Anal. Calcd. for $C_{19}H_{22}ClNO$: Cl, 11.23. Found: Cl, 11.73.

Methiodide of 3-Methoxy-10,11-dimethyl-5,6,8,9,10,11-hexahydronaphth[2,1-g]isoquinoline (XIVa).—The base from 0.2 g. of the above hydrochloride was dissolved in 3 cc. of acetone, and 0.3 cc. of methyl iodide and 0.1 g. of powdered potassium hydroxide were added. After one hour the white methiodide was filtered, and washed free of alkali with cold water. It was recrystallized from absolute ethanol; m. p. 256–258°.

Anal. Calcd. for $C_{21}H_{26}INO$: I, 29.15. Found: I, 29.47.

3-Methoxy-10,11-dimethyl-5,6,8,9,10,11-hexahydronaphth[2,1-g]isoquinoline (XIV).—(a) The methiodide XIIa (m. p. 287–288°) absorbed one mole of hydrogen rapidly when catalytically reduced. After removal of the catalyst, the ethanol solution was concentrated, and a white **hydriodide** was precipitated by addition of ether. It was recrystallized from ethanol, and melted at 236–238°.

Anal. Calcd. for $C_{20}H_{24}INO$: I, 30.12. Found: I, 29.75.

The **base** was liberated with ammonium hydroxide and slowly distilled at about 100° in an oil-pump vacuum; m. p. 97–98°.

Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90. Found: C, 81.70; H, 7.72.

The **hydrochloride** was prepared and purified in the usual way, and melted at 200–202°.

Anal. Calcd. for $C_{20}H_{24}ClNO$: C, 72.82; H, 7.33. Found: C, 72.71; H, 7.53.

Addition of methyl iodide to an acetone solution of the base precipitated the quaternary methiodide, XIVa, identical (melting point, mixture melting point) with that obtained by the action of methyl iodide and potassium hydroxide on 3-methoxy-11-methyl-5,6,8,9,10,11-hexahydronaphth[2,1-g]isoquinoline (XIII).

(b) Base XIV was also obtained by heating the methiodide XIVa to 250° in an oil-pump vacuum. It was identified by melting point and mixture melting point.

Summary

The synthesis of two new phenolic amino alcohols, 2-hydroxy-7-[2-(diethylamino)-1-hydroxyethyl]-9,10-dihydrophenanthrene and 2-hydroxy-7-[3-(diethylamino)-1-hydroxy-*n*-propyl]-9,10-dihydrophenanthrene, is described.

The synthesis of two isoquinoline derivatives of the 9,10-dihydrophenanthrene series, 10,11-dimethyl-5,6,8,9,10,11-hexahydronaphth[2,1-g]isoquinoline and 3-methoxy-10,11-dimethyl-5,6,8,-9,10,11-hexahydronaphth[2,1-g]isoquinoline (?), is described.

The starting materials, 9,10-dihydrophenanthrene-2-aldehyde and 2-methoxy-9,10-dihydrophenanthrene-7-aldehyde, were obtained by the Rosenmund method from the corresponding phenanthroic acid chlorides, while the intermediate products, 2-(2-aminoethyl)-9,10-dihydrophenanthrene and 2-methoxy-7-(2-aminoethyl)-9,10-dihydrophenanthrene, were prepared by the Curtius reaction from the corresponding β-dihydrophenanthrylpropionic acids.

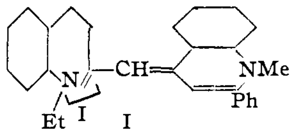
WASHINGTON, D. C. RECEIVED FEBRUARY 23, 1940

[JOINT CONTRIBUTION FROM THE KODAK RESEARCH LABORATORIES AND THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

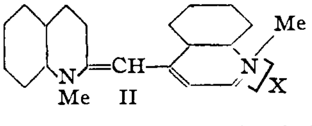
Color and Constitution. I. Halochromism of Anhydronium Bases Related to the Cyanine Dyes[1]

BY L. G. S. BROOKER, R. H. SPRAGUE, C. P. SMYTH AND G. L. LEWIS

In their work on the structure of the isocyanines, Kaufmann and Vonderwahl[2] brought forward evidence which they interpreted as indicating the static configuration I for 1-ethyl-1′-methyl-2′-phenyl-2,4′-cyanine iodide. They heated the dye in a high vacuum and obtained ethyl iodide and a base having the composition of a methylphenylquinolylidenequinaldine, and this was considered to prove that the iodine atom was attached to the nitrogen atom of the quinaldine nucleus.



I



II

On the other hand, as a result of their experiments on the oxidation of 1,1′-dimethyl-2,4′-cyanine acetate, Mills and Wishart[3] felt that it was justifiable to accept II as the formula of this substance rather than the alternative structure in

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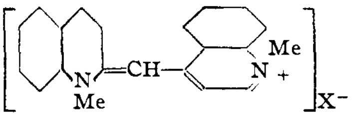
[1] Communication No. 755 of the Kodak Research Laboratories. Presented in part before the Organic Section of the American Chemical Society at the September, 1937, meeting at Rochester, New York.

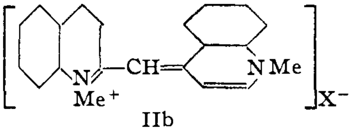
[2] Kaufmann and Vonderwahl, *Ber.*, **45**, 1407 (1912).

[3] Mills and Wishart, *J. Chem. Soc.*, **117**, 579 (1920).

which the nitrogen atom of the quinaldine nucleus is quaternary, but they recognized that the two forms might be virtually tautomeric. Since then, much evidence has been accumulated in favor of such tautomerism.[4] This conception has been amplified by the theory of resonance[5] according to which the molecule of a cyanine dye such as II is considered to be a resonance hybrid between two extreme states, the intense colors of the cyanines being attributed to such resonance. Thus, in the case of II, which is highly colored, we have the resonance scheme IIa ←→ IIb.



