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IX. Spectra of Dye Molecules

Absorption and Resonance in Dyes[1-3]

LESLIE G. S. BROOKER
Kodak Research Laboratories, Rochester, New York

1. INTRODUCTION

THE problem of tracing the relation between structure and light absorption in organic compounds is one that is almost as old as organic chemistry itself. Two main methods of attack have been developed. The older method consists of determining the constitution of colored compounds and noting by what peculiarities of structure they differ from non-colored compounds. This may be termed the classical organic chemical method. It has proved of immense value, but it is in essence nothing more than a correlation between two sets of facts which it cannot otherwise relate, and does not provide the means to tell *why* absorption occurs.

The newer method of attack is based on the primary quantum mechanical concept that absorption is possible where an atom or molecule may exist in states corresponding to different energy levels. The mathematics involved in calculating the position of absorption bands of even the simplest molecules is, however, very difficult, and up to the present no satisfactory mathematical treatment of the more complex dye molecules has been presented.

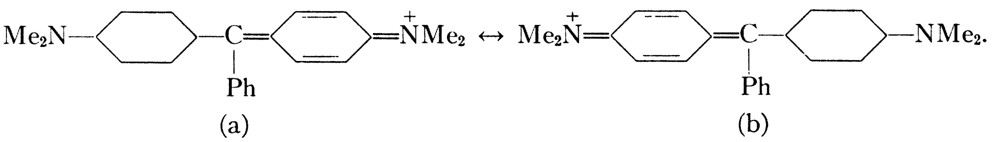
The original results[4] which constitute the bulk of the present review follow the classical organic chemical method. Certain relationships are traced and explanations suggested which are based on simple concepts derived from the resonance theory. It is felt that an appreciable advance would result from the quantitative application of quantum mechanical principles to these specific relationships.[5]

The first great advance in the correlation of chemical structure and light absorption was the discovery that all colored organic compounds are extremely unsaturated in character. Later on it was found that the unsaturation present in dyes was of a special kind, a chain of atoms in the molecule being linked together by alternate single and double linkages, forming what is now called a conjugated chain.

In relatively recent years the nature of the unsaturation in dye molecules has been further defined. It has been recognized that the conjugated chain is in many cases capable of more or less easy reversal of the linkages, this being associated with the concept of resonance.

Thus, seven years ago, Bury[6] pointed out that the great majority of dyes could be represented as resonance hybrids, that is, the molecules were such that the formulae could be written in two and sometimes in more ways which differed only in the position of an electron.

In malachite green, for example, the dye cation may be written with the charge first on one nitrogen (Ia) and then on the other (Ib), and in this case the two structures are identical. One



(I)

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[1] Contribution No. 864 from the Kodak Research Laboratories, Rochester, New York.

[2] Also presented in part as the Lee Memorial Lecture at the University of Chicago, January 21, 1942.

[3] The collaboration of the following is gratefully acknowledged: Homer W. J. Cressman, Grafton H. Keyes, Robert H. Sprague, Frank L. White, W. Waldo Williams, Gertrude Van Zandt. As a group we are deeply indebted to Dr. L. A. Jones and Mr. E. E. Richardson and their collaborators for generously providing us with the absorption data.

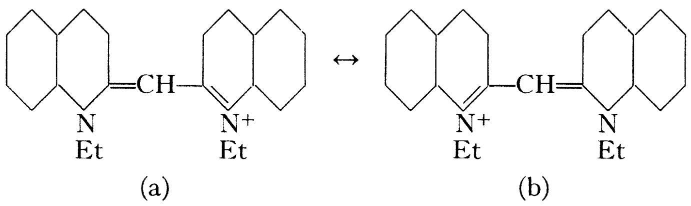
[4] Some of these results have been published as a series of papers on Color and Constitution. (a) Brooker, Sprague, Smyth, and Lewis, J. Am. Chem. Soc. **62**, 1116 (1940); (b) Brooker, White, Keyes, Smyth, and Oesper, *ibid.* **63**, 3192 (1941); (c) Brooker and Sprague, *ibid.* **63**, 3203 (1941); (d) Brooker and Sprague, *ibid.* **63**, 3214 (1941); (e) Brooker, Keyes, and Williams, *ibid.* **64**, 199 (1942); (f) Other results are as yet unpublished in detail.

[5] Cf. following paper by A. L. Sklar [Rev. Mod. Phys. **14**, 294 (1942)].

[6] C. R. Bury, J. Am. Chem. Soc. **57**, 2115 (1935).

structure is derived from the other merely by changing the position of an electron, but in passing from one to the other, the whole sequence of alternate single and double linkages in the conjugated chain joining the nitrogen atoms is reversed.

A second example (II) is very similar. It is the cation of a cyanine dye derived from quinoline. Here again the two structures are identical and the linkages of the conjugated chain are reversed in proceeding from one structure to the other.



(II)

In cases such as these, the actual state of the dye is considered to lie somewhere in between the structures given, these being called extreme or limiting structures, but to have lower energy than either of them, due to quantum mechanical resonance interaction.

2. VINYLENE SHIFT

It is characteristic of many compounds containing conjugated chains that these chains may be increased in length by adding additional vinylene (—CH=CH—) groups, giving rise to vinylene-homologous series characterized by the grouping —$(CH{=}CH)_n$—.

In such series the shift in λ_{max} which results from increasing the length of the conjugated chain by adding a vinylene group (which may be called the vinylene shift) is almost invariably in the direction of longer wave-length, but the *amount* of the shift varies considerably from series to series.

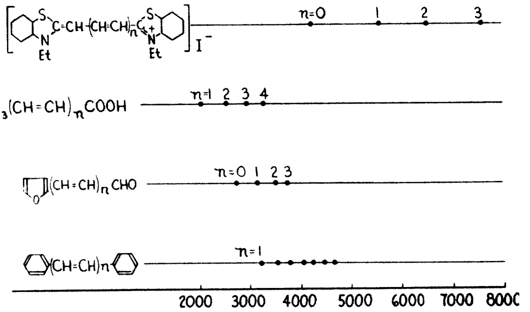


FIG. 1. Absorption maxima in A (λ_{max}) of four vinylene homologous series. For the cyanine series at the top of the figure, the values are for solutions in methanol. For the series $CH_3(CH=CH)_nCO_2H$ the values are for solutions in ethanol [Hausser *et al.*, Zeits. f. physik. Chemie **B29**, 371 (1935)]. For the series $C_4H_4O(CH=CH)_nCHO$ the values are for solutions in ethanol [König, Ber. **58**, 2559 (1925)] and for the series $Pb(CH=CH)_nPh$ the values are for benzene solutions [Hausser *et al.*, Zeits. f. physik. Chemie **B29**, 384 (1935)].

For example, the cyanine series shown at the top of Fig. 1 is typical of symmetrical polymethine dyes, the successive shifts being large and more or less evenly spaced with respect to λ. The first shift in several of these series is often larger than those succeeding, but thereafter the shifts remain roughly constant at about 1000A,[7] even up to $n=5$.[4f]

Many other vinylene homologous series, however, are known, of which three typical series are shown in Fig. 1. These series, which have largely been investigated by W. König and by Kuhn and Hausser, are characterized by shorter vinylene shifts than those shown by the cyanines, and the successive shifts show a tendency to diminish as *n* increases. Thus, whereas the upper set of points may be termed ***non-convergent***, the lower sets tend to be *convergent.*

Some understanding of the relationship between the two types of series has emerged from the comparison which follows.

3. RELATION BETWEEN VINYLENE SHIFT AND DEGENERACY OF THE EXTREME RESONANCE STRUCTURES

The set of cyanines (III) shown in Fig. 1 has been compared with the corresponding anhydrobases (IV) (Fig. 2).[4a, f] The two series of compounds are very closely related structurally, the cyanines being the ethiodides of the bases. The

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[7] N. I. Fisher and F. M. Hamer, Proc. Roy. Soc. (London) **A154**, 703 (1936).

full absorption curves in methyl alcohol are shown and the maxima are also picked out. There is obviously a considerable difference in the two sets of absorptions. Whereas the cyanines form a non-convergent series, the vinylene shifts for the bases are smaller and converge strongly, the difference between the value of λ_{max} of a cyanine and of the base with the same chain length becoming more marked the higher the value of n in the formulae. Since for a given value of n, the conjugated chain in both III and IV is of the same length, but the absorptions are very different, it follows that the mere presence of a conjugated chain is insufficient to determine the absorption.

It is possible, however, to draw a very clear distinction between the two series of compounds. The cyanine ions are seen to be resonance-hybrids between two identical low energy structures (IIIa and IIIb), i.e., the quantum mechanical degeneracy of these structures is complete. Resonance may be supposed to occur in the molecules of the bases also, but here it is not possible to devise two identical extreme structures. Of the most probable low energy structures, IVa and IVb, the dipolar structure IVb undoubtedly is of higher energy due to charge separation, so that the degeneracy of these structures is incomplete.

