resemblance was not found, at least at the temperature studied. Sodium sulfate forms a double salt with the chlorate, $3Na_2SO_4 \cdot NaClO_3$,[6] a solid solution with the bromate,[7] and two double salts with the iodate, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$.[8] It is not impossible, of course, that the results here reported are partially metastable, and that more complex, stable phases have simply failed to crystallize.

(6) Ricci and Yanick. This Journal, **59**, 491 (1931).

(7) Ricci, ibid., **57**, 805 (1935).

(8) Foote and Vance, Am. J. Sci., **19**, 203 (1930).

Summary

1. The ternary systems Na_2MoO_4–$NaClO_3$–H_2O, Na_2MoO_4–$NaBrO_3$–H_2O and Na_2MoO_4–$NaIO_3$–H_2O have been studied at 25°. Unlike the corresponding sodium sulfate systems, these are of the simple type, involving neither double salts nor solid solutions at this temperature.

2. Some observations are reported on the interference of molybdate in the iodometric titration of iodate and bromate.

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[Contribution from the Chemical Laboratory of the University of California]

The Spectra of the Doubly Charged Positive Ions of Some p,p'-Diaminotriphenylmethane Dyes

By Bert M. Tolbert and Gerald E. K. Branch

In two recent investigations by the authors[1] the spectra of some N-phenylated p,p'-diaminotriphenylmethyl ions were measured and compared with the spectrum of malachite green. In this article we shall report measurements of the spectra of the second ions of the same dyes, and compare the effects of phenylations with those on the spectra of the first ions.

The formulas of the second ions used are shown

The ions II, III, IV and V are tautomeric, thus the tautomer of III is $C_6H_5N^+H_2C_6H_4C(C_6H_5)=C_6H_4=N^+(CH_3)_2$. These tautomers lack the resonance arising from the conjugation of the terminal phenyl groups and the rest of the molecule. For this reason we believe that they exist at much lower concentrations then the ions II, III, IV and V.

Experimental Procedure

The spectra of the second ions were measured with a Beckman quartz spectrophotometer, using 1-cm. cells. A slit width of 0.02 mm. was used in the visible, but this was progressively increased more than tenfold as the measurements were carried to shorter wave lengths. The molarities of the dyes were of the order of magnitude of 10^{-5}. In two cases (VI and VIII) the concentrations were varied but no changes of molecular extinction coefficients were observed for a twofold change of concentration. The spectra were measured from 800 to 240 mμ. The dyes were dissolved as their color bases (carbinols or methyl ethers). These color bases were the same materials that had been used to measure the spectra of the first ions. Descriptions of them can be found in the references already given.

The solvent was glacial acetic acid. This solvent was chosen because the spectra of the first ions had been measured in it, because in acetic

(1) Tolbert, Branch and Berlenbach. This Journal, **67**, 887 (1945); Branch, Tolbert and Lowe, ibid., **67**, 1693 (1945).
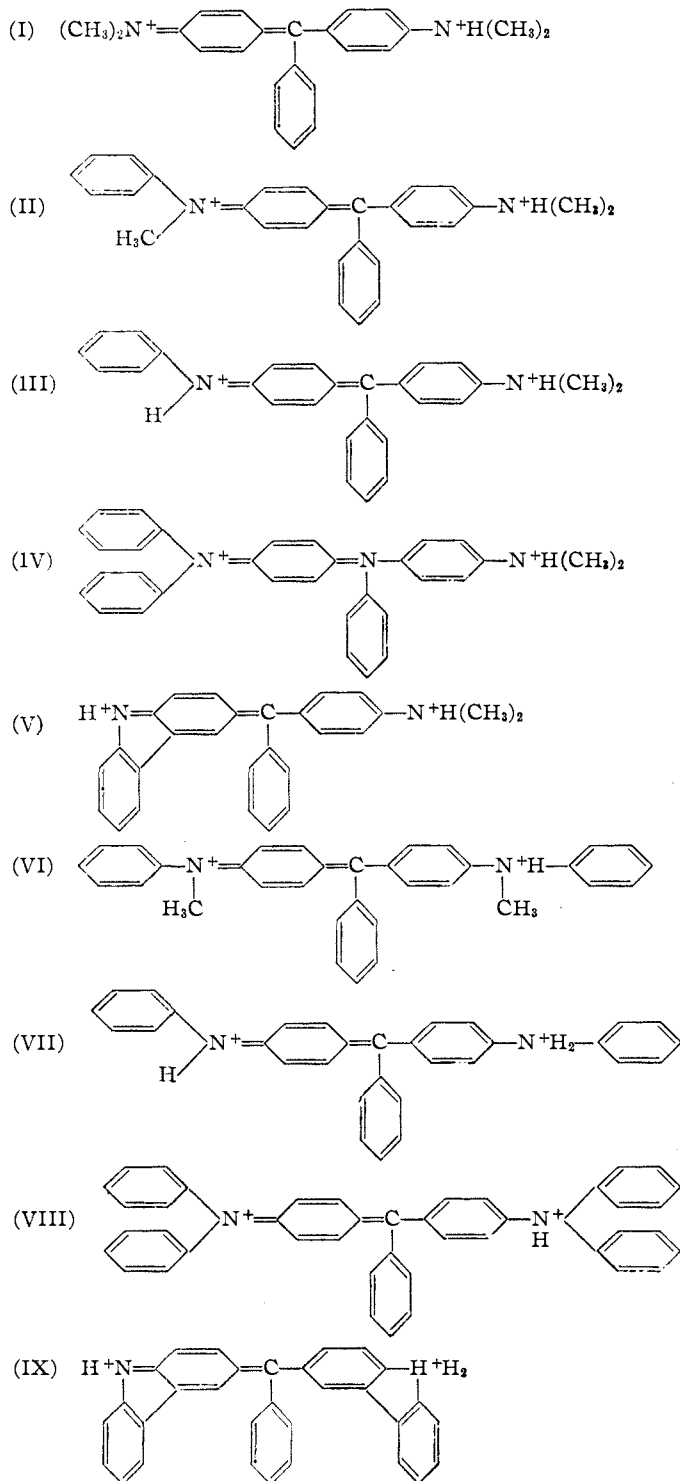
acid, the equilibria between the quinoidal second ions and their benzenoidal solvates are rapidly achieved and favor the quinoidal ions, and because acetic acid is a solvent in which very weak bases can be readily neutralized. This last property of the solvent is important, for the first ions of many of these dyes are exceedingly weak bases.

