[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Absorption Spectra of Some N-Acetyl Derivatives of *p,p'*-Diaminotriphenylmethane Dyes

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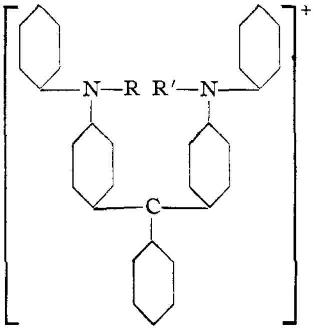
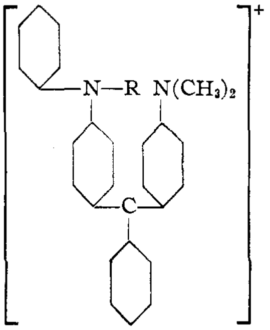
To explain the spectra of 3,3'-dicarbazylmethyl ion and N-dimethyl-*p*-amino-3-carbazylphenylmethyl ion, Branch, Tolbert and Lowe[1] suggest that in a diaminotriphenylmethane dye, the expected bathochromic effect of N-arylation is qualified by hypsochromic effects due to the reduction of the basicities of the amino groups. They cite the following four effects: when both amino groups are equally reduced in basicity, (1) the bathochromic effect of the substituents is less than would be expected from the extension of the conjugated system, and in extreme cases the substituents will have hypsochromic effects; and (2) the frequency difference between the *x*- and *y*-bands diminishes as the basicities of the amino groups are reduced. When the basicity of only one of the amino groups is reduced, the upset of the balance of basicities of the amino groups (3) reduces the wave lengths of the absorption bands[2]; and (4) increases the susceptibility of the frequency of the absorption bands to change of solvent. These four effects increase as the basicities are progressively reduced, but theoretically they should reach a limit, for reduction of the basicities should eventually produce an ion that is optically equivalent to a triphenylmethyl ion in the case of the symmetrical dyes, and to a monoaminotriphenylmethyl ion in the case of the unsymmetrical dyes.

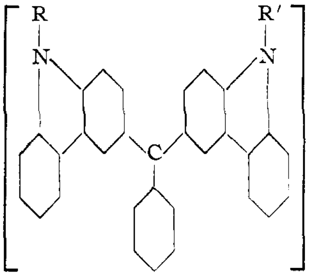
In view of the above observations, it was thought advisable to measure the spectra of two related diaminotriphenylmethane dyes in which the basicities of the amino groups have been reduced by both arylation and acylation, one of the dyes being symmetrical, and the other being unsymmetrical. The dyes chosen were N,N'-diacetyl-N,N'-diphenyl-*p,p'*-diaminotriphenylmethyl ion (formula I) and N-dimethyl-N'-acetyl-N'-phenyl-*p,p'*-diaminotriphenylmethyl ion (formula II). Attempts were also made to obtain the spectra of the monoacetyl derivative of viridine green (formula III) and the carbazole analogs (formulas IV, V and VI). These attempts were successful except in the case of IV. The second stage of acetylation of the carbazyl dye was very incomplete, and the product easily reverted to the monoacetyl derivative VI. Hereafter these acetylated dyes will be referred to by their formula numbers.



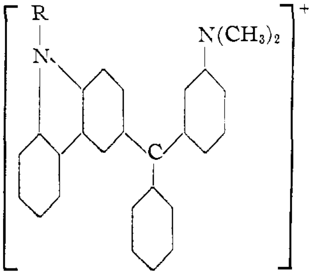
I. R = R' = $COCH_3$
III. R = $COCH_3$, R' = H
VII. R = R' = H



II. R = $COCH_3$
VIII. R = H



IV. R = R' = $COCH_3$
VI. R = $COCH_3$, R' = H
IX. R = R' = H



V, R = $COCH_3$
X, R = H

These dyes were prepared as carbinols or methyl ethers by acetylating the carbinols or methyl ethers of the appropriate dyes, and by decomposing the reaction product with water. The formulas of the mother substances are shown in formulas VII, VIII, IX and X.

Many of the acetylated color bases are so weak that an acidic solvent as well as a strong acid is necessary to convert them to their ions. For this reason acetic acid was chosen as a solvent in which the spectra of the ions of all the compounds could be measured. In addition to acetic acid chloroform was used as the solvent for II and V, and methanol, acetone and water as solvents for II.

In acetic acid solutions, sulfuric acid whose density was 1.84 g./ml. was used as the acidifying agent. The concentrations have been given in volume per cent. of sulfuric acid of the above given

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(1) Branch, Tolbert and Lowe, THIS JOURNAL, 67, 1693 (1945).

(2) See Brooker, Sprague, *et al.*, *Rev. Mod. Physics*, 14, 275 (1942); THIS JOURNAL, 67, 1875 (1945); 67, 1889 (1945).

density. The chloroform was acidified with traces of hydrochloric acid gas. The concentrations were not measured. Hydrochloric acid was also the acidifying agent in methanol and water. The normalities have been given. The acetone was acidified with 12 *N* aqueous hydrochloric acid. Hence when much acid was used the solvent was a mixture of acetone and water, but in slightly acidified solutions the solvent was essentially acetone. The concentrations have been given in volume per cent. of 12 *N* hydrochloric acid.

Results

The spectra of the acetylated dyes are shown in Figs. 1 to 6.

