The Spectra of Some Diaminotriphenylmethane Dyes in Concentrated Sulfuric Acid

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A diaminotriphenylcarbinol has three basic structures, namely, the two amino groups and the triphenylcarbinol structure. Under sufficiently acidic conditions it should neutralize three equivalents of acid. The final product would be a di-substituted triphenylmethyl ion. The, substituent radicals are aminium not amino groups. The aminium group is not an auxochrome, and hence the third ion of the dye should not absorb light of long wave lengths. Triphenylmethyl ion absorbs very little light at wave lengths longer than 450 mμ.

However Hill, Branch and Patapoff[1] observed a band at 678 mμ in the spectrum of viridine green (II) in concentrated sulfuric acid. This band could belong to neither the first nor the second ion, for under less acidic conditions the first ion is entirely converted to the second ion, whose longest band has its maximum at 495 mμ. Nor can one believe that a simple derivative of triphenylmethyl ion could have a strong absorption band with a maximum at 678 mμ. The authors of the above mentioned paper suggested that the band at 678 mμ was due to an intermediate product in the sulfonation of the dye, for on standing the band at 678 mμ was replaced by another at 580 mμ.

For further study of this phenomenon, the spectra of several diaminotriphenylmethane dyes were measured in a mixture of two volumes of acetic acid and ninety-eight volumes of concentrated sulfuric acid (d. 1.84 g./ml.). The spectra were measured immediately after making up the solutions, and after the solutions had stood twenty-six days at room temperature. In general the spectra changed on standing. No attempts were made to measure the rates and extents of these changes.

The formation of an ion of the dye, or an addition of sulfuric acid to the dye would be reversed when a solution in sulfuric acid is diluted with acetic acid. Sulfonation and decompositions would not be reversed. To study the nature of the irreversible changes, solutions in concentrated sulfuric acid were allowed to stand for a week, diluted with acetic acid, and their spectra compared with those of freshly prepared solutions in the same mixture of sulfuric acid and acetic acid. Generally sulfonation does not produce a large change in the spectra of the first and second ions of these dyes, but it must greatly reduce the basicity of the dye. When the spectra of a dye and its sulfonation derivative are measured at an acidity at which either the dye or the derivative exists as a mixture of first and second ions, the ratio of absorption by the first ion to that by the second ion is greater for the derivative than for the parent dye, and the two spectra differ markedly, and in an expected way.

(1) Hill. Branch and Patapoff. THIS JOURNAL. **67**, 545 (1945).

We think that the most illuminating results we obtained were those with malachite green (I), viridine green (II) and the N,N-dimethyl derivative of viridine green (III). The formulas of these dyes as their second ions are shown below
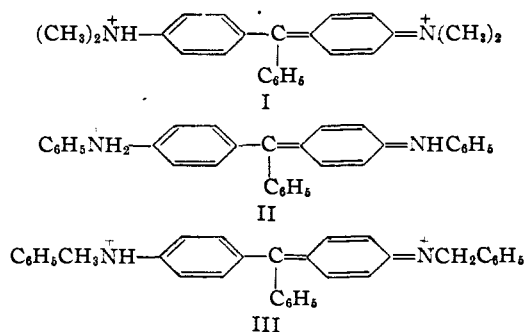

The results obtained with I were in sharp contrast with those obtained with II and III. We shall first describe and discuss the results with these three dyes, treating II and III as a unit. We shall then present and briefly discuss the spectra of five other dyes.

Malachite Green (I).—The spectrum of malachite green in concentrated sulfuric acid is shown in Fig. 1. This spectrum changed in no detectable way after standing for twenty-six days at room temperature. When a solution in concentrated sulfuric acid was allowed to stand for a week, and then diluted with acetic acid, the molecular extinction coefficients were, within experimental error, the same as those of a freshly prepared solution of (I) in the same solvent over the entire range of wave lengths measured (700 mμ to 300 mμ). Apparently no sulfonation or other irreversible reaction occurred.

The spectrum of malachite green in concentrated sulfuric acid is very similar to that of triphenylmethyl ion, and quite unlike that of the second ion of malachite green. This can be seen from the following comparison of the spectral data: For malachite green in concentrated sulfuric acid, $\lambda_1 = 434$ mμ, $\epsilon_1 = 3.2 \times 10^4$, $\lambda_2 = 388$ mμ, $\epsilon_2 = 2.7 \times 10^4$, $\lambda_3 = 288$ mμ, $\epsilon_3 = 2.3 \times 10^3$; for triphenylmethyl ion,[2] $\lambda_1 = 431$ mμ, $\epsilon_1 = 4 \times 10^4$, $\lambda_2 = 404$ mμ, $\epsilon_2 = 4 \times 10^4$, $\lambda_3 = 289$ mμ, $\epsilon_3 = 2 \times 10^3$; for the second ion of malachite green,[3] $\lambda_1 = 450$ mμ, $\epsilon_1 = 3.0 \times 10^4$, $\lambda_2 = 322$ mμ, $\epsilon_2 = 5.5 \times 10^3$, $\lambda_3 = 262$ mμ, $\epsilon_3 = 9.5 \times 10^3$. There seems little doubt that in concentrated sulfuric acid malachite green changes to an ion very similar to triphenylmethyl ion. The formula of this ion is IV.