The acid to convert the first to the second ions was concentrated sulfuric acid whose density was 1.84 g./cc. The amounts of sulfuric acid were determined by volume. We shall give the concentrations of sulfuric acid as volume percentages, so that henceforth a per cent. of sulfuric acid connotes that volume of sulfuric acid of density 1.84 g./cc. made up to 100 volumes with glacial acetic acid. No significant solvent effect of change in the proportions of acetic acid and sulfuric acid on the spectra of the dyes was observed, so we have assumed that differences in the wave lengths of bands are due to differences in structure alone, even though the measurements may have been made in very different proportions of acetic acid and sulfuric acid.

A mixture of our acetic acid (boiling range 0.1°) and sulfuric acid after standing showed absorption when compared with a freshly prepared, but otherwise similar mixture. This absorption extended over the range measured, but was greatest from 260–280 mμ. The extinction of a two per cent. sulfuric acid that had stood for seven days was 0.3 at 260 mμ. This absorption was probably due to the action of the sulfuric acid on traces of impurities in the acetic acid. Errors due to this cause were eliminated by filling the comparison cell of the spectrophotometer with a mixture of acetic acid and sulfuric acid that had not only the same composition, but was also the same age as the mixture used to dissolve the dye.

To obtain the spectrum of a second ion, it is better to eliminate the first ion than to correct for the absorption due to the first ion. To make

(I) $(CH_3)_2N^+$=⟨⟩=C—⟨⟩—$N^+H(CH_3)_2$

(II) H_3C, ⟩N^+=⟨⟩=C—⟨⟩—$N^+H(CH_3)_2$

(III) H, ⟩N^+=⟨⟩=C—⟨⟩—$N^+H(CH_3)_2$

(IV)   ⟩N^+=⟨⟩=N—⟨⟩—$N^+H(CH_3)_2$

(V) H^+N=⟨⟩=C—⟨⟩—$N^+H(CH_3)_2$

(VI)   ⟨⟩—N^+=⟨⟩=C—⟨⟩—N^+H—⟨⟩ H_3C CH_3

(VII) H, ⟩N^+=⟨⟩=C—⟨⟩—N^+H_2—⟨⟩

(VIII)   ⟩N^+=⟨⟩=C—⟨⟩—N^+⟨ H

(IX) H^+N=⟨⟩=C—⟨⟩—H^+H_2

sure that the first ion was reduced to negligible concentrations, the following general procedure was adopted. The spectrum was measured in a series of mixtures of acetic acid and sulfuric acid of increasing sulfuric acid concentrations. When the x-band of the first ion was reduced to insignifi-

cant proportions it was assumed that the spectrum was that of the second ion. The spectrum was then measured at still higher concentrations of sulfuric acid, to note whether there was any further change in the spectrum. Only very insignificant effects of excess sulfuric acid could be observed up to 50% sulfuric acid. At still higher concentrations of sulfuric acid, marked changes in the spectra were observed. These we attributed to the formation of new species of the dye. Their effects will not be discussed in this paper, but we hope that they will be the subject of a later publication. This general procedure was found to be applicable to the second ions I, II, III, IV, VI and VII.

The first ions of VIII and IX are such weak bases that their absorptions are predominant over those of the second ions in 50% sulfuric acid. In consequence we have had to obtain the spectra of the second ions from measurements in 98% sulfuric acid. In these solutions these dyes are not present only as their second ions. However, in each case there is a strong band that is indubitably the x-band of the second ions. We shall discuss only these bands in considering the spectra of the second ions VIII and IX.

In all the dyes except V the x-bands of the first and second ions are resolved in mixtures of the two ions. It is the y-band of the first ion that interferes with the determination of $\lambda_{max.}$ of the x-band of the second ion. So when the x-band of the first ion is insignificant, one is assured that there is nothing to interfere with the measurement of the bands of the second ion. But in mixtures of the first and second ions of V, the x-bands of the two ions are not resolved, and one cannot tell that the first ion has been removed by observing the disappearance of its x-band. For this reason we have given the spectrum in a solution containing enough sulfuric acid to warrant the belief that a dye of this type would be almost completely converted to the second ion.

The changes of the spectrum of V with the concentration of sulfuric acid warrant a description. When the color base is dissolved in acetic acid containing no sulfuric acid the spectrum from 260 mμ upwards consists of three main bands at 586, 417 and 295 mμ. The first two are simple, but the last has subsidiary maxima. This is the spectrum of the first ion free from the second ion. The bands at 586 and 417 mμ are the x- and y-bands, respectively. When small quantities of sulfuric acid are added the maxima of these bands

are shifted toward the violet, and they become less sharp, but do not develop shoulders. The maximum at 295 mμ remains but becomes less prominant and a new maximum develops at 264 mμ. Thus with 4% sulfuric acid there are maxima at 552, 400, 295 and 264 mμ. As the sulfuric acid is increased the maximum of the longest band decreases to 529 mμ, and the band gets sharper, while the band at 295 mμ disappears. This process reaches completion around 25% sulfuric acid, from this point up to 98% sulfuric acid there is no further change in the longest band, and the absorption from 300–260 mμ. Presumably at 25% sulfuric acid the first ion is absent. However, there are changes in the spectrum between 400 and 300 mμ as the sulfuric acid concentration is increased above 25%. At this concentration there are two maxima in this region, one at 390 mμ and the other at 355 mμ. As the concentration of sulfuric acid is increased the maximum at 355 mμ grows at the expense of that at 390 mμ, and the latter becomes a shoulder on the former band. Presumably the second ion exists in isomeric forms whose proportions change with the change of the solvent. Both isomers have bands very close to 529 and 264 mμ, and change in their proportions does not alter the spectrum in these regions, but the y-bands of the isomers are sufficiently different to be resolved. No resolution of y-bands of isomers of second ions were observed with the other dyes. The spectrum shown for V was obtained in 50% sulfuric acid. In it the main maximum of the y-band is at 355 mμ. We shall use this wave length for comparison with the maxima of the y-bands of the other second ions. Dye V is also peculiar in that its spectrum in 98% sulfuric acid shows no radical difference from spectra in solutions less concentrated with respect to sulfuric acid.