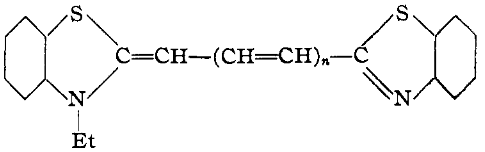
IIa



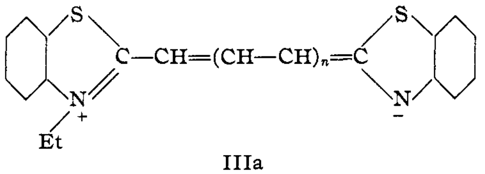
IIb

There can be no doubt that resonance of this type is very closely related to the occurrence of color in many organic compounds, and resonance structures have been assigned to practically all the principal dye types.[5] The subject has been particularly well worked out for dyes of the triphenylmethane series where it has been shown that so treating a dye that a possible mode of resonance is restricted results in the characteristic absorption of the dye being profoundly modified.[6]

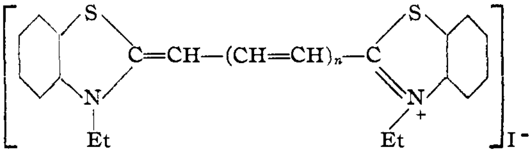
In the present work, we have endeavored to throw further light on the nature of resonance in the cyanines by comparing the series of three symmetrical cyanines derived from benzothiazole (IV, $n = 0, 1, 2$) with the series of tertiary bases (III, $n = 0, 1, 2$) obtained from them by removal of the elements of ethyl halide by heating with diethylaniline according to the method of Schwarz.[7]



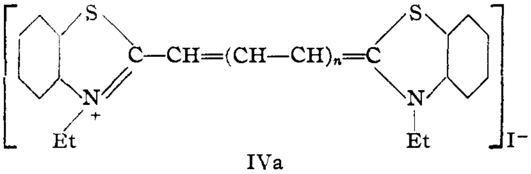
III



IIIa



IV



IVa

Of the three bases, that with the shortest chain ($n = 0$) was first prepared using another method by Mills,[8] who obtained it as a pale yellow crystalline substance. Its methyl alcoholic solution has an extremely pale yellow color. The next higher vinylene homolog ($n = 1$) was made by Schwarz and Gevaert Photo-Producten, N. V.,[7] who describe it as slightly yellow colored and add that it absorbs only the short wave end of the visible spectrum without having a distinct maximum. We find, however, that its methyl alcoholic solution absorbs in the blue part of the spectrum and shows a well-defined maximum. The base with the longest chain ($n = 2$) has not hitherto been described. It forms lustrous reddish needles which dissolve in methyl alcohol to give a rather dull brownish-red solution.

In every case, a solution of one of these bases in methyl alcohol is markedly lighter in color than a solution of the cyanine with the same length of chain, the colors of the cyanines in solution being yellow ($n = 0$), bluish-red ($n = 1$) and blue ($n = 2$).

The absorptions of all six compounds in methyl alcohol are given in Fig. 1, and these curves reveal striking relationships. The positions of the absorption maxima are given in Table I, differences also being shown.

From Fig. 1 and Table I, it can be seen that in every case, a base (III) absorbs nearer the shorter waves than the cyanine with a chain of the same

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(4) (a) Mills and Braunholtz, *J. Chem. Soc.*, **121**, 1489 (1922); (b) Hamer, *ibid.*, 206 (1928); (c) Kuhn, Winterstein and Balser, *Ber.*, **63**, 3176 (1930); (d) Ogata, *Proc. Imp. Acad. Tokyo*, **8**, 119 (1932); (e) Ogata, *Bull. Inst. Phys. and Chem. Research, Tokyo*, **13**, 549 (1934); (f) Brooker and Keyes, THIS JOURNAL, **57**, 2488 (1935).

(5) Bury, *ibid.*, **57**, 2115 (1935).

(6) Taylor and Baker, Sidgwick's "Organic Chemistry of Nitrogen," Oxford Univ. Press, New York, N. Y., 1937, p. 88.

(7) Schwarz and Gevaert Photo-Producten, N. V., United States Patent 2,169,434.

(8) Mills, *J. Chem. Soc.*, **121**, 455 (1922).

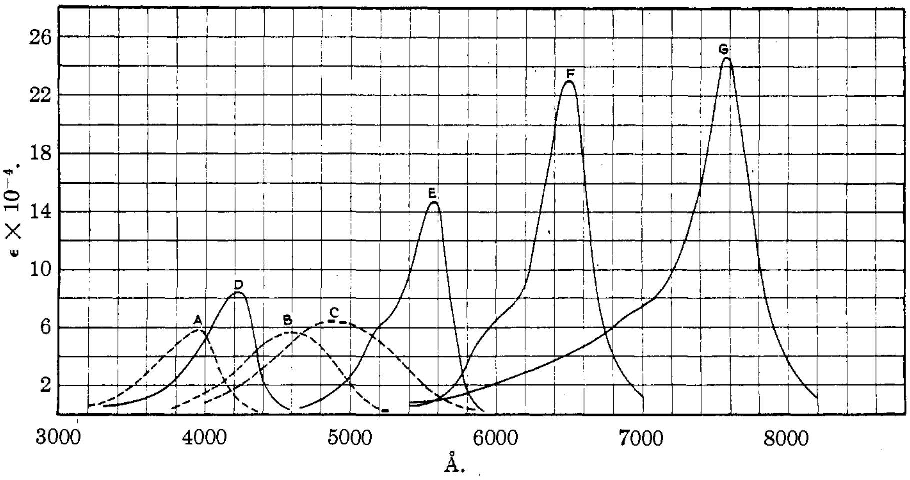

Fig. 1.—Absorption curves in methyl alcohol: A, B, C, = III, n = 0, 1, 2, respectively; D, E, F, G = IV, n = 0, 1, 2, 3, respectively.

TABLE I

Compound	Absorption max. Å.	Differences		Max. value of $\epsilon \times 10^{-4}$
III, $n = 0$	3960	> 620		5.85
III, $n = 1$	4580	> 320	270	5.65
III, $n = 2$	4900		995	6.4
IV, $n = 0$	4230	> 1345	1600	8.45
IV, $n = 1$	5575	> 925		14.8
IV, $n = 2$	6500	> 1080		22.9
IV, $n = 3$	7580			24.6

length. Furthermore, whereas it has been amply demonstrated that increasing the length of the polymethine chain joining the nuclei in a cyanine dye shifts the absorption toward the longer waves,[9] it can be seen that a similar relationship also holds in the series of tertiary bases. Here also lengthening the conjugated chain joining the nitrogen atoms shifts the absorption toward the red, but the amounts of the shifts are considerably smaller than with the cyanines. Whereas addition of a vinylene group to the cyanine IV, n = 0, produces a shift of 1345 Å., addition of vinylene to the base III, n = 0, produces a shift of only 620 Å., and addition of a further vinylene results in shifts of 925 and 320 Å. in the cyanine and base series, respectively. It follows that the difference in absorption between a cyanine and a base of the same chain length becomes greater with increasing length of the vinylene chain. There is only a difference of 270 Å. between base and cyanine in the series n = 0, this difference increasing to 995 Å. where n = 1 and to 1600 Å. where n = 2.

