLECULES[1,2]

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CONTENTS

I. INTRODUCTION

It is possible to account for the color of organic compounds very simply: a compound will be colored when it can exist both in a ground state and in an excited state to which it is capable of being raised by the absorption of visible radiation. Such a statement tells nothing, of course, about the chemical structure of colored compounds, but chemists have evolved theories which correlate structure with absorption, some of those current today being lineal descendants of the old chromophore–auxochrome theory of Witt, greatly extended and expressed in terms of modern electronic concepts, and illuminated and explained by quantum physics.

In considering the absorptions of an array of different compounds from this standpoint, one becomes conscious of the operation of a number of different factors, some outlined fairly clearly, others but dimly, though not all of these are likely to apply in any one instance. The future progress of the study of the relation between color and chemical structure is, in fact, likely to require the elucidation of a considerable mass of detail, the nature of which makes it impossible to codify into a few sentences or even paragraphs.

As an example of a factor which applies in some cases but not in others, one may cite an effect of considerable significance for the numerous dyes with two low-energy extreme resonance structures of *unequal* energy. This is the difference between these energy levels, or the "asymmetry." Considered in con-

junction with the length of the chromophoric chain, this determines what has been called the "deviation in λ_{max}," that is, the amount by which the absorption differs from that calculated by averaging the values of the two related symmetrical dyes (2). But this effect clearly plays no part in the absorption of the numerous groups of dyes which have two *identical* low-energy extreme structures.

The present paper deals with a factor which, like deviation, is completely lacking in some dyes, those that are planar, but is of great significance for many others, some of which will be discussed in detail.

## II. PLANARITY OF DYE MOLECULES

It was pointed out by Pauling (7) that resonance within conjugated systems, whereby all the linkages of the conjugated chain acquire some double-bond character, results in a tendency toward planarity of the atoms involved. The direct experimental evidence for this is not particularly extensive, but includes the determination of the planarity of the molecules of stilbene (9), *trans*-azobenzene (5) and phthalocyanine (10). It has accordingly seemed reasonable to assume that where a scale drawing of a dye molecule shows planarity to be possible, using the accepted interatomic distances, van der Waals radii, and bond angles, then the molecule will be planar, the condition being enforced by the energy of resonance stabilization. Certain dyes contain long polymethine chains $=CH—CH=CH—$ etc., which makes it possible sometimes to draw a large number of *cis–trans* isomers. Not all of these will be planar, and it has seemed plausible to restrict the choice to those that are planar, a line of argument that thus far has not been rigidly proved. In the present paper experimental evidence is for the first time adduced in support of reasoning of this kind (e.g., dye XX).

Thus far, too, relatively little has been done to determine the effect of distortion from planarity on the absorption of a given dye. The present paper is a continuation of work in this direction. The method adopted is necessarily comparative, and definite determinations of the structure of distorted dye molecules by x-ray and electron-diffraction methods still remain to be done.

III. EARLIER WORK ON EFFECT ON ABSORPTION OF DISTORTION FROM PLANARITY IN VARIOUS MOLECULES

Although the effect of steric hindrance to planarity on absorption has been examined in many substances, few of these are true dyes. Two main types of behavior may be distinguished. The great majority of studies have been made on compounds in which introduction of a "crowding" substituent is made in a molecular type characterized by the existence of a *single* low-energy resonance structure. As a rule, it is not this dominant structure, usually benzenoid, that is rendered less stable by the presence of the crowding substituent, but a higher-energy contributing structure or structures. The energetic asymmetry of the extreme structures of the molecule is thereby increased, and the absorption shifts to shorter wave lengths. Reduction in intensity is shown at the same time, because of the reduced overlap of the electronic orbitals.

Thus, Remington (8) compares the absorption of dimethylaniline (I) with that of dimethyl-o-toluidine (II), the drawings of which are approximately to scale.[3]
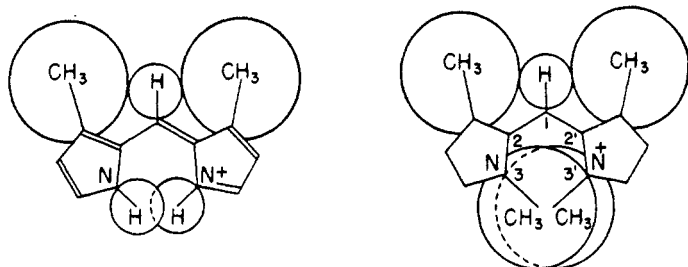
I

Dimethylaniline

II

Dimethyl-o-toluidine
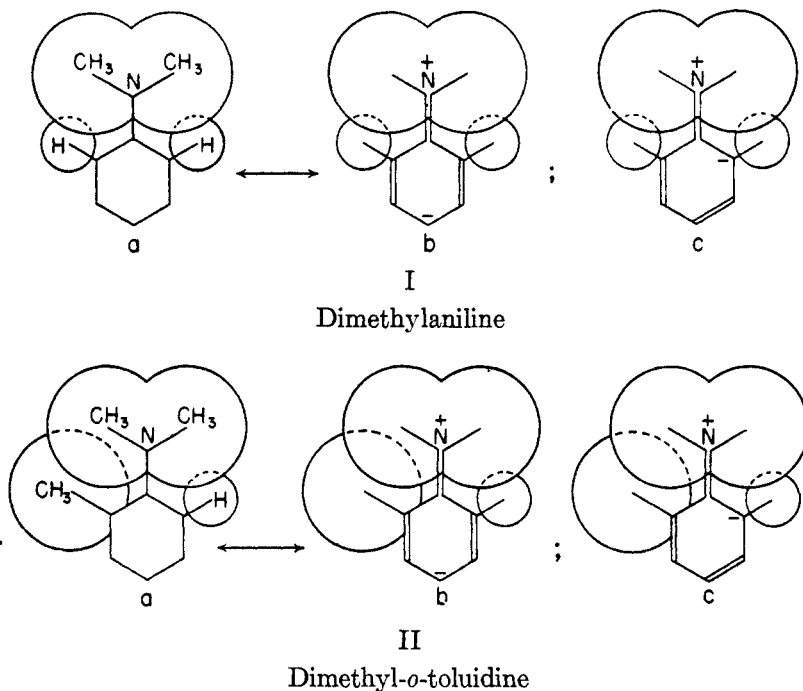
In I there is the possibility of resonance between the uncharged structure Ia and polar structures of the type of Ib and Ic. In Ia the $(CH_3)_2N-$ group is linked to the benzene ring by a single bond about which free rotation is permitted, but in Ib and Ic this linkage becomes a double bond, the geometry of which requires the carbons of the methyl groups to be coplanar with the atoms of the C_6H_5- group. The drawings indicate a rather small amount of crowding in this planar arrangement, which can almost certainly be accommodated without departure of the carbons and nitrogen of the $(CH_3)_2N-$ group from planarity with the phenyl group.

In II, on the other hand, the o-methyl group will undoubtedly crowd the dimethylamino group to a serious extent in the planar arrangements IIb and IIc, resulting in increase in their energy, although in IIa the crowding can be eased by rotation about the $N-C_6H_5$ single bond, with not much change in energy. The resulting increased separation of the energy levels of IIa and of IIb and IIc relative to Ia and to Ib and Ic results in diminished resonance interaction, but in absorption at shorter wave length of the band corresponding to the particular transition under consideration.

Examples similar to the above are relatively numerous in the literature, but only a single example has been described where crowding substituents were

[3] The dimensions used in the drawings in this paper are those listed by Jones (6).

introduced into a compound, a dye, for which two identical low-energy structures could be written. In this case Brunings and Corwin (4) compared the absorptions of the symmetrical ions III and IV.

III	IV
$\lambda_{max} = 4730$ A. in chloroform	$\lambda_{max} = 5100$ A. in chloroform
$\epsilon_{max} = 13.5 \times 10^4$	$\epsilon_{max} = 5.7 \times 10^4$

It was noted that in structure III, which was plausibly assumed by Brunings and Corwin to be the most likely for the compound, the two pyrrole rings could be nearly if not quite coplanar, for the van der Waals radii of the hydrogen atoms attached to the nitrogens overlap, as shown, to an extent that can probably be accommodated with maintenance of planarity by adjustment of bond angles alone. If these hydrogen atoms are replaced by methyl groups, giving IV, planarity is no longer possible if anything like normal bond angles, bond distances, and van der Waals radii are preserved. Brunings and Corwin suggested that the following accommodations could be made: (a) increase in the bond angles 1, 2, 2', 3, and 3', (b) some penetration of the normal van der Waals radii, and (c) some departure from planarity. These accommodations, it was suggested, require energy which must be deducted from the resonance energy, a conclusion which requires a *symmetrical* dye such as IV to absorb at *longer* wave lengths than III, and which agreed with the experimental results. Furthermore, such departure from planarity as resulted from the crowding would cut down the overlap of the π-electronic orbitals with consequent reduction of intensity of absorption, and this relationship is to be seen in the curves published by Brunings and Corwin, although it was not specifically referred to by them.