(2) Orndorf. Gibbs. McNulty and Shapiro. *ibid.*, **49**, 1545 (1927).

(3) Tolbert and Branch. *ibid.*, **69**, 1083 (1947).

$(CH_3)_2\overset{+}{N}H$—⟨ ⟩—$\overset{\cdot}{\underset{\underset{C_6H_5}{|}}{C}}$—⟨ ⟩—$\overset{+}{N}H(CH_3)_2$

IV
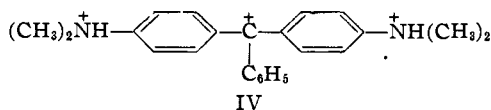
In Fig. 1 the spectrum is not shown further toward the red than 560 mμ. The measurements were made beyond 700 mμ, but there was no absorption in this region. Malachite green does not show the phenomenon observed by Hill, Branch and Patapoff with viridine green.
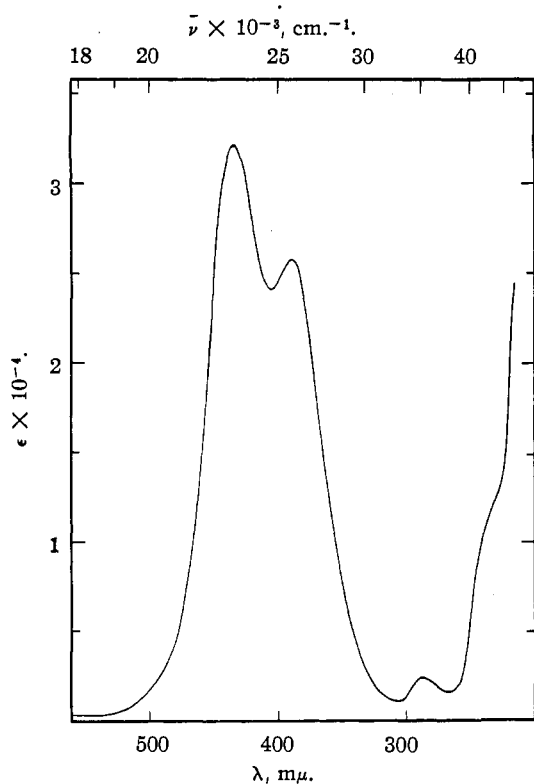

Fig. 1.—Spectrum of malachite green (I) in concentrated sulfuric acid.

Viridine Green and its Dimethyl Derivative.— The spectra of freshly prepared concentrated sulfuric acid solutions of II and III are shown in Fig. 2. The data for these spectra are $\lambda_1 = 677$ mμ, $\epsilon_1 = 1.9 \times 10^4$, $\lambda_2 = 512$ mμ, $\epsilon_2 = 2.1 \times 10^4$, $\lambda_3 = 349$ mμ, $\epsilon_3 = 1.1 \times 10^4$, $\lambda_4 = 269$ mμ, $\epsilon_4 = 1.3 \times 10^4$ for II, and $\lambda_1 = 710$ mμ, $\epsilon_1 = 2.25 \times 10^4$, $\lambda_2 = 485$ mμ, $\epsilon_2 = 2.3 \times 10^4$, $\lambda_3 = 270$ mμ, $\epsilon_3 = 1.3 \times 10^4$ with shoulders in the neighborhoods of 580 mμ, 450 mμ, and 350 mμ for III. The data for the second ions of these dyes are $\lambda_1 = 495$ mμ, $\epsilon_1 = 2.5 \times 10^4$, $\lambda_2 = 350$ mμ, $\epsilon_2 = 1.3 \times 10^4$, $\lambda_3 = 266$ mμ, $\epsilon_3 = 1.95 \times 10^4$ for II, and $\lambda_1 = 485$ mμ, $\epsilon_1 = 3.2 \times 10^4$, $\lambda_2 = 330$ mμ, $\epsilon_2 = 8.6 \times 10^3$, $\lambda_3 = 270$ mμ, $\epsilon_3 = 1.3 \times 10^4$ for III. The spectra in concentrated sulfuric acid are evidently those of the second ions with the spectra of other molecular species of the dyes superimposed on them. In both cases the new species have strong absorption bands in the neighborhood of 700 mμ.
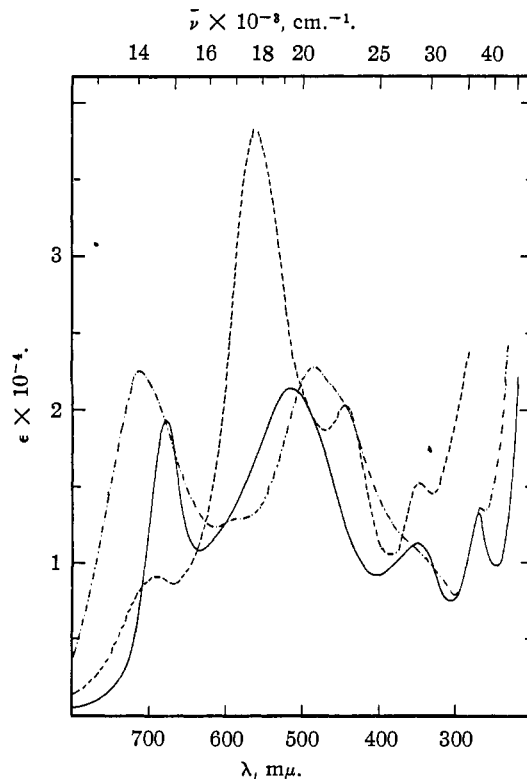

