Paper partition chromatography[7] of an alcoholic solution of the final product revealed no contamination by other flavonoid or other visible or fluorescent pigments. Mixed chromatograms of this morin with an authentic sample of pure morin prepared by vacuum sublimation techniques[4] produced only one pigment zone. The melting point of the final product (289–290° dec.) was not depressed when this material was mixed with authentic morin.

Discussion

Considerable swelling of the resin bed occurs when the alcohol replaces the water on the column. The resin bed expands vertically in columns of 2 in. diameter and thus no danger of breakage is involved.

Morin has a strong affinity for many metal ions. The ash content of samples of morin prepared by the method described in this paper ranged from 0.1 to 0.2 per cent. Further passes through a cation exchange resin will reduce the ash content even more. Morin prepared from the same starting material by non-ion exchange methods had an ash content of 1 per cent. The latter method involved concentration of an aqueous extract, recrystallization from aqueous alcohol solution, precipitation of the potassium salt and recrystallization from 60% acetic acid.

The use of an ion exchange resin for the isolation and purification of morin and other flavonoid compounds appears to be a practical method for both large and small scale laboratory preparations.

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[7] S. H. Wender and T. B. Gage, *Science*, **109**, 287 (1949).

NORMAN, OKLA. RECEIVED JANUARY 27, 1951

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

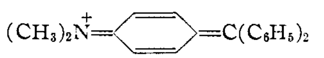
The Absorption Spectra of Some N-Substituted *p*-Aminotriphenylmethyl Ions

BY HAROLD WALBA AND GERALD E. K. BRANCH

This paper shows the spectra of the quinoidal ions of some *p*-aminotriphenylcarbinols. These ions have been chosen so that in each case one can find in the literature the spectrum of an ion differing only in the presence of a *p*-$NH(CH_3)_2^+$ group. The *p*-aminotriphenylcarbinols have also been chosen so that in one case the terminal groups have no resonance interaction with amino nitrogen, but in the other various degrees of resonance interaction between the nitrogen atom and its terminal groups exist. This series has been obtained by using *p*-dimethylaminotriphenylcarbinol as the example in which there is no resonance interaction of the terminal groups, and deriving other carbinols by replacing the dimethylaniline with methyldiphenylamine, diphenylamine, N-acetyldiphenylamine, triphenylamine, carbazole or N-acetylcarbazole. The purposes behind the choice of carbinols were (1) to measure the effect of the *p*-$NH(CH_3)_2^+$ group on the spectrum, (2) how the resonance interactions of unsaturated terminal groups affect the spectrum and (3) how they affect the effect of the *p*-$NH(CH_3)_2^+$ group.

The spectra of the quinoidal ions all have three strong bands, which we have called the first, second and third band, starting from the band with the longest wave length. The third band is very little affected by terminal unsaturated groups or by a *p*-$NH(CH_3)_2^+$ group. On the other two bands a *p*-$NH(CH_3)_2^+$ is normally hypsochromic. The resonance interaction is bathochromic on the second band. The wave length of the first band increases with that of the second band to a maximum and thereafter decreases. The separation of the first and second bands increases with the wave length of the second band to a maximum and thereafter decreases. The hypsochromic effect of the $NH(CH_3)_2^+$ group on the first band decreases as the wave length of the second band increases and eventually becomes bathochromic. The above peculiar relationships are explained on the basis of the following assumptions. (1) The first band is the *x*-band. (2) The second band is the *y*-band. (3) The labile charge is distributed over the molecule by resonance, but is chiefly on the nitrogen atom in the ion of *p*-dimethylaminotriphenylcarbinol. (4) The resonance interaction of unsaturated terminal groups tends to push the labile charge to the other end of the molecule. (5) The $NH(CH_3)_2^+$ group has the opposite effect. (6) Location of labile charge in the $C(C_6H_5)_2$ group is bathochromic on the second band. (7) Unequal distribution of the labile charge between the two ends of the molecule is hypsochromic on the first band. These assumptions have been embodied in empirical equations giving the wave numbers of the first bands and those of the first bands of the *p*-$NH(CH_3)_2^+$ derivatives as functions of the wave numbers of the second bands of the ions of the monoaminotriphenylcarbinols. Values calculated from these equations agree fairly well with those observed with one exception. The exception is $CH_3CO(C_6H_5)^+N{=}C_6H_4{=}C(C_6H_5)C_6H_4NH(CH_3)_2^+$. The suggested tautomerization is the transference of the proton from the $NH(CH_3)_2^+$ to the oxygen atom. This is similar to the *p*-nitroso derivative of dimethylaniline, where the spectrum shows that the proton shifts from the $NH(CH_3)_2^+$ group to the oxygen atom.