In the cyanine series, the value of $\epsilon_{\text{max.}}$ increases continuously as the series is ascended, this being in agreement with the findings of Kuhn and Hausser[10] in series of polyene compounds that they examined. The difference between the values of $\epsilon_{\text{max.}}$ for IV, n = 1 and IV, n = 2 is, however, much greater than that between IV, n = 2 and IV, n = 3.

In the series of bases, the values of $\epsilon_{\text{max.}}$ are very close together, and the first member actually has a slightly higher value than the second, although the value for the third member is the highest of the three. However, these values are decidedly lower than those for the corresponding cyanines.

In the cyanine series, the two extreme resonance states IV and IVa are identical and have the same internal energy. The mobility of the linkages in the conjugated chain is therefore very great, and since there is a full ionic charge available for resonance, this reaches a high level of perfection. These conditions appear to give rise to absorption curves which rise, in the first few members, to a high value of $\epsilon_{\text{max.}}$, and which are widely separated with respect to wave length.

On the other hand, the bases III are not ionized structures, and no alternative formula for III can be written in which the sequence of single and double linkages of the conjugated chain between the nuclei is reversed and in which the nitrogen atoms are in the normal tri- or tetra-covalent states. However, there is a certain amount of probability for the alternative configuration IIIa.

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(9) *Cf.* in particular, (a) Fisher and Hamer, *Proc. Roy. Soc.* (London), **A154**, 703 (1936); (b) Beilenson, Fisher and Hamer, *ibid.*, **163**, 138 (1937).

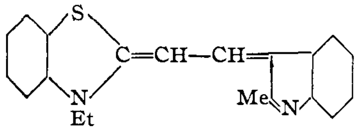
(10) Hausser, *Z. tech. Physik.* **15**, 10 (1934); note especially Fig. 20.

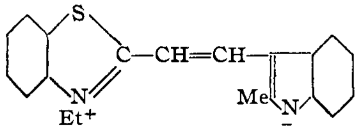
In particular, this gives an explanation of why addition of alkyl halide takes place solely at the right-hand benzothiazole nucleus. The negatively charged nitrogen atom is free to accept a proton or alkyl while the nitrogen of the left-hand nucleus will not do so because it is already quaternary. The resonance scheme III$\longleftrightarrow$IIIa is, therefore, suggested for these bases which thus resemble the anhydronium bases of Robinson and coworkers.[11] Since III and IIIa are not identical, the actual state of the molecule will tend to approach the more stable of the two configurations, thereby becoming, in corresponding measure, less of a resonance hybrid. Resonance will therefore be more restricted in the bases than in the cyanines, and this accords with the observed lighter colors of the former.

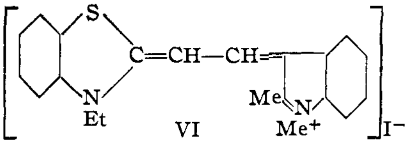
Of the two configurations III and IIIa, it seems probable that the former is the more stable, so that the actual state of the molecule will be closer to III than to IIIa. In the latter, the negatively charged nitrogen atom seems likely to be the least stable part (the quaternary nitrogen is a normal structure), and it would follow that if the negatively charged nitrogen could be rendered more stable, the whole configuration IIIa would become more stable. This would result in resonance being increased in the base which, in turn, would be accompanied by a deepening of color.

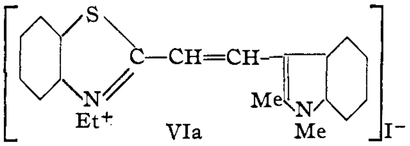
Now pyrroles and indoles with hydrogen attached to nitrogen will in general yield potassium derivatives and hence show a strong tendency to form negatively charged ions in which $>\overline{\underset{\bullet}{N}}$ is stable.

We have accordingly prepared the base 3-[(3-ethyl-2(3)-benzothiazolylidene)-ethylidene]-2-methyl-indolenine (V) by condensing 2-methyl-3-indolealdehyde with 2-methylbenzothiazole ethiodide in acetic anhydride solution. This base dissolves in methyl alcohol to give a yellowish orange solution which is actually deeper in color than the solution of its methiodide VI made either by the addition of methyl iodide to V or by condensing 1,2-dimethyl-3-indolealdehyde with 2-methylbenzothiazole ethiodide. The absorption curves are shown in Fig. 2. The maximum absorption of V determined in pyridine is at 5060 Å., there being an inflection at shorter wave length and the maximum of VI in the same solvent is at 4970 Å. (Pyridine was chosen for the absorptions because in dilute methyl alcoholic solution there was a tendency on the part of V to develop a maximum at 4830 Å. corresponding to the acidified form. Addition of a few drops of piperidine deepened the color so that the maximum moved to 5070 Å., corresponding closely with the maximum developed in pyridine alone.)


V


Va


VI


VIa

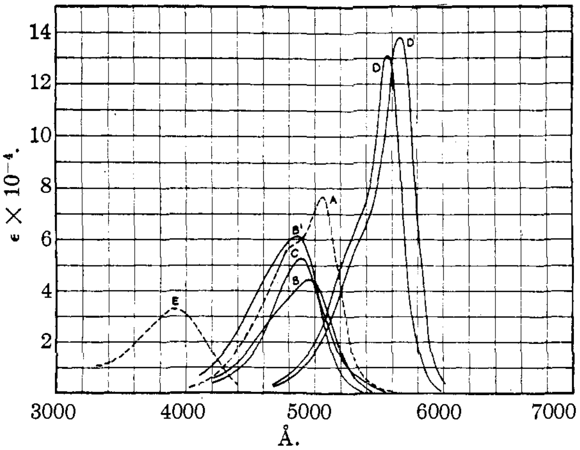


Fig. 2.—Absorption curves: A, 3-[(3-ethyl-2(3)-benzothiazolylidene)-ethylidene]-2-methyl-indolenine (V) in pyridine; B and B', [3-ethyl-benzothiazole-(2)]-[1,2-dimethyl-indole-(3)]-di-methine-cyanine iodide (VI) in pyridine and nitromethane, respectively; C, bis-[1,2-dimethyl-indole-(3)]-methine-cyanine iodide (VIII) in nitromethane; D and D', 3,3'-diethyl-thiacarbocyanine iodide in nitromethane and pyridine, respectively; E, 3-(β-2-benzothiazolyl-vinyl)-1,2-dimethyl-indole (IX) in pyridine.