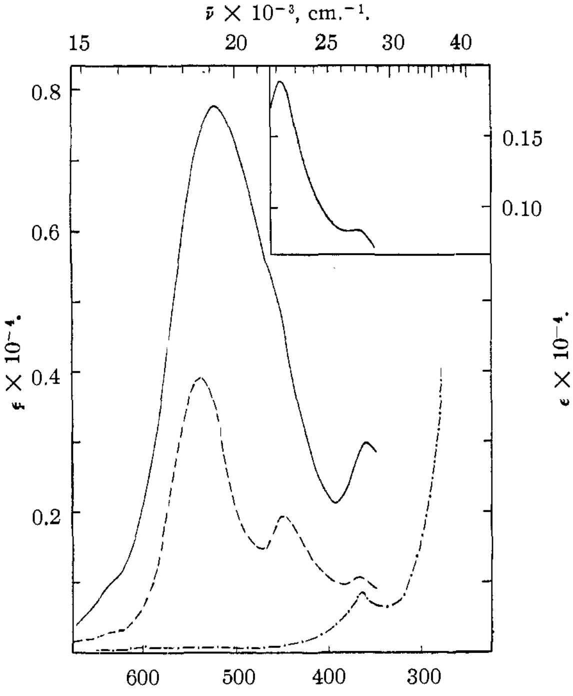

Fig. 1.—Spectra of mono- and di-acetyl derivatives of viridine green VII: —, III in acetic acid and 3.9% sulfuric acid; ---, I in acetic acid and 3.9% sulfuric acid; -·-·-, I in acetic acid. Inset shows spectrum of I from 350 to 462 mμ corrected for presence of color bases.

In this article we are primarily concerned with the x- and y- bands of the quinoidal first ion, and since the spectra show more than two bands it will be necessary to state why certain bands in the observed spectra were assumed to be these bands.

The x- and the y- bands of the quinoidal ions would be expected to occur at wave lengths longer than 350 mμ. For the purpose of this discussion we shall call this spectral region the visible and the region of higher frequency the ultraviolet.

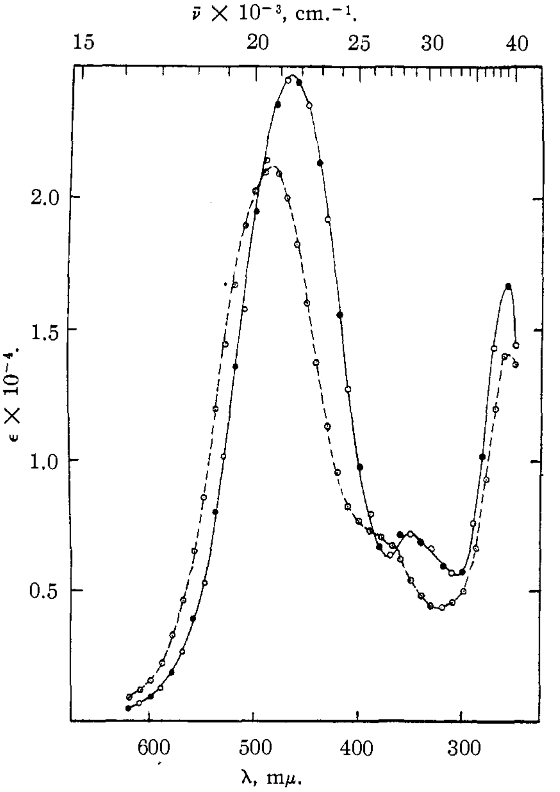

Fig. 2.—Spectra of II in acetic acid: ---, II in pure acetic acid; —, II in acetic acid and 3 or 4% sulfuric acid, ○ in 3% sulfuric acid, ● in 4% sulfuric acid.

The spectra of all the acetylated dyes show one prominent band in the visible. This is indubitably the x-band of the quinoidal ion. On the shorter wave length side of this band there are either one or two weaker bands in the visible region. In some cases the two bands are not resolved but form a shoulder that extends to about 350 mμ. It is noteworthy that all spectra with the exception of the color base of VI show enhanced absorption in the neighborhood of 360 mμ. We do not think that the bands near 360 mμ are the y-bands. We have called them a-bands and shall discuss them later. We have assumed that the y-bands are the bands that appear between the x- and the a-bands, either as well defined bands (*e. g.*, II in chloroform, see Fig. 3) or as a part of a shoulder (II in acetic acid, Fig. 2). Sometimes the y-band is completely submerged in the x-band or superimposed on the a-band (II in 12 *N* hydrochloric acid, Fig. 3).

The spectral data have been collected in Table I. In the table the maximum of the y-band has been given under λ_y if there was a distinct band. Otherwise we have given the range of the shoulder or indicated a minimum by "min." under this heading.

It may be noted that the small bands in the 600 mμ region that appear in many of the spectra are not listed in Table I. The positions of these bands always are close to those of the x-bands of the parent dyes,[1,3] and the bands always disappeared

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(3) Tolbert, Branch and Berlenbach, THIS JOURNAL, **67**, 887 (1945).