IV. FURTHER STUDIES OF BRUNINGS–CORWIN EFFECT IN CYANINES OF PYRROLE SERIES

One phase of the present work started from this point. The higher vinylogs of III and IV—namely, V and VI, respectively—were first prepared. Because of the longer conjugated chains present in these dyes, the number of possible *cis-trans* isomers is large, but if planarity is to be maintained many of these structures are improbable, and of the various possibilities for the one compound, formula V appears the most probable, while VI is selected from several configurations which are almost equally probable and almost exactly isosteric.

V

$\lambda_{max} = 5950$ A. in chloroform
$\epsilon_{max} = 17 \times 10^4$
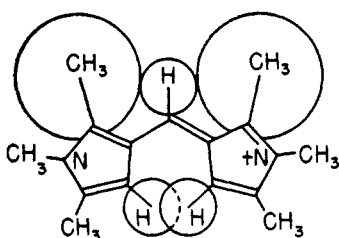
VI
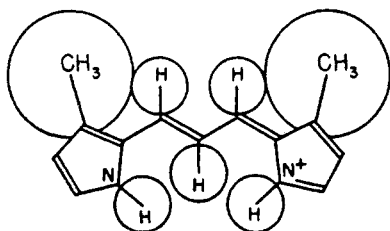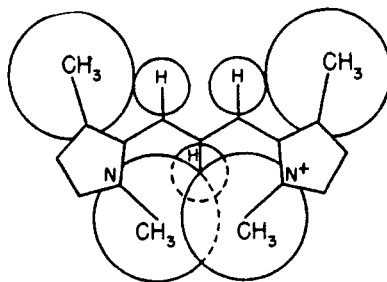
$\lambda_{max} = 5810$ A. in chloroform
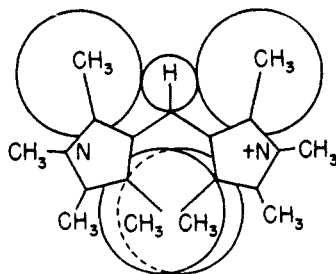$\epsilon_{max} = 17 \times 10^4$

Only very minor adjustments, if any, of bond angles are required to render V comfortably coplanar. In VI, also, the methyl groups do not give rise to anything like the crowding that they do in IV, and in VI planarity can probably be maintained by adjustment of bond angles alone, which would not require much energy. Dye VI would not therefore be expected to absorb at markedly longer wave lengths, nor with markedly lower ϵ_{max} than V, nor in fact does it. Actually it absorbs at distinctly shorter wave length when the absorptions are compared in chloroform, the reason for which is not clear. The maxima are much closer in methyl alcohol, but in this solvent V is extremely unstable, and the value for ϵ_{max} is quite unreliable.

Further confirmation of Brunings and Corwin's viewpoint that crowding a *symmetrical* dye out of planarity results in a shift of λ to longer wave lengths was provided by another set of comparisons to which precisely similar arguments may be applied. Dye VIII, which is crowded from planarity, actually absorbs at markedly longer wave lengths and with greatly lower ϵ_{max} than VII, but between the higher vinylogs, IX and X, there is no such marked difference, the values of λ_{max} being very close and those of ϵ_{max} being of the same order. In this set of four dyes, the absorptions in methyl alcohol were very similar to those in chloroform.
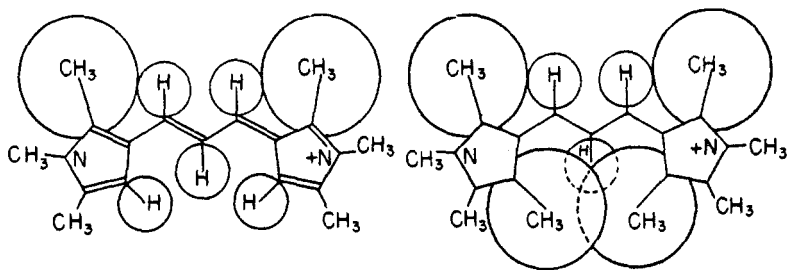

VII

$\lambda_{max} = 4460$ A. in chloroform
$\epsilon_{max} = 3.5 \times 10^4$

VIII

$\lambda_{max} = 4790$ A. in chloroform
$\epsilon_{max} = 1.25 \times 10^4$

IX   X

λ_{max} = 5360 A. in chloroform λ_{max} = 5340 A. in chloroform
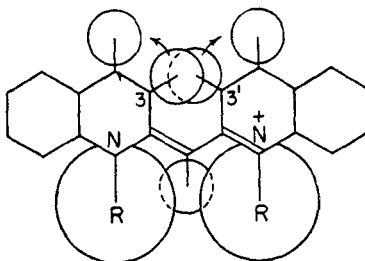ϵ_{max} = 6.3 × 10⁴ ϵ_{max} = 7.6 × 10⁴

The fact that the absorptions of VII and VIII differ markedly could not of itself safely be ascribed to the greater size of the methyl groups in VIII relative to hydrogen. It is conceivable that some property of the methyl group other than its mere size might be responsible for the effect, in part if not wholly. However, the close correspondence of the absorptions of IX and X renders this possibility unlikely.

In general, in fact, substitution of an alkyl group for hydrogen in the *nucleus* of a symmetrical cyanine, in such a position that no crowding results, has only a minor effect on the absorption in alcohol. Thus, increases in size of the R alkyl groups attached to nitrogen in dyes XI and XIII produce but slight shifts, and substitution of methyl groups in the 6- and 6′-positions of XIII (R = CH₃) to give XXIV is similarly without much effect. The same cannot be said for groups of a decidedly polar character, such as ethoxy and chloro, and for this reason the present studies have been limited to crowding effects produced by alkyl groups, where the electronic effects are minimal.

V. CROWDING EFFECTS IN CYANINES OF QUINOLINE SERIES

Investigations have also been carried out in the quinoline series, the absorptions of the cyanines XI and XII being compared. The most plausible drawing shows that there is a certain amount of crowding between the hydrogen atoms in

XI

$$R = CH_3 \begin{cases} \lambda_{max} = 5200 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 7.2 \times 10^4 \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5235 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 7.6 \times 10^4 \end{cases}$$

a   b

c

XII
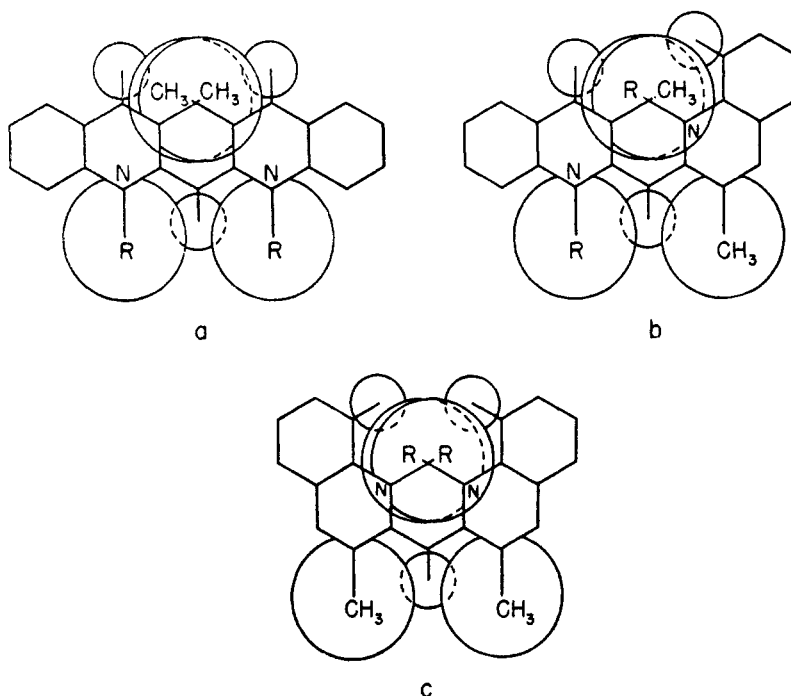
$$R = CH_3 \begin{cases} \lambda_{max} = 5270 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 4.1 \times 10^4 \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5460 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 4.5 \times 10^4 \end{cases}$$

the 3- and 3'-positions of the quinoline rings in XI, but it seems likely that this can be accommodated without substantial departure from planarity by small displacements as indicated by the arrows. In any event, the absorption of the dye in alcohol is very little affected by replacing the N-methyl groups by ethyl, although it will be seen later that this type of replacement commonly has a marked effect on a dye molecule that is crowded out of planarity.

In the 3,3'-dimethyl derivative, the three projections for which (XIIa, XIIb, and XIIc) are about equally probable, the crowding is much more pronounced, and all three show marked overlapping of the van der Waals radii of two of the alkyl groups.[4] Furthermore, a result of the hexagonal geometry of the rings in

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[4] The fact that there are several projections for XII of about equal probability, at least from the standpoint of crowding, raises the possibility, in this and similar cases, of the coexistence in solution of stereoisomers corresponding to several structures. Moreover, even if the choice were restricted to but one structure, let us say XIIa, but the nuclei were twisted out of a common plane, then the molecule could exist in two enantiomorphic modifications. These would be of identical energy and would absorb identically, but the existence of the two different sorts of molecule would very possibly be unfavorable to the close packing which seems to occur in an aggregated state. If, now, the separate structures XIIa, XIIb, and XIIc can exist, then each will be represented by two enantiomorphic modifications, making a total of six distinct molecular species.