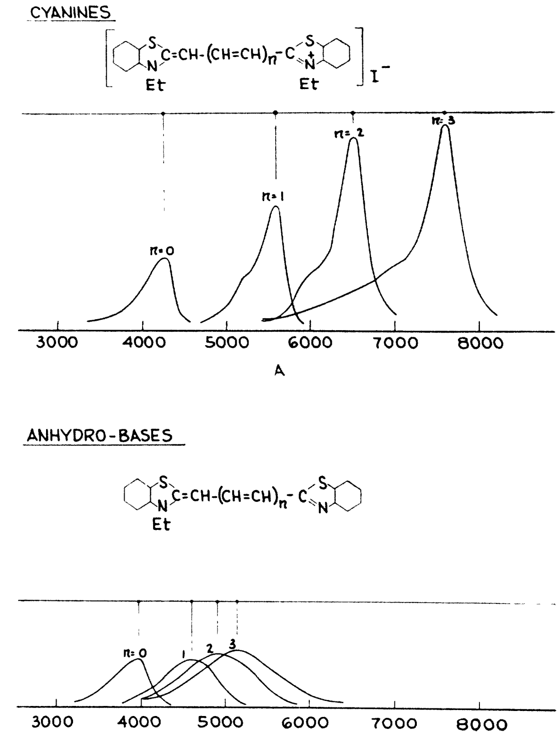
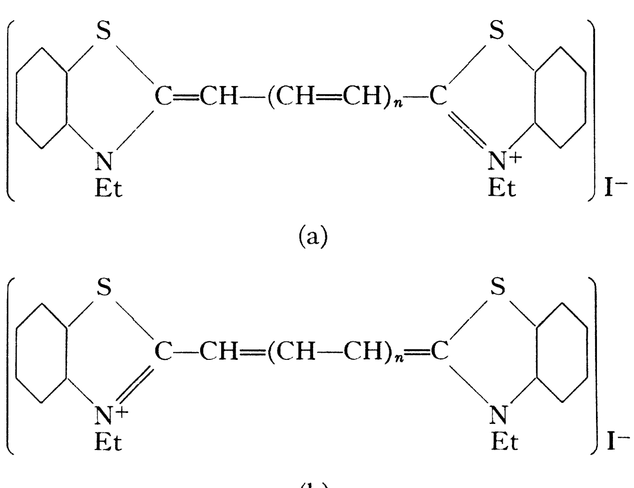


FIG. 2. Comparison of the absorptions and vinylene shifts of two series.

This is felt to be a fundamental distinction, and for example the three lower series in Fig. 1 are those in which the individual compounds are resonance hybrids between two non-identical extreme low energy structures. This view receives confirmation in the following Sections 4 and 5.

4. DEVIATION OF UNSYMMETRICAL CYANINES

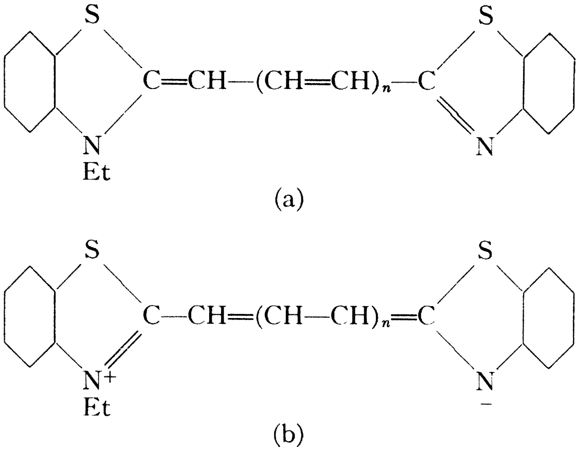
A cyanine dye is said to be symmetrical when the two terminal nuclei are the same, as in dyes



(a)

(b)

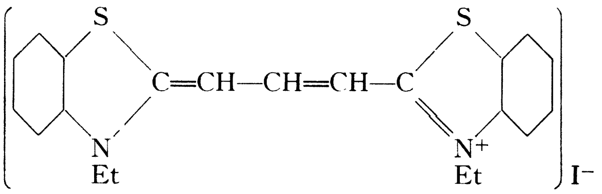
(III)

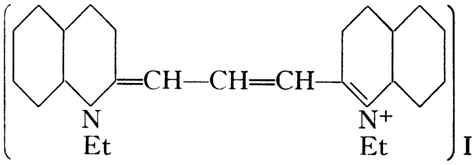

(a)

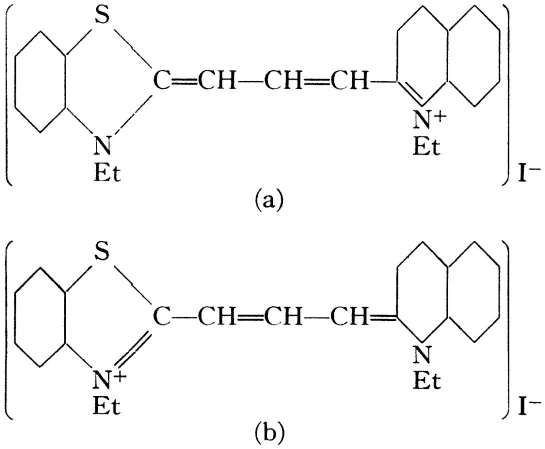
(b)

(IV)

V and VI. As a consequence each of these is represented by two identical extreme resonance structures, in one of which the positive charge of the cation is associated with the right-hand N atom (as shown) and in the other with the left-hand N atom (not shown). In dye VII, on the other hand, the two nuclei are different, and hence the extreme resonance structures, VIIa and VIIb, are not identical.


(V)


(VI)


(a)

(b)

(VII)

In such a dye it is very likely that the two nuclei will not have exactly the same basicity,[8] and if the reasonable definition is used that a strongly basic nitrogen takes up an additional positive charge to become quaternary more readily than a weakly basic nitrogen, then the more basic of the nitrogen atoms in VII will

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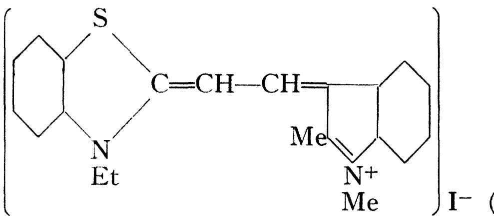
[8] Cf. Section 14.

have a greater attraction for the + charge than the other. If it is supposed that the quinoline nucleus is the more basic of the two, then VIIa will be preferred to VIIb and the dye will be a resonance hybrid between two structures of unequal energy.

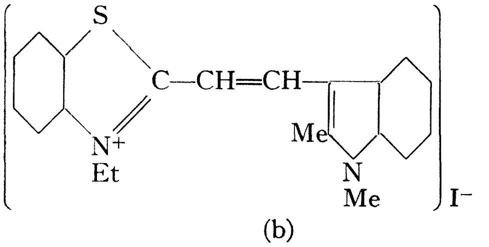
In actual fact, the absorption of VII agrees very well with that calculated as the mean of the absorptions of V and VI,[4c] of which it may be regarded as the structural hybrid, and it seems reasonable to suppose that it would absorb at this point only if the relationship between the structures were the same, or much the same, as that existing in the symmetrical dyes. Thus, judging by the absorptions, there appear to be no grounds for supposing that there is an abnormal condition in the molecule of VII compared with V and VI.

If a strongly basic nucleus is combined with a quite feebly basic nucleus in an unsymmetrical dye, however, good agreement no longer exists between λ_{max} obs. and λ_{max} calc.[9] from the related symmetrical dyes. This condition holds in VIII where the strongly basic benzothiazole ring is combined with the feebly basic indole ring. The structure VIIIb in which the benzothiazole nitrogen is quaternary must be strongly preferred, and this structure will therefore dominate.



(VIII)

(a)



(b)

In this case λ_{max} obs. lies at appreciably shorter wave-length than that calculated, the difference, or *deviation*, amounting to 365A.[4a] (See Fig. 3.)

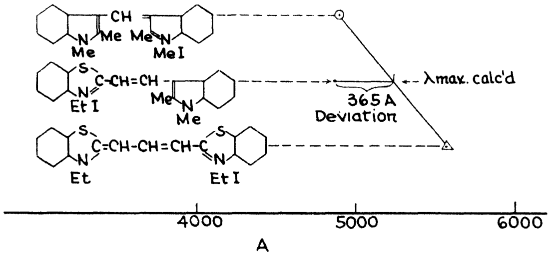


FIG. 3. Absorption maxima of three cyanine dyes.

It seems logical to suppose that this deviation would be increased by still further increasing the imbalance of basicity between the two nitrogens, and vice versa, and this prediction is actually found to hold.

5. VARIATION OF DEVIATION WITH CHAIN LENGTH; RELATION BETWEEN DEVIATION AND VINYLENE SHIFT[4e]

The series of unsymmetrical cyanines (I) shown in Fig. 4 apparently have their nuclei sufficiently balanced with respect to basicity for the deviation to be small irrespective of the length of the conjugated chain. These deviations amount only to 45, 15, and 35A for $n=0$, 1, and 2, respectively.

The benzothiazole nucleus (that at the left in the formula), however, is commonly regarded as less basic than quinoline (at the right), and it was desired to see what would happen if the basicity of the benzothiazole nucleus were reduced still further.

This was accomplished by replacing the N-ethyl group by phenyl, (Series II) for, if the N-ethylbenzothiazole nucleus is regarded as derived from ethylaniline, then the N-phenyl derivative must be regarded as derived from the much less basic diphenylamine. Comparisons were carried out as before and it was found that the deviations were larger than in Series I, particularly for the longer chain lengths, and were all in the direction of shorter wave-length from the calculated means.

Because of these results, the basicity of the benzothiazole nucleus was reduced still further by introducing an *o*-nitro substituent into the N-phenyl group (Series III). It was not found possible to prepare the symmetrical dye containing the two N-*o*-nitrophenylbenzothiazole nuclei where $n=0$, so that it was not possible to

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[9] Cf. Section 17.

