low the melting point, it melted at 78°, solidified and melted again at 84°.

Anal. Calcd. for $C_{19}H_{17}BrO$: C, 66.86; H, 5.0. Found: C, 66.9; H, 5.3.

Oxidative Fission of the Furan.—In order to work at lowered temperature propionic acid was used as the medium instead of the usual acetic acid. One gram of the furan was suspended in 12.5 cc. of propionic acid and 1.5 cc. of concd. nitric acid at −12°. The temperature rose to −3°. Upon chilling again and allowing to stand for a total of fifteen minutes, the mixture was poured into ice water. The resulting yellow oil was extracted into ether and on evaporation of the solvent the compound was obtained in crystalline form; yield, 0.5 g. of melting point 74–75°. Upon repeated crystallization the melting point was 77–78° and the product was identified by mixture melting point with a sample of the *cis*-unsaturated diketone. It gave a 10° mixture melting point depression with the starting material.

Nitric Acid Oxidation of 3-Mesitoyl-5-mesityl-2-methyl-4-phenyl-furan (VII)

2-Acetyl-1,4-dimesityl-3-phenyl-2-butenedione-1,4 (VIII).—It had been found previously[3] that the nitric acid oxidation of the furan (VII) did not go at room temperature and that at the boiling point of the medium only intractable products were obtained. The following procedure was developed to produce the unsaturated triketone (VIII).

To a suspension of 4.5 g. of the furan in 45 cc. of concd. acetic acid was added dropwise 4.5 cc. of concd. nitric acid. The temperature was maintained at 40–45° for twenty-five minutes. On cooling 2.75 g. of crystals separated; melting point, 132–133°. Upon diluting the filtrate with water and crystallizing the resulting amorphous

precipitate from ethanol the yield was brought to 3.2 g. After repeated crystallization from ethanol it was obtained as fine colorless needles of melting point 133.5–134.5°.

Anal. Calcd. for $C_{30}H_{30}O_3$: C, 82.16; H, 6.9. Found: C, 82.1; H, 7.3.

Acid hydrolysis (refluxing concd. acetic acid containing 10% by volume of concd. hydrochloric acid) gave intractable products. Alkali hydrolysis (short refluxing in 5% ethanolic sodium hydroxide) gave a new substance which has not yet been investigated.

Reduction.—Attempts to obtain the saturated triketone by reduction failed; in every attempt only the furan (VII) was produced.

(a) A suspension of 0.3 g. of VIII and 0.6 g. of sodium hydrosulfite in 20 cc. of 70% ethanol was refluxed for one and one-half hours, partially evaporated and diluted with water; 0.27 g. of crystals separated and on recrystallization from ethanol was identified as the furan by mixture melting point.

(b) Hydrogenation at atmospheric pressure in ethanol with Raney nickel showed absorption of one molecule of hydrogen and gave the furan in 75% yield.

Summary

The synthesis of two series of unsymmetrical unsaturated 1,4-diketones with one terminal mesityl group is outlined. The nitric acid oxidation of two typical furans with one α-mesityl group proceeded without difficulty and gave the corresponding unsaturated 1,4-diketones. The bearing of this on the mechanism is discussed.

Color and Constitution. II.[1] Absorptions of Some Related Vinylene-Homologous Series*

By L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth and P. F. Oesper

The absorptions of many vinylene homologous series have been examined in the past, and these may be divided into two main categories, those series the members of which have an ionic charge available for resonance, and those in which this is not the case.

Among the latter series may be listed those studied by König and more recently by Hausser and Kuhn of which the first members are furfurol,[2] *p*-dimethylaminobenzaldehyde,[3] acetalde-

hyde (or crotonaldehyde),[4] crotonic acid,[4] stilbene[5] and furoic acid.[6] These are characterized by showing differences in $\lambda_{max.}$ between successive vinylene homologs which are relatively small, usually less than 500 Å., and these differences diminish as the vinylene series is ascended. Thus in the series $CH_3(CH{=}CH)_n COOH$, the difference between the values of $\lambda_{max.}$ (in EtOH), where $n = 1$ and $n = 2$, is 500 Å., that between $n = 2$ and $n = 3$ is 400 Å., and the next shift is 330 Å. For the series furyl-$(CH{=}CH)_n CHO$,

* Communication No. 816 of the Kodak Research Laboratories.

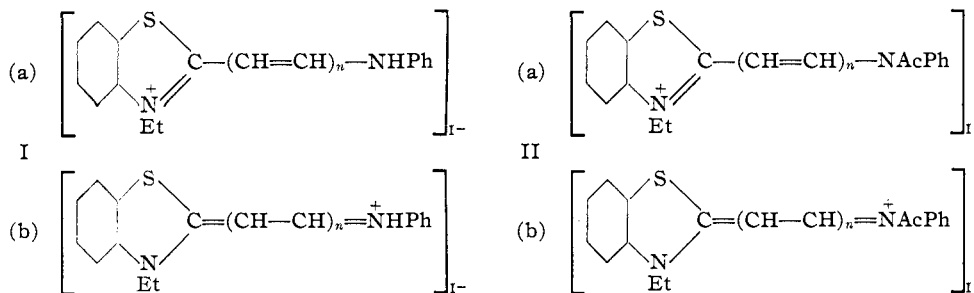(1) Part I, Brooker, Sprague, Smyth and Lewis, This Journal, **62**, 1116 (1940).

(2) König, *Ber.*, **58**, 2559 (1925).

(3) König, Schramek and Rösch, *ibid.*, **61**, 2074 (1928).

(4) Hausser, Kuhn, Smakula and Hoffer, *Z. physik. Chem.*, **B29**, 371 (1935).

(5) Hausser, Kuhn and Smakula, *ibid.*, **B29**, 384 (1935).

(6) Hausser, Kuhn, Smakula and Deutsch, *ibid.*, **B29**, 378 (1935).

the shift between $n = 0$ and $n = 1$ (in EtOH) is 420 Å., those succeeding being 360 and 230 Å. In the diphenylpolyene series $Ph(CH=CH)_n Ph$, the shift from $n = 1$ to $n = 2$ for the principal bands is 330 Å., when the absorptions are determined in benzene, and succeeding shifts are 250, 270, 200, 210, 200 Å., so that here there is no regular decrease, but nevertheless the last three differences are lower than the first three. In series such as these, where the vinylene difference between the lowest members is not great and succeeding differences tend to decrease as the series is ascended, deep colors such as blue are extremely difficult to attain, even with long conjugated chains.

Series in which the members have an ionic charge available for resonance comprise preeminently the polymethine dyes, of which the cyanines have been extensively studied.[7,8] The absorptions of these series are characterized by vinylene shifts which are of the order of 1000 Å., and there is no decrease in the magnitudes of these shifts as the series are ascended from the simple cyanines to the tricarbocyanines. In these compounds, therefore, deep colors are very commonly encountered.

A vinylene-homologous series of tertiary bases has recently been described,[1] these being bases of which the thiacyanine dyes are the ethiodides. These bases resemble the polyenes of Kuhn and Hausser in that they do not have an ionic charge available for resonance and they are relatively light in color and show relatively small vinylene shifts. It was deduced that, although resonance occurs within their molecules, the two extreme resonance configurations to which each base may be referred differ widely in stability. On the other hand, the thiacyanines have an ionic charge available for resonance and show the wide vinylene shifts characteristic of compounds which may be referred to two identical extreme resonance configurations.

The present work was started with a comparison of two further vinylene-homologous series, these being the anilino-vinylene-benzothiazole ethiodides (I)[9] and their acetyl derivatives (II).