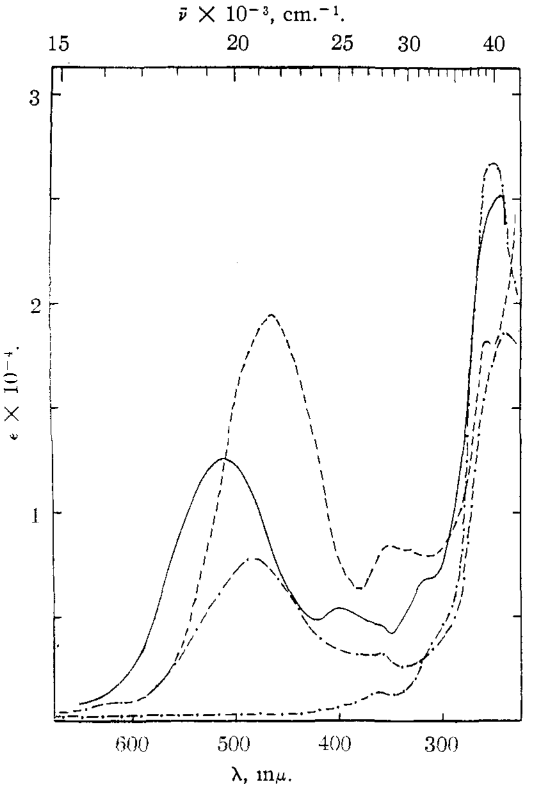


Fig. 3.—Spectra of II: -·-·-, color base of II in methanol; --·--·--, II in methanol and 5×10^{-4} N hydrochloric acid: —, II in chloroform acidified with hydrogen chloride gas; ---, II in 12 N aqueous hydrochloric acid. The concentration of the dye was not measured in aqueous hydrochloric acid, and ϵ is in arbitrary units.

when sufficient acid was added to convert the parent dyes to their doubly charged ions. In the case of II in 12 N hydrochloric acid a band appears at about 340 mμ which corresponds to the y-band of the second ion of its parent dye VIII. In view of these observations we have assumed that the bands were due to traces of the parent dyes that were either retained from the preparation or formed in the solvents in which the spectra were taken. No corrections were made in the absorption curves for the presence of these dyes, and the data in Table I were corrected only as already indicated, since it can be calculated from the size of the x-bands that absorption due to the weaker bands of the parent dyes cannot cause serious errors in the spectra.

In addition to the absorption of such impurities the observed spectra may also contain absorption due to the color bases, the benzenoidal first ions, and the quinoidal and benzenoidal second ions.

We have assumed that no appreciable amounts of second ions were present when the solvent was chloroform containing insufficient acid to neutralize the base, or when it was glacial acetic acid, 0.43 N aqueous hydrochloric acid, or acetone with 1% 12 N hydrochloric acid added. None of these solvents would completely convert the first ion of malachite green to the second ion, although it is presumably a much stronger base than the first ions of the acetylated dyes. If the addition of acid to any one of the above solvents did not cause a shift in the positions of the bands we have assumed that no second ion was formed.

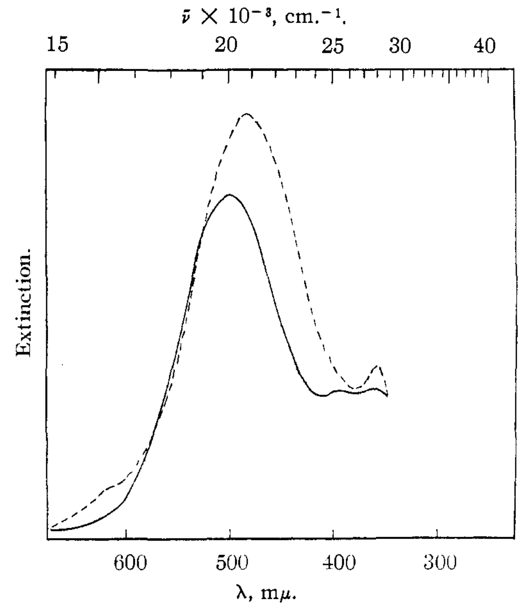


Fig. 4.—Spectra of II in acetone: —, II in acetone and 1% aqueous 12 N hydrochloric acid; -----, II in acetone and 25% aqueous 12 N hydrochloric acid.

The color bases and the benzenoidal ions should not absorb in the visible region and hence do not interfere with the position of the x- and y-bands of the quinoidal first ions. However, their presence would lead one to calculate a low molecular extinction coefficient. No correction could be made for the presence of the benzenoidal first ions, since the compositions of the equilibrium mixtures of the benzenoidal and quinoidal ions were not known. The molecular extinction coefficients given in Table I are therefore characteristic of such mixtures rather than of the pure quinoidal ions.

In some cases a correction was applied for the presence of free color base. This was possible when changing the acid concentration caused no change in λ_x. The fraction of the conversion to the first ion was then calculated from the equation

$$\alpha_1 = (\epsilon_1 c_2 - \epsilon_2 c_1)/(\epsilon_2 c_2 - \epsilon_2 c_1)$$

where α is the fraction converted to the ion, c is the concentration of the acid and ϵ is the molecular extinction coefficient at a wave length where the base does not absorb divided by the molality of the dye without reference to whether it is the color base or the ion.