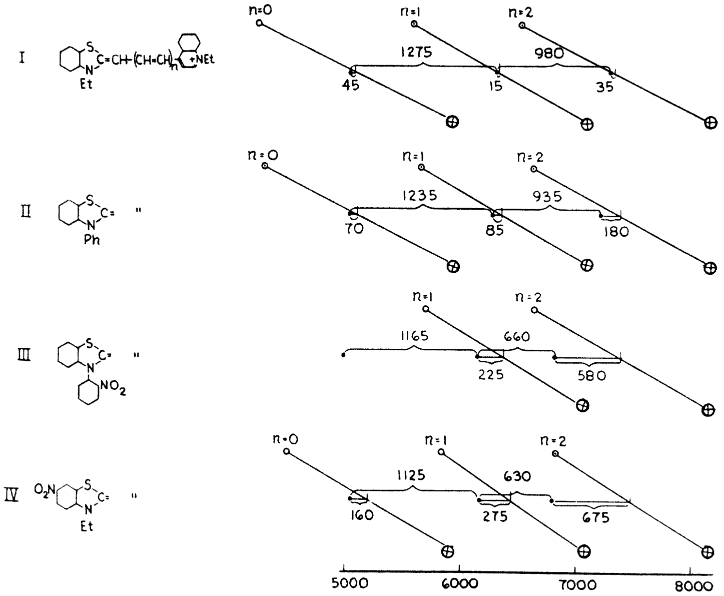

FIG. 4. Absorption maxima of thia-4′-cyanines and related symmetrical dyes in MeOH: ⊙ sym. thiacyanine; ⊕ sym. 4,4′-cyanine; · unsym. dye; | calculated mean.

determine the deviation for the first member, but the deviations for the dyes with longer chains were still greater than in II, and when $n=2$ the deviation was very great indeed (580A).

It therefore appears that although the benzothiazole and 4-quinoline nuclei do not differ sufficiently in basicity for appreciable deviations to occur in the series of dyes I, yet increasing the imbalance of basicity between the two nuclei, as in II and III, causes unmistakable deviations to appear, and here the *deviation is the greater the higher the value of n.* Furthermore it is seen that the *deviation for a given chain length is greater, the greater the degree of imbalance of basicity between the nuclei.* These results are typical of a much greater mass of data on the absorption of vinylene homologous unsymmetrical cyanines.

In a further set of comparisons, IV, (Fig. 4), the basicity of the benzothiazole nucleus was reduced by introducing a nitro group into the 6-position. The deviations are even greater in this series than in III, from which it would appear that this is the most effective of the methods used here for reducing the basicity of the benzothiazole nucleus. In IV, the deviation where $n=2$ is so great (675A) that this dye actually absorbs at shorter wave-length than either of the related symmetrical dyes.

Whereas the very small deviations in series I do not cause the second (and more significant) vinylene shift to be reduced much below the average of 1000A of non-convergent symmetrical series, in IV the second vinylene shift is only 630A and this series converges sharply. It therefore appears that introduction of a considerable structural asymmetry (non-degeneracy) into a vinylene homologous series the members of which are symmetrical or at least non-deviating, tends to render the series convergent.

In the symmetrical dyes there are always two identical low energy structures, and this appears to be the prerequisite for non-convergence. Introduction of asymmetry tends toward the production of a single low energy structure, and here the series converges to an extent which is determined by the asymmetry.

To return to the convergent series of Fig. 1, it is seen that in these series a single low energy structure is dominant, this being the formula actually shown in the figure in each case. In these cases it seems probable that the deviations for these dyes, if they could only be determined, would be very considerable indeed. This procedure is out of the question, however, since the corresponding parent compounds are not known, but, since it is seen from the dyes of Fig. 4 that a large deviation gives a dye which, *ceteris paribus*, absorbs at relatively short wave-length, then the next best criterion of asymmetry of the lowest energy resonance structures is absorption at short wave-length and convergence of the series. These properties are certainly shown by the three lower series in Fig. 1.

6. ORDER OF BASICITY OF HETEROCYCLIC NUCLEI

Since the deviation of an unsymmetrical cyanine of given chain length depends on the imbalance of basicity between the nitrogen atoms, it follows that if a number of different nuclei are combined with one constant nucleus to give a series of unsymmetrical dyes, then the relative basicities of the different nuclei may be ascertained by measuring the deviations.

This has been carried out with a series of twelve nuclei, the 2,5-dimethyl-1-phenylpyrrole nucleus being chosen as the constant nucleus (Fig. 5).[4f] The 1-phenylpyrrole ring is acknowledged to be very feebly basic, hence small deviations will be shown by nuclei that are likewise feebly basic, and larger deviations by nuclei that are strongly basic.

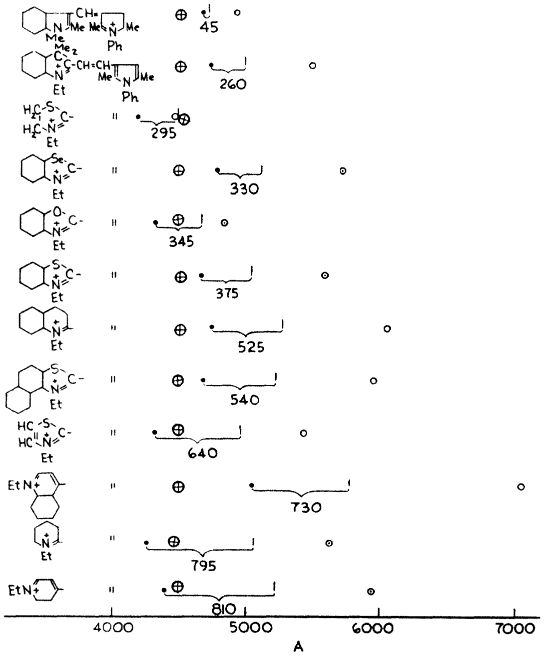

FIG. 5. Order of basicity of twelve heterocyclic nuclei. Values of λ_{max} in MeOH are shown as follows: · unsym. cyanine; ⊕ sym. cyanine with two pyrrole nuclei; ⊙ second sym. cyanine; | calculated mean between ⊕ and ⊙.

The deviations actually range from −45A for feebly basic indole to 810A for strongly basic pyridine, so that the order obtained is the expected one, at least for the nuclei at the extremes of the list. A further analysis of the order obtained for the nuclei is given in Section 14.

7. SENSITIVITY RULE

It is interesting that the benzothiazole and 4-quinoline nuclei give very different deviations in Fig. 5 (375 and 730A, respectively) although when these nuclei are combined with each other (top of Fig. 4) the deviations are very small indeed. This appears contradictory at first sight but the facts are reconciled in the following treatment:

In Fig. 6 is shown the effect on the deviation of replacing one nucleus by another. At the top, one benzothiazole nucleus of the symmetrical dye is replaced by 2-quinoline, and this in turn by 4-quinoline. The symmetrical dye has, of course, zero deviation, and the *effect* on this deviation is small throughout, the two unsymmetrical dyes in this comparison having only small deviations.

At the bottom of the figure the benzothiazole nucleus is replaced by 2-quinoline as before, but

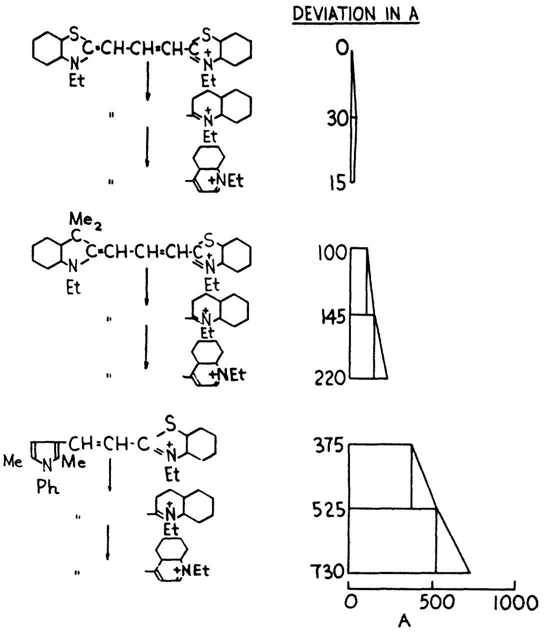

FIG. 6. Effect on the deviation of the replacement of one nucleus by another.

the replacement is now carried out on an unsymmetrical dye which itself shows a large deviation (375A) and the effect on the deviation is to increase it to 525A. Replacement of 2- by 4-quinoline increases the deviation still further to 730A.

It may therefore be said that *where a change of structure produces a small effect on the deviation of a symmetrical dye, the same change in structure produces a much greater effect on the deviation of a highly unsymmetrical dye.*[4c]

The comparisons in the center of Fig. 6 show the replacements carried out starting with a moderately asymmetric dye, as evidenced by its deviation of only 100A. Here the effects are greater than those in the first series but less than those in the third. It may therefore be concluded that in considering replacements of this kind, *the effect on the deviation is the greater, the less the degeneracy of the extreme structures and the greater the deviation of the compound undergoing the change.*[4c]

The phenomenon is further illustrated in Fig. 7. It has already been seen (in Fig. 4) that the effect of introducing a nitro group into the less basic nucleus (benzothiazole) of V, giving VI (Fig. 7) is to increase the deviation from 15 to 275A, a very considerable increase. If the same structural asymmetry is introduced into the symmetrical dye I, however, giving II, the effect on the deviation is very small, 20A. Thus it is seen that although the nuclei of V are not sufficiently out of balance to give a large deviation, the molecule is yet sufficiently asymmetric to respond strongly to an additional asymmetry.