Fig. 2.—Spectra of dyes II, III and VIII in concentrated sulfuric acid: — dye II, –·–·– dye III, – – – dye VIII.

When solutions of II and III in concentrated sulfuric acid were allowed to stand and then diluted with acetic acid, the spectra of the resulting solutions were typical of first ions of diaminotriphenylmethane dyes, though at the same concentration of sulfuric acid the spectra of the parent dyes were those of mixtures of the first and second ions. This is illustrated in Fig. 3 for the case of II, at two volume per cent. of sulfuric acid. This is shown by the following data. For the first ion of II, $\lambda_x = 637$ mμ, $\epsilon_x = 4.7 \times 10^4$, $\lambda_y = 447$ mμ, $\epsilon_y = 1.3 \times 10^4$. With two per cent. of sulfuric acid $\lambda_x = 638$ mμ, $\epsilon_x = 2.9 \times 10^4$, and there was absorption covering the regions of the x-band of the second ion ($\lambda = 495$ mμ) and the y-band of the first ion ($\lambda = 447$ mμ). At this acidity an appreciable amount of the parent dye was converted to its second ion. But when II was allowed to stand for a week in concentrated sulfuric, the spectral data for the solution after it had been diluted to two per cent. sulfuric acid was $\lambda_x = 630$ mμ, $\epsilon_x = 4.4 \times 10^4$, $\lambda_y = 454$ mμ, $\epsilon_y = 1.6 \times 10^4$. This spectrum is very similar to that of the first ion of II. The irreversible change produced on standing in sulfuric acid was one that produces only small changes in the spectrum, but markedly decreases the basicity of the first ion. Evidently the irreversible reaction was sulfonation of benzene rings.
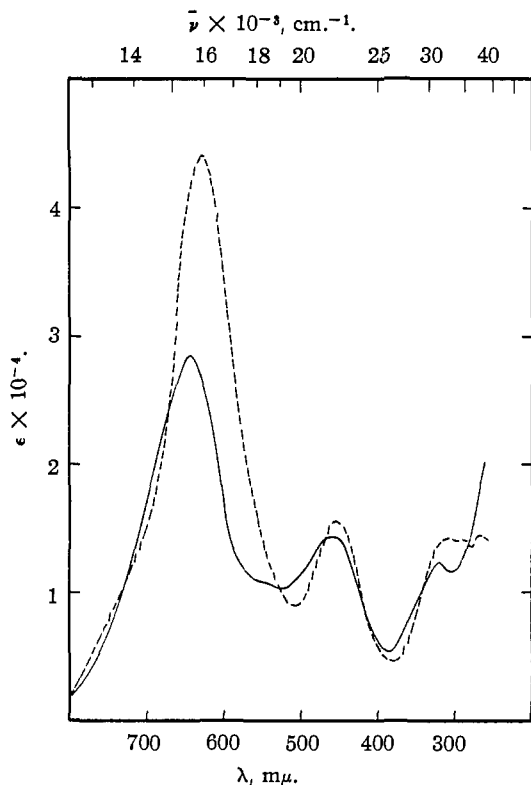
Fig. 3.—Spectra of dye II in acetic acid with 2% of sulfuric acid, before and after standing in concentrated sulfuric acid for a week: — after, - - - before.

Fig. 4.—Spectra of dye II in concentrated sulfuric acid before and after standing for twenty-six days: — before, - - - after.