Tolbert and Branch[1] have measured the absorption spectra of the second ions of a set of *p,p'*-diaminotriphenylcarbinols, in which one of the amine components was dimethylaniline in each case, and the other was varied, being dimethylaniline, methyldiphenylamine, diphenylamine, triphenylamine or carbazole. In this article we are reporting the absorption spectra of the ions of the corresponding set of *p*-monoaminotriphenylcarbinols, the amine components being dimethylaniline, methyldiphenylamine, diphenylamine, triphenylamine or carbazole. The formulas of the ions are I, II, III, IV and V. Those of the second ions of the corresponding set of diamino compounds are I', II', III', IV' and V'.

I


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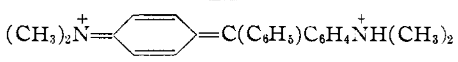
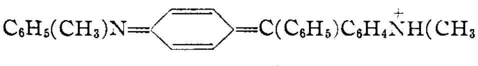


II


II'


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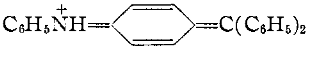

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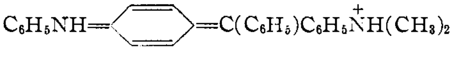

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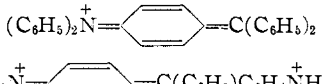

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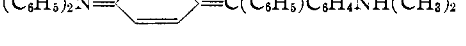

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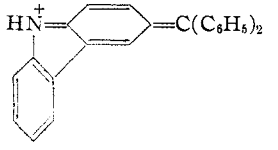
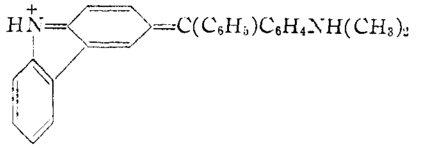
[1] B. M. Tolbert and G. E. K. Branch, THIS JOURNAL, **69**, 1083 (1947).

V 

V′ 

The resonances in the two sets are very similar, and their spectra should parallel each other, that of each member of a set being like that of the corresponding member of the other set, and the variations within a set being like those within the other set.

The Color Bases.—The color bases, either carbinols or methyl ethers, were made either by the action of phenyl-Grignard reagent on the appropriate ketone, or by the action of diphenyldichloromethane on the appropriate aromatic amine in the presence of anhydrous aluminum chloride. Except for II, either the carbinol or methyl ether was obtained as colorless crystals giving a correct analysis. No color base of II was obtained in crystalline form, but its perchlorate crystallized, and gave a correct analysis.

The structures of the compounds were shown by the syntheses, analyses and spectra of the ions. Synthesis and analysis showed each carbinol to be a one to one combination of diphenylhydroxymethyl radical and a radical of the aromatic amine used. The similarity of the spectrum of its ion to the second ion of the corresponding *p*,*p*-diaminotriphenylcarbinol showed that the central carbon atom of the radical was para to the amino group of the aromatic amine.

The Spectra of the Color Bases.—The spectra of the color bases and those of the aromatic amines from which they were made were measured in methanol solution. In this solution the color bases are methyl ethers. These spectra are shown in Figs. 1 and 2. The spectra of the color bases are sufficiently like those of the aromatic amines that one would have no difficulty in spotting which color base is derived from which aromatic amine.

In general the group $C(OCH_3)(C_6H_5)_2$ has a bathochromic effect on the spectrum of the amine as shown in Table I, which gives the spectra data for the color bases of I, II, III and IV and the appropriate amines.