XII is to make the overlap greater than in the tetramethylpyrrole derivatives IV and VIII. The Brunings–Corwin effect might therefore have been expected to be greater for XII than for IV or VIII, and it was consequently a matter of surprise that although XII does indeed absorb at longer wave lengths than XI, the shift in λ_{max} is only 70 A., compared with 370 A. for IV (in chloroform) and 330 A. for VIII (in chloroform). However, the intensity of the absorption of XII is significantly below that of XI.

In view of the small shift in λ in passing from XI to XII it seems necessary to invoke arguments in addition to those brought forward by Brunings and Corwin. It might be argued that since free rotation can take place about single but not about double bonds, the linkages of the bridge in a crowded cyanine dye such as XII will tend to become of single-bond character. This results in the favoring of intermediate structures such as XIId and especially XIIe at the expense of other intermediate structures and of the extreme structures. Because of this redistribution of energy levels, a lightening of color could very well result

XIId   XIIe
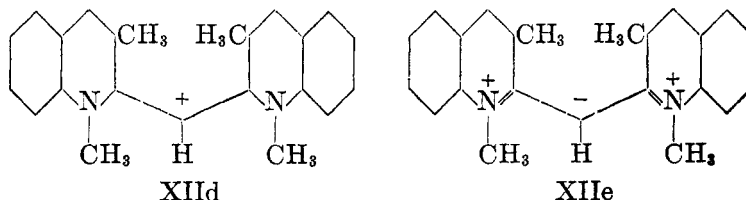
(1), which, largely counteracting a deepening of color due to the causes cited by Brunings and Corwin, could conceivably produce the relationship actually observed.
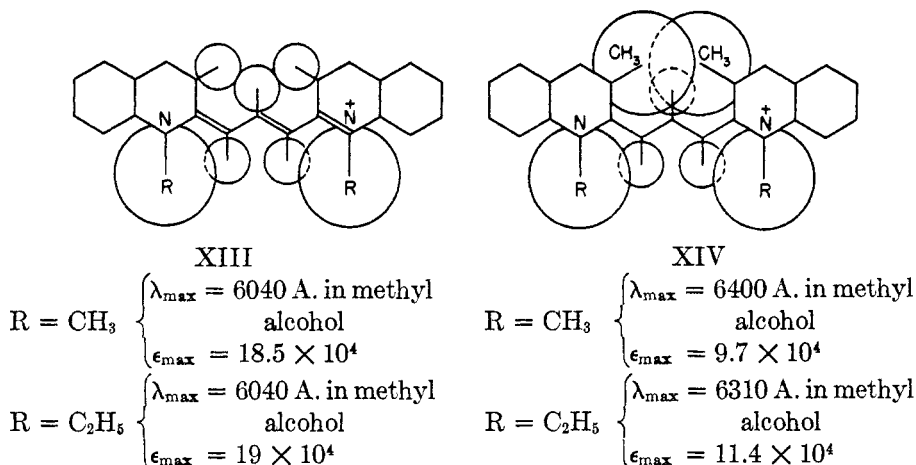
Whether this suggestion is valid is at present uncertain, but it should be mentioned that a similar method of approach proved unsatisfactory in dealing with the absorptions of certain dyes (XXIX and XXX) which will be discussed later.

If the methyl groups attached to the nitrogens of XI and XII are replaced by ethyl, the different effects produced are characteristic of each type. As mentioned above, λ_{max} for XI is scarcely affected by the change, the figure for the diethyl dye being only 35 A. different at 5235 A., and ϵ_{max} remains of the same order, the diethyl dye having a value of 7.6×10^4. This kind of behavior is quite generally shown by symmetrical or nearly symmetrical cyanine dyes for which planar structures can be drawn. On the other hand, replacement of the methyl groups attached to nitrogen in XII by ethyl has a pronounced effect on the absorption, λ_{max} being shifted 190 A. to 5460 A., although ϵ_{max} is not much affected. Although it is possible, either in a drawing or a model, so to dispose of the $-CH_3$ groups of the ethyl radicals that the molecule does not appear more crowded, in actual fact replacement of methyl by ethyl appears to increase the effective van der Waals radius of the group, the Brunings–Corwin effect becoming more pronounced.

The higher vinylene homologs of XI and XII, i.e., XIII and XIV, were also compared. The drawing of XIII, the most probable formula for the dye, in-

dicates that planarity of the molecule can be attained with only minor adjust-
ment, if any, of bond angles, a conclusion supported by the fact that the alcoholic
absorption is virtually unaffected by substitution of the N-methyl groups by
ethyl. The crowding in XIV is much more severe than in XIII, although de-
cidedly less than in XII. Nevertheless, the shift in λ_{max} of 360 A. in passing

$$XIII \qquad\qquad\qquad XIV$$

$R = CH_3$ $\begin{cases}\lambda_{max} = 6040 \text{ A. in methyl} \\ \qquad\text{alcohol} \\ \epsilon_{max} = 18.5 \times 10^4\end{cases}$ $R = CH_3$ $\begin{cases}\lambda_{max} = 6400 \text{ A. in methyl} \\ \qquad\text{alcohol} \\ \epsilon_{max} = 9.7 \times 10^4\end{cases}$

$R = C_2H_5$ $\begin{cases}\lambda_{max} = 6040 \text{ A. in methyl} \\ \qquad\text{alcohol} \\ \epsilon_{max} = 19 \times 10^4\end{cases}$ $R = C_2H_5$ $\begin{cases}\lambda_{max} = 6310 \text{ A. in methyl} \\ \qquad\text{alcohol} \\ \epsilon_{max} = 11.4 \times 10^4\end{cases}$

from XIII to XIV (both with R = CH₃) is much greater than in passing from
XI to XII (R = CH₃), so that quite obviously there is no simple relationship
between a given area of overlap in the projections of these dyes and the shift to
longer wave lengths. The considerably lower value of ϵ_{max} for XIV than for
XIII is in agreement with the requirements of a distorted molecule for XIV.

One possible contributing reason why less crowding in XIV (relative to XII)
produces a greater shift is that the restoring force to any attempted deformation,
i.e., the resonance stabilization, is less for the dye of longer chain length (XIV).
Another factor may be the readjustment of the energy levels of the extreme and
intermediate structures mentioned above.

There still remains the possibility that at least part of the shift in passing from
XIII to XIV may be due to some property of the methyl groups in the 3- and 3'-
positions other than their bulk, although the considerably reduced ϵ_{max} of XIV
indicates distortion from planarity. In this connection it is instructive to con-
sider dye XX, which may be regarded as derived from XIII by insertion of
—CH₂CH₂— between positions 3 and 9, enabling planarity to be preserved.
This dye (XX) absorbs at markedly longer wave lengths than XIII, so that an
aliphatic substituent may, if only rarely, have a strong effect on the absorption,
even in the absence of distortion from planarity.

When the N,N'-dimethyl groups in XIV are replaced by ethyl groups, the
effect, surprisingly, is to *reduce* the amount of the shift. The reason for this is
not clear, but at any rate this result is quite exceptional and stands alone against
a large body of data in which increasing the crowding in an already crowded
system intensifies the Brunings–Corwin effect.

Comparisons carried out in the 4,4'-cyanines XV and XVI gave results in line with the general Brunings–Corwin concept. The 1,1'-dimethyl-4,4'-cyanine (XV) is crowded to an extent that can doubtless be readily accommodated by adjustment only of bond angles. The 3,3'-dimethyl derivative (XVI) on the

XV
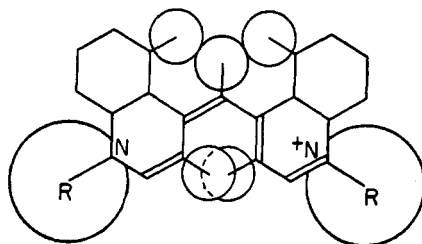
$$R = CH_3 \quad \begin{cases} \lambda_{max} = 5885 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 8.6 \times 10^4 \end{cases}$$

$$R = C_2H_5 \quad \begin{cases} \lambda_{max} = 5910 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 8.8 \times 10^4 \end{cases}$$

a   b

XVI
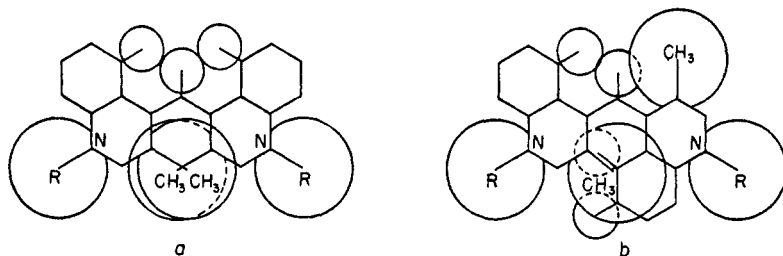
$$R = CH_3 \quad \begin{cases} \lambda_{max} = 6140 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 5.0 \times 10^4 \end{cases}$$

$$R = C_2H_5 \quad \begin{cases} \lambda_{max} = 6150 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 5.4 \times 10^4 \end{cases}$$

other hand, is strongly crowded, however it is drawn. We accordingly find that XVI absorbs at appreciably longer wave length than XV (the difference is 255 A.) and with significantly lower ϵ_{max} (5.0 instead of 8.6×10^4).

