tively, which may be taken as the values of the electrostriction of the solvent.

The limiting slopes of the partial molal heat capacities and volumes for α-alanine and β-alanine have been calculated from a modification of the Fuoss theory of dipolar solute interaction. Observed and calculated slopes agree within a factor of about 10 for the heat capacities and slightly better for the volumes.

The differences in the heat capacities and volumes at infinite dilution have been estimated from an electrostatic standpoint. The calculated values are approximately one-third of the experimental.

An article that will appear shortly in the *Chemical Reviews* will discuss the theoretical considerations in detail.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 15, 1941

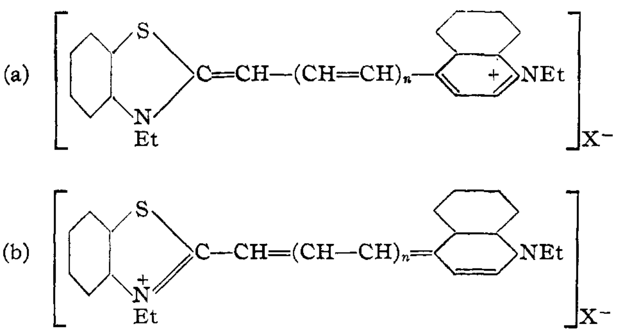
[COMMUNICATION NO. 833 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. V.[1] The Absorption of Unsymmetrical Cyanines. Resonance as a Basis for a Classification of Dyes

BY L. G. S. BROOKER, G. H. KEYES AND W. W. WILLIAMS

For a number of years it has been accepted as axiomatic that the absorption band of an unsymmetrical cyanine should be intermediate in position between those of the parent symmetrical dyes. Thus Mills and Odams[2] considered the structure of 2,4′-carbocyanine to be confirmed by the fact that it absorbed almost exactly midway between 2,2′- and 4,4′-carbocyanine.

From the resonance standpoint, however, this relationship would not necessarily be expected. An unsymmetrical dye differs from a symmetrical dye in the important respect that the two extreme resonance configurations of the former are not identical. Thus, for example, 1′,3-diethylthia-4′-cyanine iodide (I, $n = 0$), which has two different nuclei, is represented by the two distinct configurations: (a) in which the 4-quinoline nitrogen is quaternary and (b) in which the benzothiazole nitrogen is quaternary. If now the basicities of these two rings are not identical, or, more precisely, if the relative stabilities of the N^{III} and N^{IV} forms of the benzothiazole and 4-quinoline rings differ, (a) and (b) would not be expected to have the same energy, since that configuration should be the more stable in which the nitrogen of the more basic nucleus is quaternary. The degeneracy of the configurations should therefore be incomplete, a condition which is obviously impossible with a symmetrical dye.



I

It has been suggested that if it happens that the two nuclei of an unsymmetrical cyanine have the same basicity, so that the two extreme resonance configurations are of equal energy, then absorption should occur at a point midway between the absorptions of the parent symmetrical dyes. If, however, the nuclei are not equally basic, so that the configurations do not have the same energy, then absorption should occur at a shorter wave length than this intermediate position.[1]

Since a rather wide variety of nuclei have been combined in unsymmetrical cyanines, it might have been expected that this latter situation would be commonly encountered, but, in actual fact, although many dozens of these dyes have been examined in recent years,[3] agreement between the found and calculated values of $\lambda_{\max.}$ is reasonably good, and no consistent tendency for absorption to occur at significantly shorter wave length than the calculated, has been reported.

It would seem that in these unsymmetrical dyes the nuclei that were combined together were not sufficiently different in basicity for deviations to appear, the highly degenerate cyanines not being as sensitive to small changes in structure as

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[1] Part IV, THIS JOURNAL, **63**, 3214 (1941).

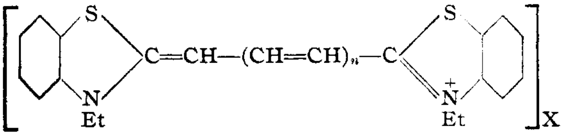
[2] Mills and Odams, *J. Chem. Soc.*, **125**, 1913 (1924).

[3] (a) Beilenson, Fisher and Hamer, *Proc. Roy. Soc.* (London), **A163**, 138 (1937); (b) Yoshimura and Sakurai, *Bull. Inst. Phys. and Chem. Res., Tokyo*, **16**, 1270 (1937).

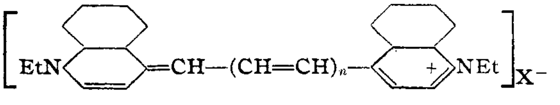
less highly degenerate dyes.[4] However, where the two nuclei of an unsymmetrical cyanine differ strongly in basicity, the two resonance configurations will differ in energy sufficiently for the absorption to be hypsochromically affected. Two examples of this have been reported, the feebly basic indole ring being combined in one instance with the much more strongly basic benzothiazole nucleus and in the other with the 4-quinoline nucleus, and the deviation was considerable in each case.[5]

In the present work we have examined additional examples of unsymmetrical cyanines in which the nuclei differ in basicity in varying degrees, and have also studied the effect produced by increasing the length of the conjugated chain in such dyes.

In the first set of comparisons the three unsymmetrical dyes (I)(n = 0, 1 and 2) were compared with the related symmetrical thiacyanines (II) and 4,4′-cyanines (III) For all three values of n the agreement between the observed values of $\lambda_{\max.}$ and those calculated as the arithmetic means of the values of $\lambda_{\max.}$ of II and III is very close (Fig. 1). Using wave numbers, however, the agreement between $\tilde{\nu}_{\max.\ \text{obsd.}}$ and $\tilde{\nu}_{\max.\ \text{calcd.}}$ as the arithmetic mean of the values of $\tilde{\nu}_{\max.}$ of the symmetrical dyes is not so good, the observed values actually lying at somewhat shorter wave numbers (*i. e.*, longer wave lengths) than those calculated, so that the deviations are in the opposite direction to those anticipated. For n = 0, 1 and 2 the deviations may, therefore, be expressed as -380, -190, -100 cm.$^{-1}$, respectively, these values corresponding to -95, -70 and -55 Å., respectively. Nevertheless, the mode of comparison using the arithmetic mean of the wave numbers (which corresponds to the harmonic mean of the wave lengths) is preferable from an energy standpoint, and is used exclusively throughout the remainder of this paper; in any event, these deviations are not very great.



II



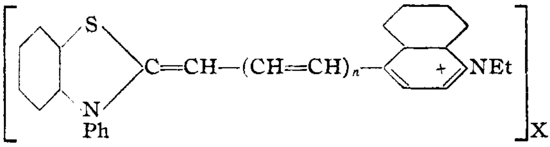
III

From these results it is possible to follow one of two lines of argument. It may be assumed, from the lack of deviations in the direction of shorter wave length, that the resonance structures in I are almost, although possibly not completely, degenerate, thus presupposing something approaching a linear relationship between non-degeneracy and deviation. Or, it may be assumed that the non-degeneracy of I is appreciable, but that deviation and non-degeneracy are connected by something of the nature of an exponential relationship, so that a departure from complete degeneracy by a significant, although not large, amount will produce but an insignificant deviation. A closer analysis of this problem, however, must be carried out using methods other than those at the command of the present writers.

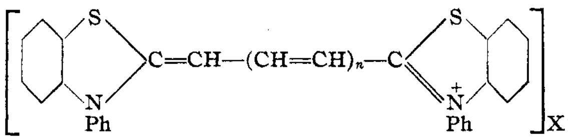
The optical data for the dyes dealt with above and others described in this paper are given in Table I.

Of the nuclei present in I, that derived from benzothiazole is doubtless the less basic. If this basicity were to be reduced still further, the imbalance of basicity might be increased to the point where significant deviations in the expected direction were produced.