TABLE I

SPECTRAL DATA OF COLOR BASES AND AMINES

Compound	λ_1 in mμ	$\epsilon_1 \times 10^{-4}$	λ_2 in mμ	$\epsilon_2 \times 10^{-4}$
Color base I	305	0.21	262	1.88
Dimethylaniline	298	0.22	252	1.27
	Δλ = 7		Δλ = 10	
Color base II	298	1.57	250	0.93
Methyldiphenylamine	290	1.24	244	0.94
	Δλ = 8		Δλ = 6	
Color base III	293	2.60	...	..
Diphenylamine	285	2.06	...	..
	Δλ = 8			
Color base IV	302	2.98	290–295[a]	..
Triphenylamine	295	2.30	...	..
	Δλ = 7			

[a] This band was observed as a shoulder on the first band.

The spectrum of carbazole has a set of three weak bands, for two of which maxima were observed at 335 and 323 mμ, ε 3 × 10^3 and 2.9 × 10^3; this is followed by a strong band at λ 294 mμ, and then a great absorption region with three maxima at 252, 244 and 233 mμ, the last having the greatest extinction coefficient (ε 4 × 10^4). The spectrum of the color base of V has a set of three weak bands, for two of which maxima were observed at 338 and 325 mμ, ε 2.5 × 10^3 and 3.6 × 10^3; this is followed by three strong bands at 294, 260 and 237 mμ, the final peak rising to ε 5 × 10^4. This is very nearly the same spectrum as that

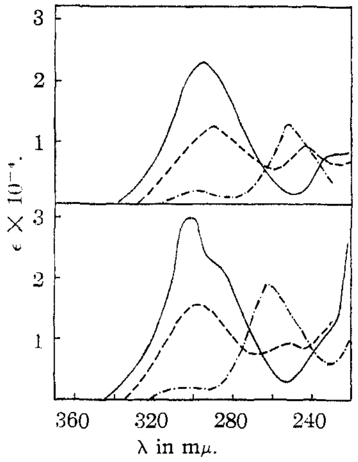


Fig. 1.—Spectra of aromatic amines and of *p*-aminotriphenylmethyl methyl ethers derived from them. The spectra of the amines are in the upper half, those of the color bases in the lower half: —, triphenylamine and color base of IV; - - -, methyldiphenylamine and color base of II; -·-·-, dimethylaniline and color base of I. The solvent was methanol.

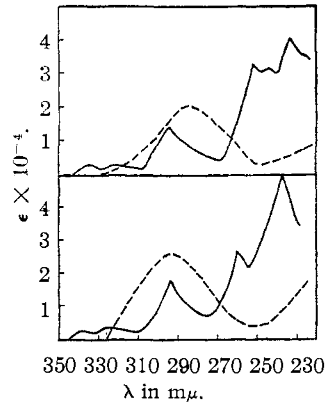


Fig. 2.—Spectra of aromatic amines and of *p*-aminotriphenylmethyl methyl ethers derived from them. The spectra of the amines are in the upper half, those of the color bases in the lower half: —, carbazole and color base of V; - - -, diphenylamine and color base of III. The solvent was methanol.

obtained by Branch, Tolbert and Lowe[2] for the color base of V′. These data were three weak bands at 340, 325 and 312 mμ, and three strong bands at 294, 263 and 237 mμ, the last having ε 5.3 × 10⁴. In the color base of V′ a shoulder was found at 243–247 mμ on the 237 mμ band. The lack of this shoulder in the color base of V is probably experimental error, for it was also found in the spectrum of dicarbazylphenylcarbinol.

Generally a compound with three nearly equivalent groups interacting with a central atom has its principal band at a wave length near to that of the principal band of the compound with only two of the groups, but the compound with only one group has its principal band at a shorter wave length. This rule seems to be broken in the amines and color bases, for λ_1 of the mono-, di- and triphenyl compounds are all nearly the same. The probable reason is that the large second bands, rather than the small first bands, of dimethylaniline and the color base of I correspond to the first bands of the other amines and color bases.

The second bands of methyldiphenylamine and the corresponding color base are probably *y*-bands. Apparently the methyl group can, but the hydrogen atom cannot produce a *y*-band with λ_{max} greater than 220 mμ.

The symmetry of triphenylamine forbids a *y*-band, but the corresponding color base, IV, has a *y*-band which is very near to the *x*-band. In the color base one of the three aryl groups attached to the nitrogen atom differs from the other two.