We never succeeded in freeing the color base of II from impurities that absorb strongly in the ultra violet. For this reason its spectrum is given only in the visible.

Results and Discussion

The spectra of the second ions are shown in Figs. 1, 2, 3 and 4. The wave lengths of the maxima of the principal bands and the molecular extinction coefficients at these wave lengths are collected in Table I. Only bands that can definitely be assigned to the second ion are included in the table. Molecular extinction coefficients have been calculated on the basis of total second ion irrespective of whether it is in the quinoidal form or present as the second ion of the benzenoidal acetate. Molecular extinction coefficients have been omitted in the table where appreciable quantities of substances other than the second ions must have been present.

In the range 240 mμ and upwards, the spectra of the second ions consists of three main bands, which we shall call the x-, y- and x'-bands. The
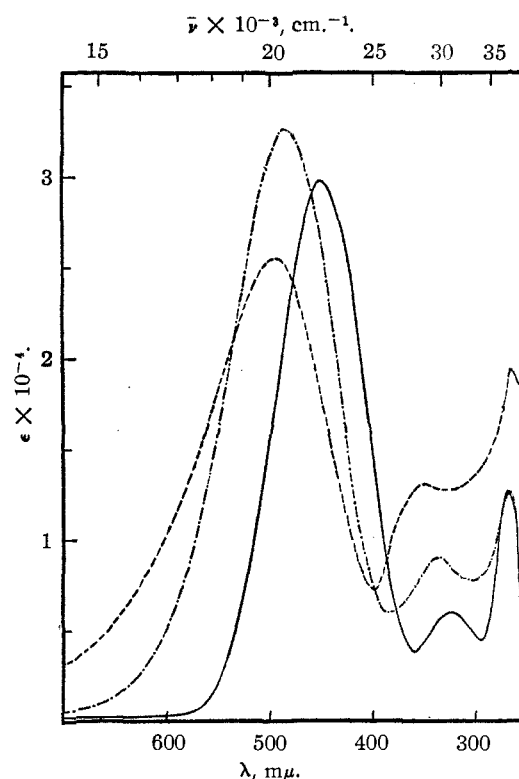

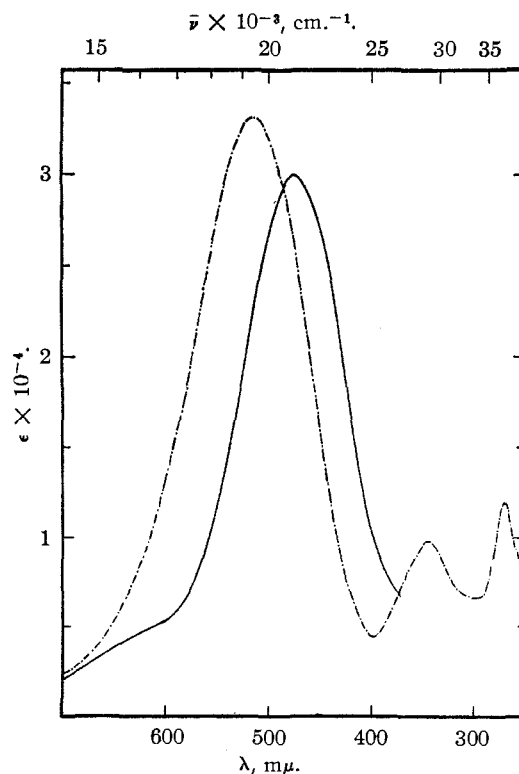Fig. 1.—Absorption spectra of second ions: ———— I, - - - - - VII, —·——·—— III.

Fig. 2.—Absorption spectra of second ions: ———— II, —·——·—— IV.

$\nu \times 10^{-3}$, cm.$^{-1}$.

Fig. 3.—Absorption spectra of second ions: ———— VI, —·——·——· V.

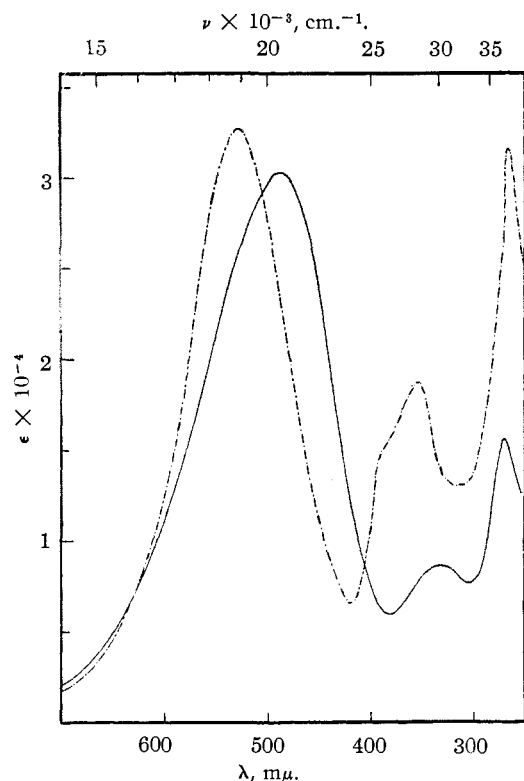$\bar{\nu} \times 10^{-3}$, cm.$^{-1}$.