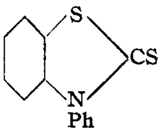
The absorptions of the vinylene homologs IV (n = 0, 1, 2) were therefore compared with those of the related parent dyes V (n = 0, 1, 2) and III (n = 0, 1, 2). In the preparation of dyes IV and V 2-methyl-3-phenylbenzothiazo-



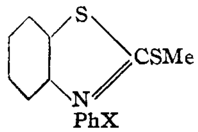
IV



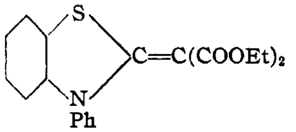
V



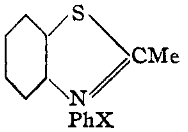
VI



VII



VIII



IX

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[4] Brooker and Sprague, This Journal, **63**, 3203 (1941).

[5] Brooker, Sprague, Smyth and Lewis, *ibid.*, **62**, 1116 (1940).

TABLE I

Dye	Anion	Solvent	A	B	C	D	E		Deviations,	
			$\lambda_{max.}$ obsd., Å.	$\lambda_{max.}$ calcd. as arithmetic mean, Å.	$\lambda_{max.}$ calcd. as harmonic mean, Å.	$\tilde{\nu}_{max.}$ obsd., cm.$^{-1}$	$\tilde{\nu}_{max.}$ calcd., cm.$^{-1}$	B − A, Å.	C − A, Å.	D − E, cm.$^{-1}$
I (n = 0)	I^-	MeOH	5025	5070	4930	19900	20280	45	−95	−380
I (n = 1)	I^-	MeOH	6300	6315	6230	15870	16060	15	−70	−190
I (n = 2)	I^-	MeOH	7280	7315	7225	13740	13840	35	−55	−100
II (n = 0)	I^-	MeOH	4230	..	..	23640	...	..	..	...
II (n = 1)	I^-	MeOH	5575	..	..	17930	...	..	..	...
		$MeNO_2$	5565	..	..	17970	...	..	..	...
II (n = 2)	I^-	MeOH	6500	..	..	15380	...	..	..	...
		$MeNO_2$	6540	..	..	15290	..	..	..	...
III (n = 0)	I^-	MeOH	5910	..	..	16920	...	..	..	...
III (n = 1)	I^-	MeOH	7050	..	..	14180	...	..	..	...
III (n = 2)	I^-	MeOH	8130	..	..	12300	...	..	..	...
IV (n = 0)	I^-	MeOH	5030	5100	4970	19880	20120	70	−60	−240
IV (n = 1)	ClO_4^-	MeOH	6265	6350	6270	15960	15950	85	0	10
IV (n = 2)	I^-	MeOH	7200	7380	7300	13890	13700	180	100	190
V (n = 0)	I^-	MeOH	4290	..	..	23310	...	..	..	...
V (n = 1)	I^-	MeOH	5645	..	..	17710	...	..	..	...
		$MeNO_2$	5655	..	..	17680	...	..	..	...
V (n = 2)	I^-	MeOH	6625	..	..	15100	...	..	..	...
		$MeNO_2$	6650	..	..	15040	...	..	..	...
X (n = 0)	ClO_4^-	MeOH	4985	..	..	20060	...	..	..	...
X (n = 1)	ClO_4^-	MeOH	6150	6375	6300	16260	15870	225	150	390
X (n = 2)	ClO_4^-	MeOH	6810	7390	7310	14680	13680	580	500	1000
XI (n = 1)	I^-	MeOH	5695	..	..	17550	...	..	..	...
		$MeNO_2$	5690	..	..	17570	...	..	..	...
XI (n = 2)	ClO_4^-	MeOH	6645	..	..	15050	...	..	..	...
		$MeNO_2$	6700	..	..	14930	...	..	..	...
XII (n = 0)	I^-	MeOH	5045	5205	5105	19820	19580	160	60	240
XII (n = 1)	I^-	MeOH	6170	6445	6385	16210	15660	275	215	550
XII (n = 2)	I^-	MeOH	6800	7475	7420	14710	13480	675	620	1230
XIII (n = 0)	Cl^-	MeOH	4495	..	..	22240	...	..	..	...
XIII (n = 1)	Cl^-	MeOH	5835	..	..	17140	...	..	..	...
		$MeNO_2$	5900	..	..	16950	...	..	..	...
XIII (n = 2)	I^-	MeOH	6820	..	..	14660	...	..	..	...
		$MeNO_2$	6905	..	..	14480	...	..	..	...
XIV (n = 1)	I^-	$MeNO_2$	5280	5835	5825	18940	17180	555	545	1760
XIV (n = 2)	I^-	$MeNO_2$	5700	6775	6765	17540	14780	1075	1065	2760
XV (n = 0)	ClO_4^-	$MeNO_2$	6100	..	..	16390	...	..	..	...
XV (n = 1)	ClO_4^-	$MeNO_2$	7010	..	..	14270	...	..	..	...
XVI (n = 1)	Cl^-	$MeNO_2$	5735	6000	6000	17430	16670	265	265	760
XVI (n = 2)	I^-	$MeNO_2$	6510	6960	6955	15360	14380	450	445	980
XIV (Ph in place of Et)										
(n = 1)	ClO_4^-	$MeNO_2$	5465	5880	5870	18300	17040	415	405	1260
(n = 2)	I^-	$MeNO_2$	6020	6830	6820	16610	14660	810	800	1950
XIV (o-nitrophenyl in place of Et)										
(n = 1)	ClO_4^-	$MeNO_2$	5605	5895	5890	17840	16980	290	285	860
(n = 2)	ClO_4^-	$MeNO_2$	6390	6855	6850	15650	14600	465	460	1050
XVII	I^-	MeOH	5780	5810	5800	17300	17250	30	20	50
XVIII	I^-	MeOH	5800	5940	5935	17240	16850	140	135	390
XIX	I^-	MeOH	6000	5950	5925	16670	16880	−50	−75	−210
XX	Cl^-	MeOH	6320	..	..	15820	...	..	..	...
XX (H in place of 6-NO_2)										
	I^-	MeOH	6040	..	..	16560	...	..	..	...

lium iodide (IX) served as the starting point, this salt being prepared by a synthesis of a new type.

The thione VI was obtained from 3-phenyl-2-(3)-benzothiazolone[6] by the action of phosphorus pentasulfide in boiling xylene, and addition of

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[6] Passing, *J. prakt. Chem.*, **153**, 1 (1939).

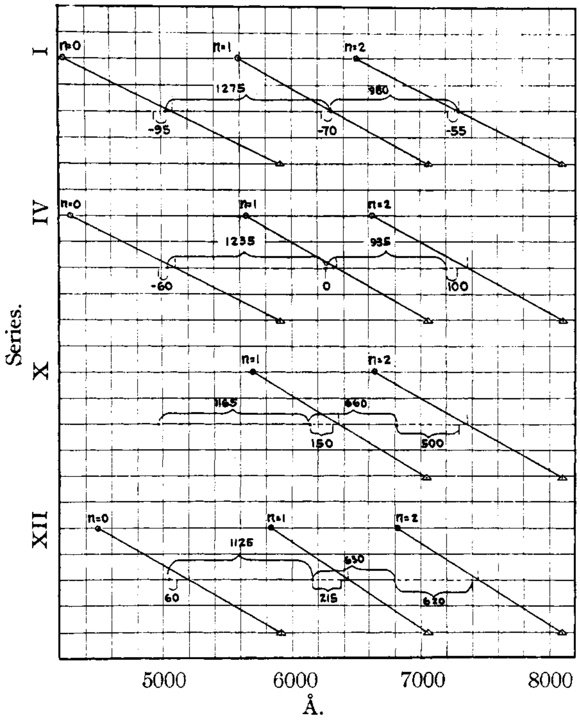


Fig. 1.—Absorption maxima (Å.) of cyanine dyes in methyl alcohol: ●, unsymmetrical cyanines of series I, IV, X and XII; ⊙, related symmetrical thiacyanines; △, related symmetrical 4,4′-cyanines; |, harmonic mean between ⊙ and △; ¦, arithmetic mean between ⊙ and △; ---, deviation, also indicated by ⌣; ⌢ indicates vinylene shift.

methyl *p*-toluenesulfonate yielded VII. In VII the methylmercapto group was very reactive, and condensation occurred with ethyl malonate under the influence of triethylamine to give VIII. This underwent hydrolysis with hydrochloric acid, followed by spontaneous decarboxylation, to give IX, and the salt underwent condensation with the appropriate intermediates to give the dyes.