With the exception of the carbazole compound, the color bases have much stronger absorptions at 220 mμ than the corresponding amines. This absorption is probably due to the $C(OCH_3)(C_6H_5)_2$ radical.

TABLE II

SPECTRA DATA FOR THE IONS

Ion	Solvent	λ_1 in mμ	$\epsilon_1 \times 10^{-4}$	λ_2 in mμ	$\epsilon_2 \times 10^{-4}$	λ_3 in mμ	$\epsilon_3 \times 10^{-4}$
I	$CHCl_3$	476	3.53	350	0.88	...[a]	..[a]
I	CH_3OH	463	1.52	341	.38	263	0.52
I	CH_3COOH	462	3.36	343	.75	263	1.14
I′	CH_3COOH	450	2.95	322	.55	262	0.95
II	$CHCl_3$	495	3.74	355	.92	267	1.06
II	CH_3OH	486	3.80	348	.88	265	1.15
II	CH_3COOH	486	3.78	350	.90	265	1.20
II′	CH_3COOH	475	..[b]	...[b]	..[b]	...[b]	..[b]
III	$CHCl_3$	502	3.65	357	1.07	...[a]	..[a]
III	CH_3OH	491	3.69	352	0.92	268	1.06
III	CH_3COOH	491	3.69	352	.98	268	1.10
III′	CH_3COOH	483	3.26	337	.91	265	1.25
IV	$CHCl_3$	535	3.83	368	1.22	...[a]	..[a]
IV	CH_3OH	522	3.90	360	1.10	265	1.17
IV	CH_3COOH	522	3.85	361	1.12	265	1.11
IV′	CH_3COOH	515	3.32	348	0.99	270	1.19
V	$CHCl_3$	537	2.90	377	1.83	...[a]	..[a]
V	CH_3OH	529	2.84[d]	373	1.61	...[c]	..[c]
V	CH_3COOH	529	3.12	372	1.80	263	2.93
V′	CH_3COOH	529	3.27	355	1.89	264	3.18

[a] Too much CCl_3COOH to obtain spectrum in this region. [b] Substance was not pure enough to make measurements valid. [c] Absorption from color base observed. [d] This value is low owing to incomplete neutralization.

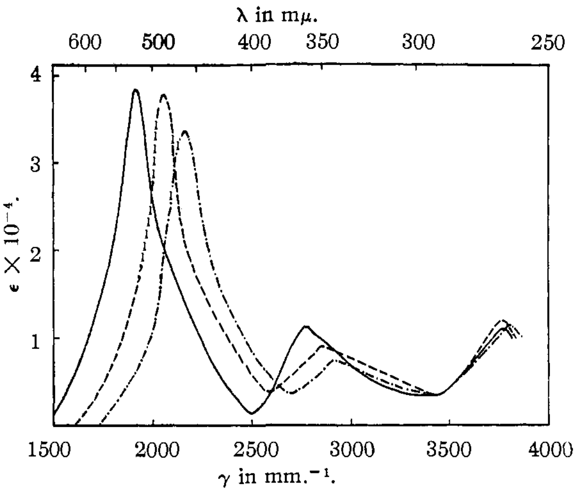


Fig. 3.—Spectra of *p*-aminotriphenylmethyl ions in acetic acid: —, IV; - - -, II; -·-·-, I.

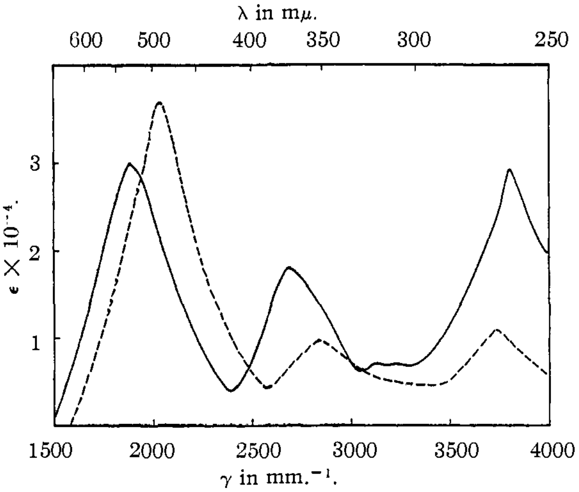


Fig. 4.—Spectra of *p*-aminotriphenylmethyl ions in acetic acid: —, V; - - -, III.