König[12] already has prepared several bases of the type of V, and he noted that they showed a "kind of reversed halochromism" in that they

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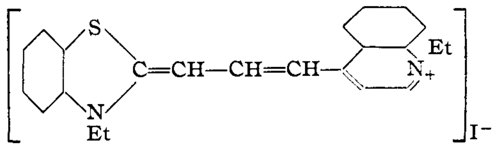
[11] *Cf.* Freak and Robinson, *J. Chem. Soc.*, 2013 (1938).

[12] König, *J. prakt. Chem.*, [2] **86**, 514 (1912).

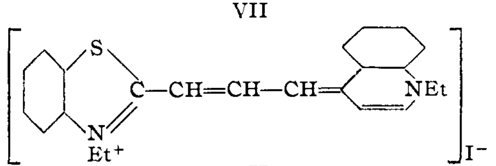
were deeper in color than their salts, but no explanation of this unusual state of affairs has so far appeared.

We now suggest that the known tendency of indole to yield an indolyl anion renders the configuration Va relatively more stable than the corresponding configuration IIIa and hence the actual state of the compound represented by the resonance scheme V ⟷ Va is closer to an intermediate position, *i. e.*, the base is more truly a resonance hybrid, than a base represented by III ⟷ IIIa. We consider, then, that V ⟷ Va represents a relatively high degree of resonance but, even so, it is remarkable that this base is deeper colored than its methiodide, in which a full ionic charge is available for resonance. The explanation of this apparent anomaly appears to lie in the fact that the methiodide VI, considered as an unsymmetrical cyanine, is exceptionally light in color.

Most of the unsymmetrical cyanines studied by Dr. Hamer and her colleagues[9b] have absorption maxima which agree fairly well with the calculated mean values of the related parent dyes, agreement being rather better in the carbocyanine than in the simple cyanine or dicarbocyanine series. This would seem to indicate that the internal energies of the two extreme resonance states of such unsymmetrical cyanines are very nearly the same. For example, the two extreme states in the case of 1′,3-diethylthia-4′-carbocyanine iodide (VII and VIIa) must have nearly equal probability. This is understandable in view of the fact that although benzothiazole is considered to be somewhat less basic than quinoline, these bases are nevertheless comparable types, so that no very marked preference for the positive charge will be shown by either of the nitrogen atoms in dyes of this type, *i. e.*, VII will not be appreciably favored over VIIa or *vice versa.*

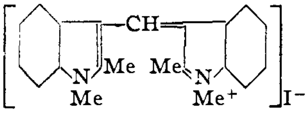


VII



VIIa

In the present case, the methiodide VI (or VIa) is a dimethine cyanine which may be considered as a cross between the two symmetrical dyes, *bis*-[1,2-dimethylindole-(3)]methine-cyanine iodide (VIII) and 3,3′-diethylthiacarbocyanine iodide (IV, $n = 1$), but unlike the unsymmetrical cyanines hitherto described,[9b] the absorption of VI lies at markedly shorter wave length than the mean of the absorptions of the parent symmetrical dyes, and in fact, its absorption maximum in nitromethane actually lies at shorter wave length than that of the lighter of the parent dyes (VIII) (Fig. 2), and this constitutes the first recorded instance of an unsymmetrical cyanine absorbing in this way. (Nitromethane was chosen as solvent for the comparison because VIII was unstable in pyridine or in alcoholic solution.)



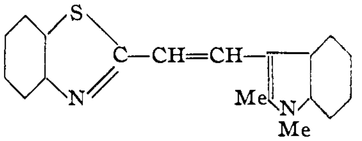
VIII

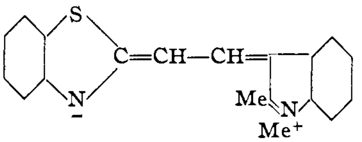
Since indoles are very weak bases and form salts with difficulty, it seems likely that of the two extreme resonance configurations VI and VIa, that in which the indole nitrogen is quaternary (VI) will be appreciably less stable than that in which the positive charge is associated with the more strongly basic benzothiazole nitrogen (VIa). Thus the actual state of the compound will tend to approach VIa in the resonance scheme VI ⟷ VIa with consequent diminution of resonance which will cause the color to be lightened.

The "reversed halochromism" of V may be attributed, therefore, to a combination of two related factors. The first is that the base is deeply colored because it resonates strongly according to the scheme V ⟷ Va, this being traceable to the stability of $>\ddot{N}$ in the indole ring in Va. The second is that the methiodide is unusually light in color because in it resonance is inhibited due to the relative instability of one of the resonance configurations (VI) traceable in turn to the weak basicity of the indole nitrogen. The net result is that the base is more deeply colored than its methiodide.

Since in some cases salt formation causes deepening of color and in others lightening of color, it is clear that it is theoretically possible for salt formation to bring about no color change at all. Actually, those instances appear to be more numerous in which a deepening of color occurs, and the term halochromism usually implies this, but a lightening of color is no less significant from a theoretical standpoint.

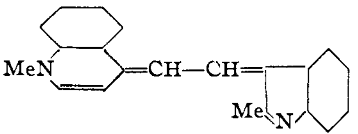
That the mere presence of an indole nucleus in an anhydronium base does not give rise to unusually deep colors may be deduced from the following consideration. The base 3-(β-2-benzothiazolyl-vinyl)-1,2-dimethylindole (IX) was prepared by condensing 1,2-dimethyl-3-indolealdehyde with 2-methylbenzothiazole in the presence of hydrochloric acid and basifying the product.