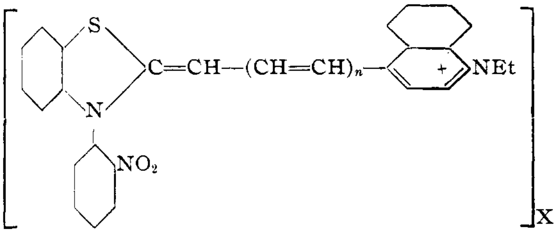
Replacement of the ethyl groups attached to the benzothiazole nuclei in I and II by phenyl, to give series IV and V, respectively, must strongly reduce the basicity of the benzothiazole nuclei, for if the N-ethylbenzothiazole nucleus is regarded as derived from ethylaniline, then the N-phenylbenzothiazole nucleus must be regarded as derived from the considerably less basic diphenylamine.

The effect of this replacement in the symmetrical dyes is to deepen the color somewhat in every case, the bathochromic shifts being 60, 70 and 125 Å. for $n = 0$, 1 and 2, respectively. In the unsymmetrical dyes (IV), the deviations are in full accord with the supposition that in these dyes the difference of basicity between the nuclei is greater than in I. For $n = 0$ the deviation is -60 Å., a reduction from the value of -95 Å. for I ($n = 0$). For $n = 1$ the deviation is zero compared with -70 Å., but for $n = 2$ it is 100 Å. compared with the value of -55 Å. for I (Fig. 1). The effect on the deviation, therefore, increases with n.

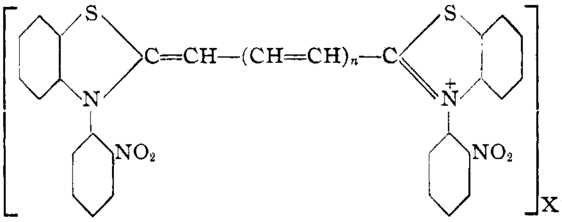
Similar dyes (X and XI) were next prepared in which the group attached to the benzothiazole nitrogen was *o*-nitrophenyl, the necessary 2-methyl-3-*o*-nitrophenylbenzothiazolium iodide for which was described by Evans and Smiles.[7] The absorptions of the symmetrical dyes lie at slightly longer wave lengths than those of the dyes V, the bathochromic shifts being 50 and 20 Å. for $n = 1$ and 2, respectively, but a comparison of the two series where $n = 0$ was not possible because all attempts to prepare XI ($n = 0$) by the acetic anhydride-amyl nitrite method[8] were unsuccessful.

In the unsymmetrical dyes X, the *o*-nitrophenyl group will render the benzothiazole nucleus still less basic than that in IV, and will thus further increase the imbalance in basicity between the heterocyclic nuclei. The deviations for this set of dyes would therefore be expected to be greater than those of IV, and this actually is the case. For $n = 1$ the deviation of X is 150 Å. and this is increased to 500 Å. where $n = 2$ (Fig. 1).

This increase in deviation with increase in the value of n is characteristic and appears to be a general phenomenon, further examples of which are provided in the present paper. The result of this effect is that the vinylene shifts tend to decrease on ascending the series, and thus the shift in series



X



XI

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[7] Evans and Smiles, *J. Chem. Soc.*, 1263 (1935).

[8] Fisher and Hamer, *ibid.*, 2502 (1930).

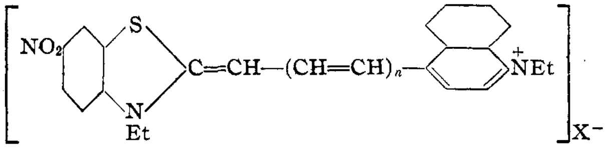
X, from $n = 1$ to $n = 2$, is only 660 Å., whereas it is 935 Å. between the corresponding members of series IV.

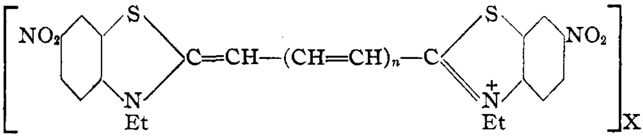
The successive vinylene shifts in series II are 1345 Å. ($n = 0$ to $n = 1$), 925 Å. ($n = 1$ to $n = 2$) and 1080 Å. ($n = 2$ to $n = 3$),[5] the last two values being roughly constant at about 1000 Å., although the first value is appreciably larger than this value. Nevertheless, as a general rule, the vinylene shifts between successive maxima in symmetrical cyanine series are roughly constant at about 1000 Å., and this figure shows no sign of decreasing significantly for the longer chain lengths.[9] With this property in mind such series may be termed "non-convergent."[10]

Series I is also practically non-convergent, the second (and more significant) vinylene shift being 980 Å. ($n = 1$ to $n = 2$), but in IV the second vinylene shift is appreciably lower at 935 Å. and in X the figure is 660 Å. and the maxima of these dyes converge strongly. It therefore appears that non-convergent cyanines are essentially those the members of which are each represented by two resonance configurations of the same or very nearly the same energy, while the converging series are those, the members of which are represented by resonance configurations that differ more or less widely in energy. Since the deviation for a given chain length and the degree of convergence increase in the order I, IV, X, it may be concluded that *the greater the difference of basicity between the two nuclei of an unsymmetrical cyanine, and therefore the greater the difference in energy between the two extreme resonance configurations, the greater will be the deviation for a given chain length and the greater the degree of convergence of the series.*

Other series showing strong convergence that have been described in earlier papers include the anhydronium bases (III) in Part I,[5] the acetanilidovinyl compounds (II) and the anils (VII) of Part II,[11] and the styryl bases (I and X), and to a less extent their alkiodides (II and XI, respectively) of Part III.[4]

If a nitro group is introduced into the 6-position of the benzothiazole nuclei of the dyes I, the series XII (n = 0, 1, 2) results, and in a further set of comparisons the absorptions of these were compared with those of the related parent dyes XIII (n = 0, 1, 2) and III (n = 0, 1, 2).


XII


XIII

The effect of the nitro substituent will be to reduce strongly the basicity of the benzothiazole nuclei, but in each of the symmetrical dyes XIII, the two benzothiazole nitrogen atoms, although less basic than those in II, are still identical, and there is complete degeneracy of the structures. The effect of introducing the two nitro groups into a dye II, giving a dye XIII, is to deepen the color in every case, the amount of the shift being roughly constant and being 270 Å. for $n = 0$, 260 Å. for $n = 1$ and 320 Å. for $n = 2$. Expressed in wave numbers, however, the shifts decrease steadily from $n = 0$ to $n = 2$ (Table I).

The dyes XII show deviations that are even greater than those shown by X, the figures for XII being 60, 215 and 620 Å. for n = 0, 1 and 2, respectively. The final deviation is actually so great that the dye absorbs at shorter wave length than the lighter of the parent dyes, XIII ($n = 3$).