The Spectra of the Ions.—The spectra of the ions were measured in chloroform, methanol and acetic acid solutions. Those of the second ions of the diamino compounds were measured only in acetic acid solution. The spectra of I, II, III, IV and V in acetic acid are shown in Figs. 3 and 4. The spectra data in the three solvents are given in Table II, which also includes the data for the second ions of the diamino compounds.

In all but one case, the extinction coefficients are for complete neutralization of the color base, as shown by no increase of absorption with increase of acidity, and absence of the bands of the color base. The color base of V was not completely neutralized in methanol at concentrations of hydrochloric acid as high as it was thought advisable to use. Consequently the value given for ϵ_1 and ϵ_2 of V in methanol are too low. Its third band was obscured by the spectrum of unneutralized color base.

The acids used were trichloroacetic acid in chloroform, anhydrous hydrochloric acid in methanol, and sulfuric acid in acetic acid. Unfortunately both the dilute and the concentrated solutions of

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[2] E. K. Branch, B. M. Tolbert and W. Lowe, THIS JOURNAL, **67**, 1693 (1945).

trichloroacetic acid in chloroform were so concentrated that the far ultraviolet bands could not be observed. However, the experiment was repeated with II, using more dilute trichloroacetic acid, and it was found that II gives a third band in chloroform very similar to that in other solvents. Presumably this would be true for the other ions.

The spectra of the *p*-aminotriphenylmethyl ions, like those of the second ions of the diamino ions, have three bands in the range 240–260 mμ. The relative intensities of the bands of any member of the monoamino series are very similar to those of the corresponding member of the other series. For instance the relative intensities of the three bands of I and V are, respectively, 1, 0.22 and 0.34, and 1, 0.58 and 0.93. For I′ and V′ the corresponding figures are 1, 0.19 and 0.34, and 1, 0.58, and 0.97. In both series λ_1 and λ_2 increase from the first to the fifth member. This is not true of λ_3. The value of λ_3 is nearly independent of the member and the series. Apparently the two sets of ions are spectroscopically very closely related.

The $NH(CH_3)_2^+$ group is hypsochromic on the first and second bands. However, the hypsochromic effect on the first band decreases from member to member, and has disappeared in the fifth member, so λ_1 for V and V′ are the same.

When λ_1 is plotted against λ_2, the points fall fairly well on a smooth curve, apparently having a maximum near V. The question arises whether the series can be extended to members in which λ_1 decreases with λ_2, and in which the $NH(CH_3)_2^+$ group is bathochromic instead of hypsochromic. Before giving the experimental answer to these questions, we shall attempt a theoretical one.

If one writes the formula of I as $(CH_3)_2NC_6H_4{}^+$-$C(C_6H_5)_2$, the axis of polarizability of the first band would be through the dimethyl-*p*-anilino radical and between the two phenyl radicals. The band would be that of a carbonium ion with two basic groups competing for the charge, the more basic group being the dimethylanilino radical, the less basic one the combined pair of phenyl radicals. The second band is a *y*-band, its axis being perpendicular to the *x*-axis described above. It can be attributed to excitation of the $(C_6H_5)_2C^+$ radical, and may be compared to the principal band of diphenylmethyl ion. Although the polarizability of the dimethylanilino radical does not affect the wave length of this band, it has an indirect hypsochromic action on it by withdrawing a considerable amount of the charge from the $(C_6H_5)_2$-C^+ radical, and λ_2 is considerably smaller than λ of diphenylmethyl ion.

The other compounds are derived by the introduction of unsaturated groups whose main resonance interactions are due to mesomers of the type $C_6H_5{}^-{=}{}^+N(R)C_6H_4C(C_6H_5)_2{}^+$. Mesomers of the type $C_6H_5{}^+{=}N^+(R)C_6H_4C(C_6H_5)_2{}^-$ are less important owing to the unfavorable distribution of the charges. This resonance reduces the basicity of the anilino group, puts more of the charge on the $C(C_6H_5)_2$ radical, and hence is bathochromic on the second band. The $\bar{\nu}_2$ value can be used as a measure of the basicity of the anilino group.