In these dyes the alkyl groups attached to the nitrogens do not lie in a crowded area, even in XVI, and accordingly it is found that in neither dye does replacement of the N,N'-dimethyl groups by ethyl have an appreciable effect on λ_{max}. There seems to be a tendency for the values of ϵ_{max} to be somewhat higher for the diethyl than for the dimethyl dyes, but determinations of intensity are more subject to experimental error than those of wave length.

Another way of introducing a crowding effect into the molecule of a simple cyanine such as XI is by replacing the hydrogen of the —CH= group of the bridge by alkyl, as in XVII. The drawings show that severe crowding must

result, even when the group introduced at the center of the molecule is methyl. The effect on the absorption is extraordinary. Absorption data for different values of R^1, R^2, and R^3 in formula XVII are given in table 1.

TABLE 1

Absorption data for dyes XI and XVII

R^1	R^2	R^3	λ_{max} (IN METHYL ALCOHOL)	$\epsilon \times 10^{-4}$ (IN METHYL ALCOHOL)
	In XVII			
			A.	
CH_3	H	CH_3	5200	7.2
CH_3	H	C_2H_5	5225	7.0
C_2H_5	H	C_2H_5	5235	7.6
CH_3	CH_3	CH_3	5745	3.5
CH_3	CH_3	C_2H_5	5770	2.7
C_2H_5	CH_3	C_2H_5	5840	2.1
CH_3	C_2H_5	CH_3	5760	3.1
CH_3	C_2H_5	C_2H_5	5830	2.6
C_2H_5	C_2H_5	C_2H_5	5910	2.0
CH_3	$n\text{-}C_3H_7$	CH_3	5750	3.2
CH_3	$n\text{-}C_3H_7$	C_2H_5	5830	2.7
C_2H_5	$n\text{-}C_3H_7$	C_2H_5	5900	2.1

a   b
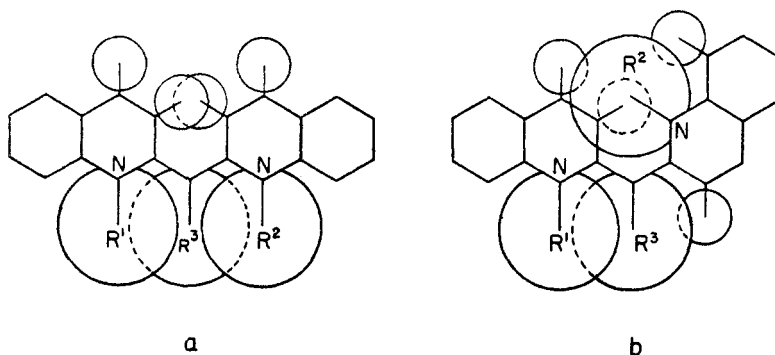
XVII

The N,N'-dimethyl dye has its absorption maximum in alcohol shifted by no less than 545 A. on introduction of the third methyl group at the center, while ϵ_{max} is approximately halved. The substitution in fact converts a pinkish-orange dye into one that is reddish-violet, a change of a magnitude that had not previously been encountered when the first observation of this kind was made several years prior to the publication of Brunings and Corwin's paper.

As has already been noted, the alcoholic absorption of XI is practically un-affected by increase in size of the N-alkyl groups, but the absorption of the

trimethyl dye is, in general, more sensitive to increase in size of any of the three alkyl groups.   However, it is the first change of chain hydrogen to chain methyl which produces by far the greatest effect.   Thereafter, increase in size of the alkyl groups from methyl to ethyl produces shifts that, on the whole, are much less although appreciable.   Increase in size of the central group from ethyl to n-propyl is virtually without effect, on either λ_{max} or ϵ_{max}.

The absorption maxima of the dyes in table 1 (excepting the three dyes with $R^3 = n$-propyl) are plotted in figure 1.   The general tendency toward increase
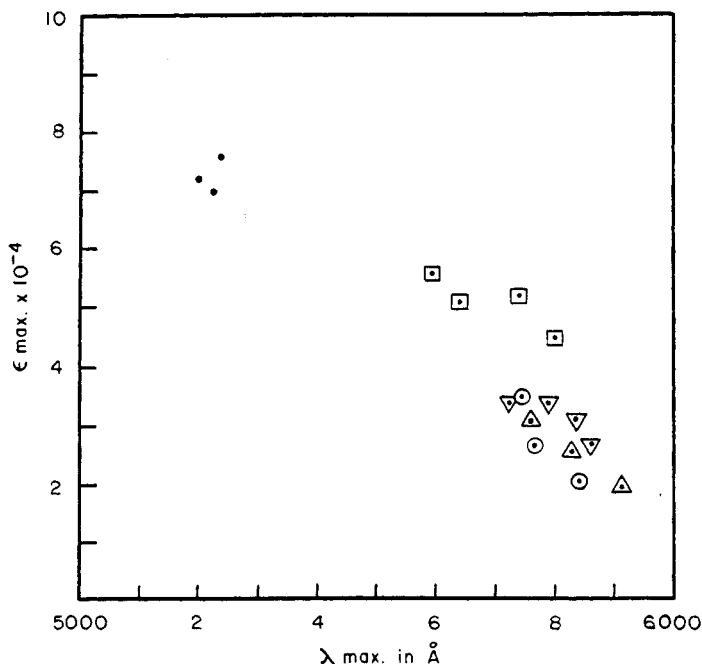

FIG. 1. Plot of λ_{max} against ϵ_{max} for dyes XI, XVII, XVIII, and XIX.   ●, dyes XVII with $R^3 = H$ (dyes XI); ⊙, dyes XVII with $R^3 = CH_3$; △, dyes XVII with $R^3 = C_2H_5$; ▽, dyes XVIII; □, dyes XIX.

in λ_{max} and decrease in ϵ_{max} with increasing crowding of the molecule can be seen very plainly.

These dyes apparently follow the Brunings–Corwin pattern in a straight-forward manner, yet we cannot be certain that the shifts are wholly due to crowding from planarity.   The dyes XVII, aside from being crowded, have a substituent in the chain between the nuclei, and it is barely possible that this might, for some reason not connected with its size, exert a bathochromic effect similar to that of the ethylene group in XX.   Nevertheless, the low values of ϵ_{max} of these dyes indicate much distortion from planarity, and it is therefore likely that most of the bathochromic shift shown by these dyes is attributable to the same cause.

It is certain, at any rate, that the shifts which result from *increasing* the size of the alkyl group in the already crowded trimethyl dye XVII ($R^1 = R^2 = $

$R^3 = CH_3$) must be ascribed almost wholly to increased distortion from planarity.

It is interesting to speculate just how great a shift in λ and how great a reduction in ϵ could be achieved through the distortion from planarity of a given model molecule. We are not yet in a position to answer these questions fully. Difficulties of synthesis must be reckoned with, and although we are not yet certain, our observations appear to indicate that there are limits to the size of crowding substituents, on the favorable side of which dye condensations take place with fair yields of product, but beyond which the condensations fail suddenly and completely. At any rate it is worthy of note that by introducing a

TABLE 2

Absorption data for dyes XVIII, XIX, and XX

R^1	R^2	λ max. (IN METHYL ALCOHOL)	$\epsilon \times 10^{-4}$ (IN METHYL ALCOHOL)
In XVIII			
		A.	
CH_3	CH_3	5725	3.4
C_2H_5	CH_3	5835	3.1
CH_3	C_2H_5	5790	3.3
C_2H_5	C_2H_5	5860	2.7
In XIX			
CH_3	CH_3	5595	5.6
C_2H_5	CH_3	5740	5.2
CH_3	C_2H_5	5640	5.1
C_2H_5	C_2H_5	5800	4.5
In XX			
CH_3	CH_3	6380	15.2
C_2H_5	C_2H_5	6410	19.0

central ethyl group into the N,N'-diethyl dye XI, λ_{max} is shifted by no less than 675 A., from 5235 to 5910 A., while ϵ_{max} is reduced to almost a quarter of its original value, from 7.6×10^4 to 2×10^4.

Up to the present, the dyes dealt with have all been structurally symmetrical, it being possible to write two identical extreme low-energy structures for any of

a   b
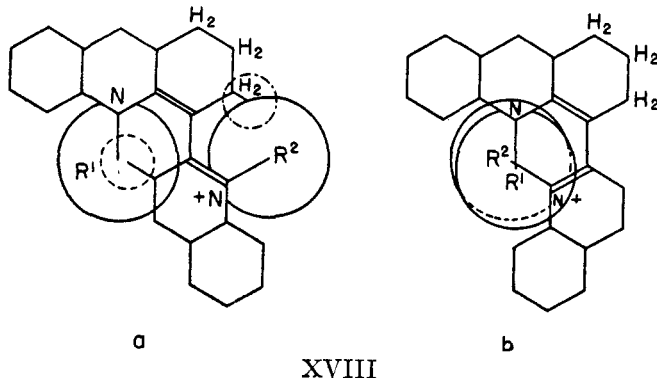
XVIII

them.   In the dyes XVIII, which contain a tetrahydroacridine ring linked to one of ordinary quinoline, this strict structural symmetry is no longer present. Nevertheless, the dyes XVIII resemble XVII in that they are both quinoline 2,2'-cyanines with a central alkyl substituent, but in XVIII this alkyl group is bent back to join up to one of the quinoline rings in the 3-position.   Owing to this, it is not possible to devise an extended structure for XVIII analogous to XVIIa, and the only planar projections to choose between are XVIIIa and XVIIIb.   Of these XVIIIa is the less crowded, and therefore the more plausible, and the choice is confirmed by the following results.   If XVIIIa is correct, there should be sensitivity to change in the size of R^1 but much less to that of R^2.   (The hydrogen atoms indicated with alternate dots and dashes are those of a $>CH_2$ group and are not in the plane of the quinoline rings.   However, they will probably crowd R^2 to some extent.)   On the other hand, if XVIIIb is the projection which most nearly represents the molecule, there should be equal sensitivity to R^1 and R^2, since increase in size of either will increase the crowding. The data in table 2 show that λ_{max} is roughly twice as sensitive to change in size of R^1 as to change in size of R^2, pointing to XVIIIa rather than XVIIIb.