From the relations existing between the series I, IV and X, it seems safe to conclude that introduction of the 6-nitro group is the most effective method of lowering the basicity of the benzothiazole nucleus of the three methods adopted.

The different degrees of convergence presented by the four unsymmetrical series suggest that there may be every gradation between a typically non-convergent series such as a set of vinylene homologous symmetrical cyanines, and a strongly convergent series such as XII. A further increase in the imbalance of basicity between the heterocyclic nuclei in XII would be expected to give rise to an even greater degree of convergence.

It has been shown that in a dye of the type of

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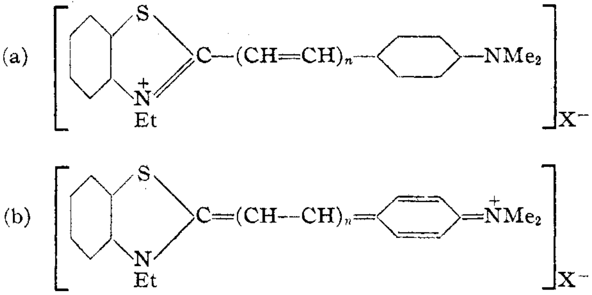
(9) Fisher and Hamer, *Proc. Roy. Soc.* (London), **A154**, 703 (1936).

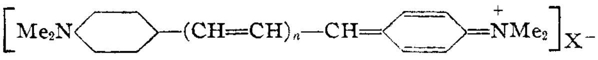
(10) If the wave numbers of the absorption maxima of a non-converging series are represented by $\nu_1, \nu_2, \nu_3, \nu_4, \ldots$, where $\nu_1 < \nu_2 < \nu_3 < \nu_4$, then the wave lengths are represented by $1/\nu_1, 1/\nu_2, 1/\nu_3, 1/\nu_4, \ldots$, and non-convergence is expressed by $1/\nu_2 - 1/\nu_1 = 1/\nu_3 - 1/\nu_2 = 1/\nu_4 - 1/\nu_3$ or $\nu_1 - \nu_2/\nu_1\nu_2 = \nu_2 - \nu_3/\nu_2\nu_3 = \nu_3 - \nu_4/\nu_3\nu_4$. If adjacent differences are considered, then $\nu_1 - \nu_2/\nu_1 = \nu_2 - \nu_3/\nu_3$ and similarly $\nu_2 - \nu_3/\nu_2 = \nu_3 - \nu_4/\nu_4$ and so on. Thus, the difference between the first and second wave numbers, divided by the first, is equal to the difference between the second and third, divided by the third.

(11) Brooker, White, Keyes, Smyth and Oesper, THIS JOURNAL, **63**, 3129 (1941).

2-*p*-dimethylaminostyrylbenzothiazole ethiodide (XIV, $n = 1$), the benzene ring lying in the conjugated chain lessens the degeneracy of the configurations by favoring that in which it is in the benzenoid state, XIVa. Reduction of the basicity of the heterocyclic nucleus, however, was shown to favor the alternative configuration XIVb, thereby neutralizing the effect of the benzene ring to a corresponding extent. The net degeneracy of the configurations is thereby increased, and this results in a lowering of the deviation between $\lambda_{\max}$ obsd. and that calculated from the carbocyanine and Michler's hydrol blue (XV, $n = 0$).[4]

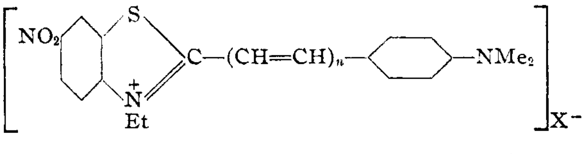


XIV



XV

It follows that if the ethyl group in XIV ($n = 1$) were to be replaced by phenyl and then by *o*-nitrophenyl, the resulting dyes would be expected to show progressively smaller deviations. Furthermore, since the introduction of a 6-nitro group into the benzothiazole ring was found to be still more effective in reducing the basicity of the benzothiazole nucleus, the 6-nitro dye, XVI ($n = 1$), would be expected to show the lowest deviation of all four styryl dyes.



XVI

These predictions have been realized. Whereas XIV ($n = 1$) shows a deviation of 545 Å., replacement of N-ethyl by phenyl results in the deviation being reduced to 405 Å. and that for the *o*-nitrophenyl compound is 285 Å. Finally, the deviation for XVI ($n = 1$) is 265 Å. (*cf.* Table I and Fig. 2).

Increasing the length of the vinylene chain in these styryl dyes gives greater deviations, thus illustrating the general rule that when a member of a vinylene homologous series shows a deviation, that deviation is increased in the next higher vinylene homolog.

Where $n = 2$, the dye XIV may be regarded as the structural cross between the thiadicarbocyanine (II, $n = 2$) and the next higher vinylene homolog of Michler's hydrol blue[12] (XV, $n = 1$) and the deviation amounts to 1065 Å. The deviations are reduced in the same order as before, for that for the phenyl dye is 800 Å., that for the *o*-nitrophenyl derivative is 460 Å. and that for the 6-nitro derivative (XVI, $n = 2$) is 445 Å.

Consistent, too, with its having the greatest deviation of the four styryl dyes, and therefore being the least degenerate, the ethyl derivative, XIV, shows the smallest vinylene shift (420 Å.) when n is increased from 1 to 2, and as the net degeneracy of the dyes is increased by lowering the basicity of the benzothiazole ring, so the vinylene shift is, in general, increased. Thus, for the corresponding N-phenyl dyes the vinylene shift is 555 Å., and for the *o*-nitrophenyl dyes it is 785 Å. The shift for the 6-nitro dyes, XVI, should, according to the argument, be still greater, but actually it is slightly lower (775 Å.). However, the deviations for the 6-nitro dyes are only slightly lower than those for the *o*-nitrophenyl dyes, and although the shift between the former might therefore be expected to be slightly more than 785 Å. rather than less, it is not felt that this exception constitutes a serious challenge to the views expressed.

As the degeneracy of an unsymmetrical cyanine I is reduced step by step in the series of replacements leading to IV, X and XII, so the molecule should become increasingly sensitive to a given small chemical change, according to the general rule already given.[4] On the other hand, the same series of replacements in the styryl dyes, XIV, gives increasing degeneracy of the dye molecule, and the rule requires that in this case the sensitivity to a small chemical change should progressively decrease.

The figures are in agreement with this hypothesis. While replacement of an ethyl group in I ($n = 2$) by a phenyl group causes an increase of deviation of 155 Å., the same replacement carried out in XIV ($n = 2$), reduces the deviation by 265 Å., so that of the two dyes undergoing replacement, the less degenerate styryl is the more responsive to the structural change. At the other

[12] König and Seifert, *Ber.*, **67**, 2112 (1934).

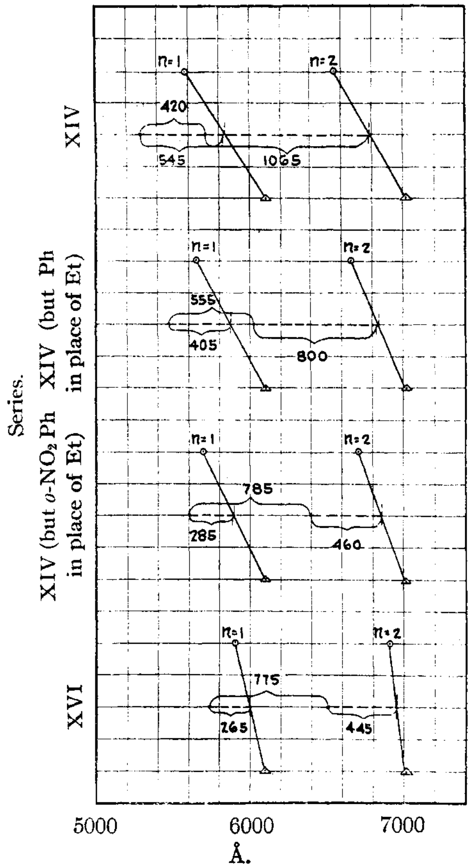


Fig. 2.—Absorption maxima (Å.) in nitromethane: ●, dyes XIV, those with phenyl and 2-nitrophenyl in place of ethyl in XIV, XVI; ⊙, related symmetrical thiacyanines; ◬, XV; |, harmonic mean between ⊙ and ◬; ¦, arithmetic mean; ---, deviation, also indicated by ⏟; ⏞ indicates vinylene shifts.