Anilinovinyl compounds of the type of I ($n = 1$) have been prepared by Piggott and Rodd[10a] who condensed quaternary salts containing reactive methyl (2-methylbenzothiazole ethiodide in the case of I) with diphenylformamidine. By carrying out the reaction in the presence of acetic anhydride, the corresponding acetanilido derivatives such as II ($n = 1$) were obtained. By replacing the diphenylformamidine in the latter reaction by β-anilinoacrolein anil, the same authors succeeded in preparing acetanilido compounds such as II ($n = 2$),[10b] while Zeh prepared anilino compounds such as I ($n = 3$) by condensing quaternary salts such as 2-methylbenzothiazole ethiodide with glutaconaldehyde dianilide hydrobromide.[11]

We have now prepared the six compounds (I and II, $n = 1, 2$ and 3). The three acetanilido derivatives (II) were obtained by condensing 2-methylbenzothiazole ethiodide with diphenylformamidine, β-anilinoacrolein anil hydrochloride (IV, $n = 1$), and glutaconaldehyde dianilide hydrochloride (IV, $n = 2$), respectively, in acetic anhydride solution. These acetanilido compounds are very reactive and among other reactions condense with primary aromatic amines with elimination of the elements of acetanilide, and the anilino derivatives were conveniently obtained by treating the acetanilido compounds with aniline.

The three anilino compounds give solutions which are pale yellow, reddish-orange and blue for $n = 1, 2$ and 3, respectively, whereas solutions

(7) Fisher and Hamer, *Proc. Roy. Soc.* (London), **A154**, 703 (1936).
(8) Beilenson, Fisher and Hamer, *ibid.*, **A163**, 138 (1937).
(9) More strictly, Ia ↔ Ib. For the sake of simplicity compounds are referred to throughout this paper by simple Roman numerals, although their representation from the resonance standpoint may require more than one formula.
(10) Imperial Chemical Industries, Ltd., Piggott and Rodd, (a) British Patent 344,409 (1931); (b) British Patent 355,693 (1931).
(11) Agfa Ansco Corporation, United States Patent 2,131,864; *cf.* I. G. Farbenindustrie Aktiengesellschaft, British Patent 438,449 (1935).
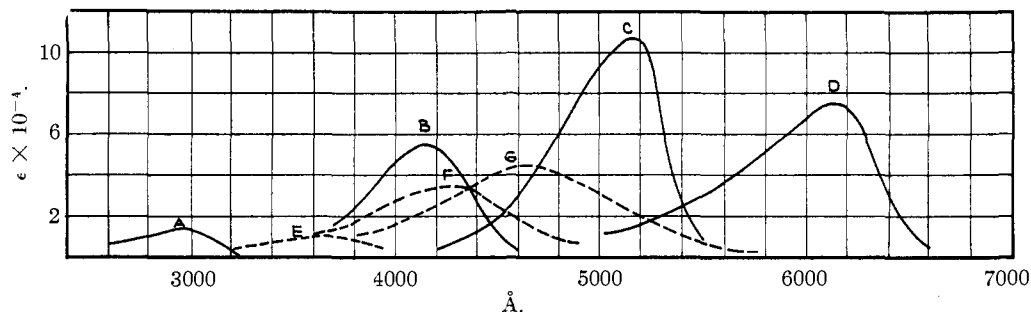
Fig. 1.—Absorptions in methyl alcohol: A, B, C. D = I, n = 0, 1, 2, 3, respectively; E, F, G = II, n = 1, 2, 3, respectively.

of the corresponding acetanilido compounds are almost colorless, yellow and orange, taken in the same order, so that in these series an anilino compound is always deeper in color than its acetyl derivative. In addition, 2-anilinobenzothiazole ethiodide (I, n = 0) was prepared by condensing 2-phenylmercaptobenzothiazole ethiodide with aniline, or, in better yield, by the direct union of 2-anilinobenzothiazole and ethyl iodide. This is colorless in solution. Attempts were also made to prepare the corresponding acetanilido compound but were unsuccessful.

TABLE I

Compound	λ_{max}. (MeOH), Å.	Differences, Å.	ϵ_{max}. $\times 10^{-4}$
I, n = 0	2985		1.4
1	4140	1155	5.5
2	5160	1020	10.7
3	6125	965	7.6
II, n = 1	3640		1.0
2	4260	620	3.5
3	4610	350	4.4
III, n = 0	4230		8.45
1	5575	1345	14.8
IV, n = 1	3825		5.0
2	4850	1025	6.5
V, n = 1	4430		5.1
2	5280	850	9.5
VI, n = 0	5235		7.6
1	6040	805	19.4
VII, n = 0	3020		1.1
1	3940	920	3.8
2	4480	540	5.9
3	4850	370	6.8
VIII, n = 0	2930		1.3
1	4000	1070	4.6
2	4965	965	10.7
3	5975	1010	13.3
IX, n = 2	4490		8.1
X, n = 0	2950		0.8
1	3880	930	5.1
2	4830	950	14.2
3	5840	1010	21.8
XI	4820		13.4
XII	4130		4.8

The absorptions of the seven compounds in methyl alcoholic solution are given in Fig. 1, the optical data for these as well as for other compounds dealt with in this paper being tabulated in Table I.
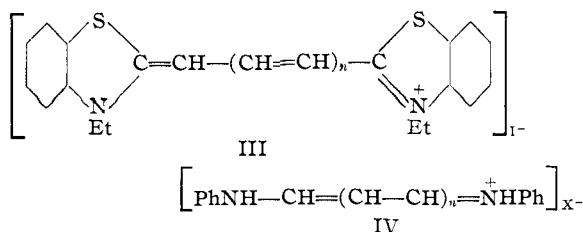
From these data it is seen that the shift on passing from an anilino compound (I) to its next higher vinylene homolog is of the order of 1000 Å., whereas in the acetanilido series (II) the shifts are considerably less than this figure and diminish markedly as the series is ascended. The difference between the values of λ_{max}. for an anilino compound (I) and its acetyl derivative (II) therefore increases with the value of n. For the compounds n = 1, the difference is 500 Å., and this rises to 900 Å. for n = 2, and to 1515 Å. where n = 3. The values of ϵ_{max}. for the acetanilido compounds are markedly less than the values for the corresponding anilino compounds, but it may be noted that the steady rise in ϵ_{max}. in passing from Curve A to B and then to C, is not maintained in D.

The relationship between these two sets of absorption curves is therefore strongly reminiscent of that found to exist between those of the vinylene homologous thiacyanine dyes and the related anhydronium bases,[1] and reasoning similar to that used in this earlier comparison provides a satisfactory explanation in the present one.