This equation is a rough approximation for it assumes that the activities of the reactants and products of the neutralization of the color base are proportional to their concentrations. This

TABLE I

SPECTRAL DATA

Formula number of dye	Solvent and acid	Molecular species present	λ_x mμ	$\epsilon_x \times 10^{-4}$	λ_y mμ	$\epsilon_y \times 10^{-4}$	λ_a mμ	$\epsilon_a \times 10^{-4}$	λ_u mμ	$\epsilon_u \times 10^{-4}$
I	CH_3COOH	Color base	...	..	...	..	364	0.08	[a]	[a]
I	CH_3COOH +3.9% H_2SO_4	First ion[b]	539	0.5	450	0.2	367	0.05	[a]	[a]
II	$CHCl_3$ + HCl	First ion + color base	512	1.3	398	0.5	365	0.4	245	2.5
II	CH_3COOH	First ion[b]	486	2.5	400–360		[c]	[c]	256	1.7
II	CH_3COOH + 4% H_2SO_4	First or[d] second ion	464	2.5	Min 370		355	0.7	260	1.7
II	CH_3OH	Color base	...	..	...	..	360	0.13	252 290–310	2.7
II	CH_3OH + 5 × 10^{-4} *N* HCl	First ion[b]	484	0.8	360–400		[c]	[c]	240	1.9
II	H_2O + 0.43 *N* HCl	First ion + color base	470	[e]	Min 385		360	[e]	250–260 230–240	[e]
II	H_2O + 12 *N* HCl	First or[d] second ion	468	[e]	Min 380		320–360		255	[e]
II	CH_3COCH_3 + 1% 12 *N* aq. HCl	First ion	498	[e]	393	[e]	360	[c]	[a]	[a]
II	CH_3COCH_3 + 25% 12 *N* aq. HCl	First or[d] second ion	482	[e]	Min 380		360	[e]	[a]	[a]
III	CH_3COOH +3.9% H_2SO_4	First ion	522	0.82	Min 394		360	0.3	[a]	[a]
V	$CHCl_3$ + HCl	First ion + color base	522	.12	389	0.05	370	0.05	[a]	[a]
V	CH_3COOH	First ion + color base	515	.20	390	0.10	370	0.09	[a]	[a]
V	CH_3COOH + 5% H_2SO_4	First or[d] second ion	530	0.55	390	0.30	355	0.36	295–300 260–270	
VI	CH_3COOH	Color base	...	..	...	..	...	..	282 264	2.6 3.3
VI	CH_3COOH + 5% H_2SO_4	First ion[b]	563	3.5	452	1.4	370	1.0	270	3.0

[a] Spectrum was not measured in the ultraviolet. [b] Molecular extinction coefficients have been corrected for absorption of color base present. [c] *a*-Band is part of shoulder. [d] λ_x changed with the acidity, so it is not known to what extent the second ion was present. [e] Molecular extinction coefficients were not measured.

assumption must be far from true in the solutions used. But the corrections were made only in cases where the conversions were nearly complete at the higher concentration of acid.

Discussion

The *x*- and *y*-Bands.—Any diaminotriphenylmethane dye can be considered as derived from malachite green by substituting the *p*-radicals of other aromatic amines for one or both of the *p*-dimethylaniline radicals. Since all the unsymmetrical dyes under discussion have one dimethylaniline radical, any aromatic amine gives rise to two dyes, symmetrical and unsymmetrical. In general, these substituted radicals will differ in their power to neutralize the central carbonium ion, *i. e.*, they will differ in what Brooker has called the "effective basicity,"[2] and it is the difference in this effective basicity that determines the magnitude of the four effects mentioned in the introduction.

Arranging the amines in an assumed order of effective basicity, Branch, Tolbert and Lowe[1] give a table in which the four effects are expressed in a semiquantitative way. For each amine they give (1) the difference in the wave numbers of the *x*-bands of malachite green ($\bar{\nu}_{x_0}$) and the symmetrical dye ($\bar{\nu}_x$), (2) the difference in the wave numbers of the *y*- and *x*-bands ($\bar{\nu}_y$ and $\bar{\nu}_x$) of the symmetrical derived dye, (3) the difference between the wave number of the *x*-band of the unsymmetrical dye ($\bar{\nu}_x$) and the arithmetic mean of the wave numbers of the *x*-bands of malachite green and the derived symmetrical dye ($\bar{\nu}_{mean}$), and (4) the difference in the wave numbers of the *x*-bands of the unsymmetrical dye dissolved in acetic acid and dissolved in chloroform.

To add N-acetyldiphenylamine to the amines in this table it is necessary to obtain λ_x and λ_y of I in acetic acid and λ_x of II in acetic acid and in chloroform. These bands were found at 539 and 450 mμ and at 486 and 512 mμ, respectively. With these data we have added N-acetyldiphenylamine to the amines in the table. Table II is this expanded table.

Although the effective basicity does not necessarily correspond to ordinary basicity, there can be no doubt that N-acetyldiphenylamine is correctly placed at the bottom of the table.