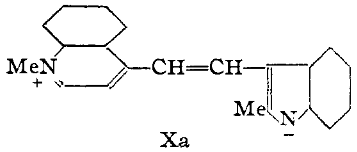

IX

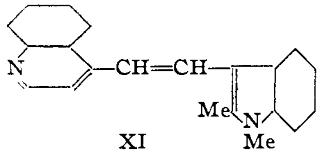

IXa

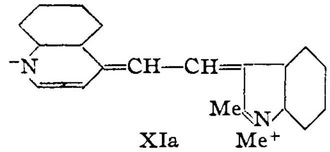
The second extreme resonance configuration of this substance, IXa, contains a negatively charged benzothiazole nitrogen which we have suggested is not as stable as the corresponding negatively charged nitrogen in Va, and also a quaternary indole nitrogen which we have argued above is also unstable. It will be concluded, therefore, that IXa is an especially unstable configuration and consequently the base will tend strongly to approach IX with corresponding loss of its resonance-hybrid character, and this will result in its having a relatively light color. This argument is supported by the facts, for IX is almost colorless in solution, its absorption maximum in pyridine being at 3920 Å. (Fig. 2, Curve E). Its structure was confirmed by the fact that it gave VI (or VIa) on treatment with ethyl iodide.

In a further set of comparisons, two isomeric bases were compared, 2-methyl-3-[(1-methyl-4(1)-quinolylidene)-ethylidene]-indolenine (X) and 1,2-dimethyl-3-(β-4-quinolyl-vinyl)-indole (XI).


X

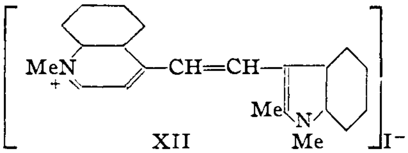

Xa

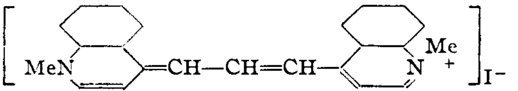

XI


XIa

The first of these was prepared by condensing lepidine methiodide with 2-methyl-3-indolealdehyde in acetic anhydride solution and basifying the product, and the second by condensing lepidine with 1,2-dimethyl-3-indolealdehyde in the presence of hydrochloric acid and basifying the product. Of these bases, X is much the deeper colored of the two, its bluish purple pyridine solution having two absorption maxima of comparable strength at 5710 and 6160 Å., the former being somewhat the stronger (Fig. 3, A). On the other hand, XI gives only a pale yellow solution in pyridine which absorbs very weakly indeed with its maximum at 3940 Å. (Fig. 3, B), and these results can be correlated with the probability of much greater resonance mobility in X ⟷ Xa than in XI ⟷ XIa for precisely similar reasons to those advanced in the case of V and IX, respectively.

Both X and XI add methyl iodide readily to give the same methiodide XII, and this has $\lambda_{\text{max.}}$ at 5390 Å. in pyridine (Fig. 3, C) so that it is lighter in color than X but much deeper in color than XI. In this case XII may be regarded as


XII


XIII

the cross between the two symmetrical dyes VIII and 1,1′-dimethyl-4,4′-carbocyanine iodide XIII, and once again XII absorbs at markedly shorter wave length than the mean of the wave lengths of maximum absorption of these two,[13] for, it

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(13) For this comparison, it was hoped to obtain the absorptions of all three substances in the same solvent. Curves D and C′ (Fig. 3) are those of VIII and XII in nitromethane but dilute solutions of XIII in this solvent proved to be extremely unstable, and

is suggested, a reason similar to that advanced in the case of VI.

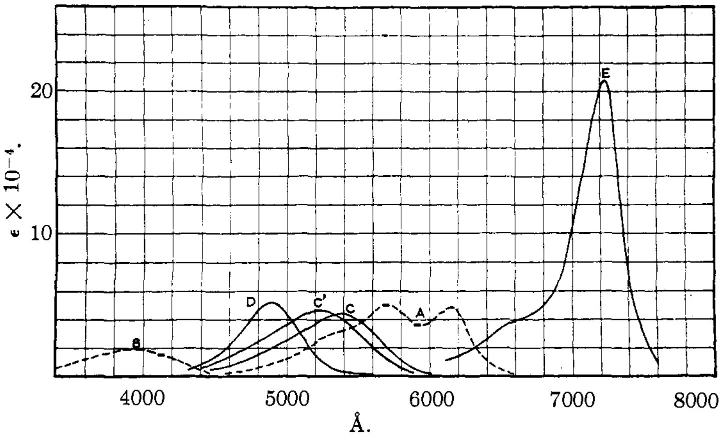


Fig. 3.—Absorption curves: A, 2-methyl-3-[(1-methyl-4(1)-quinolylidene)-ethylidene]-indolenine (X) in pyridine; B, 1,2-dimethyl-3-(β-4-quinolyl-vinyl)-indole (XI) in pyridine; C, [1,2-dimethylindole-(3)]-[1-methylquinoline-(4)]-dimethinecyanine iodide (XII) in pyridine, C′ in nitromethane; D, bis-[1,2-dimethylindole-(3)]-methinecyanine iodide (VIII) in nitromethane; E, 1,1′-dimethyl-4,4′-carbocyanine iodide (XIII) in pyridine.

Independent confirmation of the theories developed here to account for the colors of the anhydronium bases III ($n = 1$), V, IX, X and XI has been provided by a study of their dipole moments. If the suggested dipolar configurations were significant in defining the structures of these bases, then the dipole moments would be expected to be much higher than those calculated from the classical formulas. Further, since it has been argued that the dipolar configurations Va and Xa play more important parts in the resonance schemes V $\longleftrightarrow$ Va and X $\longleftrightarrow$ Xa than IXa and XIa do in the schemes IX $\longleftrightarrow$ IXa and XI $\longleftrightarrow$ XIa, it should follow that the dipole moments of the first pair of bases should be markedly higher than those of the latter. These expectations have been fully realized. Not only were the dipole moments of the bases in all cases markedly higher than those calculated from the classical formulas, but those of the deeply colored bases V $\longleftrightarrow$ Va and X $\longleftrightarrow$ Xa were much higher than those of the corresponding lighter colored bases IX $\longleftrightarrow$ IXa and XI $\longleftrightarrow$ XIa.