According to the resonance theory, the anilino compounds I may be considered as resonance hybrids between the two extreme configurations Ia and Ib, while structurally an anilino compound may be regarded as the cross between a dye of the thiacyanine series III and a dye of the series IV. For example, 2-(4-anilino-butadienyl)benzothiazole ethiodide (I, n = 2) is the structural cross between 3,3'-diethylthiacarbocyanine iodide (III, n = 1) and glutaconaldehyde dianilide hydriodide (IV, n = 2). Both of these latter dyes are

$$\left[\begin{array}{c} \text{\Large benzothiazole} \\ \text{Et} \end{array} C{=}CH{-}(CH{=}CH)_n{-}C \begin{array}{c} \text{\Large benzothiazole} \\ \overset{+}{N} \\ \text{Et} \end{array} \right] I^-$$

III

$$\left[PhNH{-}CH{=}(CH{-}CH)_n{=}\overset{+}{N}HPh \right] X^-$$

IV

symmetrical and each gives rise to two identical extreme resonance configurations. A comparison of the absorption curves of these three dyes (Fig. 2) shows that the cross has an absorption band which comes close to being the mean of the absorptions of the parent symmetrical dyes. The arithmetical mean of the wave lengths of maximum absorption of these latter is 5210 Å. (IV, $n = 2$, has $\lambda_{max.}$ 4850 Å. and III, $n = 1$, has $\lambda_{max.}$ 5575 Å.), and the observed value for I, $n = 2$, is 5160 Å., and this near approach to a mean relationship may be interpreted as indicating a degree of degeneracy of the resonance structures of the unsymmetrical dye almost if not quite as high as that in the parent dyes.
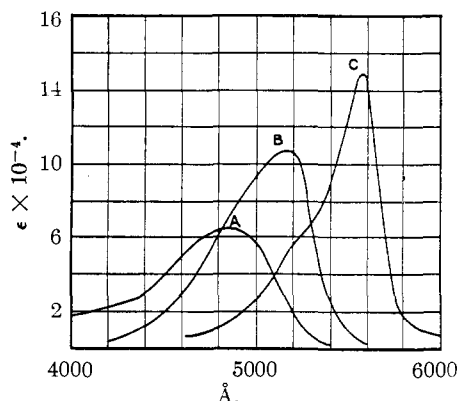
Fig. 2.—Absorptions in methyl alcohol: A = IV ($n = 2$), B = I ($n = 2$), C = III ($n = 1$).

If a similar comparison is made with the next lower vinylene homologs of the above dyes, however, the results are not so regular. In this series we may regard 2-(2-anilinovinyl)-benzothiazole ethiodide (I, $n = 1$) as the cross between 3,3'-diethylthiacyanine iodide (III, $n = 0$) and β-anilinoacrolein anil hydriodide (IV, $n = 1$). The curves are given in Fig. 3, from which it is seen that the absorption of the unsymmetrical dye (I, $n = 1$) lies much nearer to that of the deeper colored symmetrical dye (III, $n = 0$) than to the other. This result is unexpected, since, even if the resonance structures of an unsymmetrical dye were as fully degenerate as those of the parent
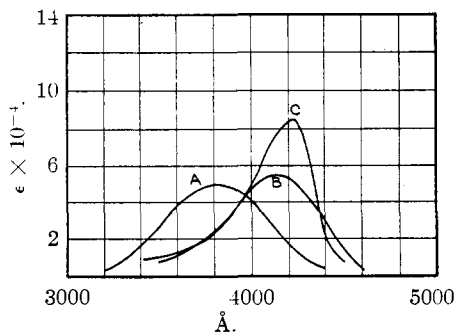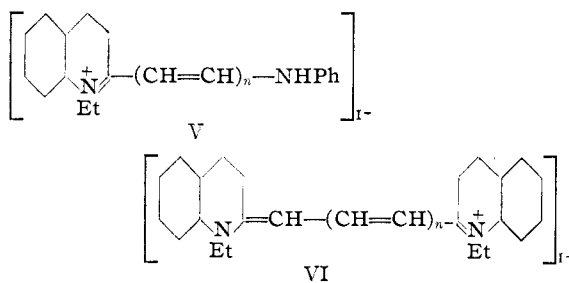
Fig. 3.—Absorptions in methyl alcohol: A = IV ($n = 1$), B = I ($n = 1$), C = III ($n = 0$).

symmetrical dyes, it could at most be expected to absorb midway between them and not at longer wave length. However, it is not entirely surprising that some discrepancies arise in the application of this argument to the first members of vinylene homologous series, where the chain connecting the nitrogen-containing nuclei is short. The argument is based upon the theorem that an unsymmetrical cyanine in which the two resonance structures are completely degenerate should have an absorption at the mean of those of the parent dyes. Although this theorem appears quite reasonable for the higher members of the vinylene-homologous series, it may very well break down at the first members where the nitrogen-containing nuclei are sufficiently close to influence each other. It is hoped to consider this point more fully in a later paper.

It is noteworthy that the two anilinovinyl dyes of the quinoline series (V, $n = 1$ and 2) both give absorptions which agree reasonably well with

$$\left[\begin{array}{c} \text{\Large quinoline} \\ \overset{+}{N} \\ \text{Et} \end{array} {-}(CH{=}CH)_n{-}NHPh \right] I^-$$

V

$$\left[\begin{array}{c} \text{\Large quinoline} \\ N \\ \text{Et} \end{array} {=}CH{-}(CH{=}CH)_n{-} \begin{array}{c} \text{\Large quinoline} \\ \overset{+}{N} \\ \text{Et} \end{array} \right] I^-$$

VI

the requirements of the mean relationship. In the case of V ($n = 1$), the parent dyes are VI ($n = 0$) and IV ($n = 1$), which have $\lambda_{max.}$ at 5235 and 3825 Å., respectively, their mean being 4530 Å. The observed value is 4430 Å., the difference being in the expected direction. For V ($n = 2$), the calculated and observed values are 5445 and 5280 Å., respectively, so that here the discrepancy is somewhat greater although still in the same di-

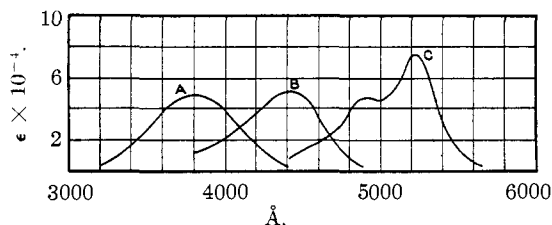rection. The absorptions are given in Figs. 4 and 5.

Fig. 4.—Absorptions in methyl alcohol: A = IV (n = 1), B = V (n = 1), C = VI (n = 0).
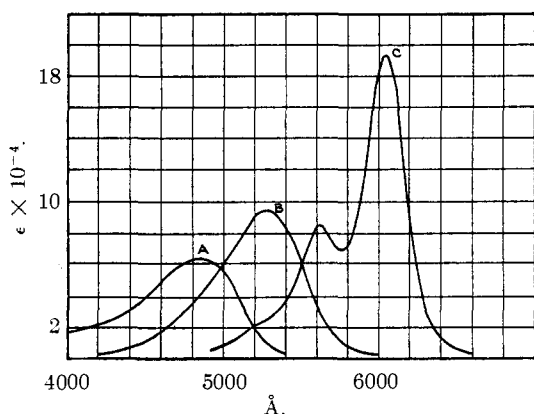

Fig. 5.—Absorptions in methyl alcohol: A = IV (n = 2), B = V (n = 2), C = VI (n = 1).

With the exception noted above, therefore, the comparisons of the absorptions of the unsymmetrical anilino dyes I and V (n = 1, 2) with those of the related symmetrical dyes indicate that the degeneracy of the resonating structures is almost if not quite as complete in the unsymmetrical dyes as in the symmetrical.

This points to a close approximation in energy of the two extreme configurations Ia and Ib (similarly with Va and Vb) which, in turn, indicates that the two nitrogen atoms in these unsymmetrical dyes are of nearly the same basicity when linked together by the polymethine chain.

It is now readily understandable why the acetyl derivatives II should in each case be lighter than the corresponding anilino compounds I. The basicity of the —NHPh groups in the latter is greatly reduced by the replacement of hydrogen by acetyl and the salt-forming tendency of the group is diminished accordingly. The extreme configuration represented by IIa in which the nitrogen of the —NAcPh group is tertiary is therefore much more stable than IIb in which it is quaternary, and the actual state of an acetyl

compound therefore tends to approach IIa rather than IIb, the two resonating structures thereby becoming less degenerate in corresponding measure. This causes absorption to occur at markedly shorter wave length than in the case of the corresponding strongly resonating anilino compound I, as will be discussed in detail in a later paper. Thus, although the acetanilido compounds are ionized and have an ionic charge available for resonance, this is suppressed, because a marked difference in basicity between the two nitrogen atoms causes the two extreme resonance configurations to differ widely in stability. The situation is therefore similar to but probably more extreme than that existing in certain unsymmetrical cyanines described in an earlier paper,[1] in which the combination of two heterocyclic nuclei of widely different basicity (e. g., indole and 4-quinoline) had the effect of rendering the dye lighter in color than would have been expected from a consideration of the absorptions of the parent symmetrical dyes.