Since with carbazole the lack of basicity is great enough to make $\bar{\nu}_x$ of the symmetrical dye greater than $\bar{\nu}_x$ of malachite green, it was expected that

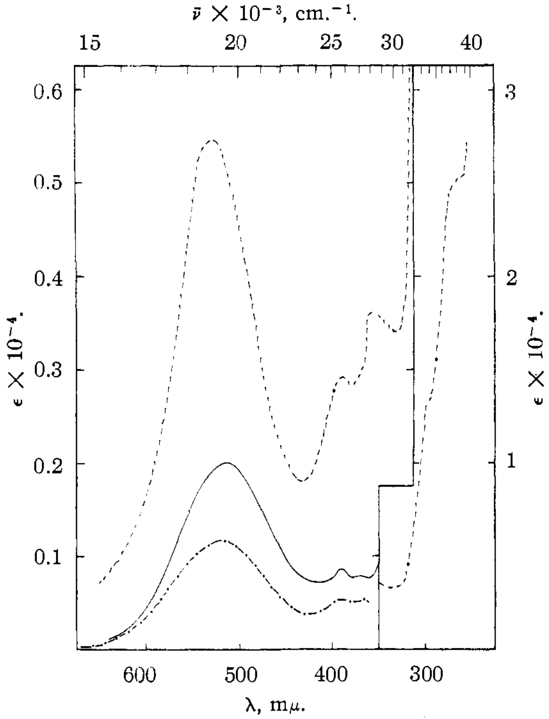


Fig. 5.—Spectra of V: —, V in acetic acid; ---, V in acetic acid and 5% sulfuric acid; -·-·-·-, V in chloroform acidified with hydrogen chloride gas. Inset is ultraviolet spectrum in acetic acid and in 5% sulfuric acid with changed units of ϵ.

$\bar{\nu}_x$ of I would be still greater. This expectation was confirmed, as can be seen from the value -2430 cm.$^{-1}$ of $\bar{\nu}_{x_0} - \bar{\nu}_x$ for N-acetyldiphenylamine.

TABLE II

EFFECTS OF LOWERING THE EFFECTIVE BASICITY

Base substituted for dimethylaniline	$\bar{\nu}_{x0} - \bar{\nu}_x$ for sym. dye $\times 10^{-2}$, in cm.$^{-1}$	$\bar{\nu}_y - \bar{\nu}_x$ for sym. dye $\times 10^{-3}$, in cm.$^{-1}$	$\bar{\nu}_{mean} - \bar{\nu}_x$ for unsym. dye $\times 10^{-2}$ in cm.$^{-1}$	Solvent effect in cm.$^{-1}$
Dimethylaniline	0	7.24	0	52
Methyldiphenylamine	3.3	6.94	− 1.40	129
Diphenylamine	4.3	6.67	− 1.89	154
Triphenylamine	12.0	6.35	− 3.71	224
Carbazole	− 3.5	6.00	− 7.63	1150
N-Acetyldiphenylamine	−24.3	3.66	−32.3	1070

The separation of the *x*- and *y*-bands is shown in the third column of Table II. As expected, the separation of the bands of I is much smaller than that of the dyes derived from more basic amines.

The hypsochromic effect of the upset of the balance of basicities is much greater in II than in any of the other unsymmetrical dyes (see column 4).

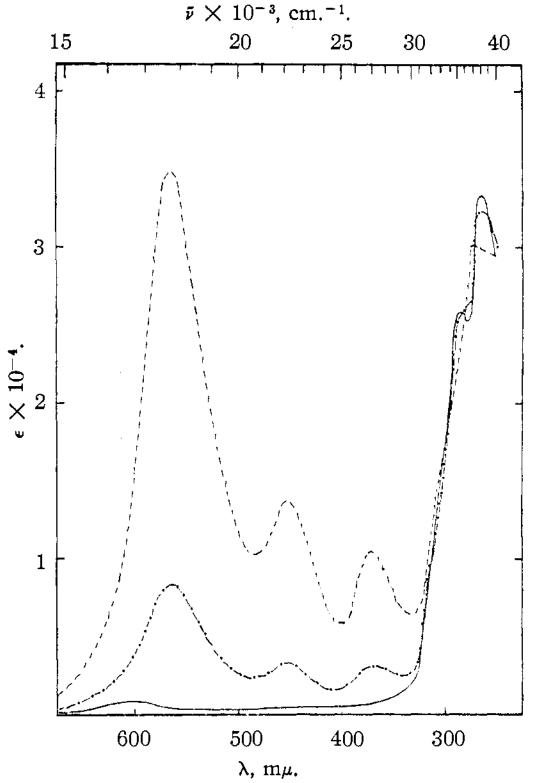
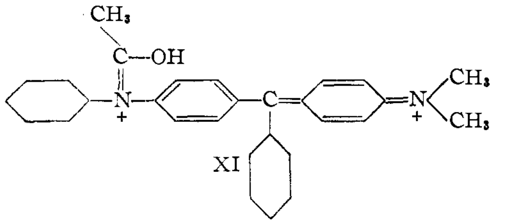


Fig. 6.—Spectra of VI: —, VI in acetic acid; -·-·-, VI in acetic acid and 0.1% sulfuric acid; ---, VI in acetic acid and 5% sulfuric acid.

The solvent effect (column 5) shows that the spectrum of II varies with the solvent much more than is normal for a diaminotriphenylmethane dye. The variation is in the predicted direction, λ_x in chloroform being greater than in the other solvents (acetic acid, acetone, methanol, and water). However, the solvent effect is less than that found for the unsymmetrical carbazyl dye X, although the difference in the basicities of the two amino groups in X is less than in II. Branch, Tolbert and Lowe predicted that continuous reduction of the basicity of one of the two amino groups would at first increase the solvent effect, but would eventually reduce it. If they are correct, the solvent effect should be smaller for V than for II. The solvent effect for V was found to be 260 cm.$^{-1}$.