There is only one linkage in XVIII about which rotation can occur,—namely, that between the rings.   It would seem reasonable to expect that the single-bond character of this linkage would thereby be increased, thus, in turn, increasing the concentration of positive charge on the quinoline nitrogen, rather than that of the tetrahydroacridine ring.   An asymmetry could thus be created which does not exist, for instance, in XVII.   Such an asymmetry should, if sufficiently great, give rise to a deviation in λ_{max}, but in all probability there is no significant deviation in the present case, for when the absorption maxima of the dyes XVIII are plotted in figure 1, they fall quite close to those given by dyes XVII, where R^3 has a value somewhere between CH_3 and C_2H_5.

The set of four dyes XIX was also prepared from 2,3-trimethylenequinoline. These are similar in structure to XVIII, but the replacement of a six- by a five-membered ring reduces crowding in the neighborhood of both R^1 and R^2.   Here
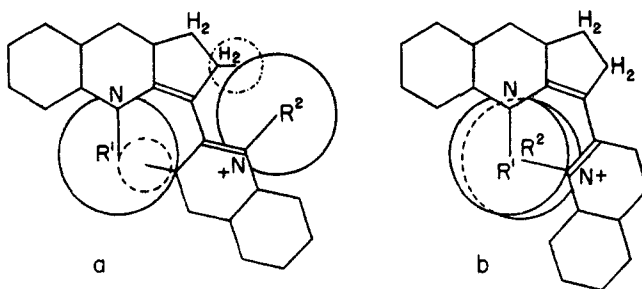

XIX

again the data show (table 2) that there is decidedly greater sensitivity to change in size of R^1 than of R^2, thus favoring XIXa over XIXb.

It is at first sight surprising that the shift when R^1 is changed from CH_3 to C_2H_5 is actually greater in XIX than in XVIII, since the latter is the more crowded model. The following explanation for this is suggested: In the dyes XVII, substitution of hydrogen by CH_3 at R^3 causes a very large shift in λ and a drop in ϵ, but beyond this point, further increases in size of R^1, R^2, and R^3 produce considerably smaller effects. It is as if the greater part of the total imaginable distortion for this particular molecular model, and its consequent optical effect, were already realized when $R^1 = R^2 = R^3 = CH_3$. If one now pictures a somewhat similar model but in which the R^1 and R^2 groups are not as close together as in XVII, then substitution of CH_3 for hydrogen at R^3 would produce less distortion and use up a smaller amount of the total realizable shift for this model, so that a *further* increase in size of one of the R groups could have a relatively *greater* effect than in XVII itself.

It is suggested that XVIIIa and XIXa (both with $R^1 = R^2 = CH_3$) are analogous to the two models just discussed at the stage where $R^3 = CH_3$. Distortion will be greater in XVIIIa than XIXa, and the former will be nearer to the position of maximum realizable distortion and be less sensitive to further crowding. Increase in size of the R^1 group thus has a smaller effect than in XIXa.

The positions occupied by the absorption maxima of dyes XIX in figure 1 are in agreement with this interpretation. Alternatively, these points are about what would be expected if it were possible to introduce a group somewhat smaller than methyl, but of similar electronic influence, into the R^3 position of XVII.

Whereas for a dye XIX the choice of structures lies between one that is crowded (XIXa) and one that is more crowded (XIXb), the choice being decided in favor of the former, for the next higher vinylogs the choice is between a structure that is not crowded (XXa) and one that is (XXb), not to include others, not
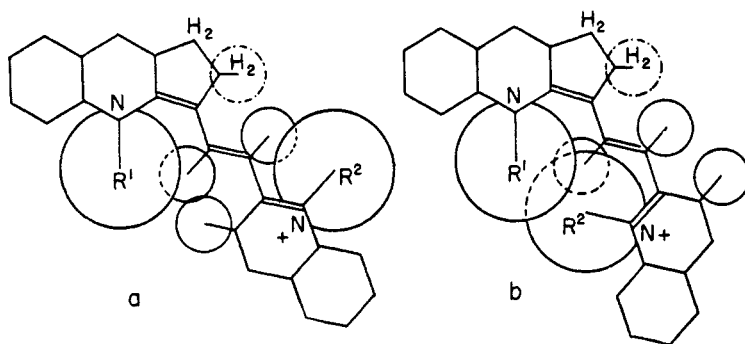

XX

shown, that are even more crowded. The crowding in XXa is so slight that the molecule could undoubtedly become coplanar by adjustment of bond angles alone, and there should be no sensitivity to change in size of R^1 or R^2, such as exists in XIX. On the other hand, XXb requires sensitivity to both R^1 and R^2.

In actual fact, the N,N-dimethyl and diethyl dyes absorb with values of λ_{max} that are very close (table 2), so that there is definite experimental evidence in favor of XXa.

Dye XX has already been referred to as being considered derivable from the carbocyanine XIII by joining carbon atom 3 of one of the quinoline rings to the first carbon of the bridge through an ethylene ($-CH_2CH_2-$) group, and without loss of planarity. But the most favored arrangement of the rings is not the same for the two dyes, and perhaps this is part of the reason why the dyes XX absorb at markedly longer wave lengths than the dyes XIII.

In the following section, another comparison is made between a short-chain cyanine which is crowded, and its higher vinylog which is not. The dyes are again unsymmetrical, one nucleus being derived from 11-indeno[1,2-b]quinoline and the second from quinoline itself.
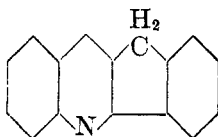
11-Indeno[1,2-b]quinoline

There are only two ways of drawing the short-chain cyanine, XXIa and XXIb, and it can be seen that the R^2 group is crowded against a hydrogen of the indeno-quinoline ring to exactly the same extent in one drawing as in the other. The
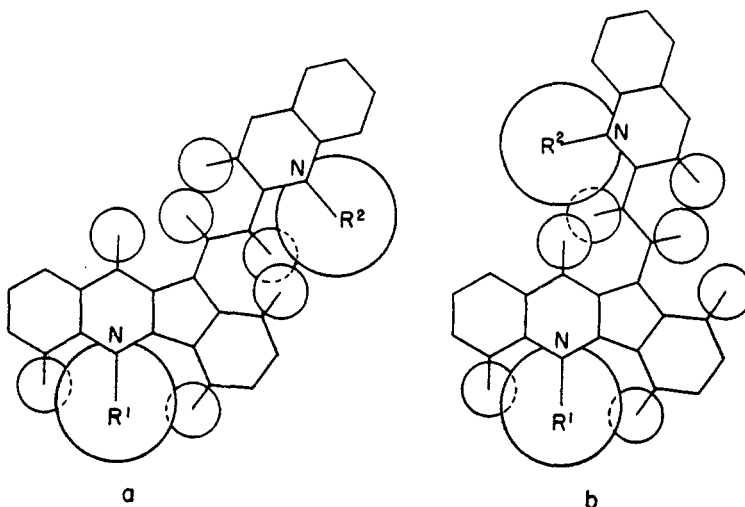

a   b
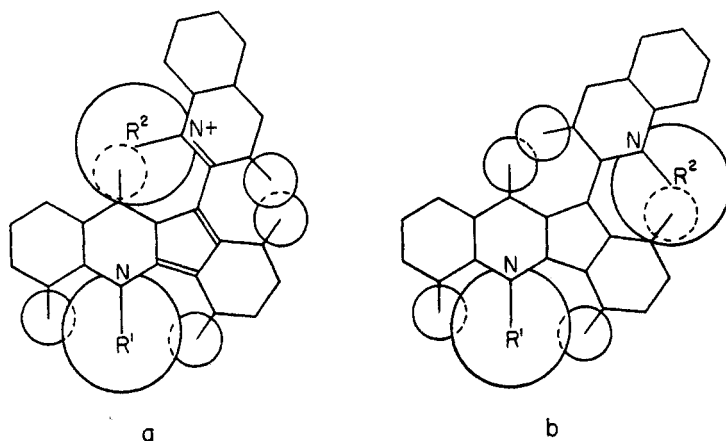
XXI

R^1 group, on the other hand, is not crowded; consequently the absorption of the dye should be sensitive to change in size of R^2 but not R^1. The data in table 3 show that this is indeed true. Changing R^1 from methyl to ethyl is almost without effect on λ_{max}, but the same change in R^2 shifts λ_{max} 90 A. in one case and 80 A. in another. The values of ϵ_{max} of all the four dyes examined, however, stay at much the same level.