On treatment with alkali, the anilino compounds lose the elements of acid to give a series of bases (VII, n = 0, 1, 2, 3)
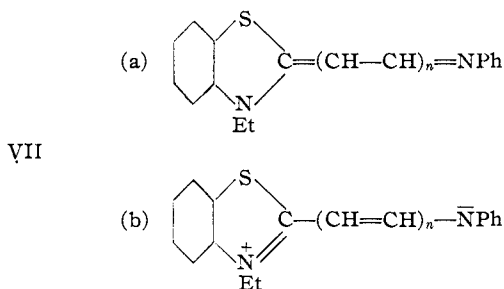
The last three members of this series resemble the acetyl derivatives (II) in that they are in every case lighter in color than the anilino compounds (I) with the same chain length. Their absorptions are shown in Fig. 6.

The shifts produced by adding vinylene are also smaller with these bases (anils) than with their hydriodides and they decrease as the series is ascended, so that the difference in λ_{max} between an anil and its hydriodide increases as the value of n in the general formula increases from 1 to 3.

The resonance scheme VIIa ↔ VIIb is suggested for these anils for precisely similar reasons to those advanced in the case of the anhydronium bases related to the thiacyanines.[1] Configuration VIIb gives an explanation of why the imino nitrogen is the center of basicity rather than the benzo-
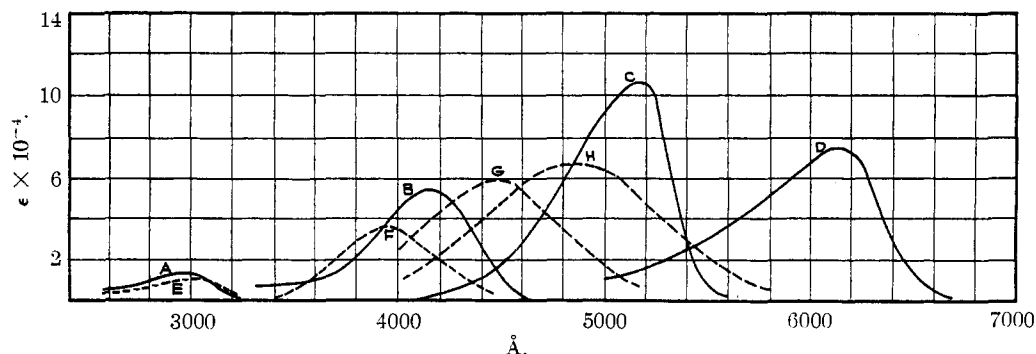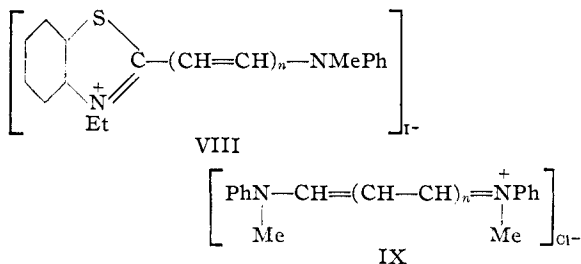
Fig. 6.—Absorptions in methyl alcohol: A, B, C, D = I (n = 0, 1, 2, 3), respectively; E, F, G, H = VII (n = 0, 1, 2,) 3, respectively.

thiazole nitrogen, and it also explains the fact that the dipole moments of these compounds are higher than those calculated from the classical formula VIIa, especially for the higher values of n (Table II). The methods adopted in these determinations were identical with those described in an earlier paper.[1] The —NHPh group is not very acidic, however, whence it follows that the —$\overline{N}$Ph group in VIIb is correspondingly unstable, so that of the two extreme resonance configurations, VIIa will be the more favored. The actual state of an anil will tend to approach VIIa, therefore, and the compound will consequently be lighter in color than the hydriodide which has almost completely degenerate resonating structures.

The first member of the anil series (VII, n = 0) is anomalous in that it absorbs at longer wave length than its hydriodide, although the difference between them is not great. A clear explanation of this is, at the moment, lacking, but whatever the reason, the fact remains that the halochromic shift brought about on passing from an anil to its hydriodide depends not only in *amount* but also in *direction* on the length of the conjugated chain in the compounds, and this appears to be the first vinylene-homologous series in which this has been observed.

That the phenylimino nitrogen is the center of basicity in the anils may be deduced from the following. The four anils combined readily with methyl p-toluenesulfonate to give a series of methylanilino salts which were converted into the iodides (VIII, n = 0, 1, 2, 3). The constitution of these compounds follows

$$\left[\begin{array}{c} S \\ \overset{+}{N} \\ Et \end{array} C-(CH{=}CH)_n-NMePh \right] I^-$$

VIII

$$\left[\underset{Me}{PhN}-CH{=}(CH{-}CH)_n{=}\overset{+}{N}\underset{Me}{Ph} \right]_{Cl^-}$$

IX

from the fact that the triiodide corresponding to

TABLE II

Mole fractions (C_2), dielectric constants (D), densities of solutions in benzene (d), polarizations at 25° (P_2), molar refractions (MR_D), polarizations at 25° (P_∞), observed moment (μ) and calculated moment (μ calcd.).
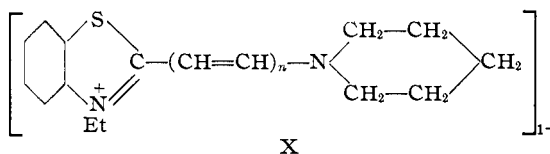
Compound	C_2	D	d	P_2	MR_D	$P_\infty(25°)$	$\mu(\times 10^{18})$	μ calcd. ($\times 10^{18}$)
VII (n = 0)	0.000000	2.2784	0.87222	(P_1 = 26.758)				
	.002416	2.2981	.87416	182.5				
	.004927	2.3218	.87615	191.4	76	192 ± 3	2.37 ± 0.03	1.6 ± 0.6
	.009690	2.3639	.87985	191.3				
	.014089	2.4040	.88306	192.8				
VII (n = 1)	.000000	2.2831	.87226	(P_1 = 26.826)				
	.004640	2.3927	.87620	409.6				
	.008453	2.4903	.87960	416.1	85	443 ± 20	4.17 ± .12	2.0 ± .6
	.017452	2.7015	.88731	397.7				
	.023206	2.8339	.89205	388.3				
VII (n = 2)	.000000	2.2831	.87226	(P_1 = 26.826)				
	.004310	2.4525	.87621	635				
	.006027	2.5241	.87782	637	94	680 ± 20	5.32 ± .10	2.0 ± .6
	.011982	2.7520	.88317	605				
	.017223	2.9565	.88796	587				

VIII ($n = 3$) was obtained when 2-methylbenzothiazole ethiodide was condensed in acetic anhydride with glutaconaldehyde dimethylanilide chloride (IX, $n = 2$),[12] this mode of preparation establishing the attachment of the methyl group to the anilino nitrogen and not the benzothiazole nitrogen. Furthermore, the next lower homolog (VIII, $n = 1$) underwent condensation with 2-methylbenzothiazole ethiodide to give 3,3'-diethylthiacarbocyanine iodide, the elements of methylaniline clearly being eliminated in this reaction, thus confirming the structure.