Fig. 4.—Absorption spectra of second ions: ———— VIII, - - - - - IX.

two longest of these bands can be due only to the quinoidal ions. The x'-bands cannot be definitely assigned to the quinoidal ions, for the second ions of the benzenoidal acetates are presumably present in the solutions, and these compounds might have absorption bands in the region where the x'-bands were observed (264–270 mμ). The x-bands are the strongest (ϵ_x *circa* 3×10^4). The y-bands are from one half to a third as strong as the x-bands. The x'-bands in general have extinctions between those of the x- and y-bands. Superficially, the spectra of the second ions are like those of the first ions with the extinctions reduced, and the maxima of the bands shifted to shorter wave lengths.

The x-Bands.—The x-band of a second ion is a smooth curve without shoulders or other irregu-
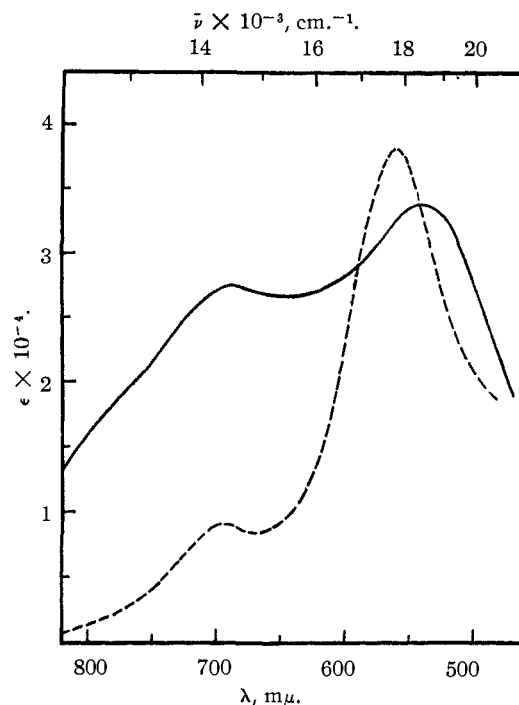
larities. The absorption falls off less rapidly on the long wave length side than on the other. This lack of symmetry cannot be attributed to tautomers, geometric isomers nor traces of the first ion. The phenomenon was observed in cases such as malachite green in which tautomers and geometric isomers are not possible. Traces of the first ion generally would produce a subsidiary maximum, a shoulder or other irregularity. The spectrum of II (Fig. 2) is an example of the effect of a trace of the first ion. The x-band of a first ion of a triphenylmethane dye generally shows some irregularity on its short wave length side. This was not observed in any of the second ions. In general the x-band of a first ion is sharper than that of the second ion.

The formulas of the dyes under consideration are all derivable from that of malachite green by substituting p-radicals of aromatic amines for p-

TABLE I
ABSORPTION MAXIMA AND THEIR MOLECULAR EXTINCTION COEFFICIENTS

Number and formula of second ions, R = C₁₉H₁₃	% H₂SO₄	λ_x in mμ	ε_x × 10⁻⁴	λ_y in mμ	ε_y × 10⁻⁴	λ_x' in mμ	ε_x' × 10⁻⁴
I	[(CH₃)₂HNRN(CH₃)₂]⁺⁺	4	450	2.95	322	0.55	262	0.95
II	[(CH₃)₂HNRNCH₃C₆H₅]⁺⁺	4	475	..	...	..	...	..
III	[(CH₃)₂HNRNHC₆H₅]⁺⁺	4	483	3.26	337	.91	265	1.25
IV	[(CH₃)₂HNRN(C₆H₅)₂]⁺⁺	10	515	3.32	348	.99	270	1.19
V	[(CH₃)₂HNC₆H₄C(C₆H₅)C₁₂H₈N]⁺⁺	50	529	3.27	355	1.89	264	3.18
VI	[CH₃C₆H₅HNRNCH₃C₆H₅]⁺⁺	50	485	3.20	330	0.86	270	1.25
VII	[C₆H₅H₂NRNHC₆H₅]⁺⁺	25	495	2.52	350	1.3	266	1.95
VIII	[(C₆H₅)₂HNRN(C₆H₅)₂]⁺⁺	98	540	..	...	..	...	..
IX	[HNC₁₂H₈C(C₆H₅)C₁₂H₈N]⁺⁺	98	560	..	...	..	...	..

radicals of dimethylaniline. One such substitution gives the formulas of II, III, IV and V and two substitutions of the same amine radical gives the formulas of VI, VII, VIII and IX. The effects of these substitutions can be expressed by the quantity $\lambda - \lambda_0$, where λ is the wave length of one of the bands of one of the ions of the derived dye, and λ_0 that for the corresponding band of the corresponding ion of malachite green. The band can be indicated by the subscript x, y or x', and the ion by the superscript I or II. Thus $\lambda_x^{II} - \lambda_{ox}^{II}$ is the effect of a substitution on the x-band of a second ion. Table II shows the effects of the substitutions on the wave lengths of the x-bands of both the first and second ions expressed in terms of $\lambda - \lambda_0$.

TABLE II

EFFECTS OF SUBSTITUTIONS ON X-BANDS

Amine substituted for $C_6H_5N(CH_3)_2$	Number of substitution	Dye number	$\lambda_x^{II} - \lambda_{ox}^{II}$ in mμ	$\lambda_x^{I} - \lambda_{ox}^{I}$ in mμ
Methyldiphenylamine	1	II	25	1
Diphenylamine	1	III	33	1
Triphenylamine	1	IV	65	9
Carbazole	1	V	79	−34
Methyldiphenylamine	2	VI	35	13
Diphenylamine	2	VII	45	17
Triphenylamine	2	VIII	90	50
Carbazole	2	IX	110	−13

In every case $\lambda_x^{II} - \lambda_{ox}^{II}$ is positive and markedly greater than $\lambda_x^{I} - \lambda_{ox}^{I}$. The latter quantity is generally positive, but is negative when either one or two carbazyl radicals are substituted. A single substitution of one of the radicals in the second ion produces a greater increase in λ_x than two single substitutions of the same radical in the first ion.