For the higher vinylog of XXI, structures XXIIa and XXIIb are the most plausible in that they show the least crowding, and in this respect they are

TABLE 3

Absorption data for dyes XXI and XXII

R¹	R²	λ max. (IN METHYL ALCOHOL)	ϵ max. $\times 10^{-4}$ (IN METHYL ALCOHOL)
	In XXI		
		A.	
CH₃	CH₃	5400	2.5
C₂H₅	CH₃	5420	2.3
CH₃	C₂H₅	5490	2.4
C₂H₅	C₂H₅	5500	2.4
	In XXII		
CH₃	CH₃	5520	5.9
CH₃	C₂H₅	5540	6.2

XXII

equivalent. (The nitrogen atoms at the ends of the chromophoric chain are not the same distance apart in the two structures, however, and it is not known at present how this affects the absorption. It seems reasonable to suppose that the farther the nitrogens are apart, and the higher the dipole moment of the transition, the higher will be the intensity of absorption.)

Neither XXIIa nor XXIIb shows serious crowding, and it seems that such as there is could be completely relieved by adjustment of bond angles. The drawings would not lead to the prediction of sensitivity of the absorption to change in size of R² in this case, and the data show this to be true. The absorptions of the dyes where R² equals methyl and ethyl differ by only 20 A.

Another interesting relationship is the close similarity of the alcoholic absorptions of the dyes XXI and XXII, where R^2 = ethyl, in spite of the difference in length of the conjugated chains. The values of λ_{max} are very close (see table 3) and it is impossible to distinguish visually between the two purplish-blue solutions. At least two factors contribute to this situation, a crowding effect and a deviation effect. The dye with the shorter chain (XXI) is deeper because of the Brunings–Corwin effect than it would be without the crowding from planarity. But the dye of longer chain-length (XXII) is not crowded; hence it will not be deepened in color for this reason.

On the other hand, the dyes are rather highly unsymmetrical, with the indenoquinoline ring predictable as the more basic of the two, using the method employed before (2). A shift of λ_{max} to *shorter* wave lengths, or "deviation," could very well result, and this would be much more pronounced for the dye with *longer* chain-length (3). The combination of these two effects could very well produce the result observed.

It is noteworthy that in spite of the planarity of the dyes XXII, they have relatively low values of ϵ_{max}. This may be the result of energetic asymmetry of the extreme structures, unsymmetrical dyes frequently behaving in this way, but this subject will not be pursued further at the present time. The difference in basicity between the nuclei is, however, probably insufficient to warrant inclusion of the dyes of shorter chain-length (XXI) among the *highly* unsymmetrical (and strongly deviating) crowded dyes described in the next section.

Since the crowding in XXI can be relieved by rotation of the nuclei about the linkage between them, this linkage should be inclined toward single-bond character. But this will induce the positive charge of the dye ion in the quinoline nitrogen, and thus increase the basicity of this ring at the expense of the indenoquinoline ring. Any tendency which XXI would have towards a deviation will therefore be expected to be reduced by this effect. Plausible as it is, however, this argument must be used with caution in view of the results obtained with certain of the styryl dyes to be described later.

If concentrated alcoholic solutions of XXI and XXII are well diluted with water, the purplish-blue solution of XXII becomes distinctly reddish, doubtless owing to the formation of a polymeric aggregate or aggregates such as is given under similar conditions by the dye pinacyanol (XIII, R = C_2H_5) (11). The solution of XXI, on the other hand, is relatively unchanged by the water and apparently does not aggregate with anything approaching the same ease as XXII, thus following the general behavior of dyes distorted from planarity. By choosing an aqueous solvent it is thus possible to obtain a solution of the dye of *longer* chain-length (XXII) that absorbs at *shorter* wave lengths than its lower vinylene homolog, an unusual relationship even under these narrowly specified conditions.

So far the crowding that has been described is such as will tend to twist the two nuclei of a cyanine dye out of a common plane. An example of crowding of a different kind is provided by XXIII. In this dye the two methyl groups of each
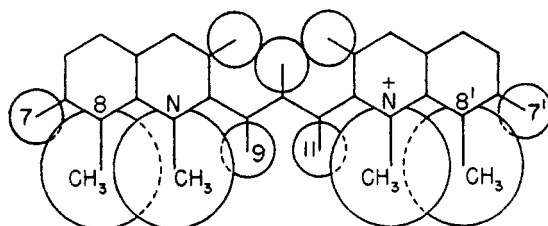
XXIII

λ_{max} = 6095 A. in methyl alcohol

ϵ_{max} = 15.7 $\times$ 10⁴ in methyl alcohol
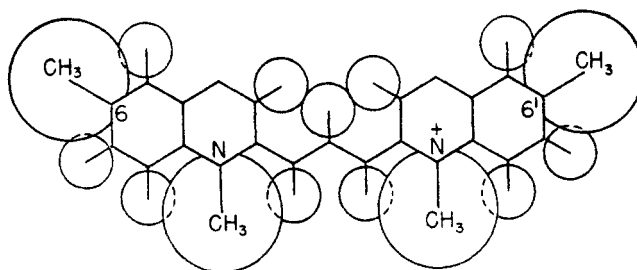
XXIV

λ_{max} = 6085 A. in methyl alcohol

ϵ_{max} = 14.3 $\times$ 10⁴ in methyl alcohol

quinoline ring crowd one another, but not in such a way as seriously to distort the conjugated chain between the nitrogens from planarity. It is thus not surprising that the alcoholic absorption of XXIII is about the same as that of the isomeric XXIV, in which the molecule can be planar.

It seems plausible that the two methyls on each ring in XXIII, prevented to some extent from repelling each other in the plane of the molecule by hydrogen atoms 7 and 9 and 7' and 11, will crowd each other so that one is thrust somewhat above and the other below the plane of the quinoline rings, thus increasing the average thickness of the molecule. More than this, it may be shown that distortion of the type suggested could give rise to several distinct molecular species, indicated by the following drawings, which are simplified plans of the molecules. The lines represent the length of the molecule in a plane and the
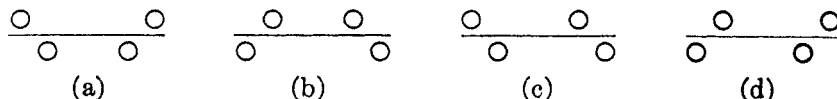
four circles in each drawing the disposition of the methyl groups. Of the four possible arrangements, (a) and (b) are identical, so that there are three possible species with one, (a) + (b), having twice the probability of the other two. Use of models shows that the disposition of the methyl groups in these different
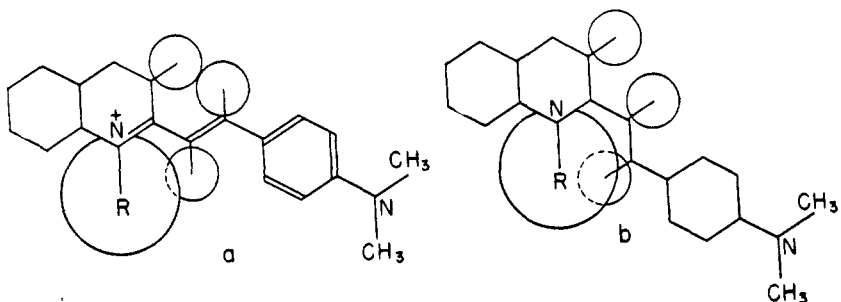
species is unfavorable to a close approach of the planar surfaces desirable for aggregate formation.

Whatever the nature of the actual distortion, it is a fact that this dye gives much less of the red aggregate in aqueous solutions than does the isomeric XXIV. Similar behavior is shown by other 2,2′-carbocyanines with substituents (e.g., Cl) in positions 8 and 8′, but not in positions 5 and 5′, 6 and 6′, and 7 and 7′.

<p style="text-align:center">VI. CROWDING EFFECTS IN HIGHLY UNSYMMETRICAL DYES OF THE
p-DIMETHYLAMINOSTYRYL SERIES</p>

Up to this point, the dyes discussed have been either symmetrical or nearly symmetrical cyanines. With these, where the appropriate comparison can be made, distortion from planarity of the resonating system responsible for absorption in the visible invariably produces a shift of λ_{max} to longer wave lengths, although the amount of the shift is not always predictable. There is always a drop in ϵ_{max} also.