The absorptions of the four methylanilino compounds (VIII) are shown in Fig. 7. They form a series with very nearly the same wave length differences between successive vinylene homologs as those of the anilino series, but the methylanilino compounds consistently absorb at somewhat shorter wave lengths than the corresponding

absorptions of IX ($n = 2$) and III ($n = 1$) (4490 + 5575) ÷ 2 = 5030 Å.

When the acetanilido compounds (II) are treated with aliphatic primary or secondary amines, reaction occurs with elimination of the elements of acetanilide and new aliphatic dye types are formed.[13] Thus from piperidine the vinylene homologous series X ($n = 1, 2, 3$) has been prepared, and the lowest homolog ($n = 0$) was obtained by treating 2-ethylmercaptobenzothiazole ethiodide with piperidine, ethylmercap-

tan being eliminated. The absorptions of this series are also shown in Fig. 7. There is much the same shift for each added vinylene as in Series I and VII, i. e., roughly 1000 Å., and the piperidino dyes absorb at somewhat shorter wave lengths than the methylanilino compounds except that the lowest piperidino homolog absorbs at very slightly longer wave length than the corresponding methylanilino compound.

A comparison has not been made between a piperidino dye and the related symmetrical dyes, but we have compared the absorption of the similarly constituted 2-(4-dimethylaminobutadienyl)-benzothiazole ethiodide (XI) (which absorbs at almost exactly the same wave
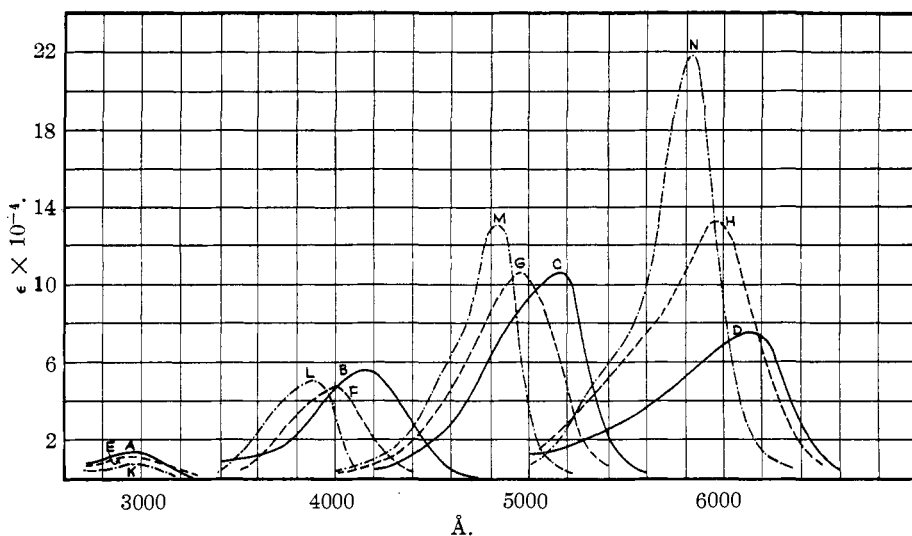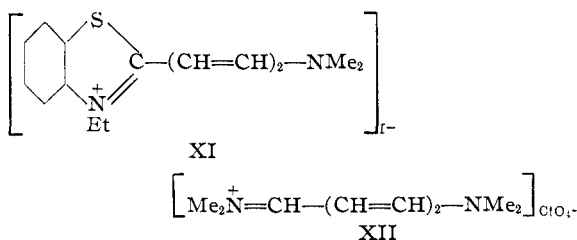
Fig. 7.—Absorptions in methyl alcohol: A, B, C, D = anilino compounds, I, $n = 0, 1, 2, 3$, respectively; E, F, G, H = methylanilino compounds, VIII, $n = 0, 1, 2, 3$, respectively; K, L, M, N = piperidino compounds, X, $n = 0, 1, 2, 3$.

anilino compounds, the average amount being 135 Å. The reason for this remains obscure, but is undoubtedly related to the fact that the dimethylanilide IX, $n = 2$, absorbs at considerably shorter wave length ($\lambda_{max.}$ 4490 Å.) than the dianilide IV, $n = 2$ ($\lambda_{max.}$ 4850 Å.).

The magnitudes of the vinylene shifts in VIII indicate that the methylanilino compounds are very strongly resonating and in confirmation of this the absorption of VIII ($n = 2$) ($\lambda_{max.}$ 4965 Å.) is found to agree very well with the mean of the

(12) Zincke, Ann., 333, 107 (1905).

(13) White and Keyes, United States Patent 2,166,736.

length as X, $n = 2$; data in Table I) with those of the related symmetrical dyes XII[14] and III ($n = 1$). In this case agreement is very good, the observed value for XI being λ_{max}. 4820 Å. and the calculated, 4850 Å. (4130 + 5575) ÷ 2. It is therefore concluded that, in the series X, the two structures are quite degenerate and comparable in degeneracy with that in the symmetrical parent dyes.

In order to bring out the relationships existing between the members of the five vinylene homologous series described in the present paper, their wave lengths of maximum absorption are plotted in Fig. 8. In the upper part of the diagram the close relationship of the anilino, methylanilino and piperidino series is apparent. These are all three considered to be highly degenerate series, both because of the wide vinylene shifts they exhibit and also because in all of the cases examined except one the absorptions of these compounds agree reasonably well with those calculated as the arithmetic means of those of the related symmetrical dyes.

In the lower part of the figure, the relationship of the highly degenerate anilino series to the less degenerate acetanilido and anil series is brought out. With but one exception, a member of one of the latter series is less deeply colored than the anilino compound of the same chain length. In the acetanilido and anil series, also, the vinylene shifts progressively decrease in a characteristic way as the series are ascended.

Comparison of Reactivities.—Compounds of the anilino (I) and acetanilido (II) types have both been used as intermediates in the preparation of cyanine dyes, condensation taking place between them and a component containing reactive hydrogen, the elements of aniline and of acetanilide, respectively, being eliminated as well as the elements of acid. Of the two types, the former, containing two degenerate structures, would be expected to be less reactive, since *ceteris paribus*,

Fig. 8.—Wave lengths of maximum absorption of members of five vinylene homologous series.

a highly degenerate compound has higher resonance stabilization and is therefore less reactive. It is accordingly interesting to compare the reaction rates of compounds of series I and II. Differences of reactivity between them have indeed been observed by Ogata,[15] but for a comparison of reactivity, the yields must be measured as functions of the t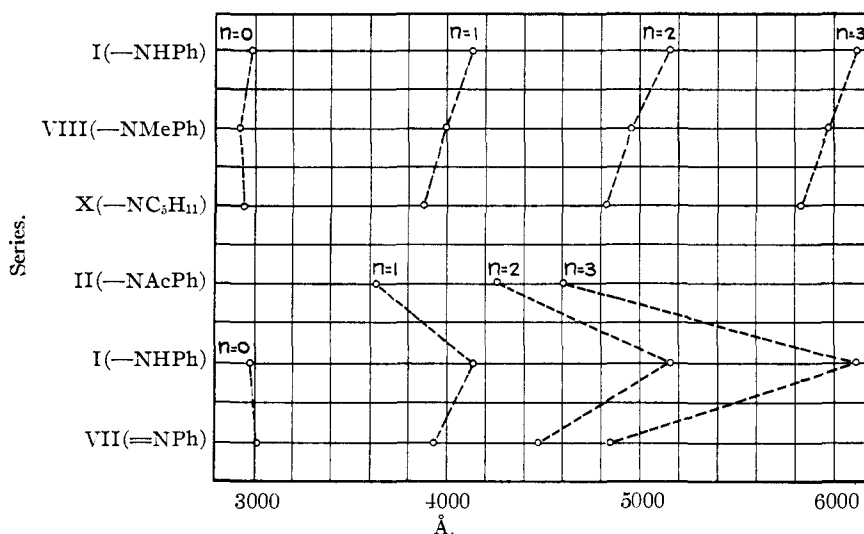ime. Furthermore, a comparison is difficult, since in the commonly used basic media, such as pyridine, the anilino derivatives may lose acid to give the corresponding anils, which, if they react further, will have their own characteristic reactivity, and in acetic anhydride, which has also been used,[16] the anilino compound may become acetylated before dye condensation takes place.