The second ion of malachite green has a conjugated system terminated by a doubly bonded tetracovalent nitrogen atom. Conjugate systems are chromophores, and if the conjugate system is extended by the substitution of a phenyl group for a terminal saturated group or atom, the wave length of the band associated with the conjugated system is increased. It is therefore to be expected that the second ion of malachite green would be colored, and that the substitution of the radical of a more arylated amine for the radical of dimethylaniline would increase λ_x.

The first ion of malachite green is a resonance hybrid of $(CH_3)_2N^+=R-N(CH_3)_2$ and $(CH_3)_2-N-R=N^+(CH_3)_2$ where R is the conjugated system $C_{19}H_{13}$. The substitution of the radical of a more arylated amine for the radical of dimethylaniline extends the conjugated system of one of the hybrids. Hence, as a rough approximation one might expect that two substitutions would have the same effect on λ_x of the first ion as a single substitution has on λ_x of the second ion. This approximation grossly underestimates the difference in the two cases.

The first ion of malachite green can be treated as a diamino derivative of triphenylmethyl ion. The amino groups extend the resonance, and so are strongly bathochromic. The bathochromic effects of the amino groups depend on their basic character and, to obtain the maximum effect, the two groups must be equally basic. When aryl groups are substituted for N-methyl groups, the basicities of the amino groups are decreased, and a hyposchromic effect is introduced which compensates to some extent for the normal bathochromic effect of the extension of the conjugated system. When the substitution occurs on only one of the amino groups, there is a further hyposchromic effect due to the upset of the balance of basicities of the two amino groups.

When the amino groups are separated by an aliphatic conjugated system a very considerable reduction in the basicities of the amino groups would be necessary to produce a strong hyposchromic effect, but in the diaminotriphenylmethane dyes the neutralizing power of the amino groups are already greatly reduced, for their action on the methyl ion is resisted by the necessity of the change from a benzenoidal to a quinoidal structure, and the consequent loss of resonance energy. The spectra of these dyes are therefore more susceptible to the hypsochromic action of loss of basicity of the amino groups than dyes of the type $R_2N(CH=CH)_nCH=NR_2^+$ and the cyanines.

The hypsochromic effect of loss of basicity of the amino group is less in the second than the first ion of a diaminotriphenylmethane dye. In the second ion one of the amino groups is neutralized by the added proton. This increases the acidity of the carbonium ion, and so to have the same hypsochromic effect a greater weakening of the basicity of the amino group is needed in the second ion than in the first. Further, the hypsochromic effects are limited by the difference between λ_{ox} and the wave length of the absorption band of triphenylmethyl ion. This difference is greater in the first ion than in the second, and hence greater hypsochromic effects are to be expected in the first ions than in the second ions. With the first ion, the hypsochromic effect of a single substitution is enhanced by the resulting inequality of basicities of the amino groups. There is no such effect in a second ion. Hence, the difference between the effect of a single substitution on λ_x of the second ion and twice the effect on λ_x of the first ion is more marked than the difference between the effect of a single substitution on λ_x of the second ion and that of a double substitution on λ_x of the first ion.

Branch, Tolbert and Lowe put the bases dimethylaniline, methyldiphenylamine, diphenylamine, triphenylamine and carbazole in that order to indicate the decreasing order of the effective basicities of their amino groups in diaminotriphenylmethane dyes. This is also the order of in-

creasing $\lambda_x^{II} - \lambda_{ox}^{II}$. Apparently there is some correlation between the bathochromic effects and the reduction of the effective basicities of the amino groups.

From the number of resonating forms one should expect the above five amines to fall into three classes with respect to basicity. Dimethylaniline should belong to the most basic class, methyldiphenylamine and diphenylamine to the next class, and triphenylamine and carbazole to the least basic class. The effectiveness of the resonance in reducing the basicity depends on the ease of obtaining coplanarity. The methyl group of methyldiphenylamine offers a steric hindrance to coplanarity, and the bond between the phenyl groups of carbazole enforces coplanarity. Hence, there is a steric factor enhancing the basicity of methyldiphenylamine and one reducing the basicity of carbazole. These steric factors should be especially effective when the radical of the amine is part of an ion of a diaminotriphenylmethane dye. Therefore, the order given for the effective basicity of the amino group of the radicals of these amines in the dyes is not unreasonable.

In the second ion of a diaminotriphenylmethane dye the terminal groups on the neutralized amino group are separated from the conjugated system by a saturated tetracovalent nitrogen atom. Normally an unsaturated group separated from a conjugated system by a saturated tetracovalent carbon atom has very little effect on the wave length of the absorption band characteristic of the conjugated system. Hence, if one assumes that the tetracovalent nitrogen and carbon atoms have the same insulating effects, λ_x values for II, III, IV and V should be respectively nearly equal to those for VI, VII, VIII and IX. This was found not to be the case. For example, in going from malachite green to II, λ_x increased by 25 mμ, but a further increase of 10 mμ was found in going from II to VI. The effect of the second phenyl group was 40% of that of the first, and the same ratio between the effects of the first and second substitutions was observed in every case.