The dielectric constants of very dilute solutions of the bases in benzene were measured at a frequency of 520 kilocycles and a temperature of 25° with a heterodyne beat apparatus described elsewhere[14] and have been used, together with the densities measured with an Ostwald–Sprengel pycnometer, to calculate the dipole moments by the usual method.[15]

In Table II there are given the mole fraction c_2 of each substance in benzene solution, the dielectric constant D and density d of the solution, and the polarization P_2 of the substance calculated from these data. As the color of several of the solutions made impossible an accurate determination of refractive index, the molar refractions, MR_D, were calculated as the sums of the atomic refractions with due regard to constitutive influences. The uncertainties in these calculated values of MR_D given in the first column of Table II are small in comparison with the errors in the values of the polarization at infinite dilution, P_∞, obtained by extrapolation of the P_2 values. The probable errors in these P_∞ values are unusually large as the result of the high dilutions at which the measurements had to be made because of the low solubilities of the substances. The resulting experimental values of the moments given in the eighth column of Table II have probable errors of about 1% except in the case of X(Xa), where it is 5%.

The last column of Table II gives the values of the dipole moments μ calcd. which the molecules should have in the absence of resonance contributions from ionic structures other than those normally found in the bonds involved. These moment values are necessarily extremely approximate, having a probable error 0.5×10^{-18}. They are calculated[16] from bond moments and from the moments of groups obtained from molecular moments in the literature, rotation around single bonds being taken into account as far as possible.[17] Uncertainty as to rotation or orientation of large groups around single bonds and, in some cases, the question of *cis* or *trans*

Curve E was determined in pyridine. In the three cases in this paper where absorptions have been determined in the two solvents (Fig. 2, B and B′, D and D′; Fig. 3, C and C′) nitromethane gives somewhat the lower value for $\lambda_{\text{max.}}$, so that by analogy, $\lambda_{\text{max.}}$ of XIII in nitromethane should lie at shorter wave length than that in pyridine. Even if an allowance of as much as 200 Å. is made for this effect, XII still absorbs at much shorter wave length than the mean of the absorptions of VIII and XIII. The value of $\lambda_{\text{max.}}$ for curve C′ (Fig. 3) is 5240 Å., and for E it is 7230 Å.

(14) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(15) Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

(16) Smyth, *J. Phys. Chem.*, **41**, 209 (1937); THIS JOURNAL, **60**, 183 (1938).

(17) See Smyth and Walls, *ibid.*, **54**, 2261 (1932).

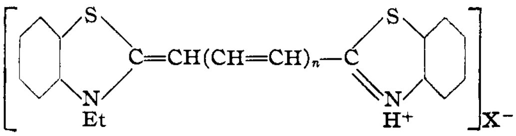
TABLE II

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_∞ (25°)	$\mu(\times 10^{18})$	μcalcd. $(\times 10^{18})$
III $\longleftrightarrow$ IIIa	0.000000	2.2760	0.87334	(P_1 = 26.668)				
(n = 1)	.001617	2.3258	.87531	521	103	525	4.51	1.6
	.004340	2.4115	.87872	500				
	.005760	2.4526	.88046	511				
	.007401	2.5010	.88230	506				
V $\longleftrightarrow$ Va	.000000	2.2760	.87334	(P_1 = 26.668)				
	.000710	2.3364	.87405	1304	100	1350	7.68	2.2
	.001299	2.3860	.87473	1285				
	.001581	2.4097	.87515	1280				
IX $\longleftrightarrow$ IXa	.00000	2.2751	.87275	(P_1 = 26.672)				
	.00169	2.3154	.87429	424	94	434	4.06	2.2
	.00322	2.3513	.87581	422				
	.00488	2.3889	.87754	416				
	.00673	2.4332	.87971	408				
X $\longleftrightarrow$ Xa	.000000	2.2760	.87334	(P_1 = 26.668)				
	.000076	2.2875	.87337	2303	96	2450	10.6	2.5
	.000144	2.2958	.87345	2090				
XI $\longleftrightarrow$ XIa	.000000	2.2751	.87275	(P_1 = 26.672)				
	.001557	2.3390	.87418	670	93	705	5.43	2.5
	.002623	2.3773	.87503	637				
	.003546	2.4083	.87569	615				

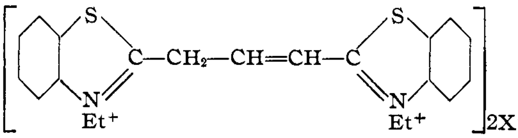
configurations contribute to the uncertainty of these calculated values. Moments calculated for dipolar structures are subject to far greater errors because of these uncertainties. The values estimated for these structures lie, for the most part, between 20 and 30 $\times$ 10^{-18}. As it seems probable that values thus calculated for such dipolar structures without knowledge of the reduction of the moments by induced shifts of charge are much too high,[16] they are omitted from Table II as misleading.

Addition of mineral acid to dilute alcoholic solutions of the anhydronium bases (III, V, IX, X and XI) gave colors which were visually indistinguishable from those of the cyanines (IV, VI, VI, XII and XII, respectively). The solutions so obtained were in most cases unstable and faded badly on trying to measure their absorptions, and we have only determined the wave lengths of maximum absorption of acidified solutions of the bases III (n = 0, 1, 2). For these three the values are 4220, 5525 and 6480 Å., respectively, and these are slightly less than the figures for the corresponding diethyl cyanines. In these cases addition of a proton gives XIV and this can resonate in similar fashion to that postulated for IV.



(XIV)

Addition of excess of mineral acid to solutions of the cyanines or of the bases discharges the color completely, indicating destruction of the conjugated system as suggested in XV.



(XV)

Acknowledgment.—We wish to thank Mr. E. E. Richardson and Dr. L. A. Jones for the absorptions and Dr. L. T. Hallett for the analyses.

Experimental

2 - [(3 - Ethyl - 2(3) - benzothiazolylidene) - methylene]-benzothiazole (III, n = 0).—3,3′-Diethylthiacyanine iodide[18] (1.3 g.) was heated to refluxing with diethylaniline (100 cc.) for two hours. The mixture was then steam distilled and the residue extracted with 500 cc. methyl alcohol and the extract concentrated to 40 cc. The base separated and was purified by two recrystallizations from methyl alcohol (charcoal) (145 cc. per g.); yield 46%, m. p. 163–164° with darkening.