Because of these complications, we have compared the time dependence of the yields of the acetanilido compound (II, $n = 1$) with that of the more deeply absorbing and therefore presumably more resonance-stabilized and less reactive methylanilino compound (VIII, $n = 1$), the condensations being carried out in boiling pyridine solution, in which medium the methylanilino compound was stable. These intermediates were condensed with 2-methylbenzothiazole ethiodide, giving 3,3'-diethylthiacarbocyanine iodide, and the yields of well-washed but not recrystallized dye given in Table III for various periods of refluxing indicate that the acetanilido compound is in fact the more reactive of the two.

(14) König and Regner, *Ber.*, **63**, 2823 (1930).

(15) Ogata, *Proc. Imp. Acad.* (Tokyo), XIII, no. 8, 325 (1937).

(16) *Cf.* Piggott and Rodd, United States Patent 2,071,899.

Table III

Yields of 3,3'-Diethylthiacarbocyanine Iodide

| Time of refluxing, minutes	Using II ($n = 1$) %	Using VIII ($n = 1$) %	Using X ($n = 1$) %
5	99	71	10
15	99	86	42
30	100	94	73

Yields of 5-[(3-Ethyl-2(3)-benzothiazolylidene)-ethylidene]-3-phenylrhodanine

Time of refluxing, minutes	Using II ($n = 1$) %	Using VIII ($n = 1$) %	Using X ($n = 1$) %
15	97	52	9
30	96	58	18
60	96	63	25

Yields of 3,3'-Diethylthiadicarbocyanine Iodide

Time of refluxing, minutes	Using II ($n = 2$) %	Using VIII ($n = 2$) %
5	89	62
15	91	70
30	96	70

In a second comparison, the two intermediates were condensed with 3-phenylrhodanine in absolute ethyl alcohol, using triethylamine to effect the condensation. In this case the product, 5-[(3-ethyl-2(3)-benzothiazolylidene)-ethylidene]-3-phenylrhodanine (XIII), a dye of the merocyanine class[17] was obtained at a considerably higher rate

XIII
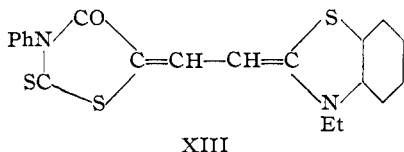
when the acetanilido compound was used.

In a further comparison, the piperidino compound X ($n = 1$) was employed as an intermediate in both the above condensations, piperidine being eliminated in these reactions, and it was found to be considerably less reactive than the methylanilino compound. Since both the piperidino and methylanilino compounds are regarded as being highly degenerate from a consideration of their absorptions, some additional factor must be responsible for the widely different rates given by the two substances.

In a final comparison, the acetanilido and methylanilino compounds (II and VIII, $n = 2$) were condensed in absolute ethyl alcohol with 2-methylbenzothiazole ethiodide to give 3,3'-diethylthiadicarbocyanine iodide, triethylamine being used to effect the condensations. Here again the methylanilino compound gave the lower rate.

(17) *Cf.* Brooker and Eastman Kodak Co., United States Patent 2,170,803.

In conclusion, we take pleasure in expressing our gratitude to Mr. E. E. Richardson, Dr. L. A. Jones and their co-workers for the absorptions, and to Dr. L. T. Hallett and his co-workers for the (micro)analyses.

Experimental[18]

2-Phenylmercaptobenzothiazole was prepared by warming 2-chlorobenzothiazole (1 mole) on a steam-bath and adding small amounts of phenylmercaptan (2 moles, *i. e.*, 100% excess) and of triethylamine (2 moles, 100% excess) alternately down a reflux condenser, shaking the while, and finally heating at 100° for twenty-four hours. Water was added after cooling, followed by an excess of caustic soda, and the base was extracted with ether. Yield was 93% of slightly yellowish liquid, b. p. 183–187° (3 mm.).

Anal. Calcd. for $C_{13}H_9NS_2$: C, 64.13; H, 3.73. Found: C, 64.45; H, 3.80.

2-Phenylmercaptobenzothiazole ethiodide was prepared by heating the above base with ethyl iodide (100% excess) at 100° for sixteen hours. After cooling, the cake of crystals was crushed and well washed with acetone; yield 70%. After recrystallization from nitromethane the cream colored crystals had m. p. 167–168° dec.

Anal. Calcd. for $C_{15}H_{14}INS_2$: I, 31.80. Found: I, 31.76.

2-Ethylmercaptobenzothiazole ethiodide was prepared by heating 2-ethylmercaptobenzothiazole with ethyl iodide (1.2 mols) at 100° for forty-three hours. The product was crushed and washed with acetone; yield 65%. A portion was recrystallized twice from a mixture of acetone and methyl alcohol; the cream colored crystals had m. p. 115–117° dec.

Anal. Calcd. for $C_{11}H_{14}INS_2$: I, 36.15. Found: I, 36.16.

2-Anilinobenzothiazole ethiodide (I, $n = 0$) was prepared by refluxing 2-phenylmercaptobenzothiazole ethiodide with excess (2 mols) of aniline in ethyl alcohol for fifteen minutes. The product was recrystallized several times from ethyl alcohol; yield 3% of cream colored crystals, m. p. 197–198° dec.

A better method was to heat 2-anilinobenzothiazole (from 2-chlorobenzothiazole and aniline) with excess of ethyl iodide (2 mols) at 100° for fifty-four hours. The viscous mass was induced to crystallize by stirring with acetone; yield 87% before and 43% after two recrystallizations from ethyl alcohol (norite).

Anal. Calcd. for $C_{15}H_{15}IN_2S$: I, 33.21. Found: I, 33.37.

2-(2-Anilinovinyl)-benzothiazole ethiodide (I, $n = 1$).— The acetyl derivative (II, $n = 1$) (1.12 g., 1 mol) was refluxed with aniline (0.3 g., 1.25 mols) in ethyl alcohol (10 cc.) for twenty minutes. Addition of ether (200 cc.) precipitated the product which was purified by two recrystallizations from methyl alcohol; yield 54%. The buff colored needles had m. p. 265–266° dec.

Anal. Calcd. for $C_{17}H_{17}IN_2S$: I, 31.10. Found: I, 31.10.

(18) All melting points are corrected.

2-(4-Anilino-1,3-butadienyl)-benzothiazole ethiodide
(I, $n = 2$).—The acetyl derivative (II, $n = 2$) was treated
with aniline as above; yield 34% of brownish needles with
m. p. 250–252° dec.

Anal. Calcd. for $C_{19}H_{19}IN_2S$: I, 29.23. Found: I,
28.93.

2-(6-Anilino-1,3,5-hexatrienyl)-benzothiazole ethiodide
(I, $n = 3$) was prepared in similar fashion to the two
lower vinylene homologs; yield 26% of dark needles with a
greenish-bronze reflex, m. p. 161–163° dec.

Anal. Calcd. for $C_{21}H_{21}IN_2S$: I, 27.57. Found: I,
27.53.