It is necessary to consider whether this lack of complete insulation by the saturated tetracovalent nitrogen atom could be an illusion produced by the tautomerism of the second ions of the unsymmetrical dyes. The spectrum given for one of these second ions is really the spectrum of a tautomeric mixture. For instance, the solution of the second ion II is a tautomeric mixture of C_6H_5-$CH_3N^+{=}C_6H_4C(C_6H_5)C_6H_4N^+H(CH_3)_2$ and C_6H_5-$CH_3HN^+C_6H_4C(C_6H_5)C_6H_4{=}N^+(CH_3)_2$. If one assumes that the saturated tetracovalent nitrogen atom completely insulates the phenyl group from the conjugated system, the x-band of the former tautomer would be very similar to that given for VI, and the x-band of the latter tautomer would be similar to that of I. In the mixture these two bands might fuse to give a band that could be mistaken for that of a single substance. The possibility of such fusion can be tested by seeing whether bands similar to the x-bands of the tautomeric second ions (II, III, IV and V) can be constructed by combining the x-band of I, with the x-bands of VI, VII, VIII and IX, or with the x-band of I, shifted so as to make its maximum coincide with that of the x-bands of VI, VII, VIII or IX. This can be done in the case of the x-band of II, whose ϵ_x was not determined. No combination of the x-bands of I and VII can give the x-band of III; though a band without shoulders and having its maximum in the right place can be constructed from the x-band of I, and a similar band shifted to make its maximum coincide with that of the x-band of VII. The value of ϵ_x for this synthetic band is much smaller than that found for III. Synthetic bands constructed in this way are entirely different from the x-bands of IV and V. This evidence favors the hypothesis that the nitrogen atom of the neutralized amino group only partially insulates the terminal aryl groups from the main conjugated system.

Since the x-bands of the tautomeric second ions are on the whole just as sharp as the x-bands of the second ions that are not tautomeric, one can assume that in the tautomeric ions one of the tautomers is always in great preponderance over the other. That the first substitution increases λ_x two and one-half times as much as the second, is readily explained by a partial insulation effect of the nitrogen atom of the neutralized amino group, and the assumption, already made, that in II, III, IV and V, the tautomer in which the proton neutralizes the dimethylamino group is predominant.

The second ions II, III, V, VI, VII and IX should exist in cis and trans forms in not very unequal quantities. The x-bands do not show any signs of this geometric isomerism. However, there should be very little difference in the x-bands of the two isomers, and the x-band of the mixture should be very similar to that of either component.

The y-Bands.—In the investigation of the spectra of the first ions of the dyes under consideration, it was found that structural changes had the same qualitative effects on the y- and x-bands, and that the frequency difference between the two bands was decreased when an effectively less basic amine was substituted for a more basic one. It is of interest to compare the frequency difference of the x- and y-bands of the second ions with those of the first ions. This has been done in Table III, by showing the values of $\bar{\nu}_y - \bar{\nu}_x$ for both ions of the dyes. Unfortunately, the values for the second ions II, VIII and IX must be omitted because of lack of sufficiently accurate data.

The data given show that the frequency differences between the x- and y-bands are much greater for the second ions than for the first ions, and that arylation of the amino groups decreases $\bar{\nu}_y - \bar{\nu}_x$ in the first ion, but generally increases it in the second ion. These effects appear somewhat con-

TABLE III
SEPARATION OF x- AND y-BANDS

Number of dye	$\bar{\nu}_y - \bar{\nu}_x \times 10^{-3}$ in cm.$^{-1}$ for 1st ion	$\bar{\nu}_y - \bar{\nu}_x \times 10^{-3}$ in cm.$^{-1}$ for 2nd ion	$\lambda_y^{II} - \lambda_{oy}^{II}$ in mμ
I	7.24	8.83	..
II	7.15	..	..
III	7.15	8.97	15
IV	6.93	9.74	21
V	6.92	9.26	32
VI	6.94	9.68	8
VII	6.67	8.37	28
VIII	6.35	..	..
IX	8.00	..	..

tradictory, for arylation, which decreases the basicity of the amino groups, has the opposite effect to the addition of a proton to the amino group, which entirely removes the basicity of the group.

According to Lewis and Calvin[2] y-bands are due to vibrations along the axis perpendicular to the principal optical axis of the molecule. The y-axis is the line passing through the central carbon atom and the para carbon atom of the non-aminated benzene ring in a first ion of a symmetrical diaminotriphenylmethane dye. In consequence, the para axis of the aminated benzene rings have components along the y-axis, so that to some extent the effects of the terminal groups on λ_x and λ_y are similar. But the hypsochromic effect of reduced basicities of the amino groups on the y-band is much less than on the x-band, for as the amino groups lose their basicities, the central carbon atom and the non-aminated benzene ring become more doubly bonded, and the resulting increase of polarizability is along the y-axis.

The case of the first ion of an unsymmetrical dye is very similar to that of the first ion of a symmetrical dye, but since the two aminated benzene rings are not equivalent, the y-axis is rotated a little from the para axis of the non-aminated ring. In consequence, the value of $\bar{\nu}_y - \bar{\nu}_x$ lies between that of malachite green and the arithmetic mean of the values for malachite green and for the corresponding symmetrical dye.

In a second ion of a diaminotriphenylmethane dye, the most polarizable part is the quinoidal structure extending from the central carbon atom to the doubly bonded nitrogen atom. The x-axis is nearly the para axis of this quinoidal structure, and the y-axis is perpendicular to the x-axis. In consequence, polarizability along the para axis of the quinoidal structure does not contribute much to the length of the y-band, and the frequency differences between the x- and y-bands are much greater in the second ions than in the first ions. Also, arylation of the second ion will affect the x-band much more than it does the y-band, and so tends to increase $\bar{\nu}_y - \bar{\nu}_x$.

This last expectation is only partially confirmed by the data. For instance, $\bar{\nu}_y - \bar{\nu}_x$ for the second

ion VII is less than that of malachite green, and $\bar{\nu}_y - \bar{\nu}_x$ of IV is greater than that of V, although λ_x of V is greater than λ_x of IV. These anomalies can be attributed to bathochromic effects of N-hydrogen atoms on y-bands. In the last column of Table III the values of $\lambda_y^{II} - \lambda_{oy}^{II}$ are shown. These values average more for the dyes derived from secondary amines (III, V and VII) than for those derived from tertiary amines (IV and VI).

One would expect that the y-bands of the geometric isomers of II, III, V, VI, VII or IX would differ more than their x-bands. The y-bands of II and IX were not measured. The y-band of V was double, and the two maxima varied in importance with the solvent. This variation suggests isomerism, and this isomerism could be the expected geometric isomerisms.