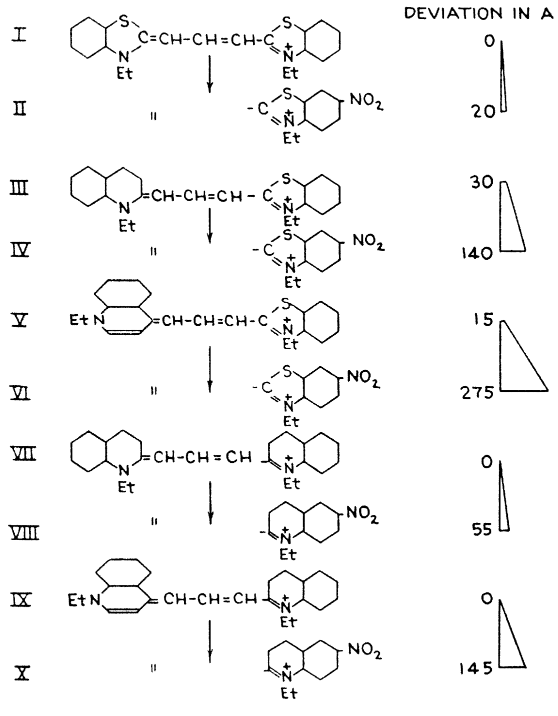

FIG. 7. Effect on the deviation of symmetrical and unsymmetrical dyes of introducing a nitro group.

From the order of basicity of the nuclei arrived at in Fig. 5 it follows that the nuclei in III (Fig. 7) are less out of balance than those in V,[10] and therefore the added asymmetry in IV produces a smaller effect (140A) than in VI.

Again, the effect on the deviation of introducing the nitro group into the symmetrical dye VII is rather small (55A), but the effect on the unsymmetrical but non-deviating dye IX is much greater.

The most reasonable explanation of all these facts would appear to be that non-degeneracy of the extreme structures and deviation are related by a parabolic type of function. The reduction of degeneracy I→II (Fig. 7) may be considered comparable in amount with the reduction in degeneracy V→VI, but the relation to deviation is such that the first change produces only a small increase in deviation whereas the second produces a large increase.

In comparisons of this kind, that dye which has the greater resonance energy (i.e., the difference in energy between the structure of lowest energy and the lowest ground state) is the most highly stabilized, and its deviation will be the least affected by an introduced small structural asymmetry.

The rule described here concerning sensitivity to a structural asymmetry would appear to be of wide application in resonance chemistry. Schwarzenbach, for example, has already observed that symmetrical dyes are less affected by changes of *p*H than unsymmetrical dyes of closely related structure.[11]

It has already been shown in Section 5 that

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[10] The higher deviation (30A) of III compared with V (15A) appears to contradict this conclusion, but these figures are too small to be significant in this sense.

[11] Schwarzenbach *et al.*, Helv. Chim. Acta **20**, 490, 627, 1596 (1937).

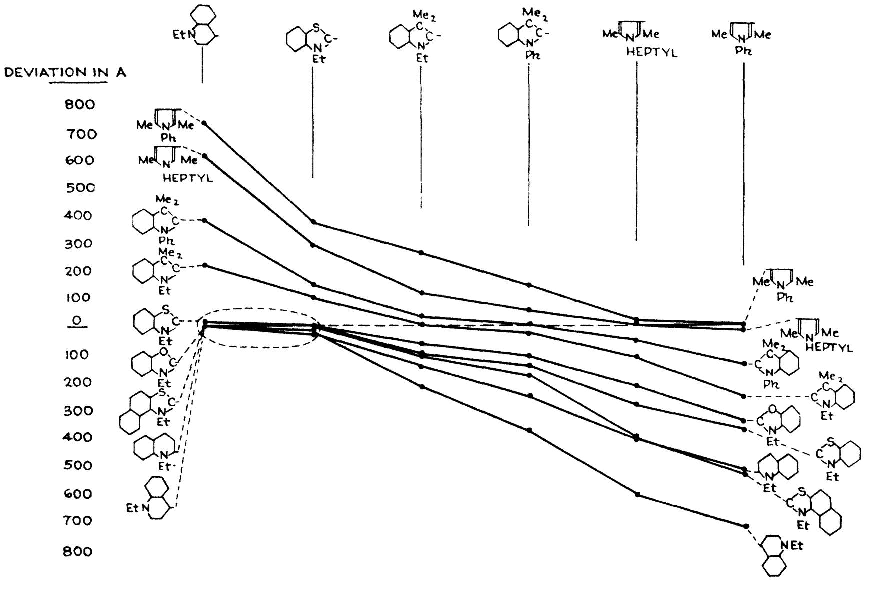

FIG. 8. Deviations of unsymmetrical carbocyanines.

in a vinylene homologous series of unsymmetrical cyanines (such as series IV, Fig. 4), the deviation increases with *n*. In this case, then, a non-degeneracy produces its greatest effect on the absorption, the longer the chain, just as in the comparisons given above, a non-degeneracy exerts its greatest effect on a dye showing the highest asymmetry.

According to the treatment worked out by Dr. Sklar,[5] the resonance energy of a series of symmetrical cyanines diminishes as *n* increases; hence the shift of λ toward the longer waves with increase in *n*. This means that a given small non-degeneracy will produce its least effect with the dye of the shortest chain, and that the effect will increase thereafter with *n*, and this is what is actually observed.

It follows from this reasoning that the significant datum in estimating the effect of an introduced structural asymmetry on a dye is the resonance energy of the latter, and not the total resonance split.[5]

There is another property, too, of cyanine dyes, that depends on the resonance energy, and this is the ease of discharge by acid. The resonating system is destroyed on acidification, and the color disappears,[12] but in a vinylene homologous series the stabilization energy of this resonating system diminishes with *n*. It is clear that the lower the resonance energy, the more readily will acid discharge occur, hence the ease of discharge of color should increase with *n*, which is precisely what is actually found for a number of series of symmetrical cyanines.[13]

8. DEVIATIONS OF UNSYMMETRICAL CARBOCYANINES[4f]

From Fig. 6 it is seen that, if their basicities are to be compared, the greatest differentiation between the three relatively strongly basic nuclei benzothiazole, 2-quinoline, and 4-quinoline is attained when they are combined with the very feebly basic 2,5-dimethyl-1-phenylpyrrole nucleus, and the deviations are compared. It is, in fact, for this reason that pyrrole is used as the constant nucleus in the comparisons in Fig. 5, for it permits of a maximum differentiation between the other nuclei which are mostly of much higher basicity. Conversely, the greatest differentiation between two feebly basic nuclei should be attained by comparing their deviations in combination with a strongly basic nucleus.

These points are brought out in Fig. 8. Here are plotted the deviations of a representative set of unsymmetrical carbocyanines. The deviations

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[12] For the mechanism of this cf. reference 4a, p. 1123.

[13] The writer wishes to thank Professors V. K. LaMer and G. H. Burrows for kindly supplying these data.

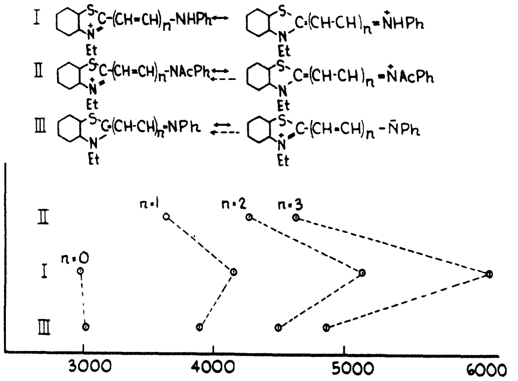

FIG. 9. Absorption maxima of three structurally related vinylene homologous series.

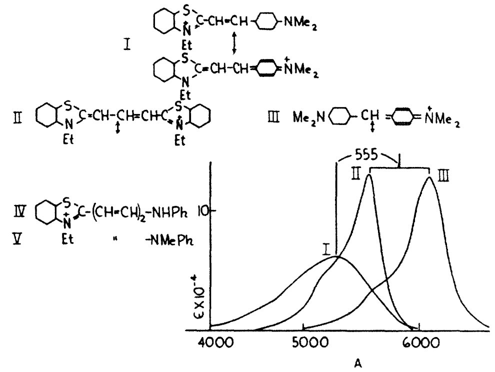

FIG. 10. Suppression of degeneracy of structures by a single benzene ring in the conjugated chain.

shown are those of carbocyanines produced by combining the nine nuclei in the upright columns with the six shown horizontally.

In the lower left-hand side of the figure, four nuclei are shown which have zero deviation when they are combined with 4-quinoline, and for one additional nucleus, benzothiazole, the figure is very small. These nuclei, then, do not differ sufficiently in basicity from 4-quinoline for appreciable deviations to be observed.

If these same five nuclei are combined with benzothiazole (second vertical column from left) the deviations are still very small, but in the third vertical column there is now sufficient difference in basicity between some of the nuclei being combined, for certain of the deviations to be considerable, and the five nuclei under consideration give deviations which differ markedly one from the other. In the fourth vertical column the magnification of the differences is continued and proceeds steadily in the two remaining vertical columns until, in that on the extreme right, the deviations shown by the five strongly basic nuclei approach maximum values.