2-(2-Acetanilidovinyl)-benzothiazole ethiodide (II, $n =$
1) was prepared by refluxing tenth molar amounts of 2-
methylbenzothiazole ethiodide and diphenylformamidine
in acetic anhydride (150 cc.) for twenty minutes. The
dark product separating on cooling was washed with water
followed by acetone and after drying was sufficiently pure
to be used for further reactions; yield 65%. Pure ma-
terial was obtained by acetylating the anilino compound
(I, $n = 1$), using acetic anhydride and pyridine (1 mol),
and separated from acetic anhydride in almost colorless
crystals, m. p. 231–233° dec.

Anal. Calcd. for $C_{19}H_{19}IN_2OS$: I, 28.19. Found: I,
28.14.

**2-(4-Acetanilido-1,3-butadienyl)-benzothiazole ethio-
dide** (II, $n = 2$) was prepared similarly to the preceding
compound but using β-anilinoacrolein anil hydrochloride
and refluxing for seventy minutes. The yield of acetone-
washed material was 58%, and this was sufficiently pure
for further reaction. Pure material was obtained by
acetylating the anilino compound (I, $n = 2$), using acetic
anhydride and pyridine and separated from acetic an-
hydride in minute brownish crystals with m. p. 233–234°
dec.

Anal. Calcd. for $C_{21}H_{21}IN_2OS$: I, 26.66. Found: I,
26.53.

In dilute methyl alcoholic solution, this substance
tended to hydrolyze on standing, a band appearing at
about 5150 Å. corresponding to the unacetylated com-
pound.

**2-(6-Acetanilido-1,3,5-hexatrienyl)-benzothiazole eth-
iodide** (II, $n = 3$) was made by the same general procedure
but using glutaconaldehyde dianilide hydrochloride and
refluxing for ten minutes. Here again the acetone-washed
product was sufficiently pure for further reaction; yield
56%. Pure material was obtained by three recrystalliza-
tions from acetic acid, from which it separated in reddish-
brown crystals with m. p. 203–205° dec.

Anal. Calcd. for $C_{23}H_{23}IN_2OS$: I, 25.27. Found: I,
25.38.

3-Ethyl-2-phenyliminobenzothiazoline (VII, $n = 0$).—2-
Anilinobenzothiazole ethiodide (0.1 mole) was suspended in
acetone (270 cc.) and a solution of sodium hydroxide (0.5
mole) in water (40 cc.) added and stirring maintained
without additional heating until solution was complete
(ten minutes). The acetone layer was concentrated to
small volume and the product precipitated by adding
water (yield theoretical) and purified by two recrystalliza-
tions from petroleum ether; yield 65% of colorless crys-
tals, m. p. 64–65°.

Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.82; H, 5.55.
Found: C, 70.62; H, 5.47.

3-Ethyl-2-(2-phenyliminoethylidene)-benzothiazoline
(VII, $n = 1$) was prepared similarly but it was necessary to
stir for forty-five minutes; yield 97% before and 80% after
two recrystallizations from ligroin (b. p. 90–120°). The
anil formed compact amber crystals with a blue reflex and
had m. p. 98–99° dec.

Anal. Calcd. for $C_{17}H_{16}N_2S$: C, 72.80; H, 5.76.
Found: C, 72.97; H, 5.94.

**3-Ethyl-2-(4-phenylimino-2-butenylidene)-benzothi-
azoline** (VII, $n = 2$) was prepared similarly to the above,
the reaction mixture being warmed gently in this case and
twice the volume of acetone being used; yield 90% before
and 77% after two recrystallizations from ligroin (b. p. 90–
120°). The orange-brown needles had m. p. 109–110° dec.

Anal. Calcd. for $C_{19}H_{18}N_2S$: C, 74.46; H, 5.92.
Found: C, 74.48; H, 6.13.

**3-Ethyl-2-(6-phenylimino-2,4-hexadienylidene)-benzo-
thiazoline** (VII, $n = 3$).—The anilino compound (I, $n = 3$)
(0.01 mole) was refluxed in 95% ethyl alcohol (40 cc.) with
powdered potassium hydroxide (0.01 mole) for five minutes.
Cold water precipitated a sticky product which was
washed with more water and purified by two recrystalliza-
tions from ligroin; yield 10% of brown crystals with m. p.
117–119° dec.

Anal. Calcd. for $C_{21}H_{20}N_2S$: C, 75.86; H, 6.07.
Found: C, 75.40; H, 6.07.

2-(N-Methylanilino)-benzothiazole ethoperchlorate
(VIII, $n = 0$).—The anil (VII, $n = 0$) was heated at 100°
with an equivalent amount of methyl p-toluenesulfonate
for one day, the product dissolved in the minimum amount
of hot methyl alcohol, and a hot aqueous solution of
sodium perchlorate added. The product was washed
with water and purified by two recrystallizations from
ethyl alcohol; yield 62% of colorless crystals, m. p. 194–
195°.

In this and in two other cases (VIII, $n = 2$; X, $n = 0$)
it was found more satisfactory to isolate the perchlorates
rather than the iodides.

Anal. Calcd. for $C_{16}H_{17}ClN_2O_4S$: C, 52.08; H, 4.65.
Found: C, 52.07; H, 4.51.

2-[2-(N-Methylanilino)-vinyl]-benzothiazole ethiodide
(VIII, $n = 1$) was prepared similarly to the above but
heating at 100° for only two hours. Sodium iodide was
used to precipitate the salt; yield 70% of bright yellow
crystals, m. p. 213–214° dec.

Anal. Calcd. for $C_{18}H_{19}IN_2S$: I, 30.07. Found: I,
29.85.

**2-[4-(N-Methylanilino)-1,3-butadienyl]-benzothiazole
ethoperchlorate** (VIII, $n = 2$) was prepared similarly, using
sodium perchlorate as precipitant; yield 60% after two
recrystallizations from methyl alcohol. The salt formed
orange-brown prisms with a brilliant green reflex and had
m. p. 236–238° dec.

Anal. Calcd. for $C_{20}H_{21}ClN_2O_4S$: C, 57.06; H, 5.03.
Found: C, 57.15; H, 5.01.

**2-[6-(N-Methylanilino)-1,3,5-hexatrienyl]-benzothiazole
ethiodide** (VIII, $n = 3$) was prepared similarly but in this
case 100% excess of methyl p-toluenesulfonate was used

and heating at 100° was continued for only thirty minutes. The yield of iodide was 19% after two recrystallizations from methyl alcohol. It formed steely blue needles and had m. p. 157–158° dec.

Anal. Calcd. for $C_{22}H_{23}IN_2S$: I, 26.76. Found: I, 26.44.

The triiodide corresponding to the above was obtained when 2-methylbenzothiazole ethiodide (6.1 g., 1 mol) and glutaconaldehyde dimethylanilide chloride (6.2 g., 1 mol) were heated to refluxing in acetic anhydride (30 cc.) for ten minutes. The solid which separated was recrystallized several times from methyl alcohol (yield 0.15 g.) and was obtained in minute dark green crystals with m. p. 194–196° dec.

Anal. Calcd. for $C_{22}H_{23}I_3N_2S$: I, 52.30. Found: I, 52.08.

The absorption of this product corresponded closely with that of the monoiodide.

2-(1-Piperidyl)-benzothiazole ethoperchlorate (X, $n = 0$).—Equivalent quantities of 2-ethylmercaptobenzothiazole ethiodide and of piperidine were heated in ethyl alcohol to refluxing for twenty minutes. Ether precipitated an oily material which was dissolved in a little hot water, precipitated with sodium perchlorate (yield 29%) and recrystallized four times from ethyl alcohol (norite, first time) (yield 12%). The colorless crystals had m. p. 129–130°.