Because of the inequality of basicity of the radical competing for the charge there is a hypsochromic Brooker effect.[3] Since in these ions only the anilino group varies, the Brooker effect depends on the basicity of the anilino group. In I the anilino group is the stronger of the competing bases. Any substitution that reduces the basicity will decrease the Brooker effect, and in consequence, will be bathochromic on the first band. Continuous reduction of the basicity of the anilino group will eventually make it the weaker of the competing bases, and after this point reduction of the basicity of the anilino group will be hypsochromic on the first band. Taking $\bar{\nu}_2$ as a measure of the basicity of the anilino group, the Brooker effect is a factor tending to make $\bar{\nu}_1$ decrease with decrease of $\bar{\nu}_2$ up to a minimum value of $\bar{\nu}_1$, but thereafter increase with decrease of $\bar{\nu}_2$.

The resonance interactions between the nitrogen atoms and the terminal groups in II, III, IV and V are bathochromic. These resonances are the same ones that reduce basicities in the anilino groups, and thereby decrease $\bar{\nu}_2$. Therefore there are two factors that make $\bar{\nu}_1$ decrease as $\bar{\nu}_2$ decreases. One of these, the Brooker effect, is inverted when the anilino group is the weaker of the two bases competing for the charge. Brooker's[3] studies of the hybrid dyes has shown that his effect is negligible for small differences in the basicities of the competing groups, but rapidly increases with the inequality of basicities. Thus were the anilino groups made the weaker of the competing bases, further decrease of its basicity would eventually make the Brooker effect again become the predominant factor, and $\bar{\nu}_1$ would increase, though $\bar{\nu}_2$ would continue to decrease, as the anilino group loses its basicity.

The chief effect of the $NH(CH_3)_2^+$ group on the first band is due to the repulsion between its charge and the other positive charge on the ion. This is equivalent to an increase of the relative basicity of the anilino group, and an increase of the Brooker effect. The group is therefore hypsochromic. However, when the anilino group has been so reduced in basicity that it has become the weaker of the competing bases, increase of the relative basicity of the anilino group would decrease the Brooker effect, and the $NH(CH_3)_2^+$ group should be bathochromic.

Neither of the above inversions were observed in the spectra of the ions I to V and I′ and V′. Apparently the inversions occur at basicities of the anilino group very near to that of the carbazyl radical, for the $\bar{\nu}_1$ values of V and V′ are the same. By extending the series to include *n*-acetyl derivatives one might expect to observe the inversions. Consequently a study was made of the first and second bands of the *n*-acetyl derivatives of III and V, and of the first bands of the acetyl derivatives of III′ and V′.

The color bases of III and V were digested with acetic anhydride, and each digest divided into three parts. The first parts were diluted with acetic acid containing enough sulfuric acid to form the ions of the acetyl compounds, and the spectra were measured.

(3) L. G. S. Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).

The second parts were diluted with acetic acid containing some sulfuric acid and enough water to hydrolyze all the acetic anhydride originally used. The solutions were allowed to stand until constant spectra were obtained. In both cases these spectra were those of the original dyes with no loss of material. Hence the only reactions on digestion were reversible acetylations, presumably N-acetylations.

The experiment on the third part was done only with the digest of III. It was diluted with acetic acid and its spectrum was measured. The λ_1 and λ_2 values were those of III. Hence very little of the acetyl derivative could have been neutralized by acetic acid. The extinctions of this spectrum corresponded to forty per cent. of III having escaped acetylation. When this spectrum is taken from that obtained from the first part, and the result is divided by 0.6, one obtains a corrected spectrum of the acetyl derivative.

The spectrum of the product of acetylation of V showed that it did not need to be corrected for the presence of V. At 600 mμ, V has more than ten times the extinction coefficient of the product of acetylation, and hence V was more than ninety per cent. acetylated. The error produced by ten per cent. of V would not be significant.

The spectra of the first parts are shown in Fig. 5. The spectra data obtained were λ_1 522 mμ, ϵ_1 3.95 $\times$ 10^4, λ_2 386 mμ, ϵ_2 1.94 $\times$ 10^4 for the acetyl derivative of *V*. When not corrected λ_1 506 mμ, ϵ_1 2.6 $\times$ 10^4, λ_2 355 mμ, ϵ_2 7.5 $\times$ 10^3 for the acetyl derivative of III. The latter data become λ_1 515 mμ, ϵ_1 2 $\times$ 10^4, λ_2 358 mμ, ϵ_2 6 $\times$ 10^3, when they are corrected for the forty per cent. of III that escaped acetylation.