Deviations have been plotted in some cases above and in others below the zero line. The reason for this is that a nucleus of intermediate basicity, such as one of the indolenines, gives a deviation when it is combined with a more strongly basic nucleus or with one that is less basic. If the deviations were to be plotted in the same direction from zero, it is possible that the same point might have to be shared by two nuclei that differed widely in basicity, and the method actually adopted avoids this difficulty and allows the nine nuclei to be arranged in descending order of increasing basicity both in the left-hand and right-hand columns. The six nuclei at the top show progressive decrease in basicity from left to right.

This chart may be used to illustrate the fact that response to a given small chemical replacement is in general greater with highly unsymmetrical dyes.

It might be pointed out that the compilations of data on unsymmetrical carbocyanines made by earlier investigators[14,15] only included dyes which fell into the region approximately indi-

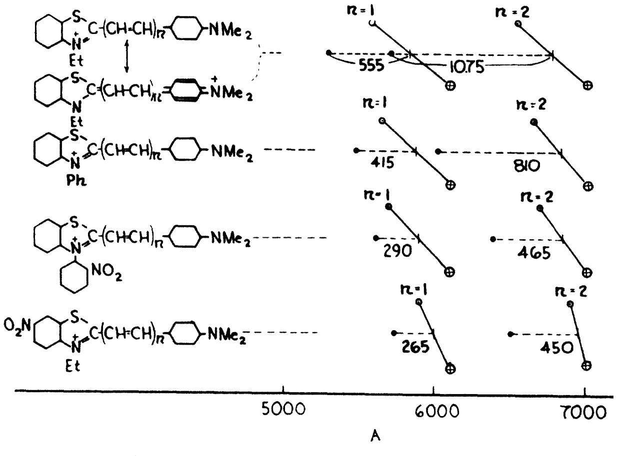

FIG. 11. Lowering the basicity of a heterocyclic nucleus in a styryl dye reduces the deviation. Values of λ_{max} in nitromethane are shown as follows: • styryl dye; ⊙ sym. cyanine; ⊕ Michler's hydrol blue type; | calc. mean.

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

[15] S. Yoshimura and S. Sakurai, Bull. Inst. Phys. and Chem. Research, Tokyo **16**, 1295 (1937).

cated by the dotted ellipse, where deviations, if present at all, are small.

9. COMPARISON OF THREE STRUCTURALLY RELATED VINYLENE HOMOLOGOUS SERIES[4b]

In Fig. 9 are compared the absorption maxima of three series of compounds which are closely related structurally. Series I is a set of ionized anilino compounds, of which the cations are shown. The maxima of this series are widely spaced and form a typically non-convergent series from which it may be deduced that the two extreme structures shown are at least sufficiently close in energy for the dyes not to show appreciable deviations.

Acetylation of the anilino group in I, giving II, must enormously reduce the basicity of the anilino nitrogen, so that the left-hand resonance structure of II is preferred. The absorptions of this series are accordingly strongly convergent.

Removal of the elements of acid from the dyes I yields the anil bases III. Here the charge separation renders the dipolar structure the less stable of the two, and this series is also strongly convergent.

Although the compounds of series II are ionized, those of series III are not. The two series present very similar pictures from the standpoint of absorption, however, and indeed the fact of their being ionized or not is immaterial; the important point is that in both series there is a considerable departure from complete degeneracy of the extreme structures for each compound.

10. SUPPRESSION OF DEGENERACY OF STRUCTURES BY A BENZENE RING IN THE CONJUGATED CHAIN[4c]

In Fig. 10, dye I is closely related to the cyanines in that it is a basic dye with the N-N auxo-chromophoric system. The dye cation is shown. It differs from those dyes that have been considered up to the present, in that it has a single benzene ring in the chromophoric chain.

This dye is also unsymmetrical, and may be regarded as the structural cross between the

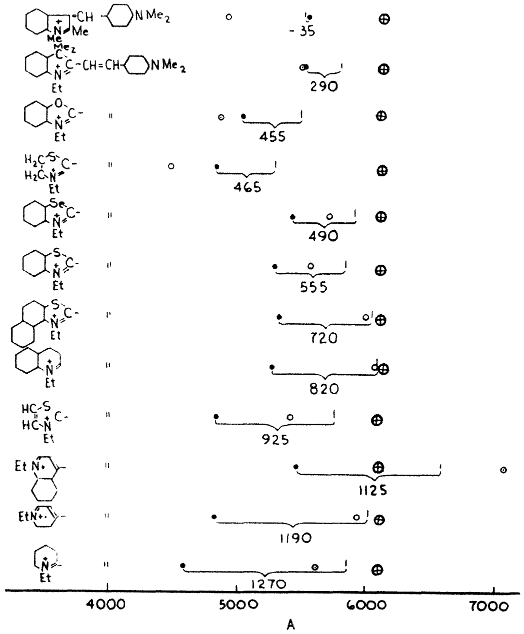

FIG. 12. Increasing deviation in a styryl dye with increasing basicity of the heterocyclic nucleus. Values of λ_{max} are in nitromethane: • styryl dye; ⊙ sym. cyanine; ⊕ Michler's hydrol blue; | calcd. mean.

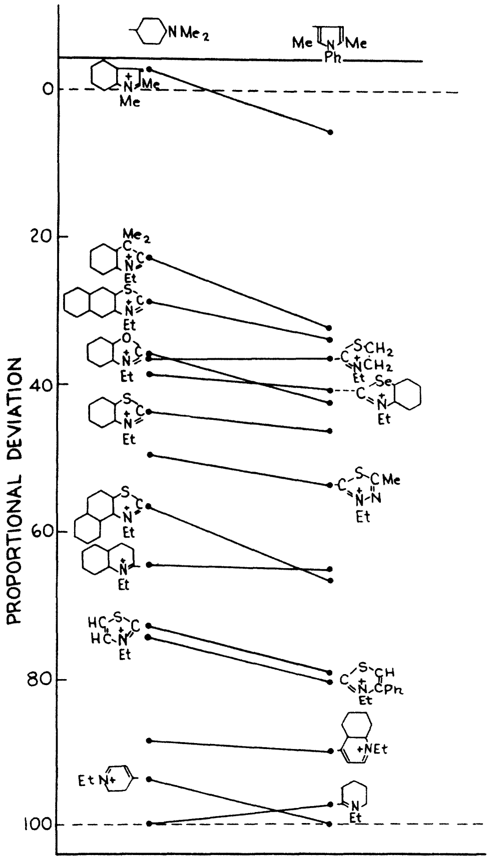

FIG. 13. Order of basicity of nuclei, a comparison of two methods.

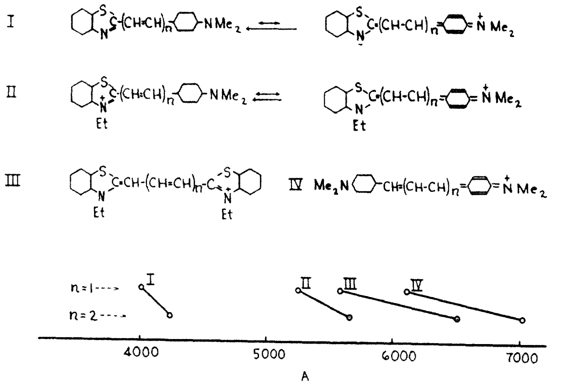

FIG. 14. Value of λ_{max} for three categories of compounds.

symmetrical dyes II and III, only one extreme resonance structure of each of which is shown; II is a cyanine and III is the diphenylmethane dye Michler's hydrol blue.

The absorptions show that I absorbs at considerably shorter wave-length than the mean of the absorptions of II and III, the deviation being 555A. This could be due to a marked difference of basicity between the nitrogen atoms, but it would seem as if the benzothiazole and dimethylaniline nitrogens are both rather strongly basic. Furthermore, the other two dyes shown, IV and V, one with the aniline residue and the other with the methylaniline residue, show very small deviations indeed.

It therefore seems much more likely that the cause of the great deviation of I is due to the presence of the single benzene ring in the chromophoric chain. This will be in the benzenoid arrangement in the upper structure but quinonoid in the lower. Of these arrangements the benzenoid is the more stabilized by resonance, hence the structure containing it will be of lower energy than the other, and hence the deviation.

In I the quinonoid structure (b) could be rendered more stable if the competition for the positive charge by the heterocyclic nitrogen were reduced, in other words, if the heterocyclic ring were to be rendered less basic. Increasing the stability of this structure would reduce the nondegeneracy of the two structures and reduce the deviation.

That this actually occurs is seen in Fig. 11. The basicity of the benzothiazole nitrogen is reduced by the means employed for the same purpose in Fig. 4 and the deviation is reduced and the vinylene shift increased (cf. where $n=2$).

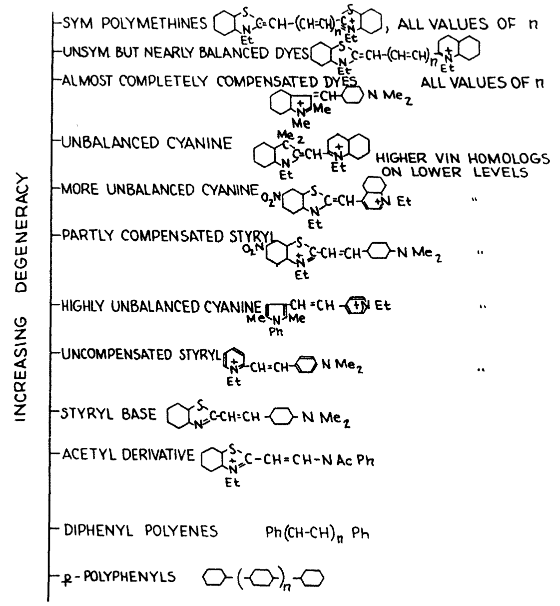

FIG. 15. Classification of dyes by degeneracy of the extreme structures.