Anal. Calcd. for $C_{14}H_{19}ClN_2O_4S$: N, 8.08. Found: N, 8.04.

2-[2-(1-Piperidyl)-vinyl]-benzothiazole ethiodide (X, $n = 1$).—The acetanilido vinyl compound (II, $n = 1$) (0.01 mol) was refluxed in ethyl alcohol (40 cc.) with piperidine (0.03 mol) for one-half hour. The product that separated was recrystallized twice from methyl alcohol (norite); yield 37% of cream colored prisms with m. p. 274–277° dec.

Anal. Calcd. for $C_{16}H_{21}IN_2S$: I, 31.71. Found: I, 31.49.

2-[4-(1-Piperidyl)-1,3-butadienyl]-benzothiazole ethiodide (X, $n = 2$).—Equimolecular proportions of the acetanilido compound (II, $n = 2$) and piperidine were refluxed in ethyl alcohol for ten minutes. After two recrystallizations from methyl alcohol the red prisms (yield 27%) had m. p. 205–207° dec.

Anal. Calcd. for $C_{18}H_{23}IN_2S$: I, 29.78. Found: I, 29.57.

2-[6-(1-Piperidyl)-1,3,5-hexatrienyl]-benzothiazole ethiodide (X, $n = 3$) was similarly prepared; yield 17% after two recrystallizations from methyl alcohol and one from acetone. The dye formed steely blue crystals with m. p. 172–175° dec.

Anal. Calcd. for $C_{20}H_{25}IN_2S$: C, 53.08; H, 5.57; S, 7.09. Found: C, 53.20; H, 5.58; S, 6.99.

2-(2-Anilinovinyl)-quinoline ethiodide (V, $n = 1$).—Equimolecular proportions of quinaldine ethiodide and of diphenylformamidine were intimately mixed and stirred in an oil-bath, the temperature being raised from 120 to 180° over a period of thirty-five minutes. The melt was allowed to solidify, crushed, and washed with acetone (yield 81%). After two recrystallizations from methyl

alcohol (norite) the amber leaflets had m. p. 282–285° dec.; yield 17%.

Anal. Calcd. for $C_{19}H_{19}IN_2$: I, 31.56. Found: I, 31.70.

2-(4-Anilino-1,3-butadienyl)-quinoline ethiodide (V, $n = 2$).—The acetyl derivative, **2-(4-acetanilido-1,3-butadienyl)-quinoline ethiodide,** was first prepared by heating equimolecular amounts of quinaldine ethiodide and of β-anilinoacrolein anil hydrochloride in acetic anhydride at the boiling point for one-half hour, the product obtained after precipitation with ether being recrystallized twice from methyl alcohol; yield 38% of brownish needles with blue reflex, m. p. 231–234° dec.

Anal. Calcd. for $C_{23}H_{23}IN_2O$: I, 27.00. Found: I, 27.04.

This was refluxed with three molecular equivalents of aniline in ethyl alcohol for one-half hour and the product recrystallized four times from methyl alcohol; yield 9% of minute dark crystals with green reflex, m. p. 238–240° dec.

Anal. Calcd. for $C_{21}H_{21}IN_2$: I, 29.65. Found: I, 29.83.

2-(4-Dimethylamino-1,3-butadienyl)-benzothiazole ethiodide (XI) was prepared in similar fashion to the piperidyl derivative (X, $n = 2$); yield 42% after two recrystallizations from methyl alcohol (norite, first time). The minute red crystals had m. p. 244–246° dec.

Anal. Calcd. for $C_{15}H_{19}IN_2S$: I, 32.87. Found: I, 32.62.

In comparing the reactivities of II ($n = 1$), VIII ($n = 1$) and X ($n = 1$) toward 2-methylbenzothiazole ethiodide, one-hundredth molar proportions of the reactants were refluxed together in 20 cc. of pyridine, for the periods indicated in Table III. In each case, ether (150 cc.) was added to complete precipitation of the product, 3,3'-diethylthiacarbocyanine iodide, which was then well washed under constant conditions with water and then acetone.

In the case of II ($n = 2$) and VIII ($n = 2$), the same proportions of reactants were refluxed together in ethyl alcohol (70 cc.), together with 1.05/100 mole of triethylamine, for the periods indicated. After chilling, the dicarbocyanine was removed and washed with acetone.

5-[(3-Ethyl-2(3)-benzothiazolylidene)-ethylidene]-3-phenylrhodanine (XIII).—In the comparative preparations of this substance, the components (0.05 molar amounts) were refluxed together in ethyl alcohol (35 cc.) with triethylamine (0.05 mole plus 5% excess) for the times indicated. The dye was filtered off and washed with methyl alcohol, but when X ($n = 1$) was used, it was necessary to remove that which had not reacted with hot methyl alcohol and unchanged 3-phenylrhodanine with hot benzene. The dye separated from acetic acid in minute prisms with a brilliant green reflex, m. p. 283–285° dec.

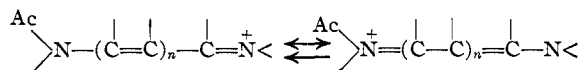*Anal.* Calcd. for $C_{20}H_{16}N_2OS_3$: C, 60.56; H, 4.07; N, 7.07. Found: C, 60.65; H, 4.21; N, 7.19.

Summary

The absorptions of five series of vinylene homologous compounds have been compared.

Three of the series are of the amidinium salt

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

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

$$\overset{Ac}{\underset{}{>}}N-(\overset{|}{C}=\overset{|}{C})_n-\overset{|}{C}=\overset{+}{N}< \;\rightleftharpoons\; \overset{Ac}{\underset{}{>}}\overset{+}{N}=(\overset{|}{C}-\overset{|}{C})_n=\overset{|}{C}-N<$$

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

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

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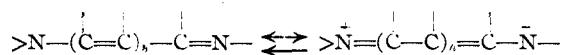
In general, these bases absorb at markedly shorter wave length than their hydr- or ethiodides (these latter constituting two of the strongly degenerate series referred to above), and, furthermore, their vinylene shifts decrease markedly as the series is ascended. This is correlated with inhibition of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

ROCHESTER, N. Y.
PRINCETON, N. J.   RECEIVED JULY 17, 1941

[COMMUNICATION No. 819 FROM THE KODAK RESEARCH LABORATORIES]

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

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

The base 2-p-dimethylaminostyrylquinoline (I)[3] dissolves in basic or in neutral solvents with a yel-

(a) / (b) structures I
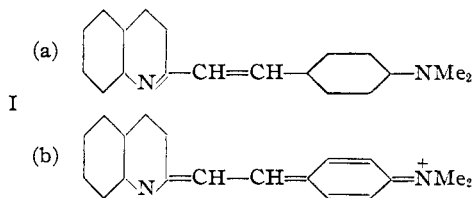
low color but exhibits halochromism in that on acidification or on treatment with methyl iodide the color is deepened to wine red. This has at-

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

Rupe, Hagenbach and Collin[4] have shown that the base gives rise to two mono-methiodides, one of which is the wine red salt referred to above, the other being almost colorless. The red isomer is also formed when quinaldine methiodide is con-
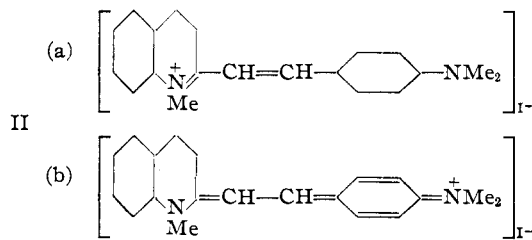
(a) / (b) structures II

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

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

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

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