The spectrum of II in acetic acid varied with the volume per cent. of sulfuric acid in a peculiar way, which can be seen by inspection of Fig. 2. As sulfuric acid was added ϵ_x increased without any change in λ_x (486 mμ), as would be expected if the color base were not completely neutralized by acetic acid alone. But when the concentration of the sulfuric acid was increased beyond 0.1%, λ_x decreased but reached a limiting value of 464 mμ at 3% sulfuric acid. The identity of the spectra in 3 and 4% sulfuric acid is shown in Fig. 2. This phenomenon is exactly what would be observed if λ_x of the first ion were 486 mμ and λ_x of the second ion were 464 mμ, and if the first ion were almost completely converted to the second ion by 3% sulfuric acid. However, these concentrations are about those necessary for the complete conversion of the parent dye VIII to its second ion, and one would naturally assume the parent dye to be a much stronger base than its N-acetyl derivative. This assumption may not be true. The difficulty of converting a first to a second ion is largely due to the loss of the strong resonance between the two nearly equivalent structures of the first ion. But acetylation by making the two structures very far from equivalent, reduces this resonance energy and so assists the formation of the second ion. This effect may compensate for the loss of basicity usually associated with acetylation. It is also possible that the proton does not add to the dimethylamino group but to the oxygen atom of the acetyl group, in spite of the fact that the basic properties of the oxygen atom of an ordinary amide are very weak. But in this case, such an ion would be greatly stabilized by resonance,' as can be seen by inspection of formula XI.



XI

If this last assumption is correct, the second ions of the acetylated dyes would be very different from the second ions of ordinary diaminotriphenylmethane dyes and the basic properties of the two classes of compounds could not be directly compared.

However, one cannot discard the possibility that the change in λ_x is a solvent effect. It seems that it would be well to reserve judgment as to whether the band at 464 mμ is due to the second ion or the first ion. Similar reservations have been made in the spectra in which the absorbing species have been given as "first or second ion" in Table I.

The dyes II and V are corresponding diphenylamine and carbazole derivatives, and the same is true for III and VI. In both these cases λ_x is greater in the carbazole than it is in the diphenylamine derivative. The same effect of substituting diphenylamine for carbazole was observed by Tolbert and Branch in the negative ions and the anhydrobases[4] and in the doubly charged positive ions,[5] but the opposite effect was observed in the first ions of VII, VIII, IX and X.[1,3]

The carbazyl radical is apparently a stronger bathochrome than the diphenylamino radical, but it has the lower effective basicity. But the hypsochromic effect of lack of basicity is due to a marked lowering of the degree of double bondedness of the connection of an amino group to the central conjugate system. In the negative ions and the anhydrobases the loss of the proton from the carbazyl radical insures a high degree of double-bondedness of this connection. In the second ions, the neutralization of one of the amino groups insures a high degree of double bondedness of the other amino group to the central conjugate system. Hence only in a singly charged positive ion can λ_x for the diphenylamine derivative be greater than λ_x for the corresponding carbazole derivative. But in the acetylated dyes the loss of basicity is already so great that it can make little difference in the hypsochromic effect whether the dye is a carbazole or a diphenylamine derivative, and hence the normally greater λ_x of the carbazole derivative is re-established even in the first ions.

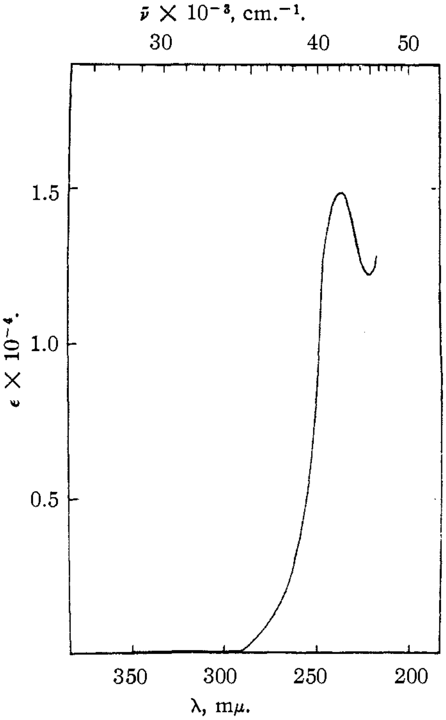


Fig. 7.—Spectrum of N-acetyldiphenylamine in methanol.

The α-Bands.—In a benzenoidal form of a diaminotriphenylmethane dye the phenyl groups are insulated from each other and one would not expect any absorption bands at markedly longer wave lengths than those which would be found in the spectra of the constituent amines or of their ions. Yet small α-bands were observed in the spectra of the color bases of the acetylated dyes derived from diphenylamine. This was quite unexpected, so bands in the region of 350–370 mμ were searched for in the spectrum of N-acetyldiphenylamine, but none were observed. We therefore suspect that the α-bands observed in the spectra of the color bases of I and of II are due to impurities. Since *p*-dimethylaminobenzophenone has a strong band in the neighborhood of 360 mμ, we think that the α-bands are due to traces

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[4] Tolbert and Branch, THIS JOURNAL, **68**, 315 (1946).