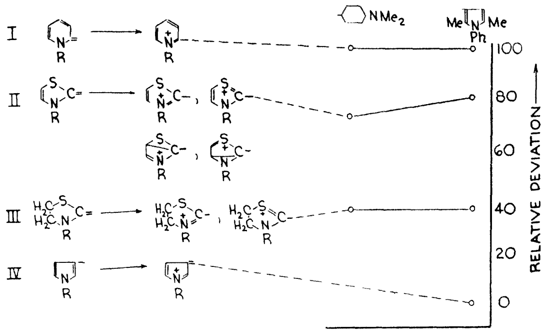

FIG. 16. Basicity of nuclei largely due to additional-double-bond stabilization.

Since the deviation of a dye of this type depends on the basicity of the heterocyclic nucleus, the order of basicity of a variety of different nuclei may be obtained by comparing the deviations. Twelve nuclei are so dealt with in Fig. 12. The smallest deviation (−35A) is given by the very feebly basic indole ring, and here the strong tendency for the more strongly basic NMe₂ group to monopolize the ionic charge must approximately neutralize the tendency for the benzene ring to concentrate the charge at the opposite end of the chain, and the extreme structures of the dye are sufficiently close in

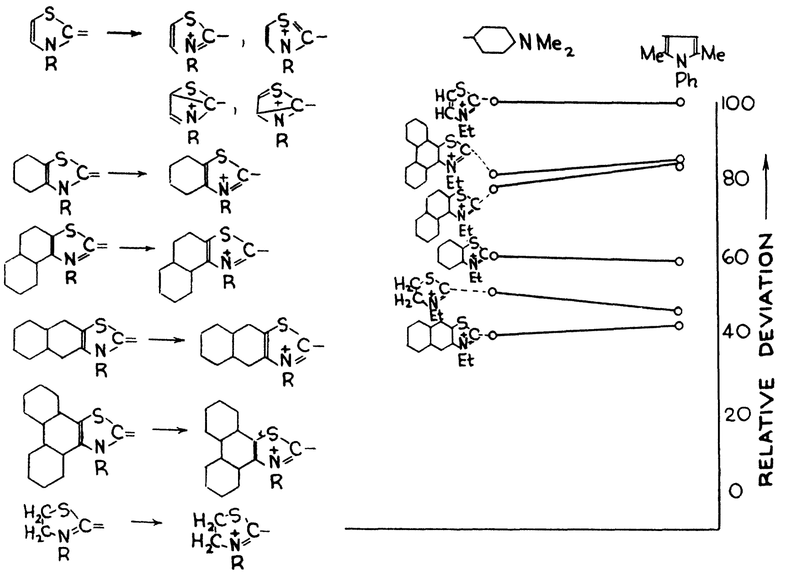

FIG. 17. Basicity of nuclei largely due to additional resonance stabilization.

energy for the deviation to be negligible. The deviations increase steadily in amount with other nuclei; the maximum value of 1270A is reached for the 2-pyridine ring.

11. COMPARISON OF TWO METHODS OF DETERMINING THE RELATIVE BASICITIES OF HETEROCYCLIC NUCLEI[4f]

It is interesting to compare the order of basicity of the nuclei obtained from the deviations in the styryl series, in Fig. 12, with those obtained from a consideration of unsymmetrical cyanines in Fig. 5. This has been done in Fig. 13.

In each series the nucleus giving the greatest deviation has been assigned 100 arbitrary units of deviation and those for the other nuclei have been determined proportionately.

The agreement between the two series is good on the whole; there is relatively little intersection of lines, which shows that the order obtained in the one series agrees reasonably well with that obtained in the other.

One reason for this, undoubtedly, is the fact that in each series, proceeding from one of the nuclei being compared, to another that is more basic, is accompanied by an increased deviation-response to increasing asymmetry of the molecule.

It might be mentioned that the absorptions for the unsymmetrical cyanine column were determined in methyl alcohol, and those for the styryls in nitromethane, but even so the agreement is good.

12. THREE CATEGORIES OF COMPOUNDS[4c]

In addition to the compounds I, II, and III of Fig. 10, there may be obtained the base I of Fig. 14 in which the benzothiazole N is not quaternary. This base may resonate as shown and the second extreme structure is a dipole. In this structure not only is the benzene ring in the relatively unstable quinonoid arrangement but the dipole is unstable in itself, because of the work which must be done in charge separation, so that this extreme resonance structure is especially unstable, and there will be a very strong preference for the uncharged structure. The degeneracy of the structures in I is therefore much lower even than in II, and although the deviation for this compound cannot be measured, it nevertheless absorbs at much shorter wavelength than II.

The vinylene shift, too, on proceeding to the next higher vinylene homolog of I is considerably lower than for II, and this in turn is lower than for the symmetrical dyes III and IV, so that once again there is a clear relationship between degeneracy of the extreme structures and absorption and vinylene shift.

13. CLASSIFICATION OF DYES BY DEGENERACY OF THE EXTREME STRUCTURES[46]

It is now possible to classify dyes according to the degeneracy of their extreme resonance structures.

Dyes in which there is complete degeneracy of these structures, such as the symmetrical polymethine dyes, are placed at the head of the list in Fig. 15. They are closely followed by dyes which are unsymmetrical but which show little or no deviation, whatever the chain length, and by dyes such as the indole benzylidene dye in which opposing forces almost exactly neutralize each other.

Then follows an unsymmetrical cyanine which shows a small but definite deviation even for the shortest chain length, and at this level only this member can be included, the higher vinylene homologs occupying progressively lower levels, since the degeneracy of the structures appears to diminish as the chain is lengthened, if we judge by the deviations. Still more highly unbalanced cyanines come still lower on the list. Sandwiched in between, there are styryl dyes in which the effect of the benzene ring is only partly neutralized, and at still lower levels, those styryls in which its effect is either not neutralized at all or even reinforced.

At a still lower level there is found a styryl base, then an acetyl derivative (cf. Fig. 9), and finally such compounds as the diphenyl polyenes and the *p*-polyphenyls in both of which classes there is a very stable single structure.

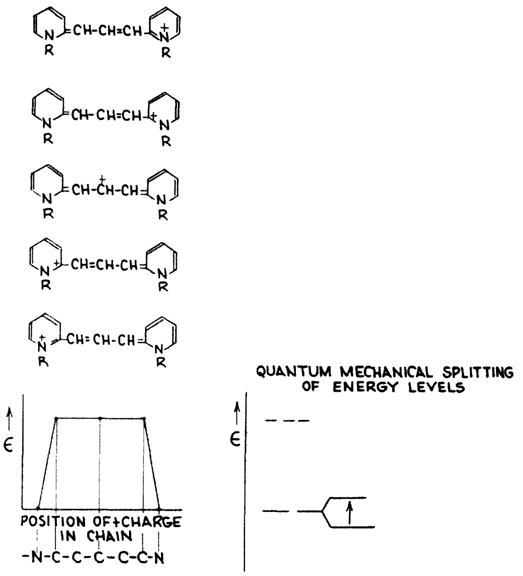

FIG. 18. Extreme and intermediate structures.

14. BASICITY OF NUCLEI LARGELY DUE TO ADDITIONAL RESONANCE STABILIZATION

In the preceding sections the "basicity" of the various nuclei employed in cyanine dyes has been identified with the relative ease with which the uncharged form of the nucleus takes up a positive charge to give the positively charged form.

It was pointed out by Dr. A. L. Sklar that in the case of pyridine (I, Fig. 16) the N^{III} nucleus has a six-membered ring with two double bonds which must be stabilized by resonance very like that present in dihydrobenzene, but in the N^{IV} ring there are three double bonds so that the stabilization is similar to that in benzene, and much greater than in the N^{III} nucleus. The tendency to pass from $N^{III} \rightarrow N^{IV}$ will therefore be very great, or, otherwise expressed, the pyridine nucleus should be very strongly "basic," which actually is the case, on the basis of the deviations in Fig. 13.

In thiazole (II, Fig. 16) the stabilization of the N^{III} nucleus is by only one double bond, but additional stabilization is attained in passing to the N^{IV} form, although the difference will not be as great as in pyridine where the N^{IV} ring is fully benzenoid. The thiazole ring is therefore less basic than pyridine which agrees with the order indicated by the deviations.

Thiazoline (III, Fig. 16) in the N^{III} form has no double bond for stabilization, but the N^{IV} form has higher stabilization corresponding to the two ways of writing the structure. However, the gain is not so great as in thiazole, for in the N^{IV} thiazole ring Dewar structures are possible too, due to the presence of two conjugated double bonds, which are not possible in thiazoline. Consequently thiazoline is less basic than thiazole, as the deviations indicate.

Finally, in a fourth category, pyrrole (IV, Fig. 16) has two double bonds in each form, and there is little if any additional resonance stabilization on acquiring the positive charge. This nucleus should therefore be found to be the least basic of the four, as indeed it actually appears to be from the deviations.