The x'-Bands.—According to Lewis and Bigeleisen[3] one should expect an overtone of the x-band to appear in the spectrum of a dye. They called these x'-bands. Their wave lengths should be a little greater than half those of the x-bands of which they are overtones. The second ions have bands in the region where x'-bands are to be expected. We have called these bands the x'-bands of the second ions, but in reality it is unlikely that they are. In a series of closely related substances $\epsilon_x/\epsilon_{x'}$ should decrease as $\lambda_x/\lambda_{x'}$ approaches two. This is not true of the second ions. For instance, $\lambda_x/\lambda_{x'} = 2$ and $\epsilon_x/\epsilon_{x'} = 1$ for V, but the corresponding values for I are 1.72 and 3.1. It is possible that the bands we have called the x'-bands of the second ions are not due to the same molecular species as the x-bands. They could be x-bands of the second ions of the benzenoidal acetates. That they vary so little in wave length from dye to dye suggests that this is the case.

Partly Neutralized Solutions.—In applying the general procedure of measuring the spectra in varying concentrations of sulfuric acid, the spectra of dyes VI and VII were measured in two, four and ten per cent. sulfuric acid as well as in more acid solutions. At these concentrations of acid the spectrum of each of these dyes showed two strong bands in the visible. One of these is the x-band of the first ion, and the other a combination of the y-band of the first ion and the x-band of the second ion. The spectra, therefore, showed that in this range both first and second ions were present in significant proportions. Normally the spectrum of a mixture of two components is given by the equation

$$\epsilon = \alpha\epsilon_1 + (1 - \alpha)\epsilon_2$$

where ϵ is the extinction at any wave length divided by the sum of the molarities of the components, ϵ_1 and ϵ_2 are the molecular extinction coefficients of the components and α is the molal fraction of one of the components. The spectra of dyes VI and VII in two, four or ten per cent. sulfuric acid cannot be made to fit this equation with any values of α. At wave lengths longer than λ_x

(2) Lewis and Calvin, Chem. Rev., 25, 273 (1939).

(3) Lewis and Bigeleisen, THIS JOURNAL, 65, 2107 (1943).

of the first ion, ϵ is greater than ϵ_1, although ϵ_1 is greater than ϵ_2. Between λ_x for the two ions a new band appears.

The phenomenon is shown in Fig. 5 for the case of VII in four per cent. sulfuric acid. In this figure the measured spectrum is shown as a full line. The dash and dot line shows a spectrum calculated by the equation with a value of α that makes the peak of the first band almost coincide with that of the observed spectrum. At the bottom of the figure the difference of the two curves is shown, but this curve has been raised a little to avoid negative extinction coefficients. This lower curve looks like the spectrum of a third component. It has maxima at 707 and 547 mμ. The observed spectrum has a shoulder around 700 mμ and a maximum at 553 mμ.
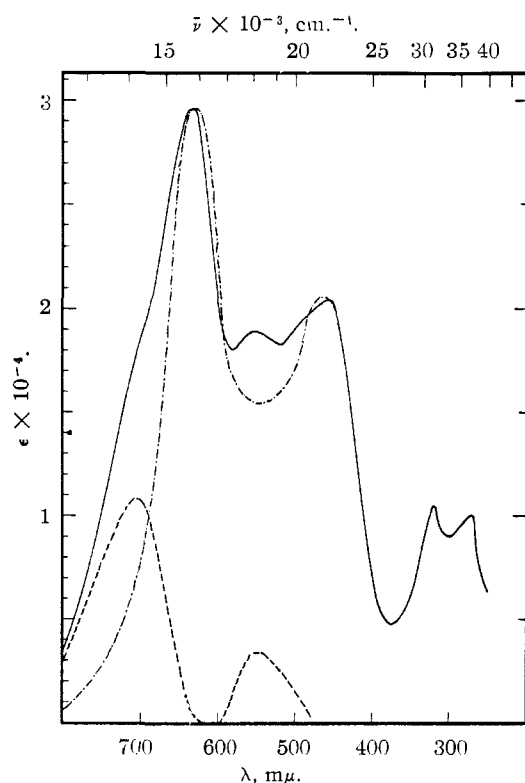
$$\bar{\nu} \times 10^{-3}, \text{cm.}^{-1}.$$

Fig. 5.—Absorption spectra of a mixture of the first and second ions of VII: ———— observed spectrum, —·—·—·—·— linear combination of spectra of first and second ions, - - - - - difference in ϵ, raised by 1×10^3. The synthetic spectrum was calculated from 450 to 800 mμ.

If one assumes that the two ions combine to form a compound, one can construct facsimiles of the observed spectra from the measured spectra of the first and second ions and an assumed spectrum having maxima in the neighborhood of 700 and 550 mμ. In these synthetic spectra, the extinction attributed to the compound at first increases with the concentration of sulfuric acid and later decreases, the maximum being in the

neighborhood of the sulfuric acid concentrations at which it is necessary to assume equal concentrations of first and second ions.

Dye VI behaves in a very similar way to dye VII, except that the first ion of VI is a weaker base than that of VII. The spectrum of the assumed compound of VI also must have maxima in the neighborhood of 700 and 550 mμ.

To test the hypothesis of a compound of the two ions being formed, the spectra of VI and VII in 4 and 10% sulfuric acid were remeasured using twice the concentration of the dye. Expressed in molecular extinction coefficients these spectra were identical to those obtained at lower concentrations of the dyes. Hence, the anomalous spectra cannot be due to reactions in which two free ions combine. To explain these experiments one can modify the hypothesis by assuming that the ions exist chiefly in clusters. In that case doubling the concentration of the dye without altering the ratio of first ion to second would approximately double the concentration of the compound, and Beer's law would hold. Combination of a first and second ion could be produced by a link between the neutralizing proton of a second ion with the amino group of a first ion.