[5] Tolbert and Branch, *ibid.*, **69**, 1083 (1947).

of *p*-acetylated derivatives of I and II. In that case the *a*-bands found in the spectra of the ions are also due to these impurities. Correction of the spectrum of I for the presence of the color base does not remove the *a*-band of the ion (see inset to Fig. 1). But this correction would not be valid for the neutralization of an impurity which is a much weaker base than the color base of I. Also, the benzenoidal first ion of the impurity might have a band in this region, and may greatly predominate over the quinoidal ion.

On the other hand the *a*-band of VI should not be attributed to an impurity. No sign of a band in this neighborhood was found in the spectrum of the color base. By analogy the *a*-band found in the spectrum of V should also be attributed to the ion. The *a*-bands of the two acetylated carbazole dyes are moderately strong. Bands in this neighborhood were found in the parent dyes IX and X. It is possible that these bands are x'-bands.[6]

The Ultraviolet Bands.—Acetyldiphenylamine, the color bases and the ions of the acetylated dyes all have strong bands in the region of 240–260mμ. These bands may be compared to the bands in the neighborhood of 300 mμ found in the spectra of malachite green and of other diaminotriphenylmethane dyes[3] and of their color bases. However, in the ordinary diaminotriphenylmethane dyes these ultraviolet bands are much less intense than the x-bands of the dyes, but in the spectra of acetylated dyes the ultraviolet bands and the x-bands are about equally intense. This seems to indicate that the proportion of benzenoidal ion present in the ion of an acetylated dye is greater than in normal diaminotriphenylmethane dyes, for the benzenoidal ion would absorb in this region. The difference between the acetylated and the normal dyes can be exemplified by the comparison of II and its parent dye VIII. For II in methyl alcohol $\epsilon_x = 0.8 \times 10^4$ and $\epsilon_u = 1.9 \times 10^4$; for VIII in the same solvent $\epsilon_x = 7.6 \times 10^4$ and $\epsilon_u = 1.65 \times 10^4$. The spectrum of N-acetyldiphenylamine has a band at 237 mμ with $\epsilon_{max.} = 1.5 \times 10^4$.

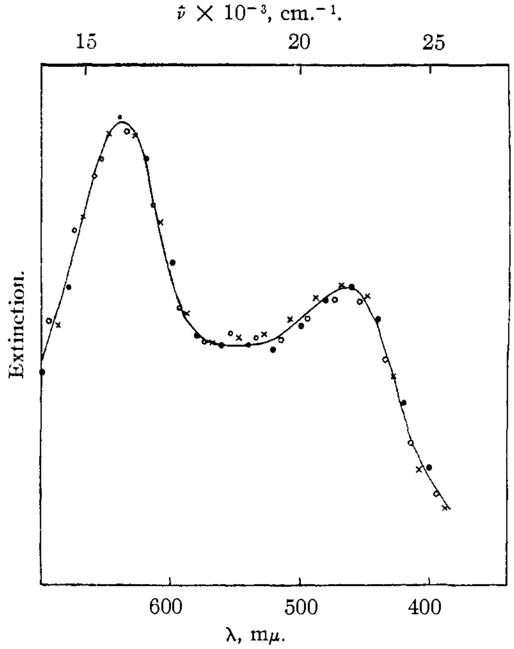

Fig. 8.—Spectra of hydrolysis products of I and III compared with that of viridine green VII in a mixture of acetic acid and sulfuric acid: ●, viridine green; ×, hydrolysis product of I; O, hydrolysis product of III.

Experimental

Preparation of the Acetylated Dyes.—Acetyl derivative I was prepared by heating VII with excess of acetic anhydride until the purple color of III was removed. The same dye was obtained by heating III with excess of acetic anhydride until its color was removed. The carbinol precipitated when the reaction product was added to water.

Acetyl derivative II was prepared by heating VIII with excess of acetic anhydride in the presence of a little zinc chloride for fifteen minutes on a water-bath. The carbinol precipitated when the reaction product was added to water.

Acetyl derivative III was prepared by warming VII with excess of acetic anhydride until the green color had changed to a purple (a few minutes). The carbinol precipitated when water was added to the mixture. It was also prepared by heating a solution of I in a mixture of water and methanol containing some hydrochloric acid. The carbinol was precipitated by dilution with water and neutralization of the acid with sodium hydroxide. The time of hydrolysis was regulated by the color. The beginning of a change from purple to green indicated that I was completely hydrolyzed and some viridine green (VII) was formed. The acetylated dye was separated from VII by taking advantage of the difference in basicity of the two color bases. The mixed color bases were dissolved in methyl alcohol 0.001 *N* with respect to hydrochloric acid. Benzene was added to the solution and then sufficient water to form two layers. The carbinol or methyl ether of III dissolved in the benzene layer, from which it was obtained by evaporation. VIII formed the chloride which is insoluble in benzene.

The acetyl derivatives V and VI were prepared from X and IX respectively by the same procedures used to prepare II from VIII and III from VII.

The carbinols of the acetylated dyes were purified by boiling their solutions in acetone with Nuchar 00 and by repeated solvent precipitation of their benzene solutions with hexane.