The spectrum of a freshly prepared solution of III in concentrated sulfuric had two regions of strong absorption. One of these was in the neighborhood of 700 mμ, and the other in the neighborhood of 500 mμ. The latter was due chiefly to the second ion, the former to a new species. The absorptions in the two regions were approximately equal. When the solution was allowed to stand the absorption in the neighborhood of 500 mμ grew at the expense of that at 700 mμ. During this period sulfonation of benzene rings occurred. Evidently sulfonation reduces the conversion of second ions to forms that absorb in the neighborhood of 700 mμ. This suggests that the forms absorbing at 700 mμ are higher ions, and that their disappearance is due to the reduction of basicity normally resulting from sulfonation.

The spectrum of II in concentrated sulfuric acid changed in a quite different way on standing. This change is shown in Fig. 4. The spectrum was measured after twenty-six days, but visual observation showed that the change was nearly complete in a day. The chief feature of the spectrum after standing is a strong band with λ = 580 mμ, and ϵ = 3.1 $\times$ 10^4. The same phenomenon was observed by Hill, Branch and Patapoff.[1]

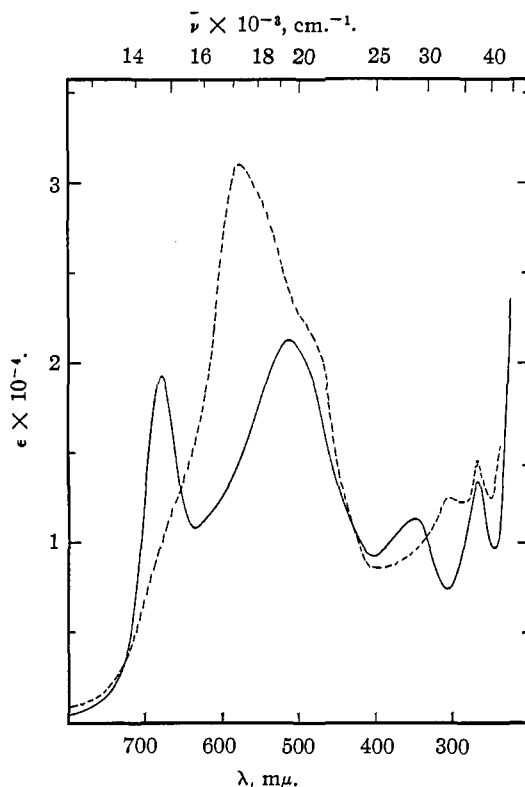To whatever compound the absorption at 580 mμ was due, it was evidently formed in good yield,

but was entirely destroyed when the solution was diluted with acetic acid.

The chief difference between II and III is that II is a secondary amine while III is a tertiary amine. The difference observed in the spectra of the two dyes on standing is best explained as due to N-sulfonation. This reaction could occur with the secondary amine II, but not with the tertiary amine III. However there is no reason to believe that the second ion of any sulfonated product of II can have a band with λ_{max} as great as 580 mμ. Sulfonation at the nitrogen atoms would greatly reduce the basicity of the dye, and hence could cause the reversion of the second ion to a first ion even in concentrated sulfuric acid. That λ_x for the first ion of the N-sulfonated dye should be markedly smaller than that for the parent dye is to be expected. The value of λ_x for the first ion of the N,N-diacetyl derivative of II is 539 mμ.
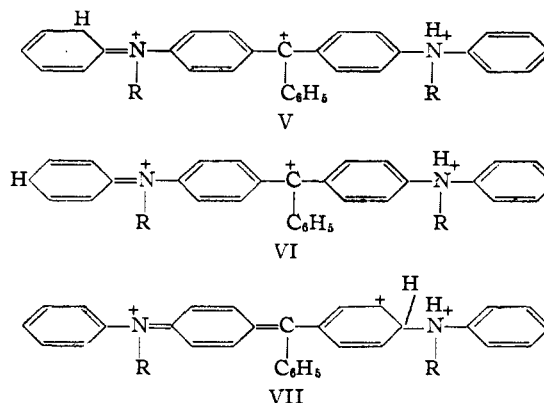
The acetyl groups are easily removed from the N-acetyl derivatives of II by hydrolysis in acid solution. By analogy one would expect that sulfonic acid groups are easily removed from N-sulfonic acid derivatives of II, by the lytic action of acetic acid. It is therefore not surprising that the band at 580 mμ disappeared when the solution was diluted. That C- as well as N-sulfonation occurred was shown by the spectrum of the diluted solution.