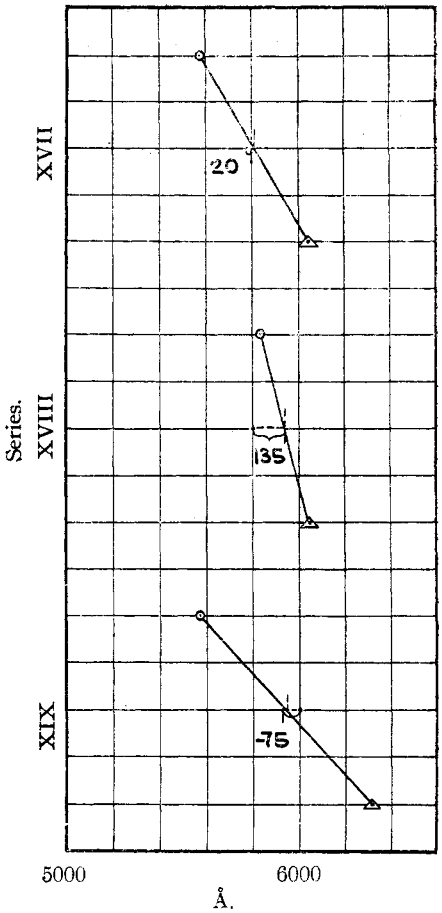


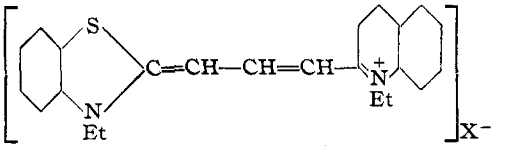
Fig. 3.—Absorption maxima (Å.) in methyl alcohol: ● unsymmetrical dyes XVII, XVIII and XIX; ⊙, related thiacarbocyanines; ◬, related 2,2′-carbocyanines; |, harmonic mean between ⊙ and ◬; ¦, arithmetic mean; ---, deviation, also indicated by ⏟.

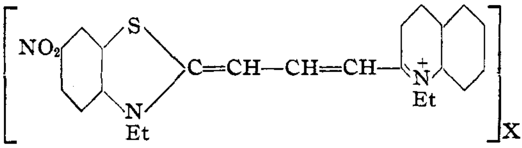
end of the scale, however, passage from the cyanine X ($n = 2$) to XII ($n = 2$) increases the deviation by 120 Å., whereas in the styryl series passage from the *o*-nitrophenyl derivative to XVI ($n = 2$) decreases the deviation by only 15 Å., and here the cyanine is clearly the more sensitive.

It should, perhaps, be pointed out that the absorption bands of the dyes under discussion, as determined in solution for the present paper, are the resultants of a number of different effects which undoubtedly vary somewhat from dye to dye, so that in any dye that wave length which might be considered characteristic of the electronic transition between the energy levels resulting from the resonance interaction of the limiting configurations may differ from $\lambda_{\text{max.}}$ as actually determined, by a greater or lesser amount. Even under these conditions, a factor which strongly influences the absorption will not be difficult to detect, but if an effect sought for is relatively small, then it will be the more readily obscured by secondary factors.

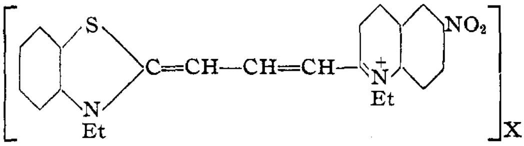
One further relationship is sufficiently striking to be given special mention. Whereas introduction of the 6-nitro group into the thia-4′-dicarbocyanine (I, $n = 2$) so reduces the degeneracy of the configurations that the absorption maximum is shifted from 7280 to 6800 Å., *i. e.*, there is a *hypsochromic* shift of 480 Å., introduction of the 6-nitro group into XIV ($n = 2$), giving XVI ($n = 2$), increases the total degeneracy of the configurations so that the absorption maximum is shifted from 5700 to 6510 Å., *i. e.*, a *bathochromic* shift of 810 Å. Thus the same chemical change carried out on the two unsymmetrical dyes produces enormously different results which are, as has been shown, capable of very simple interpretation.

The 6-nitro group having been found very effective in reducing the basicity of the benzothiazole nucleus, a comparison was made between the thia-2′-carbocyanine (XVII) and its 6-nitro derivative (XVIII). It has already been shown that XVII shows practically no deviation,[4] but in XVIII the balance of basicity between the two nuclei is upset and the dye shows a deviation of 135 Å. (Fig. 3).

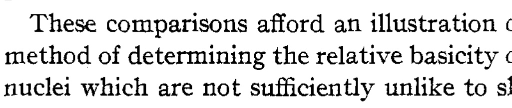

XVII


XVIII

It is interesting to compare XVIII with the isomeric dye XIX which has the nitro substituent in the quinoline nucleus.


XIX

On the assumption that the benzothiazole nucleus is initially less basic than quinoline, all the negativity of the nitro group in XVIII is available for lowering the basicity of the benzothiazole ring still further. On the other hand, some of the negativity of the nitro group in XIX must be expended in bringing the two nuclei to the same level of basicity and only the surplus negativity, if any, is available for rendering the quinoline ring less basic than benzothiazole. The difference of basicity between the rings should therefore be less in XIX than in XVIII, and the former should show less deviation. This is actually the case, for XIX absorbs with $\lambda_{\text{max.}}$ 6000 Å. and that calculated from II ($n = 1$) and XX is 5925 Å., the deviation being -75 Å. (Fig. 3).


XX

These comparisons afford an illustration of one method of determining the relative basicity of two nuclei which are not sufficiently unlike to show a significant deviation when combined directly, as in XVII. If a strongly negative substituent is introduced first into one nucleus and then into the other (*e. g.*, XVIII and XIX) that dye will show the greater deviation in which the substituent is introduced into the less basic nucleus.

Although the conclusions reached in this paper have emerged from a study of unsymmetrical cyanines and of styryl types, it is felt that they are of general application.

The significance of a dye being a resonance hybrid was stressed by Bury[13] and his concept may now be extended and dyes further classified according to the difference in energy between the extreme resonance configurations.[14] At one end of the scale there will be such dyes as the symmetrical cyanines in which these configurations have the same energy, and at the other, dyes showing the maximum difference in energy between the configurations.

Since deviation, and the degree of convergence of the first few members of the series discussed in the present paper, are both symptomatic of the non-degeneracy of the configurations; the dyes would be arranged in the order I, IV, X, XII, XVI, XIV with respect to decreasing degeneracy, although possibly XII and XVI might be interchanged.