2 - [3 - (3 - Ethyl - 2(3) - benzothiazolylidene) - propenyl]-benzothiazole (III, n = 1).—3,3′-Diethylthiacarbocyanine iodide[19] (30 g.) was heated under dry carbon dioxide with diethylaniline (600 cc.) for two hours with mechanical

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(18) Fisher and Hamer, *J. Chem. Soc.*, 2502 (1930).

(19) Hamer, *ibid.*, 2796 (1927).

stirring, some of the solvent being slowly distilled off. After concentration *in vacuo* as far as possible 300 cc. of ether was added and the base separated on chilling, and was purified by recrystallization from absolute ethyl alcohol (30 cc. per g.); yield 65%. The base formed reddish-brown crystals with double green and blue reflex; m. p. 138–140° with some decomposition.

Anal. Calcd. for $C_{19}H_{16}N_2S_2$: C, 67.79; H, 4.80. Found: C, 67.62; H, 5.09.

2 - [5 - (3 - Ethyl - 2(3) - benzothiazolylidene) - 1,3-pentadienyl]-benzothiazole (III, $n = 2$).—3,3′-Diethylthiadicarbocyanine iodide[9a] (10 g.) was heated under dry carbon dioxide with diethylaniline (500 cc.) for one hour with mechanical stirring, some of the solvent (200 cc.) being slowly distilled off during the reaction. After filtration to remove a small residue of unchanged cyanine the liquid was concentrated *in vacuo* to 25 cc. The oily residue so obtained was extracted with 50 cc. hot methyl alcohol and separated as an oil from the extract on chilling. Crystals were obtained on stirring with cold acetone (15 cc.) and were purified by recrystallization from this solvent (50 cc. per g.); yield 4%; m. p. 161–162° with some decomposition.

Anal. Calcd. for $C_{21}H_{18}N_2S_2$: C, 69.55; H, 5.01. Found: C, 69.46; H, 5.15.

3 - [(3 - Ethyl - 2(3) - benzothiazolylidene) - ethylidene]-2-methyl-indolenine (V).—The hydriodide of this base was prepared by condensing 2-methylbenzothiazole ethiodide (5.75 g.; 1 mol) with 2-methyl-3-indolealdehyde (3 g., 1 mol) in acetic anhydride (30 cc.), refluxing for two minutes; yield 93%. After two recrystallizations from methyl alcohol (190 cc. per g.) the dye formed minute reddish-brown needles with a blue reflex and had m. p. 283–284°, dec.

Anal. Calcd. for $C_{20}H_{19}IN_2S$: I, 28.45. Found: I, 28.31.

The hydriodide (2 g., 1 mol) was stirred mechanically with a mixture of 50 cc. of 20% aqueous sodium hydroxide and 75 cc. of acetone at room temperature for one-half hour. The hydriodide slowly dissolved and crystals of the base separated. The aqueous layer was drawn off and more base was obtained by concentrating the acetone layer; yield 91%. After recrystallization from acetone (50 cc. per g.) the base formed beautiful reddish-brown prisms with a bright green reflex and had m. p. 286–288° dec.

Anal. Calcd. for $C_{20}H_{18}N_2S$: C, 75.43; H, 5.70. Found: C, 75.08; H, 5.84.

[3 - Ethyl - benzothiazole - (2)] - [1,2 - dimethyl - indole-(3)]-dimethine-cyanine Iodide (VI).—(a). 2-Methylbenzothiazole etho-*p*-toluenesulfonate[20] (3.5 g., 1 mol) and 1,2-dimethyl-3-indolealdehyde (1.73 g., 1 mol) were refluxed for five minutes in acetic anhydride (15 cc.). Dye separated on chilling; yield 91%. This was converted directly into the iodide using sodium iodide; yield 95% for the conversion. The dye separated in scarlet prisms from methyl alcohol (310 cc. per g.); m. p. 269–271°, dec.

Anal. Calcd. for $C_{21}H_{21}IN_2S$: I, 27.57. Found: I, 27.52.

(b) The dye was obtained in theoretical yield when the base V (1.6 g., 1 mol) was heated under reflux with methyl iodide (2.8 g., 4 mols) in nitrobenzene (25 cc.) for four hours. The base first dissolved and then the iodide separated rapidly, crystallization being subsequently promoted by adding ether. After recrystallization analysis gave I, 27.37.

(c) When the base IX (0.5 g., 1 mol) was refluxed with ethyl iodide (1.6 g., 6 mols) for six hours, the iodide separated slowly; yield 39%. After recrystallization analysis gave I, 27.34.

The identity of specimens obtained in a, b and c was established by m. p. and mixed m. p. determinations. The absorptions were also identical.

3-(β-2-Benzothiazolyl-vinyl)-1,2-dimethylindole (IX).—2-Methylbenzothiazole (3 g., 2 mols), 1,2-dimethyl-3-indolealdehyde (1.73 g., 1 mol) and concd. hydrochloric acid (2.3 g., 2 mols) were heated together at 100° for sixteen hours. The solid mass was dissolved in hot methyl alcohol (100 cc.), basified with triethylamine, chilled and the product filtered off; yield 50%. After recrystallization from methyl alcohol (46 cc. per g.) the canary yellow crystals had m. p. 150–151° with slight decomposition.

Anal. Calcd. for $C_{19}H_{16}N_2S$: C, 74.94; H, 5.30. Found: C, 74.68; H, 5.37.

bis-[1,2-Dimethylindole-(3)]-methine-cyanine Iodide (VIII).—1,2-Dimethylindole (2.9 g., 1 mol) and 1,2-dimethyl-3-indolealdehyde (3.46 g., 1 mol) were fused together and concentrated hydrochloric acid (2 cc., 1 mol) added. Much heat was generated and the mixture was stirred without further heating for five minutes. The product was dissolved in ethyl alcohol (15 cc.) and precipitated by adding excess of aqueous sodium iodide (6 g.). The dye was washed (water then ether) and was recrystallized from methyl alcohol (30 cc. per g.); yield 35%. The brown crystals had m. p. 221–222°, dec.