The value of the λ_{max} of a diaminotriphenyl-methane dye alternately increases and decreases by 100–200 mμ as protons are removed from or added to the nitrogen atoms, the greater λ_{max} values occurring when the two nitrogen atoms have similar basicities. This alternation does not normally continue after the second ion has been reached, for on the next step both nitrogen atoms become neutralized by protons, thus insulating them from the chromophore and reducing λ_{max}. When as in II and III the alternation continues beyond the second ion, one might suppose that the amino groups have lost basicity, and the second ion has reverted to a first ion in spite of the increase in the acidity. But so great a reduction of the basicity of the amino groups would have a strong hypsochromic effect, and consequently such an explanation is not a valid explanation of the bands observed in the neighborhood of 700 mμ, for the first ions of the parent dyes have λ_{max} values a little smaller than 640 mμ. It would appear therefore that the acid reacts to form a third ion in which the terminal rings extend the chromophoric conjugated system beyond the triphenyl-methyl structure.

To assume that the band near 700 mμ is due to an addition of the acid to the π electrons of a ring as a whole is begging the question. There is no known reason why such an addition should be strongly bathochromic. We shall assume an addition of the acid to a particular atom. For such an assumption to be acceptable it is necessary that the carbonium ion charge of the product should have a greater linear range of location than is found in triphenylmethyl ion in which the linear range for the charge is from the para position of one ring to the para position of another ring (9 atoms). Otherwise λ_{max} would not be much greater than it is in triphenylmethyl ion (430 mμ). Further it is also necessary that the carbonium ion charge of the addition product shall be locatable at more atoms than it is in triphenylmethyl ion (10 atoms). Otherwise, since the product has fewer benzenoidal rings than its type IV tautomer, and is for that reason very unstable with respect to its tautomer, it could not exist in appreciable quantities without the compensating factor of greater resonance of the charge.

We shall consider only the three product whose formulas are shown below. Other possibilities either could not absorb in the 700 mμ region, or are not acceptable for the same reasons that lead us to reject VII. In the formulas the added acid is represented by an H, and R is a methyl group when the parent dye is III, and a hydrogen atom when the parent dye is II.
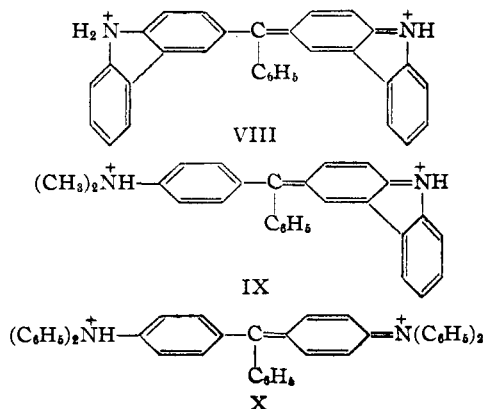
In VII, the charge may vibrate over thirteen atoms, and consequently such a product might account for the high value of λ_{max}. But there are only ten locations for the charge in VII, and these do not include the favored central carbon atom, but do include an already positively charged nitro-
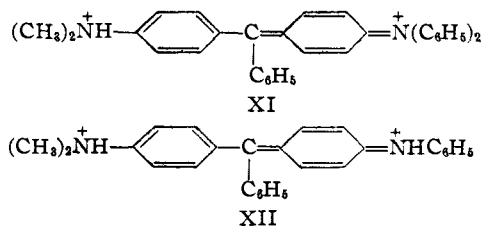

gen atom. Consequently VII must be rejected as being too unstable with respect to its type-IV tautomer. One cannot assume that the equilibrium between VII and IV is not achieved, for the formation of the addition product is a rapid reversible reaction, and a type-IV compound is formed rapidly and reversibly from malachite green.

The charge of V or VI vibrates linearly over 13 atoms. In V the number is 15 if the atoms are counted round the terminal ring. In VI there is the additional bathochromic factor of a branched system of double bonds in the terminal ring. If these carbonium ions are treated by the same rules as the cyanines, λ_{max} of V or VI should be between 200 and 300 mμ, greater than λ_{max} of triphenyl-methyl ion. That is, λ_{max} should be between 650 and 750 mμ. Both V and VI have thirteen locations for the charge, including the favored location on the central carbon atom. It is therefore possible that V and VI are stable with respect to their type IV tautomers. Since we have no preference between structures V and VI, we shall use V to mean V and/or VI.