The results now to be described for highly unsymmetrical dyes, such as 2-p-dimethylaminostyryl-3-methylquinoline methiodide (XXVI), differ significantly from those obtained with the symmetrical cyanines. Dye XXVI is related to the styryl XXV for which structure XXVa is substantially uncrowded and is therefore selected as more probable than XXVb.
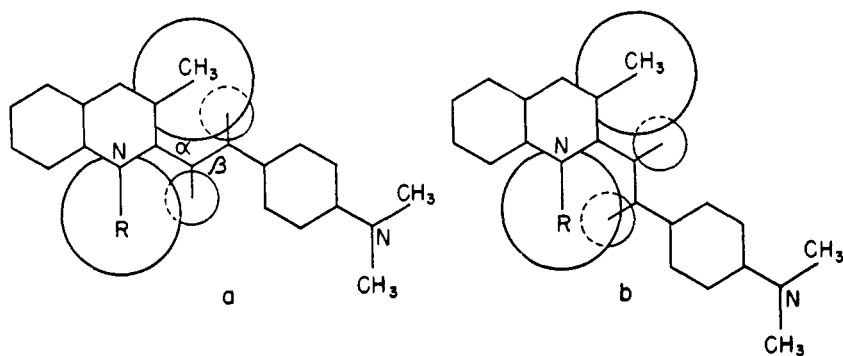

<p style="text-align:center">XXV</p>

$$R = CH_3 \begin{cases} \lambda_{max} = 5250 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 6 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5250 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 5.8 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

The lack of sensitivity to change of R from methyl to ethyl is in agreement with this choice of XXVa over XXVb. The dyes XXVI absorb at markedly *shorter* wave lengths than XXV, although with strongly reduced values of ϵ_{max}, both effects being more pronounced where R = ethyl.

An explanation which at first seemed satisfactory is as follows: Structures XXVIa and XXVIb are crowded to about the same extent and are therefore about equally probable. But both of them show a hydrogen atom of the vinylene
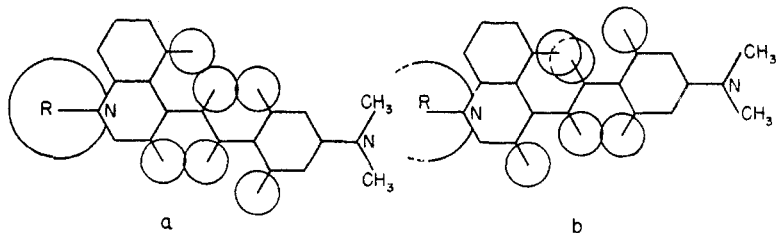
XXVI

$R = CH_3$ $\begin{cases} \lambda_{max} = 5000 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 2.7 \times 10^4 \text{ in methyl alcohol} \end{cases}$

$R = C_2H_5$ $\begin{cases} \lambda_{max} = 4930 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 2.2 \times 10^4 \text{ in methyl alcohol} \end{cases}$

chain crowding an alkyl group,—the 3-methyl group in XXVIa and the N-alkyl group in XXVIb. This crowding may be relieved by rotation about the linkages marked α and β, but use of a model shows that greater relief is obtained by rotation about α than about β. This will result in an increase of the single-bond character of α. However, this linkage is already predominantly of single-bond character, since it is a single bond in the extreme structure of lower energy, i.e., that in which the benzene ring of the styryl group is benzenoid. (The arrangement of the linkages of the conjugated chain in this structure follows that shown in XXVa.) Thus, the effect of crowding in XXVI is further to increase the stability of that structure which is already the more stable. The asymmetry of the extreme structures is therefore increased over that prevailing in XXV, resulting in an increase in deviation over that of XXV, which, in turn, could easily result in a net shift of λ_{max} to shorter wave lengths. Also, the effect would be greater, the greater the size of R.

The plausibility of this explanation was apparently confirmed by the fact that very similar results were obtained on comparing 4-p-dimethylaminostyryl-3-methylquinoline methiodide (XXVIII) with the corresponding dye lacking the 3-methyl group (XXVII). The drawings show XXVII to be uncrowded in XXVIIa and XXVIII to be about equally crowded in XXVIIIa and XXVIIIb.

XXVII

$$R = CH_3 \begin{cases} \lambda_{max} = 5440 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 4.5 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5460 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 4.6 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

a

b
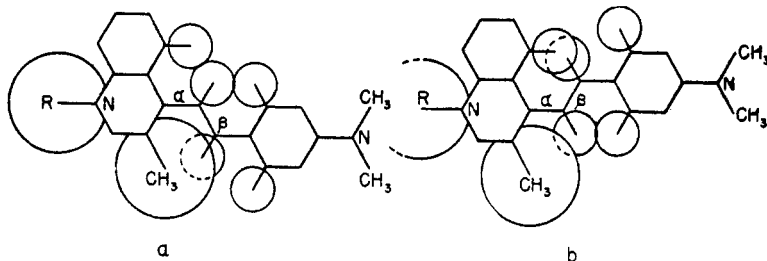
XXVIII

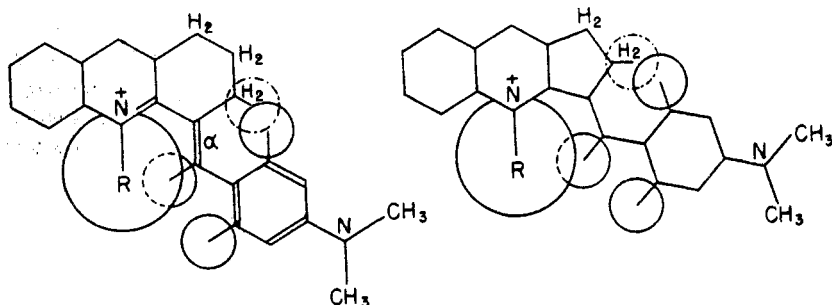$$R = CH_3 \begin{cases} \lambda_{max} = 5100 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 2.3 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5115 \text{ A. in methyl alcohol} \\ \epsilon_{max} = 2.4 \times 10^4 \text{ in methyl alcohol} \end{cases}$$

Here also the crowded dyes XXVIII absorb at *shorter* wave lengths, and with lower values of ϵ_{max}, than the related uncrowded dyes XXVII, and a precisely similar explanation may be offered to that advanced for XXV and XXVI. The crowding can better be relieved by rotation about the linkage α than about β and this will still further increase the single-bond character of α and hence the deviation of the dye, so that absorption at shorter wave lengths than XXVII is not surprising. In these dyes, however, the R groups in the quinoline nitrogen do not enter into any crowding; hence neither XXVII nor XXVIII is sensitive to increase in size of R, as the data show.

This argument, however, is not satisfactory in treating the absorptions of the styryl, or rather benzylidene, dyes XXIX and XXX. In XXIX, for which only the structure shown need be considered, there is crowding between the R

XXIX

$$R = CH_3 \begin{cases} \lambda_{max} = 5070 \text{ A. in methyl} \\ \text{alcohol} \\ \epsilon_{max} = 2.8 \times 10^4 \text{in methyl} \\ \text{alcohol} \end{cases}$$

XXX

$$R = CH_3 \begin{cases} \lambda_{max} = 5380 \text{ A. in methyl} \\ \text{alcohol} \\ \epsilon_{max} = 4.7 \times 10^4 \text{ in methyl} \\ \text{alcohol} \end{cases}$$

$$R = C_2H_5 \begin{cases} \lambda_{max} = 5010 \text{ A. in methyl} \\ \qquad \text{alcohol} \\ \epsilon_{max} = 2.1 \times 10^4 \text{ in methyl} \\ \qquad \text{alcohol} \end{cases} \qquad R = C_2H_5 \begin{cases} \lambda_{max} = 5400 \text{ A. in methyl} \\ \qquad \text{alcohol} \\ \epsilon_{max} = 4.8 \times 10^4 \text{ in methyl} \\ \qquad \text{alcohol} \end{cases}$$

group and the hydrogen of the chain. This can clearly be remedied by rotation about linkage α, which, according to the previous argument, would increase the single-bond character of this linkage. But α is a double bond in the low-energy extreme structure, the linkages of which are those shown, consequently the crowding in this particular dye would be expected to favor the higher-energy extreme structure rather than the lower, and thus *decrease* the deviation and exert a bathochromic influence. Since the effect should be stronger the larger
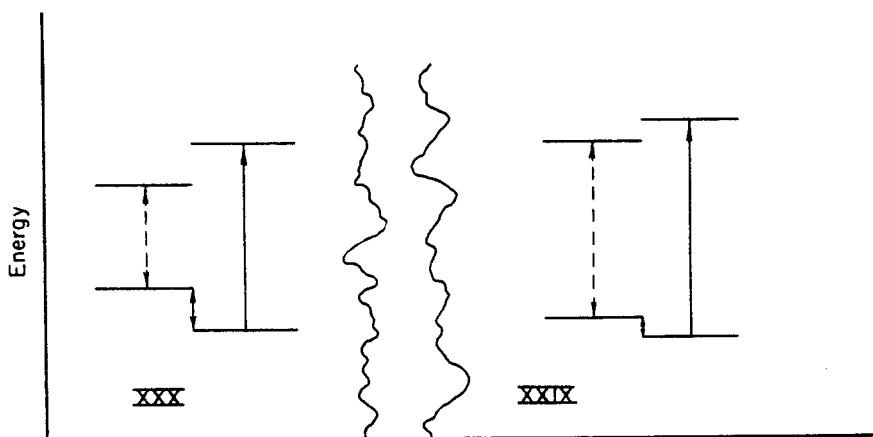

FIG. 2. Lowered resonance energy ($\leftrightarrow$) in XXIX relative to XXX gives greater separation of the levels of the extreme structures ($\leftarrow$ -- $\rightarrow$) and hence of the ground and excited states ($\longrightarrow$).

the group R, the *N*-ethyl derivative of XXIX by this reasoning should absorb at longer wave lengths than the *N*-methyl dye, whereas in actual fact the reverse is true. Furthermore, the dyes XXIX should by this reasoning absorb at longer wave lengths than the very similarly constituted dyes XXX but in which crowding is virtually absent. Again, the reverse actually holds.