It is not absolutely necessary, therefore, to use

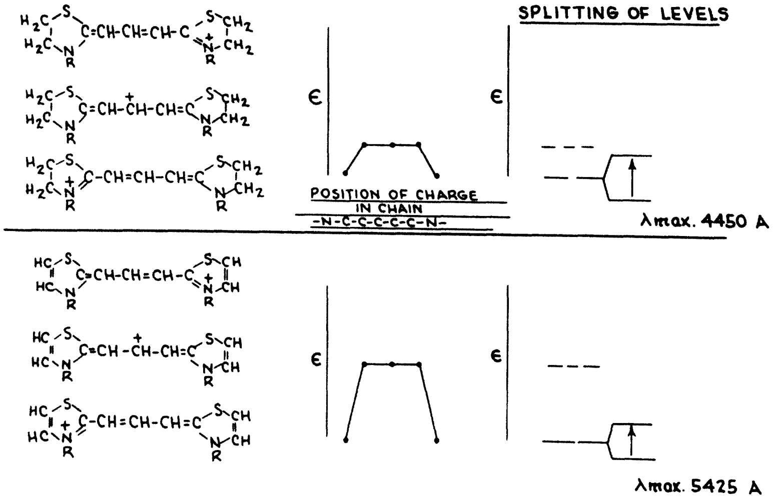

FIG. 19. Comparison of two dyes of closely related structures. Rule: the steeper the energy gradient, the deeper the color.

the term "basicity" in the foregoing treatment, and it may be replaced by a term indicating the difference in resonance stabilization in proceeding from the N^{III} form of the ring to the N^{IV} form. (In addition, the nitrogen atom itself passes from N^{III} to N^{IV} and an energy term will be involved here, but this will be the same in all nuclei.) A general expression which is suggested is "stabilization produced by introduction of an additional double bond into a ring" which may be shortened to "additional-double-bond stabilization." It is clear that this additional stabilization is very high for the pyridine ring, progressively less for thiazole and thiazoline and zero for pyrrole, and hence the basicities of these rings follow in this order.

A closer study of several nuclei containing the thiazole ring which was also suggested by Dr. Sklar is given in Fig. 17. At the top there is thiazole itself, highly stabilized in the quaternary form by two structures of the Kekulé type and two of the Dewar type, and this ring has high additional-double-bond stabilization and is quite strongly basic. The Dewar structures, it must be noted, are possible only because of the presence of the double bond in the 4,5-position.

In benzothiazole, where the 4,5-side is shared with a benzene ring, this side will not have full double bond character, for the benzene ring requires only one-half double bond character of any of the six sides. The probability of Dewar arrangements in this case is therefore not as high as in thiazole itself, and the quaternary ring will be less stabilized by them and hence this nucleus will appear less basic than thiazole.

In β-naphthothiazole, the 4,5-thiazole side shared with naphthalene has $\frac{2}{3}$ double bond character in naphthalene itself, and so the Dewar arrangements can play a greater part than in benzothiazole and the nucleus will accordingly be more basic than benzothiazole although less so than thiazole, and this it actually is, as estimated from deviations of dyes containing these nuclei.

The so-called β,β-naphthothiazole ring, on the other hand, has only $\frac{1}{3}$ double bond character in that side of the naphthalene ring which is shared with thiazole. The Dewar structures will play a small part here and the ring will be less basic than the isomeric nucleus and even than benzothiazole, and this is actually the order obtained from the deviations (Fig. 13).

In the phenanthrothiazole, the side shared between thiazole and phenanthrene has $\frac{4}{5}$ double bond character in the latter, the Dewar structures will play a greater part than in benzothiazole or even β-naphthothiazole, but less than in thiazole, and it is seen that the position occupied by this nucleus actually is in agreement with these relations.

Thiazoline, with no double bond in the 4,5-position, will have no stabilization from Dewar structures in the quaternary form, and should therefore be the least basic of all, but it is apparently anomalous in that it appears to be more basic than β,β-naphthothiazole. However, an aromatic ring tends to attract electrons, and this will reduce the basicity of a thiazole ring to which it is fused. The result is that the basicity of all these fused-ring hydrocarbon thiazoles is lower for this reason than they otherwise would be, thus accounting for the apparent anomaly.

15. ABSORPTION OF SYMMETRICAL CYANINES AND RELATIVE STABILITY OF THE INTERMEDIATE STRUCTURES

Some understanding of why symmetrical cyanines derived from different heterocyclic nuclei absorb at different wave-lengths even when the chain lengths are the same is provided by the following arguments which have arisen from a collaboration with Dr. Sklar.

According to Pauling,[16] not only extreme resonance structures of dyes must be taken into account but intermediate structures also, there being only a vanishingly small probability for transition to take place between the extreme structures in one step.

Pauling has suggested two mechanisms by which charge transference may take place, but one is preferred and this preferred mechanism is used here.

If we start with the formula at the top of Fig. 18, the positive charge is considered to move first to the carbon atom adjacent to N, then to the central C atom, then to the C atom adjacent to the second nitrogen atom, and finally to the second nitrogen atom itself.

As discussed in Section 14, the N^{IV} nucleus is stabilized by resonance of the benzene type, and the N^{III} nucleus is stabilized to a much less extent. In the transition from the topmost formula to that immediately below it, the benzenoid type of resonance is destroyed in the one ring and is replaced by that more nearly characteristic of an N^{III} ring. Two N^{III} rings are likewise present in the other two intermediate structures, so that in all of these latter, both rings are in the less stabilized state, and the energy of these structures will be higher than that of the extreme structures for that reason. In addition, C^+ is probably much less stable than N^+, and this will provide an additional reason why the extreme structures are the more stable ones.

If the relative energies of the five structures are plotted (diagram at lower left of Fig. 18), there will be two identical low levels for the extreme structures and three much higher levels for the intermediate structures.

The quantum-mechanical resonance splitting of the lower energy levels is determined, however, by the relative levels of the other contributing structures. If these are high, as shown here, the resonance splitting will be small and the light absorbed will have low frequency and long wave-length.

A comparison of two closely related dyes (Fig. 19) serves to illustrate the principle more fully.

Two symmetrical dyes of the same chain length are compared, the dye of the upper formula containing two thiazoline nuclei and the other two thiazole nuclei. In each case the two extreme structures are formulated, but only one intermediate structure is given rather than three, in order to save space.

In the upper dye, when the positive charge is transferred from N to C, a certain reduction in the resonance stabilization in the ring occurs, but this amount is not particularly great (cf. Fig. 16) and it may be supposed that the intermediate structures are not greatly higher in energy than the extreme structures, and the resonance splitting of the latter will be considerable, corresponding to absorption of light of shorter wave-length (actually λ_{max} is 4450A).

In the second dye, on the other hand, passage from the topmost extreme structure to the intermediate structure involves a considerable reduction in the resonance stabilization of the ring from which the positive charge is removed (cf. Fig. 16) and the energy of the intermediate structure(s) will be higher, relative to the extreme structures, than in the thiazoline dye. The resonance splitting of the extreme structures will therefore be less with the lower dye, and λ_{max} is actually at considerably longer wave-length, i.e., 5425A.

It will be seen that the energy gradient, or hump, from the extreme structures to the intermediate ones, is lower in the upper dye than in

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[16] L. Pauling, Proc. Nat. Acad. Sci. **25**, 577 (1939).

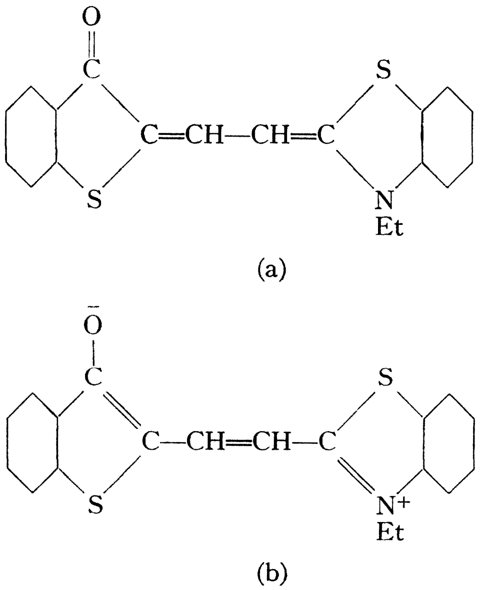
the lower, and the rule may be stated that in the case of two symmetrical dyes of closely related structures the *steeper this energy gradient the deeper will be the color.*

16. ADDITIONAL-DOUBLE-BOND STABILIZATION; A FACTOR CONTRIBUTING TO THE STABILITY OF DIPOLAR STRUCTURES IN DYES

It has been shown in Sections 14 and 15 that additional double-bond stabilization of rings is very significant in determining the relative stability of resonance structures. This concept is also useful in understanding the properties of many cyclic compounds in which the possibility exists of resonance between an uncharged structure and a dipolar structure.

In general a dipolar structure will be of considerably higher energy than the corresponding uncharged structure, at least in media of low dilectric constant, because of the work that must be done in charge separation. It will be shown, however, that in a number of cases this factor is opposed to a greater or less extent, whereas in other cases it may even be reinforced.

If two ring systems are involved in the resonance, the destabilizing effect of the dipole will be opposed if both rings are in a higher state of resonance stabilization in the dipolar than in the uncharged structure. Examples of this are provided by the merocyanine dyes, of which IX is a typical representative.