Other Phenylated Dyes.—Experiments similar to those already described were done with some other phenylated diaminotriphenylmethane dyes. We shall use formula numbers instead of the complicated names to indicate these dyes. The formulas of the second ions are given below

$(CH_3)_2\overset{+}{N}H-\langle\!\!\langle\!\!\rangle\!\!\rangle-\underset{\underset{C_6H_5}{|}}{C}=\langle\!\!\langle\!\!\rangle\!\!\rangle=\overset{+}{N}(C_6H_5)_2$

XI

$(CH_3)_2\overset{+}{N}H-\langle\!\!\langle\!\!\rangle\!\!\rangle-\underset{\underset{C_6H_5}{|}}{C}=\langle\!\!\langle\!\!\rangle\!\!\rangle=\overset{+}{N}HC_6H_5$

XII

The change of the spectrum on ageing the solutions in concentrated sulfuric acid was not investigated for VIII and IX. The results obtained with X (Fig. 5) were inconclusive. The first ion of this dye is so weakly basic that in a 50–50 mixture of acetic and sulfuric acids there was no sign of the second ion. Hence there is a probability that the first ion was present in the sulfuric acid solution, which contained a considerable amount of the second ion. The x-bands of the first ions of II and III are greatly affected by the presence of the second ion. Although the absorption by X at long wave lengths was greatly changed in going from fifty per cent. to ninety-eight per cent. sulfuric acid, one cannot say whether the change was due to the effect of the second ion on the x-band of the first ion, or the production of higher than second ions. On standing, the sulfuric acid solution of X lost its optical clarity, and no conclusion could be drawn from the spectrum.
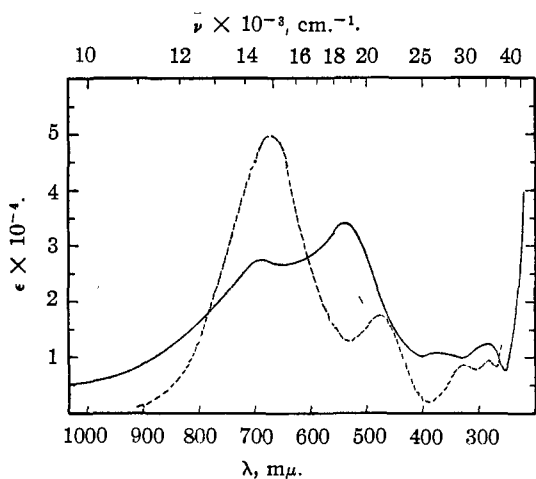

Fig. 5.—Spectra of dye X in a fifty–fifty mixture of acetic and sulfuric acids, and in concentrated sulfuric acid: — in concentrated sulfuric acid, $-\cdot--$ in fifty–fifty mixture.

The spectra observed for IX and XI indicated the presence of nothing but the second ions. The spectrum of IX in concentrated sulfuric acid was an exact replica of that shown for the second ion in reference 3. A shift of the bands toward the red was observed in XI. This is presumably a solvent effect. The spectral data for XI in sulfuric acid (Fig. 6) are $\lambda_1 = 538$ mμ, $\epsilon_1 = 3.7 \times 10^4$; $\lambda_2 = 355$ mμ, $\epsilon_2 = 1.1 \times 10^4$; $\lambda_3 = 270$ mμ, $\epsilon_3 = 1.3 \times 10^4$. The data in ten per cent. sulfuric acid

are $\lambda_1 = 515$ mμ, $\epsilon_1 = 3.3 \times 10^4$; $\lambda_2 = 343$ mμ, $\epsilon_2 = 1.0 \times 10^4$, $\lambda_3 = 270$, $\epsilon_3 = 1.2 \times 10^4$.
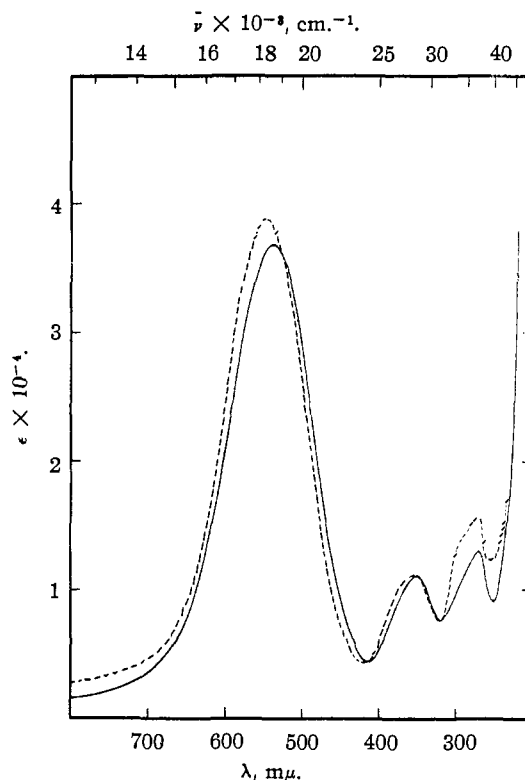

Fig. 6.—Spectra of dye XI in concentrated sulfuric acid before and after standing for twenty-six days: — before, $---$ after.