In all of these dyes, the degeneracy of the linkages in the conjugated chain in the sense $-(\overset{|}{C}=\overset{|}{C})_n-\overset{|}{C}= \longleftrightarrow =(\overset{|}{C}-\overset{|}{C})_n=\overset{|}{C}-$ is dependent to a greater or lesser extent on the participation of the auxochromic atoms, although other factors, such as that of an interposed benzene ring[4] also influence this mobility. In the absence of the conventional auxochromic atoms, however, the terminal atoms in the vinylene chain itself can take over their function as shown in XXI for the vinylene homologous dimethyl polyenes of Kuhn and Grundmann.[15] In these compounds the scheme

(a) $CH_3{}^+CH{-}(CH{=}CH)_n{-}{}^-CHCH_3$
(b) $CH_3CH{=}(CH{-}CH)_n{=}CHCH_3$ XXI
(c) $CH_3{}^-CH{-}(CH{=}CH)_n{-}{}^+CHCH_3$

XXIa (or c) ↔ XXIb provides a certain minimum degeneracy of the configurations, which will not be great because of the greatly superior stability of XXIb over the dipolar forms. Nevertheless, such series show definite although relatively small

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(13) Bury, This Journal, **57**, 2115 (1935).

(14) An account of this classification together with the results leading up to it was given at a colloquium held at the Kodak Research Laboratories in March, 1940, and was referred to by Sheppard, Lambert and Walker [*J. Chem. Phys.*, **9**, 105 (1941)]. In the meantime similar conclusions have been reached independently by Schwarzenbach [*Z. Elektrochem.*, **47**, 40 (1941)].

(15) Kuhn and Grundmann, *Ber.*, **71**, 442 (1938).

TABLE II

Compound	Reactants	g.	Medium, cc.	Refluxed, hrs.	Yield, %	Solvent, cc./g.		M. p., °C. dec.	Formula	Analyses, % Calcd.	Found
R2	R1	26	*m*-Xylene; 200	9	100, 71	EtOH	20	98–99[g]	$C_{13}H_9NS_2$	C, 64.13	64.33
	P_2S_5	25								H, 3.73	3.57
QS1	R2	12.2	...	4[a]	85,[b] —	...	..	176–177[g]	...	...	...
	R12	14.0									
R3	QS1	39.7	EtOH; 100	4.5	41, 34	EtOH	40	178–179[g]	$C_{20}H_{19}NO_4S$	C, 65.01	64.95
	R7	24.0								H, 5.19	5.14
	NEt_3	10.1									
QS2	R3	14.0	HCl (20%); 100	2	31,[c] 19	EtOH	20	209–210	$C_{14}H_{12}INS$	C, 47.57	47.35
										H, 3.43	3.45
QS3	QS2	7.0	Ac_2O; 25	0.5	45[b]	...	..	208–209	...	...	...
	R8	4.0									
R5[d]	R4	15.0	...	d	58, 53	AcOH	6	166[d,g]–167	$C_8H_6N_2O_2S$	N, 14.44	14.42
	HNO_3 (d. 1.49)	225								S, 16.51	16.38
QS6	R5	7.8	...	10[e]	56,[c] 31	H_2O	12	254–255	$C_{10}H_{11}IN_2O_2S$	I, 36.25	36.28
	R13	6.2									
QS7	QS6	21.3	EtOH; 650	15	72,[b] —	...	..	.....	...	...	...
	AgCl (freshly pptd.)	13.0									
QS14	QS10	45	...	0.25[f]	—, 82	MeOH	40	.....	...	...	...
	R8	30									
QS15	QS14	49	Ac_2O; 500	1	88[b]	...	..	.....	...	...	...
QS16	QS10	6.0	Ac_2O; 30	0.5	74, 26	EtOH	35	121–123	$C_{23}H_{23}IN_2O$	I, 27.00	27.27
	QS17	5.0									
QS11	R6	3.8	...	0.5[h]	34,[c] 18	MeOH	83	220–223	...	...	...
	R13	3.1									

[a] Heated at 100°. [b] Product washed with ether followed by acetone and used without further purification. [c] After conversion to iodide. [d] This base was prepared by Mylius [Dissertation, Berlin, p. 48 (1883)] by the action of acetyl chloride on 2-amino-5-nitrothiophenol; Mylius gives m. p. 175°. In the present method, nitration of R4 was carried out by mixing the reactants and allowing to stand at room temperature for two hours, followed by precipitation with water and ammonia. The structure was established by reducing the nitro group to amino, using sodium hydrosulfite, followed by conversion to the chloro derivative by Sandmeyer's method. This was identical (m. p. and mixed m. p.) with a specimen of authentic 6-chloro-2-methylbenzothiazole [Beilenson and Hamer, *J. Chem. Soc.*, 1225 (1936)]. [e] Heated in an oil-bath at 120–125°. [f] Fused in an oil-bath at 150–160° with constant stirring. [g] Melted without decomposition. [h] Heated in an oil-bath at 140–145°.

vinylene shifts, and it is possible that the convergence of a vinylene homologous series such as XII or XIV would reach a limit due to this effect.

The polyene hydrocarbons, then, may be regarded as a class of compounds showing a minimum degeneracy of the configurations due to the minimal participation of auxochromic atoms. They differ from the cyanines in several important respects. Thus the charged atoms in XXI which function as auxochromes, are separated by an even number of carbon atoms, whereas the chain linking the nitrogens in a cyanine is always uneven in number. Also, although XXIa and XXIc are identical, they differ from one another in the position of two electrons rather than one, and are each much less stable than the intermediate configuration XXIb, whereas the extreme configurations in a cyanine are much more stable than the intermediate carbonium configurations.

The present classification provides the key to one of the chief difficulties which, in the past, has attended attempts to correlate absorption with structure. Although there is at first sight an obvious similarity between the conjugated chains in the polyene and cyanine types, it is now seen that they present very different pictures from the resonance standpoint.

It is clearly possible to classify other dyes between these extreme types, and it is hoped to deal with this in later papers.

We wish to express our gratitude to Mr. E. E. Richardson and Dr. L. A. Jones and colleagues for the absorptions, to Dr. L. T. Hallett and colleagues for the microanalyses, and also to Dr. A. L. Sklar and Dr. G. Kornfeld for valuable discussions.

Experimental

All melting points are corrected.

Quaternary salts used are listed below:

QS1	2-Methylmercapto-3-phenylbenzothiazolium *p*-toluenesulfonate (VII)
QS2	2-Methyl-3-phenylbenzothiazolium iodide (IX)
QS3	2-(2-Acetanilidovinyl)-3-phenylbenzothiazolium iodide
QS4	2-Methyl-3-*o*-nitrophenylbenzothiazolium iodide
QS5	2-Methyl-3-*o*-nitrophenylbenzothiazolium perchlorate
QS6	2-Methyl-6-nitrobenzothiazole ethiodide
QS7	2-Methyl-6-nitrobenzothiazole ethochloride
QS8	Quinoline ethiodide
QS9	4-Iodoquinoline ethiodide