The $\bar{\nu}_1$ value of the acetyl derivative of V is greater than that of V, but its $\bar{\nu}_2$ value is less than that of V. Provisionally, it is an example of one of the expected inversions. Put in a plot of $\bar{\nu}_1$ against $\bar{\nu}_2$, it shows that ν_1 decreases to a minimum as $\bar{\nu}_2$ decreases and increases with further decrease of $\bar{\nu}_2$. The minimum is near $\bar{\nu}_1$ of V. The acetyl derivative of III does not show the inversion. Acetylation of III is bathochromic on both first and second bands. The $\bar{\nu}_1$ of the acetyl derivative falls on the above curve. In the series, the acetyl derivative of III lies between III and IV. This position is peculiar in that it implies that the acetylphenylanilino acts as a more basic radical than the diphenylanilino group in these ions.

The spectra of the N acetyl derivatives of III′ and V′ were obtained by Katzenellenbogen and Branch[4] while investigating the spectra of the first ions of some acetylated diaminotriphenylcarbinols. They found that when the acidities of solutions of the N-acetyl derivatives of the color bases of III′ and V′ were increased beyond that necessary to obtain the spectra of the first ions, the spectra changed, but soon became invariant to further increase of acidity. In acetic acid only a small per cent. of sulfuric acid was necessary. They suggested that this phenomenon was due to the formation of second ions, and this is the only simple explanation. The peaks of the first bands of these ions were found at 464 mμ and 530 mμ for the acetyl derivatives of III′ and V′, respectively, in acetic acid. The $NH(CH_3)^+$ group is bathochromic by 8 mμ on the first band of the acetyl derivative of V, which makes it an example of the predicted inversion of the effect of the $NH(CH_3)_2^+$. However, in the acetyl derivative of III′, the $NH(CH_3)_2^+$ group is hypsochromic on the first band by 51 mμ, which is much more than in any of the other cases.

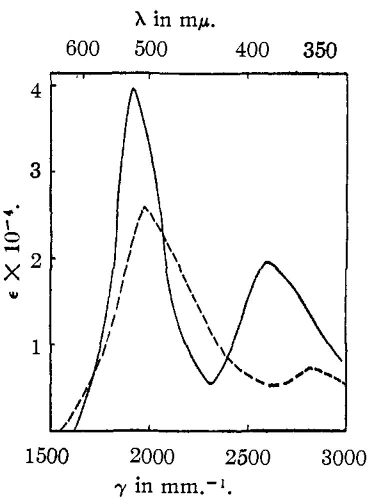

Fig. 5.—Spectra of the acetyl derivatives in acetic acid: —, acetyl derivative of V; - - -, acetyl derivative of III. The spectrum shown for the acetyl derivative has not been corrected for forty per cent. of III present in the solution.

It seems necessary that before deciding that the observed inversions are those theoretically predicted it is necessary to get some evidence as to whether or not these acetyl derivatives belong to the same structural and spectroscopical series as the other ions. To do this we shall express the relationship between $\bar{\nu}_1$ and $\bar{\nu}_2$ and the effect of the $NH(CH_3)_2^+$ by empirical equations. When the $\bar{\nu}_2$ values of acetyl derivatives fit these equations it may be assumed that they belong to one or other of the two series, but a lack of fit indicates that some disturbing factor has been introduced with acetylation. Only the factors mentioned in the previous discussion will be included in the equations, and only the simplest function of $\bar{\nu}_2$ will be used to express the actions of these factors. This over-simplification is not likely to lead to difficulties as the errors so introduced will be taken care of by the adjustability of constants.

In these ions the terminal groups may offer considerable steric hindrance to the coplanarity of the molecule. This steric hindrance is an important factor in the spectra, which was not considered in the discussion. However, it should not perturb the relationship between $\bar{\nu}_1$ and $\bar{\nu}_2$, which depends on the resonance interaction of the terminal groups and not on whether the interaction has been repressed by steric hindrance.