The other two dyes VIII and XII (Figs. 2 and 7) showed the presence of type V ions. A definite band, $\lambda_{max} = 680$ mμ and $\epsilon = 9 + 10^3$, was obtained with VIII. A shoulder 680–700 mμ was obtained with XII.

The spectra of III, VIII and XII cannot be accounted for by bands in the neighborhood of 700 mμ and absorption by the second ions. In all three dyes some of this extra absorption was in the neighborhood of 450 mμ. This extra absorption appeared as a shoulder on the x-band of the second ion in III, as a small band, with $\lambda = 446$ mμ in VIII and as the most intense band ($\lambda = 440$ mμ) in the spectrum of XII. Since the strengths of these absorptions are related inversely to the intensity of the absorption by type V ions, presumably they are not due to type V ions; but to some other species, which we think is the type IV ion.

Terminal aryl groups on both nitrogen atoms are insulated in a type IV ion, but those on only one of the nitrogen atoms of a second ion are insulated. Hence the basicity of the second ion depends chiefly on the terminal groups on one nitrogen atom. Hence the relative basicities of the second ions should be correlated to the relative basicities of the less basic of the pair of amines out
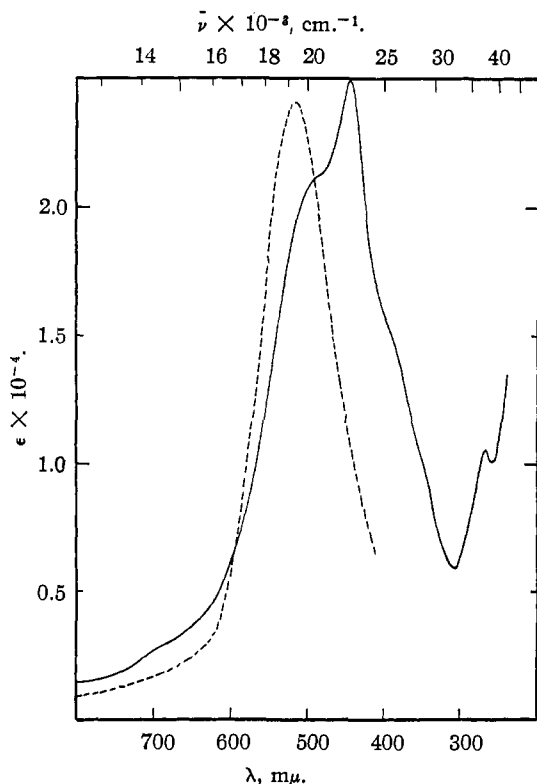
Fig. 7.—Spectra of dye XII in concentrated sulfuric acid before and after standing for twenty-six days: — before, - - - after.

Fig. 8.—Spectra of dye XI in acetic acid with 2% sulfuric acid, before and after standing in concentrated sulfuric acid for a week: — before, - - - after.

of which the dye is made, the terminal groups from the more basic amine being insulated by the addition of the proton to form the second ion from the first. To obtain a type V ion one terminal aryl group is necessary. Other terminal aryl groups are either insulated or have only a small interaction with the rest of the molecule. Hence extra aryl groups or resonance either should have only a small effect on the amount of type V ion, or if located on the already phenylated nitrogen atom should reduce the conversion of the second ion to the type V ion.

Assuming that the relative intensities of the bands roughly mirror the relative concentrations of the three species the above deductions were to some extent confirmed by the experiments. Thus the second ion of I, which is derived from dimethylaniline, was completely neutralized, the second ions of VIII, IX and XI, which are derived in part or *in toto* from the very weakly basic amines, triphenylamine and carbazole, were the least affected by sulfuric acid, and II, III and XIII were of intermediate basicity. However, the agreement between deduction and experiment was far from perfect. The insulated aryl group has the effect of stabilizing the type V ion. Thus the type V ion was abundant in II and III, but only a trace was present in XII. The type V ion of VII was found, but at the same acidity no type V ion
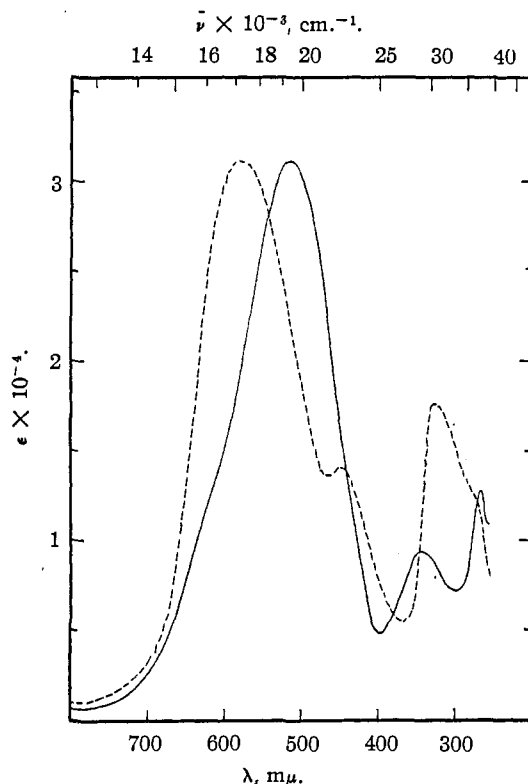
was observed in IX. Apparently the insulation is not complete. Tolbert and Branch[3] found bathochromic effects on the x-bands of the second ions leaking through the insulation.