Identification.—The acetylated dyes were identified by hydrolysis to the parent dye, which was identified by its spectrum. The hydrolysis was done with aqueous hydrochloric acid and enough ethyl alcohol to keep the dyes in solution. The parent dyes are best identified by their spectra in solutions containing both their first and second ions. An example of this method is shown in Fig. 8. This figure shows the spectra of an authentic sample of VII, a sample prepared by the hydrolysis of III and one prepared by the hydrolysis of I. Each substance was dissolved in the same mixture of acetic and sulfuric acids. The acid concentration was sufficient to convert about half of the first ion to the second ion. The three curves agree with each other within experimental error. This experiment shows that I and III hydrolyze to a product whose first and second ions respectively have the same spectra as the first and second ions of VII, and whose first ion has the same base strength as the first ion of VII.

The Spectra.—The spectra were measured with a Beckman spectrophotometer, Model DU. The concentrations of the dyes were regulated to give extinctions in the

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[6] Lewis and Bigeleisen, THIS JOURNAL, **65**, 2107 (1943).

range of 0.1 to 0.5 with a 1-cm. cell. Band widths were from 2–3 mμ. The concentrations needed varied from 3×10^{-4} to 1×10^{-6} *M*. Beer's law was tested for V and was found to be nearly valid for a ten-fold change of concentration. When mixtures of acetic acid and sulfuric acid were used as the solvent, the blank cell of the spectrophotometer was filled with a mixture of the acids of the same age and composition as that used to dissolve the dye. This was done to compensate for an increase in absorption by the solvent on standing.

Acknowledgment.—We wish to thank Dr. B. M. Tolbert for the preparation of the N-dimethyl-N′-phenyl-*p,p*′-diaminotriphenylmethyl methyl ether and the *p*-dimethylaminophenyl-3-carbazylphenylmethyl methyl ether, and Miss E. R. Carson for the preparation of the 3,3′-dicarbazylphenylmethyl methyl ether.

Summary

N,N′-Diacetyl-N,N′-diphenyl-*p,p*′-diaminotriphenylmethylcarbinol, N-acetyl-N,N′-diphenyl-*p,p*′-diaminotriphenylmethylcarbinol, N-dimethyl-N′-acetyl-N′-phenyl-*p,p*′-diaminotriphenylmethylcarbinol, N-acetyl-3,3′-dicarbazylphenylmethylcarbinol, and (N-dimethyl-*p*-aminophenyl)-(N-acetyl-3-carbazyl)-phenylmethylcarbinol have been prepared and their spectra measured in acetic acid, and in some cases in other solvents.

These spectra are discussed on the basis of hypsochromic effects resulting from the lowering of the effective basicity of the amino groups by acetylation.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Ultraviolet Absorption Spectra of α,β-Unsaturated Ketones Conjugated with an Aromatic Nucleus[1]

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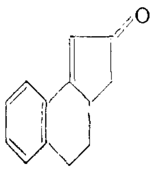
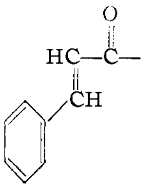
During the past five years we have had occasion to prepare a number of α,β-unsaturated ketones in which the double bond was in conjugation with an aromatic nucleus as well as with the carbonyl group. We are now reporting the ultraviolet absorption spectra of these compounds and of other unsaturated ketones closely related to them. The results confirm the α,β-unsaturated nature of certain of these ketones in which other locations of the double bond were possible, and lead to some interesting conclusions regarding the correlation of absorption spectrum with structure in this class of unsaturated ketones which has not been reported on very extensively before.

Ketones Related to Benzalacetone.—The spectrum of the ketone I[3] was found to be almost identical with that of benzalacetone (II), as can be seen in Fig. 1. This clearly indicates that the ketone possesses the same conjugated system present in benzalacetone as shown in formula I, rather than the alternate structure with the double bond between the five- and six-membered rings, which would be a possibility from the method of preparation. The occurrence of the main maximum at exactly the same wave length (286–287 mμ) for both ketones is coincidental, however, and the result of several compensating factors.[4]



I



II

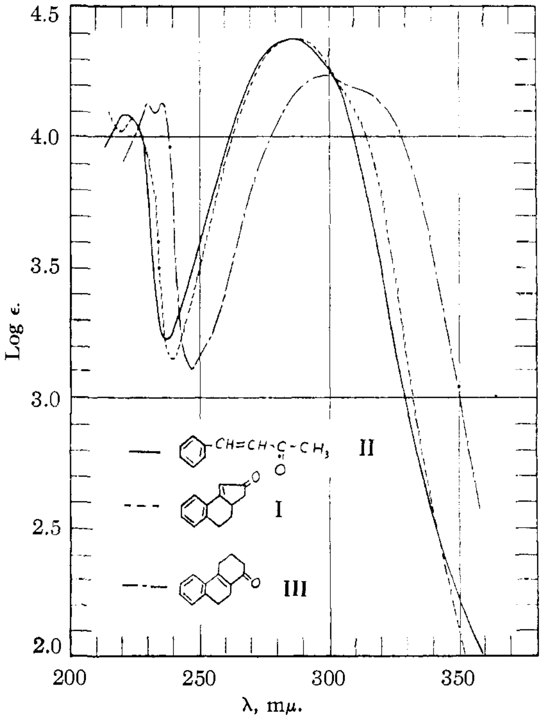


Fig. 1.

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[3] Wilds and J. A. Johnson, THIS JOURNAL, **68**, 86 (1946).

[4] The effect of the additional β-substituent and the exocyclic double bond in I, tending to shift the maximum toward longer wave lengths, is offset by the opposite effect of the five-membered ring.