TABLE III

	Dye	Formula	Components,	g.	Medium,	cc.	Re-fluxed, min.	Yield, %	Solvent,	cc./g.	M. p., °C., dec.	Formula	Analyses, %	Calcd.	Found
D1	1′-Et-3-Ph-thia-4′-cy. iodide	IV, *n* = 0	QS1 QS10 NEt_3	2.15 1.5 0.5	EtOH	10	10	40, 32, 18[a]	EtOH	15	277–279	$C_{25}H_{21}IN_2S$	I,	24.92	25.18
D2	1′-Et-3-Ph-thia-4′-carbocy. perchlorate	IV, *n* = 1	QS3 QS10	1.0 0.6	C_5H_5N	10	10	60, 40, 35	EtOH	150	241–243	$C_{27}H_{23}ClN_2O_4S$ $+ C_2H_5OH$	C, H,	62.96 5.29	62.92 4.68
D3	1′-Et-3-Ph-thia-4′- dicarbocy. perchlorate	IV, *n* = 2	QS2 QS16 NEt_3	1.8 2.4 0.5	EtOH	15	8[b]	25, 13,[c] 8	MeOH	180	170–171	$C_{29}H_{25}ClN_2O_4S$ $+ CH_3OH$	C, H,	63.74 5.17	63.31 4.71
D4	1′-Et-3-*o*-nitro-Ph-thia-4′-cy. perchlorate	X, *n* = 0	QS5 QS8 KOH	1.9 4.3 0.9	EtOH	25	15	—, 19, 12	MeOH	150	284–286	$C_{25}H_{20}ClN_3O_6S$	C, H,	57.06 3.83	57.17 3.90
D5	1′-Et-3-*o*-nitro-Ph-thia-4′-carbocy. perchlorate	X, *n* = 1	QS5 QS15	0.75 0.9	C_5H_5N	15	10	54, 27, 18[a]	EtOH	150	223–225	$C_{27}H_{22}ClN_3O_6S$	S,	5.81	5.84
D6	1′-Et-3-*o*-nitro-Ph-thia-4′-dicarbocy. perchlorate	X, *n* = 2	QS5 QS16 NEt_3	1.9 2.4 0.5	EtOH	15	5	55, 22, 7[a]	MeOH	150	195–196	$C_{29}H_{24}ClN_3O_6S$	C, H,	60.24 4.19	60.10 4.22
D7	1′,3-DiEt-6-nitro-thia-4′-cy. iodide	XII, *n* = 0	QS7 QS9 NEt_3	2.6 4.1 2.0	EtOH	50	20	8, 3, 2	MeOH	1200	307–309	$C_{21}H_{20}IN_3O_2S$	I,	25.13	25.11
D8	1′,3-DiEt-6-nitro-thia-4′-carbocy. iodide	XII, *n* = 1	QS7 QS15	0.65 1.1	C_5H_5N	20	10	85, 62, 31	MeOH	1000	299–301	$C_{23}H_{22}IN_3O_2S$	I, S,	23.89 6.03	23.59 6.16
D9	1′,3-DiEt-6-nitro-thia-4′-dicarbocy. iodide	XII, *n* = 2	QS7 QS16 NEt_3	0.65 1.1 0.5	EtOH	50	5	23, 15, 11	MeOH	1000	218–220	$C_{25}H_{24}IN_3O_2S$	S,	5.75	5.72
D10	3,3′-DiPh-thiacy. iodide	V, *n* = 0	QS1 $CH_2(COOH)_2$[i]	2.0 1.0	C_5H_5N	10	45	64, 50, 36	EtOH	40	Above 315	$C_{27}H_{19}IN_2S_2$	C, H,	57.62 3.40	57.84 3.48
D11	3,3′-DiPh-thiacarbocy. iodide	V, *n* = 1	QS2 $CH(OEt)_3$	1.8 1.5	C_5H_5N	10	15	83, 76, 62	EtOH	50	276–277	$C_{29}H_{21}IN_2S_2$	I,	21.58	21.36
D12	3,3′-DiPh-thiadicarbocy. perchlorate	V, *n* = 2	QS2 R9	1.8 1.0	C_5H_5N	10	15[d] hrs.	47, 17,[c] 10	MeOH	250	226–228	$C_{31}H_{23}ClN_2O_4S_2$	C, H,	63.39 3.95	63.33 4.07
D13	3,3′-Di-*o*-nitro-Ph-thia-dicarbocy. perchlorate	XI, *n* = 2	QS5 QS17 AcONa (fused)	1.9 1.3 1.7	Ac_2O	15	5[e]	68, 50, 24[a]	MeOH	250	257–258	$C_{31}H_{21}ClN_4O_8S_2$	C, H, S,	54.96 3.13 9.48	54.90 3.16 9.61
D14	3,3′-DiEt-6,6′-dinitrothiacy. chloride	XIII, *n* = 0	QS7 diphenylnitrosamine	1.3 0.5	Ac_2O	10	15[e]	17[f]	MeOH	570	326–328	$C_{19}H_{17}ClN_4O_4S_2$	N,	12.06	11.82
D15	3,3′-DiEt-6,6′-dinitrothiacarbocy. chloride	XIII, *n* = 1	QS7 CH(OEt)	1.3 0.75	Ac_2O	20	15	65, 40, 8[a]	MeOH	375	278–280	$C_{21}H_{19}ClN_4O_4S_2$	N,	11.42	11.29
D16	3,3′-DiEt-6,6′-dinitrothiadicarbocy. iodide	XIII, *n* = 2	QS6 QS17	3.5 1.3	C_5H_5N	30	15[e]	42, 33[g]	....	..	274–276	$C_{23}H_{21}IN_4O_4S_2$	C, H, I,	45.38 3.48 20.86	45.69 3.77 20.46
D17	2-*p*-Dimethylaminostyryl-3-Ph-benzothiazolium perchlorate	XIV (Ph in place of Et), *n* = 1	QS2 R10	1.4 0.6	EtOH[h]	15	15	57,[c] 47, 37	EtOH	150	242–246	$C_{23}H_{21}ClN_2O_4S$	C, H, N,	60.42 4.63 6.14	60.44 4.70 6.01

D18	2-(4-*p*-Dimethylaminophenyl-1,3-butadienyl)-3-Ph-benzothiazolium iodide	*n* = 2	QS2 R11	1.8 0.9	EtOH[k]	15	10	68, 56, 20[l]	EtOH	100	168–170	$C_{25}H_{23}IN_2S$	C, 58.79 H, 4.54	58.62 4.55
D19	2-*p*-Dimethylaminostyryl-3-*o*-nitro-Ph-benzothiazolium perchlorate	XIV (*o*-nitro-Ph in place of Et), *n* = 1	QS5 R10	0.75 0.6	EtOH[h]	15	10	35, 25, 20	EtOH	180	185–186	$C_{23}H_{20}ClN_3O_6S$	C, 55.01 H, 4.02	55.09 4.25
D20	2-(4-*p*-Dimethylaminophenyl-1,3-butadienyl)-3-*o*-nitro-Ph-benzothiazolium perchlorate	*n* = 2	QS5 R11	1.9 0.9	EtOH[k]	15	5	100, 51, 19[a]	MeOH	100	221–222	$C_{25}H_{22}ClN_3O_6S$	C, 56.84 H, 4.19 S, 6.07	57.05 4.27 6.03
D21	2-*p*-Dimethylaminostyryl-6-nitrobenzothiazole ethochloride	XVI, *n* = 1	QS7 R10	0.65 0.4	Ac_2O	20	10	92, 62, —	MeOH	300	256–258	$C_{19}H_{20}ClN_3O_2S$	N, 10.78	10.72
D22	2-(4-*p*-Dimethylaminophenyl-1,3-butadienyl)-6-nitrobenzothiazole ethobromide	XVI, *n* = 2	QS7 R11	1.3 0.8	EtOH[k]	35	30	20[m]	MeOH	750	220–222	$C_{21}H_{22}BrN_3O_2S$	Br, 17.36	17.06
D23	1′,3-DiEt-6-nitro-thia-2′-carbocy. iodide	XVIII	QS7 QS13	0.65 1.1	C_5H_5N	20	10	77, 61, 50	MeOH	1000	291–293	$C_{23}H_{22}IN_3O_2S$	I, 23.89 S, 6.03	23.75 5.97
D24	1′,3-DiEt-6′-nitro-thia-2′-carbocy. iodide	XIX	QS12 QS11	0.9 0.7	C_5H_5N	20	10	66, 47, 38	MeOH	1000	293–295	$C_{23}H_{22}IN_3O_2S$	I, 23.89 S, 6.03	23.68 6.21
D25	1,1′-DiEt-6,6′-dinitro-2,2′-carbocy. chloride	XX	QS11 $CH(OEt)_3$	6.9 12.0	C_5H_5N	150	40	33,[n] 19, 14	MeOH	1100	306–309	$C_{25}H_{23}ClN_4O_4$	C, 62.67 H, 4.84 N, 11.70	62.12 4.70 11.88

[a] After a further third recrystallization. [b] Heated at 60–70°. [c] After conversion to perchlorate. [d] Reaction mixture allowed to stand at room temperature. [e] Heated at 100°. [f] After six recrystallizations. [g] Satisfactory analytical results were obtained with unrecrystallized dye which was washed successively with hot water, acetone and chloroform. [h] Plus piperidine as catalyst. [i] Method of Kendall (B. P. 431,140). [k] No catalyst needed. [l] After five recrystallizations. [m] After being converted to bromide, and then several recrystallizations from methyl alcohol. [n] After converting the crude iodide to chloride using freshly precipitated silver chloride and cresol as solvent (method of Brooker, U. S. Patent 2,245,249).