Anal. Calcd. for $C_{21}H_{21}IN_2$: I, 29.65. Found: I, 29.62.

2 - Methyl - 3 - [(1 - methyl - 4(1) - quinolylidene) - ethylidene]-indolenine (X).—The hydriodide of this base was prepared by condensing lepidine methiodide (14.3 g., 1 mol) with 2-methyl-3-indolealdehyde (8 g., 1 mol) by refluxing in acetic anhydride (50 cc.) for three minutes. Dye separated from the hot solution; yield 72%. After recrystallization from methyl alcohol (600 cc. per g.) the dye formed brownish coppery crystals with m. p. 319–320°, dec.

Anal. Calcd. for $C_{21}H_{19}IN_2$: I, 29.79. Found: I, 29.60.

The hydriodide was basified in similar fashion to V; yield quantitative. The base separated from acetone (330 cc. per g.) as dark blue needles m. p. 249–251° dec.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.50; H, 6.08; N, 9.40. Found: C, 83.91; H, 6.35; N, 9.21.

König[12] gives m. p. 240°. His analysis is that of $C_{21}H_{18}N_2{\cdot}2CHCl_3$.

1,2-Dimethyl-3-(β-4-quinolyl-vinyl)-indole (XI).—An excess of lepidine (3 g., 2 mols) was heated with 1,2-dimethyl-3-indolealdehyde (1.73 g., 1 mol) and concentrated hydrochloric acid (1.1 g., 1 mol) at 100° for sixteen hours. The hydrochloride of the base which resulted was purified by recrystallization from methyl alcohol (120 cc. per g.); yield 2 g. of red needles, and was suspended in cold methyl alcohol and basified by the addition of triethylamine. A

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[20] Brooker and White, THIS JOURNAL, **57**, 550 (1935).

yellow solid separated and was recrystallized from methyl alcohol (160 cc. per g.); yield 43%. The yellow needles had m. p. 192–193° slight dec.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.50; H, 6.08; N, 9.40. Found: C, 83.84; H, 6.10; N, 9.29.

[1,2 - Dimethylindole - (3)] - [1 - methylquinoline-(4)]-dimethine-cyanine Iodide (XII).—(a) Lepidine methiodide (1.43 g., 1 mol) was condensed with 1,2-dimethyl-3-indolealdehyde (0.86 g., 1 mol) by refluxing in acetic anhydride (15 cc.) for three minutes. Dye separated from the hot mixture; yield 68%. After recrystallization from methyl alcohol (230 cc. per g.) the dye formed dull brownish crystals with m. p. 297–298° dec.; yield 59%.

Anal. Calcd. for $C_{22}H_{21}IN_2$: I, 28.83. Found: I, 28.82.

(b) The dye was obtained when the base X (0.5 g., 1 mol) was heated on a steam-bath to refluxing with methyl iodide (2 g., 8 mols) in nitrobenzene (10 cc.) for two hours; yield 88%. Found: I, 28.88 after recrystallization.

(c) XII was similarly obtained from XI; yield 81%. Found: I, 28.95 after recrystallization. The identity of the specimens from a, b and c was established by m. p. and mixed m. p. determinations and by absorptions.

Summary

A number of cyanine dyes have been compared with respect to absorption with the bases derived from them by removal of the elements of alkyl halide. In most cases the bases are lighter in color than the corresponding cyanines, but this is not invariably the case. These facts may be explained on the basis of the resonance theory. Certain of the arguments used have been confirmed by dipole moment determinations.

ROCHESTER, N. Y.
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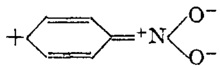
RECEIVED FEBRUARY 15, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Steric Inhibition of Resonance in Aromatic Nitro Compounds[1]

BY G. W. WHELAND AND A. A. DANISH[1a]

From a study of dipole moments, Birtles and Hampson have concluded[1b] that, in the aromatic nitro compounds, the resonance with quinoid structures of the type I[2] is sterically inhibited



I

when the nitro group lies between methyl groups in the two ortho positions. The work described in the present paper was undertaken in order to obtain chemical evidence bearing upon this hypothesis.[3]

The particular problem investigated was that presented by the striking effect of para nitro groups upon the acid strengths of the phenylmethanes. While triphenylmethane has been assigned[4] a pK value greater than 33, its trinitro derivative, 4,4′,4″-trinitrotriphenylmethane (hereafter called simply trinitrotriphenylmethane) is sufficiently acidic for its salts to be stable in aqueous alcohol.[5] It seems probable that resonance of the sort considered is at any rate partially responsible for this greater acidity of the trinitro derivative, since the quinoid structures increase the positive electrostatic potential at the position of the ionizable hydrogen atom, and since, moreover, the negative ion can be stabilized by resonance with these quinoid structures to a greater extent than the undissociated molecule.

If the above reasoning is correct, and if the contention of Birtles and Hampson is justified, it follows that 3,3′,3″,5,5′,5″-hexamethyl-4,4′,4″-trinitrotriphenylmethane (hereafter called simply trinitrotrixylylmethane) should be appreciably less acidic than trinitrotriphenylmethane. The former compound was, accordingly, prepared, and its acid strength was investigated in a manner analogous to that employed by Conant and Wheland[6] and by McEwen.[4] The sodium salts of both trinitrotriphenylmethane and trinitrotrixylylmethane are characterized by intense purple colors, and, consequently, the position of the equilibrium between either methane and its salt can be estimated colorimetrically. Since

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(1) Abstract of a thesis presented by A. A. Danish to the faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science, December, 1938.

(1a) Present address: VioBin Corporation, Chicago, Illinois.

(1b) R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937), see also C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939).

(2) L. E. Sutton, *Proc. Roy. Soc.* (London), **A133**, 668 (1931); *Trans. Faraday Soc.*, **30**, 789 (1934).

(3) Since the present research was started, several papers have appeared dealing with the steric inhibition of resonance from the chemical point of view. These have provided strong support for the existence of such an effect in various types of compounds, but apparently little work of this sort has been done with nitro compounds. See for example, W. G. Brown, A. H. Widiger and N. J. Letang, THIS JOURNAL, **61**, 2597 (1939); G. Baddeley, *Nature*, **144**, 444 (1939).

(4) W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936).

(5) V. v. Richter, *Ber.*, **21**, 2475 (1888).

(6) J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932).