The main thesis of this article is that the bands observed in the neighborhood of 700 mμ could have been due to a third ion that is tautomeric with the type IV ion, and derivable from it by a tautomeric shift of a proton from a nitrogen atom to an ortho or para position of a terminal aryl group. The arguments for this conclusion apply equally to a shift of this type from both nitrogen atoms. Against this double shift it can be argued that the band in the red was also found in the sulfuric acid solution of XII, which has only one terminal aryl group, and that calculation of λ_{max} of the product of a double shift, by methods used to predict λ_{max} values in cyanines, gives too large a value. Neither of these arguments is conclusive. The absorption in the red observed in XII was so small that it could have been due to an impurity with terminal groups on both nitrogen atoms. The amount needed would be too small to detect by analysis, or in the spectra of the first and second ions. Such an impurity could have been formed by disproportionation. Indeed Tolbert and Branch actually separated from the crude preparation of some of these dyes small amounts of dyes with spectra characteristic of triaminotriphenyl-

methane dyes. Although there is little doubt that structures like V represent oscillators very similar to the cyanines, it is not known that the constant for the increase of λ_{max} with the number of interpolated double bonds would be the same as that found in cyanines. Were this constant half of what it is in the cyanines, the observed λ_{max} would indicate the double shift.

With the exception of I, in all solutions in sulfuric acid that had stood, absorption due to third ions diminished. On dilution, such solutions, again with the exception of I, gave spectra that were characteristic of a diaminotriphenylmethane dye, but of one whose first ion was less basic than the first ion of the corresponding parent dye. It is natural that sulfonation should decrease the basicities of both first and second ions.

On standing, the spectra of XI changed very little (Fig. 6). That it had sulfonated was shown by the spectrum after dilution (Fig. 8). This spectrum was chiefly that of a first ion as can be seen from the bands in the far ultraviolet. However the main band comes at a wave length that is short for a phenylated dye. In dye XI the two amino groups are sufficiently different in basicities for the Brooker effect to be appreciable, on sulfonation of the terminal phenyl groups the difference of basicities of the two amino groups is increased, and the hypsochromic Brooker effect becomes accentuated. The appearance of the spectrum showed that there was a mixture in the solution as would be expected, since sulfonation would have reached different degrees in different molecules. Some second ions were probably present, but their bands were obscured by those of the first ions.

Experimental

The spectra were measured with a Beckman spectrophotometer. The experimental details and the materials were all the same as those described or given by reference in the author's paper on the spectra of the second ions.[3] One detail should be repeated because of its special importance in this work. The mixtures of acetic and sulfuric acids in the comparison cell of the spectro-

photometer were compounded and aged in the same way as the liquid in which the dye was dissolved. This was necessary to compensate for absorption, especially in the ultraviolet, that developed when mixtures of the two acids were aged. The absorption developed especially fast in mixtures of approximately equal proportions. In general the method of compensating for the charring appears to have been successful. The greatest error would have arisen when solutions that were treated with concentrated sulfuric acid were diluted. Heating was not always avoided during dilution. In solutions made in this way, the spectra at wave lengths less than 300 mμ should be considered dubious.

Summary

The spectra in concentrated sulfuric acid of malachite green and some more phenylated diaminotriphenylmethane dyes were measured.

The spectrum of malachite green was so similar to that of triphenylmethyl ion, that it was assumed that, in concentrated sulfuric acid, malachite green exists as a triply charged ion with a structure similar to that of triphenylmethyl ion except for two dimethylaminium ion groups at the p and p' positions.

With some of the phenylated dyes bands were observed in the neighborhood of 700 mμ. These bands have been attributed to the addition of a proton to one of the terminal benzene rings, resulting in a carbonium ion compounded of a large number of mesomers, differing from each other in the location of the charge, and the distribution of the double bonds. This mesomeric ion can be considered as a triphenylmethyl ion in which the conjugate system has been extended by three more double bonds. Bands attributed to this type of ion were found mixed with bands due to the second ion and to ions of the simple triphenylmethyl type. They were prominent only when both amino groups were phenylated, though a small band in the neighborhood of 700 mμ were found in one case in which only one of the amino groups was phenylated.