QS10	Lepidine ethiodide
QS11	6-Nitroquinaldine ethiodide
QS12	2-(2-Acetanilidovinyl)-benzothiazole ethiodide
QS13	2-(2-Acetanilidovinyl)-quinoline ethiodide
QS14	4-(2-Anilinovinyl)-quinoline ethiodide
QS15	4-(2-Acetanilidovinyl)-quinoline ethiodide
QS16	4(4-Acetanilido-1,3-butadienyl)-quinoline ethiodide
QS17	β-Anilinoacrolein anil hydrochloride

Reactants used in addition to the above salts are:

R1	3-Phenyl-2(3)-benzothiazolone
R2	3-Phenyl-2(3)-thiobenzothiazolone (VI)
R3	2-Dicarbethoxymethylene-3-phenylbenzothiazoline (VIII)
R4	2-Methylbenzothiazole
R5	2-Methyl-6-nitrobenzothiazole
R6	6-Nitroquinaldine
R7	Ethyl malonate
R8	Diphenylformamidine
R9	β-Ethoxyacrolein acetal
R10	*p*-Dimethylaminobenzaldehyde
R11	*p*-Dimethylaminocinnamaldehyde
R12	Methyl *p*-toluenesulfonate
R13	Ethyl sulfate

Of the above compounds, details of the preparation of those that are new are given in Table II. Unless otherwise stated, the necessary components were heated together in the medium indicated, and the product separated on cooling. The percentage yields given are those before and after two recrystallizations from the solvent shown in the sixth column.

Appearance of the Dyes

D1	Red crystals
D2	Minute blue crystals
D3	Green needles
D4	Orange-brown powder
D5	Dull blue crystals
D6	Dull purplish powder
D7	Minute dull red crystals
D8	Minute greenish crystals
D9	Dark greenish-bronze felt
D10	Glistening yellow crystals
D11	Dark crystals with metallic green reflex
D12	Green needles with metallic reflex
D13	Dark green crystals
D14	Orange-yellow crystalline powder
D15	Dark needles with green reflex
D16	Small dark crystals with green reflex
D17	Greenish-blue prisms
D18	Dark needles with greenish metallic reflex
D19	Dark bluish crystals
D20	Dull greenish powder
D21	Dark blue powder
D22	Minute green crystals
D23	Minute green crystals
D24	Minute dark blue crystals
D25	Small dark green crystals

The dye condensations are summarized in Table III. Unless otherwise stated, the components were refluxed together in the specified medium for the period indicated, and dye (D1-25) separated on cooling. The yield of crude, but washed, dye is given followed by the yield after one and two recrystallizations from the solvent indicated. All the dyes melted with decomposition.

Summary

1. The absorption maxima of vinylene homologous symmetrical cyanines show roughly constant differences of wave length of about 1000 Å. and such series may be termed non-convergent.

2. Many unsymmetrical cyanine series in which the two nuclei do not differ too greatly in basicity are similarly non-convergent, and the individual dyes do not show considerable deviations (between $\lambda_{\text{max.}}$ obsd. and the harmonic or the arithmetic mean of the values of $\lambda_{\text{max.}}$ of the parent dyes).

3. Beyond a certain limit, however, progressively increasing the imbalance of basicity between the nuclei of an unsymmetrical cyanine tends progressively to increase the deviation for a given chain length, and this deviation is the greater, the longer the polymethine chain joining the nuclei. A vinylene homologous series of this type shows progressively shorter vinylene shifts as the series is ascended and may be termed convergent. The degree of convergence is the greater for the first few members the greater the imbalance of basicity between the nuclei.

4. Introduction of the nitro group into the benzothiazole nucleus of a dye of the thia-4′-cyanine series (I → IV) gives rise to marked deviations, but the same substitution effected in a dye of the styryl series (XIV → XVI) results in a marked reduction of deviation, dyes of this type having previously been shown to give lower deviations the lower the basicity of the heterocyclic nitrogen.[4]

5. The deviation of a polymethine dye, and the degree of convergence of the vinylene homologous series of which it is a member, are determined by the degeneracy of the limiting resonance configurations. It is suggested that a classification of dyes may be based upon this latter property. In such a classification non-deviating dyes, members of non-converging series, appear to represent one limiting type in which degeneracy is complete. The polyene hydrocarbons may represent another limit in which non-degeneracy reaches a maximum. Between these extremes all gradations are possible.

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Sterols. CXXVII. 17-Bromopregnan-3(β)-ol-20-one*

BY RUSSELL E. MARKER, HARRY M. CROOKS, JR., AND R. B. WAGNER

While there has been rather extensive study of the bromination of steroids having a ketone group in the first or second ring,[1] there has been practically no work done on the halogenation of the 20-keto steroids. There has been a patent[2] on the haloform degradation of pregnan-20-one compounds to *etio*-cholanic acids. Reichstein[3] has prepared 21-halopregnan-20-one compounds but not by means of direct halogenation.

Ruzicka and Meldahl[4] reported the preparation of 17-bromo-5-pregnen-3(β)-ol-20-one acetate by phosphorus tribromide treatment of the corresponding 17-hydroxy compound, but since their starting material came from the boron fluoride-mercuric oxide hydration of 17-ethynyl-5-androstene-3,17-diol they were undoubtedly dealing with a compound of the so-called "D-homo" series[5] and not with a true pregnane type of compound. In a report of Butenandt[6] on 16-*allo*-pregnene compounds reference is made to a thesis of Masch at Danzig, 1938, describing the prepara-

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[1] Fieser, "Natural Products Related to Phenanthrene," 1937, p. 247–250, 402–404. Butenandt and co-workers, *Ber.*, **68**, 1850, 1854, 2091 (1935); **69**, 1158, 2289, 2779 (1936); **71**, 1681 (1938); **72**, 1614, 1617 (1939); **73**, 206 (1940). Heilbron and co-workers, *J. Chem. Soc.*, 801 (1937). Inhoffen and co-workers, *Ber.*, **69**, 1134, 1702, 2141 (1936); *Naturwiss.*, **25**, 125 (1937); *Ber.*, **70**, 1695 (1937); **71**, 1720 (1938); **72**, 1686 (1939); **73**, 451 (1940). Ruzicka and co-workers, *Helv. Chim. Acta*, **19**, 1147 (1936); **20**, 244 (1937).

[2] British Patent 493,055 to I. G. Farbenindustrie.

[3] Reichstein and co-workers, *Helv. Chim. Acta*, **20**, 1165 (1937); **22**, 1124 (1939); **23**, 658 (1940).

[4] Ruzicka and Meldahl, *Helv. Chim. Acta*, **22**, 421 (1939).

[5] Ruzicka, Gätzi and Reichstein, *ibid.*, **22**, 626 (1939).

[6] Butenandt, Mamoli and Heusser, *Ber.*, **72**, 1614 (1939).