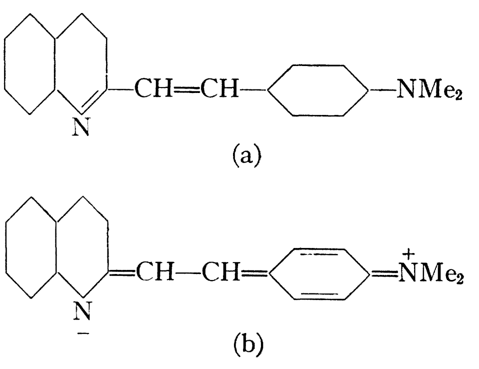


(IX)

In IXa the structure is uncharged, and its energy should be lower than that of IXb for this reason, but in the latter, each of the rings has one more double bond, and therefore higher stabilization, than the corresponding ring in (a), and the effect of the dipole is opposed. The degeneracy of the structures of dyes of this type is therefore frequently high, the dyes showing small deviations and high dipole moments.[4f]

It is interesting to note that whereas high additional double-bond stabilization of the nitrogen-containing nucleus corresponds to high basicity, high additional double-bond stabilization of the oxygen-containing nucleus corresponds to high acidity, so that the merocyanines that show small deviations are those in which a strongly basic nucleus is combined with one that is strongly acidic.

The compound represented by X is of quite a different type. Here resonance may be supposed to exist between the extreme structures (a) and (b), but now (a), which is more stable because it is a neutral structure, is also the more stable because both rings are in a more highly stabilized state than in (b). The resonance-inhibiting factors reinforce each other, therefore, and there is a relatively small participation of structure (b) which accounts for the low dipole moment of the compound.[4c] Also, the low degree of degeneracy of the extreme structures is in accord with the short wave-length absorption.



(X)

The compound XI is similar to X in that both rings are in the more highly stabilized state in the uncharged structure (a). Here again, then, there is absorption at relatively short wave-length.[17, 4c]

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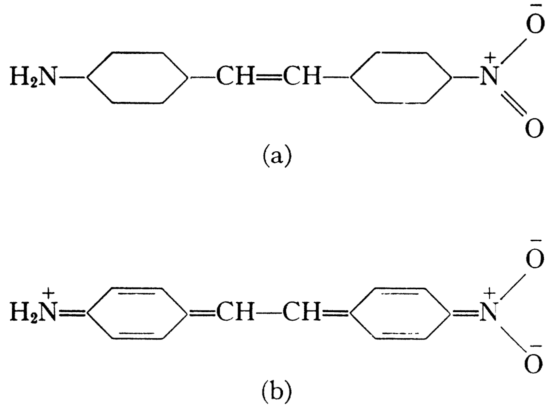
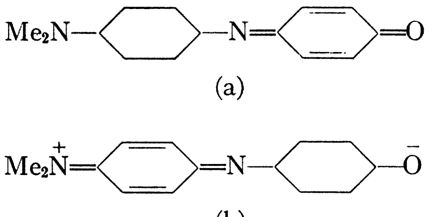
[17] M. Calvin and R. E. Buckles, J. Am. Chem. Soc. **62**, 3324 (1940).



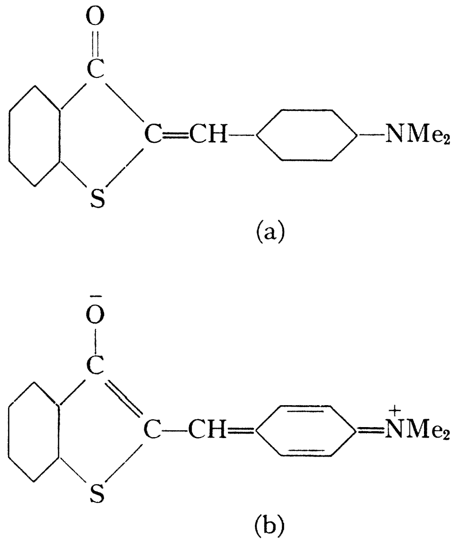
(XI)

Phenol Blue (XII) belongs to a class that is intermediate between those to which IX and X belong. In this compound one benzene ring is the more highly stabilized in (a) and the other in (b), so that the effect of the dipole is neither opposed nor reinforced by the additional double-bond stabilization factor.[4d]



(XII)

The benzylidene derivative XIII is similar in this respect, but here the two rings involved are different. The benzene ring is more highly stabilized in (a), and the thianaphthenone ring in (b), but the additional double-bond stabilizations of these rings will not be the same, that of benzene undoubtedly being the greater, and so there will be a net effect favoring (a), and this structure will also be favored because of the dipole effect. The degeneracy of the structures XIII (a) and (b) will therefore be rather strongly reduced, and compounds of this class as a rule show considerable deviations of λ_{max}.[4f]



(XIII)

Many other examples could be cited to show the interplay of these two factors, but it is hoped to present a fuller treatment of this subject elsewhere.

17. METHOD OF ARRIVING AT λ_{max} CALCULATED

In the foregoing sections the value of λ_{max} calcd. for an unsymmetrical dye has been taken as the arithmetic mean of the values of λ_{max} of the corresponding symmetrical dyes. It might reasonably be maintained that use of $\tilde{\nu}_{max}$ calc., i.e., the arithmetic mean of the corresponding wave numbers, would be preferable, and the deviations have been calculated on this basis also, but the agreement between the two methods of determining the order of basicity of heterocyclic nuclei is definitely poorer using this second method.

These two methods of comparison are shown in Fig. 20. Column I uses λ_{max} calculated arithmetically and column IV $\tilde{\nu}_{max}$ calculated arithmetically, and it is seen that there is much less intersection of lines in I so that by this purely empirical test I is preferable. In column II, $\tilde{\nu}_{max}$ is calculated harmonically, i.e., these values

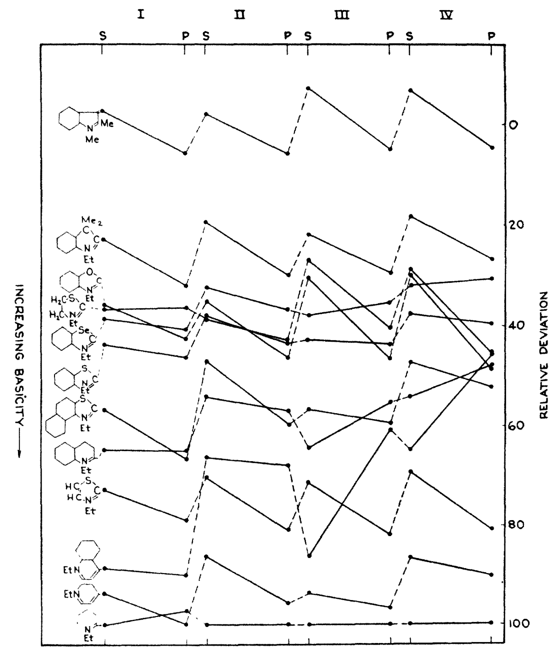


FIG. 20. Comparison of the relative basicities of heterocyclic nuclei by comparing the deviations in two series of dyes, *S*, the *p*-dimethyl-aminostyryl series (cf. Fig. 12) and *P*, the unsymmetrical 2, 5-dimethyl-1-phenylpyrrolocyanines (cf. Fig. 5). In column I deviations are obtained from $\lambda_{\max}$ calc. arithmetically; in column II, deviations are obtained by using $\tilde{\nu}_{\max}$ calc. harmonically; in column III deviations are obtained by using $\lambda_{\max}$ calc. harmonically; in column IV deviations are obtained from $\tilde{\nu}_{\max}$ calculated arithmetically.

of $\tilde{\nu}_{\max}$ correspond exactly to those of $\lambda_{\max}$ calculated arithmetically, and in column III, $\lambda_{\max}$ is calculated harmonically.

It so happens that in the comparisons involving the unsymmetrical pyrrolo-cyanines (Fig. 5), the parent dye that is common to all the comparisons, the symmetrical pyrrolo-cyanine itself, absorbs at shorter wave-length than all except one of the other symmetrical parent dyes (the thiazolino-carbocyanine; third nucleus from top of Fig. 5). In this one case, the two parent dyes absorb very close together so that it is virtually immaterial which mode of calculating the mean value is used, and the deviation will remain at much the same value by all methods.

In the styryl series, on the other hand (Fig. 12), the invariable parent dye, Michler's hydrol blue, absorbs at *longer* wave-length than all the other parent symmetrical dyes with but one exception (the 4,4′-carbocyanine; third row from the bottom). In the comparison involving the thiazoline nucleus, however (fourth row from top), the two parent dyes now absorb very far apart, so that it matters a great deal which mode of calculation is employed, and the deviation is strongly reduced if $\lambda_{\max}$ is calculated harmonically rather than arithmetically, or if $\tilde{\nu}_{\max}$ is calculated arithmetically rather than harmonically. This accounts for the pronounced upward slope from right to left of the line representing the thiazoline nucleus in column IV of Fig. 20. The marked upward slope from left to right of the line representing the 4-quinoline nucleus in the same column is explained similarly.

It is interesting that $\lambda_{\max}$ calculated arithmetically appears to be more consistent with the facts than $\tilde{\nu}_{\max}$ calculated arithmetically, and it is to be hoped that a theoretical justification will ultimately be found for this, although one is lacking at present.

It might also be mentioned that use of $\lambda_{\max}$ calculated arithmetically rather than harmonically has the advantage of eliminating a number of deviations of negative sign. Thus the deviations of the vinylene homologous series I of Fig. 4 are -95, -70, and -55A for $n=1$, 2, and 3, respectively, when $\lambda_{\max}$ is calculated harmonically,[4e] but the figures become 45, 15, and 35A, respectively, by the alternative method.