Relative Basicities.—The phenomenon described in the preceding section precludes an unequivocal determination of the degree of conversion of the first ion to the second ion. However, we shall give the percentages converted to the second ion at some concentrations of sulfuric acid obtained by the use of the equation given in the preceding section, even though this equation is not accurate. The errors in the equation should not be great enough to prevent our obtaining the order of basicities of the first ions. The calculations were made at λ_x of the first ions, except in the case of V, where 264 mμ was used as the wave length. At 0.1% sulfuric acid only I was completely converted to the second ion. At 4% sulfuric acid, I and III were almost completely converted, II was 98% converted, IV was 95% converted and the others were much less or not at all affected by the sulfuric acid. At 10% sulfuric acid I, II, III and IV were almost completely converted, VII was 90% converted, VI was 70% converted, V was 60% converted, VIII and IX were not affected. In 50% sulfuric acid IX was partially converted, but VIII was not affected. From these data the decreasing order of basicities of the first ions appears to be I, III, II, IV, VII, VI, V, IX, VIII with a possible inversion of V and VI. The range of basicities extends from I, which is partially converted to the second ion in a hundredths of a per cent. of sulfuric acid, to VIII which is only partially converted to the second ion in a mixture of 98% of sulfuric acid (d. 1.84 g./cc.) and 2% of acetic acid. The range of acidities covered is equivalent to more than 8 pH units.

From the above order one may generalize that

the substitution of a more arylated base for dimethylaniline decreases the basicity of the first ion of a diaminotriphenylmethane dye, that a second such substitution still further decreases the basicity, and that the radicals of triphenylamine and carbazole are much more effective than those of diphenylamine and methyldiphenylamine.

Summary

The spectra of the second ions of malachite green and some more highly phenylated diamino triphenylmethane dyes were measured. These spectra have been compared with those of the first ions of the same dyes.

It was found that phenylation has a much greater bathochromic effect on the x-band of a second ion than on the corresponding band of a first ion, and that the frequency differences between the x-bands and y-bands are greater in second ions than in first ions, and that phenylation increases this frequency difference in second ions, but decreases it in first ions.

It was found that the spectra of solutions containing both first and second ions were not linear combinations of the spectra of the first and second ions.

Spectrophotometric and Potentiometric Evaluation of Apparent Acid Dissociation Exponents of Various 4-Aminoquinolines[1]

BY J. LOGAN IRVIN AND ELINOR MOORE IRVIN

Albert and Goldacre[2] have demonstrated that 4-aminoquinoline has the greatest basicity (attraction for protons) of the various mono-amino derivatives of quinoline. They attribute this enhancement of basicity to stabilization of the proton-donor (cation) by resonance of the type shown in Fig. 1. In the present paper, apparent acid dissociation exponents are reported for a series of substituted 4-aminoquinolines. These compounds possess varying degrees of antimalarial activity,[3] and the data reported here will permit an attempt to correlate antimalarial activity and physiological disposition of members of this series with their basicities and, consequently, with the relative proportions of the various ionic species which are present at the pH of body fluids. Such pharmacological and physiological studies have been made by Drs. J. Taggart and J. Shannon and will be reported elsewhere.

As represented in Fig. 1, the aromatic nuclei of the 4-aminoquinolines accept a single proton in dilute aqueous solutions as determined potentio-

(1) This is one of a series of studies in connection with a program in this Department on antimalarial compounds and the biochemistry of malaria. The work reported in this paper was done on a volunteer basis in coöperation with the main program which was conducted under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and The Johns Hopkins University. A preliminary report on this work has been published (Federation Proc., 5, 139 (1946)).

(2) Albert and Goldacre, Nature, 153, 467 (1944).

(3) Some of these compounds were synthesized in the laboratories of various universities under contracts with the Office of Scientific Research and Development, and others were prepared in the laboratories of several pharmaceutical companies. Sources of the compounds are acknowledged in Table I. Data concerning these and many other compounds have been assembled by the Survey of Antimalarial Drugs and will be published as a monograph, "A Survey of Antimalarial Drugs, 1941-1945," edited by F. Y. Wiselogle. At some points in this paper, these compounds are designated by numbers preceded by the letters, SN. These are the code numbers assigned by the Office of the Survey.

metrically or spectrophotometrically. A second proton is accepted by the aromatic nucleus in very concentrated aqueous solutions of strong mineral acids, as demonstrated spectrophotometrically. Most of the compounds with which this report is concerned have an aliphatic side-chain possessing a diethylamino group which will accept a proton in dilute aqueous solutions, as determined potentiometrically. Therefore, the acid–base reactions involving these compounds in *dilute aqueous solutions* can be formulated essentially as described by Adams[4] for the case of unsymmetrical dibasic acids. However, an extension is necessary in order to show the relationship of the intrinsic constants defined by Adams to the constants which are evaluated by the spectrophotometric method, which was not treated by Adams.

Formulation of Acid-Base Equilibria

Throughout this paper activities are indicated by parentheses and concentrations by brackets. The following symbols are used: $^+$HB—B$'$H$^+$, the dipolar cation or proton-donor in which B represents the resonating aromatic nucleus and B$'$ the diethylamino group of the side-chain.

B—B$'$H$^+$ and $^+$HB—B$'$, monopolar cations (see diagram of acid–base reactions).

B—B$'$, dipolar base or proton acceptor.

[S], molar concentration of the compound. [S] = [$^+$HB—B$'$H$^+$] at the origin of the titration.

K_1 and K_2, experimental acid dissociation constants as determined potentiometrically. K_1' and K_2' are the corresponding apparent constants defined in terms of *concentrations* rather than *activities*. (Definition of the apparent constants is restricted to the specification of *constant ionic strength*).

K_S, acid dissociation constant of the group associated with the aromatic nucleus (determined spectrophotometrically). K_S', the corresponding apparent constant (at constant ionic strength).

The steps in the acid dissociation of the dipolar proton-donor, $^+$HB—B$'$H$^+$ are

(4) Adams, THIS JOURNAL, 38, 1503 (1916).