Because of these results the argument previously advanced must either be abandoned or given secondary significance, and for the present the best explanation of the facts seems to be that crowding in highly unsymmetrical dyes reduces the resonance interaction, thus increasing the separation of the levels of the structures, and hence of the levels of the ground and excited states, as shown in figure 2. Although it is shown lower in the diagram, it is not intended to imply that the low-energy extreme structure is actually lower in XXIX than in XXX, merely that the *separations* are greater in XXIX.

Since with symmetrical and nearly symmetrical cyanines of short chain-length the effect of crowding is to shift λ to longer wave lengths and with highly unsymmetrical dyes the effect is to shift λ to shorter wave lengths, it would seem as if

dyes of an intermediate classification must be capable of existence, which would show virtually no shift of λ but only a drop in ϵ_{max} as a result of crowding.   So far we have not encountered an example of this type.

VII. PROGRESSIVE INCREASE IN CROWDING IN A CONNECTED SERIES OF DYES

The dye XXXI, containing two pyridine rings linked together by a single =CH— group, is the simplest member of the series XXXI to XXXV, the higher members of which may be regarded as derived from the lower by fusion to the nuclei of benzene residues.   The absorption curves of these five dyes in methyl alcohol are shown in figure 3.
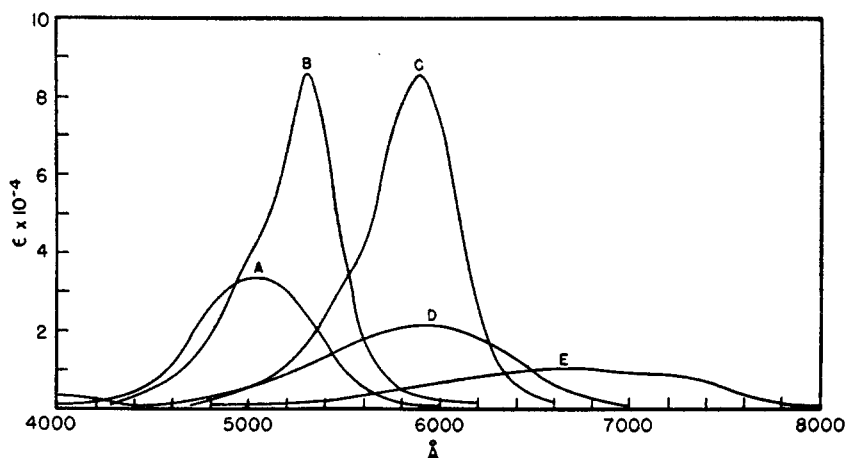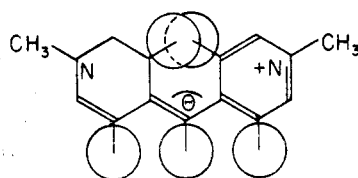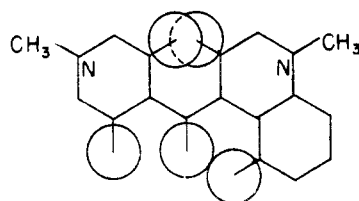

FIG. 3. Absorption spectra in methyl alcohol.   A = XXXI; B = XXXII; C = XXXIII; D = XXXIV; E = XXXV.

XXXI

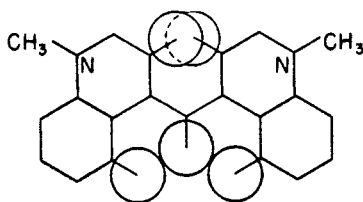λ_{max} = 5045 A. in methyl alcohol
ϵ_{max} = 3.4 × 10⁴ in methyl alcohol

XXXII

λ_{max} = 5300 A. in methyl alcohol
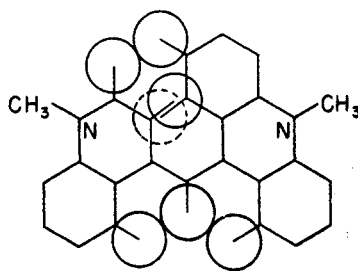ϵ_{max} = 8.7 × 10⁴ in methyl alcohol

Only the projection shown is possible for XXXI.   The crowding of the hydrogen atoms in the upper part of the figure is like that already encountered (e.g., XI) and can doubtless be accommodated very easily to preserve planarity, especially by increase in the angle θ, particularly as there is room to spare in the lower part of the figure.   However, it is noteworthy that the dye does not have a high ϵ_{max} (12).
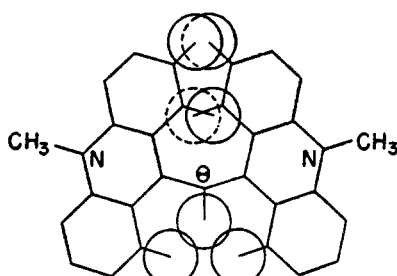
XXXIII

λ_{max} = 5885 A. in methyl alcohol

ϵ_{max} = 8.6 × 10⁴ in methyl alcohol

XXXIV

λ_{max} = 5940 A. in methyl alcohol

ϵ_{max} = 2.2 × 10⁴ in methyl alcohol

XXXV

λ_{max} = 6710 A. in methyl alcohol

ϵ_{max} = 1.1 × 10⁴ in methyl alcohol

Addition of a benzene residue to give XXXII will result in a somewhat tighter packing of the molecule in the lower part of the figure; nevertheless XXXII absorbs with a considerably higher value of ϵ_{max} and with a shift in λ toward the longer waves (12). The additional conjugation introduced as a result of adding the benzene residue is doubtless partly responsible for these effects.

Addition of a second benzene residue gives XXXIII. The molecule is still more tightly packed, and it is possible that there is now a slight distortion from planarity, sufficient to account for the fact that ϵ_{max} is not higher than the value for XXXII, in spite of the extra conjugation in the molecule.

In XXXIV the crowding is so pronounced that planarity cannot be maintained and the drop in ϵ_{max} is now very marked, although the shift in λ is very small. The band, too, is much broader than that of XXXIII. There is a still further drop in ϵ_{max} in XXXV, where the crowding must be extremely severe, and the band is very broad and flat. Solutions of this dye are a rather dull bluish-green. (The figure of XXXV is drawn with angle θ larger than normal in order to avoid confusion in the upper part of the drawing.)

There can be little doubt that a multiplicity of factors enters into the absorptions of these dyes. For one thing, the basicity of the nuclei in the three symmetrical dyes diminishes with increasing complexity, and there is reason to

believe that, other things being equal, greater depth of color is shown in a symmetrical cyanine the more basic the nucleus. This factor will thus tend to make XXXI relatively deeper in color with respect to XXXIII than it would be otherwise, and XXXIII relatively deeper with respect to XXXV. However, the Brunings–Corwin effect, operating strongly in XXXV, will make this dye much deeper in color than it would be otherwise, and will probably much more than offset the lightening effect due to the weak basicity of the acridine nucleus.

Again, dyes XXXII and XXXIV are unsymmetrical cyanines, and might be expected to show deviations. It is indeed true that these dyes absorb with λ_{max} well on the short-wave-length side of the average of the values of the related symmetrical dyes, although it is doubtful if the deviation of 165 A. shown by XXXII (the mean of 5045 and 5885 A. is 5465 A., so that the deviation is 5465 − 5300 = 165 A.) is a result solely of the unequal basicities of the nuclei. It is possible that XXXIII is somewhat deeper in color than it would be otherwise, because of the operation of the Brunings–Corwin effect, thus increasing the apparent deviation of XXXII.

The considerable deviation of 360 A. shown by XXXIV is likewise probably due in part to the difference of basicity of the nuclei composing the dye, in part to the absorption of the parent dye XXXV at very much longer wave lengths owing to the Brunings–Corwin effect. Incidentally, it is worth pointing out that with $\lambda_{max} = 6710$ A., the acridine dye XXXV is by far the deepest-colored simple (monomethine) cyanine yet described.

VIII. CONCLUSIONS

The foregoing constitutes a preliminary survey of a field that is at present by no means completely explored, and is still incompletely understood. Nevertheless, it is possible to trace certain generalities.

To the single example of a crowded symmetrical cyanine provided by Brunings and Corwin (4) many others have now been added. In almost all cases the absorption maximum is shifted to longer wave lengths as a result of crowding the two nuclei of a cyanine out of a common plane, or increasing the crowding in an already distorted molecule. (The single exception is XIV, R = C_2H_5, considered relative to the already crowded XIV, R = CH_3.) The extent of the shift, however, for a comparable amount of crowding varies from type to type. Somewhat unsymmetrical dyes behave similarly on introduction of a crowding group, but where an uncrowded dye is sufficiently unsymmetrical to show a large deviation in λ_{max}, then crowding the conjugated system out of planarity shifts the absorption to *shorter* wave lengths. The crowded dyes of both categories, however, behave alike in that they show a marked drop in ϵ_{max} compared to the related uncrowded dyes.

The connection between steric hindrance and planarity and molecular aggregation is touched on very briefly in the present paper. It is hoped to deal with this subject more fully at a later date.

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