The Brooker effect depends on a difference of basicities and not on which base is the stronger. It is proportional to a higher than first power of the inequality of basicities. The simplest function of

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[4] E. R. Katzenellenbogen and G. E. K. Branch, THIS JOURNAL, **69**, 1978 (1947).

$\bar{\nu}_2$ that it could be is proportionality to the square of $(\bar{\nu}_2 - k_2)$, where k_2 is the $\bar{\nu}_2$ at which there would be no Brooker effect. This point would be that at which the charge is as much on the two phenyl radicals as it is on the anilino group according to the qualitative discussion. It is more probable, that this point would be where the charge is equally distributed between the anilino and $C(C_6H_5)_2$ groups. For our purpose the difference is immaterial.

The simplest way of expressing the other effect of the terminal group is to make its bathochromic effect on $\bar{\nu}_1$ proportional to its effect on $\bar{\nu}_2$, that is to $\bar{\nu}_{2I} - \bar{\nu}_2$, where $\bar{\nu}_{2I}$ is $\bar{\nu}_2$ of I.

Finally another constant would be needed. Were Brooker's treatment of hybrid dyes strictly followed, this constant would be the harmonic mean of $\bar{\nu}_1$ values of malachite green and of the imaginary ion, $C(C_2H_5)_4^+$. The resultant equation is

$$\bar{\nu}_1 = k_1(\bar{\nu}_1 - k_2)^2 - k_3(\bar{\nu}_{2I} - \bar{\nu}_2) + k_4 \qquad (1)$$

In the discussion the difference between the $\bar{\nu}_1$ values of the second ions of the diamino compounds and the monoamino ions was restricted to the effect of the $NH(CH_3)_2^+$ group on the Brooker effect. This simplification gives

$$\bar{\nu}_1' - \bar{\nu}_1 = k_1(\bar{\nu}_2 - k_2 + \Delta k_2)^2 - k_1(\bar{\nu}_2 - k_2)^2 = k_1 \Delta k_2[2(\bar{\nu}_2 - k_2) + \Delta k_2] \qquad (2)$$

Where $\bar{\nu}_1'$ is $\bar{\nu}_1$ of the second ion of a diamino compound, $\bar{\nu}_1$ and $\bar{\nu}_2$ are the values for the corresponding monoamino ion, and Δk_2 arises from the decrease of basicity produced by the $NH(CH_3)_2^+$ group.

For acetic acid solutions the values chosen for the constants are 5×10^{-3} mm. for k_1, 2700 mm.$^{-1}$ for k_2, 24 mm.$^{-1}$ for Δk_2, 2×10^{-1} for k_3 and 1931 mm.$^{-1}$ for k_4. The experimental value of $\bar{\nu}_{2I}$ is 2915 mm.$^{-1}$. Table III shows the λ_1 values calculated from the above equations and constants, and the observed values.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED VALUES OF λ_1 IN ACETIC ACID

	λ_2, mμ	λ_1(obsd.), mμ	λ_1(calcd.), mμ
I	343	462	463
II	350	486	489
III	352	491	496
Acetyl III	358	515	513
IV	361	522	519
V	372	529	530
Acetyl V	386	522	519
I′	...	450	449
II′	...	475	478
III′	...	483	485
Acetyl III′	...	464	505
IV′	...	515	513
V′	...	529	530
Acetyl V′	...	530	527

The equations from which the calculated values in the above table are obtained are based on the consideration of only a few factors that govern the positions of the bands in the spectra. For instance, only a certain type of resonance has been considered as affecting the intrinsic bathochromicities of N-terminal groups and their effects on the basicities of the anilino groups. The agreement between calculated and observed values cannot be very exact, and cannot be even approximately correct for all possible cases. For instance the $(CH_3)_3N^+$ group in $(CH_3)_3N^+N(CH_3)C_6H_4C^+(C_6H_5)_2$ would have a large inductive effect lowering the basicity of the anilino group without a correspondingly large intrinsic bathochromicity, and λ_1 should be markedly less than that calculated from the value of λ_2.

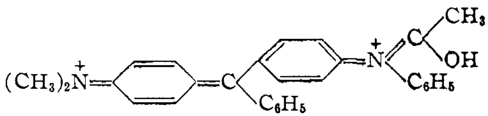
That in three of the four acetyl derivatives the calculated and observed values agree about as well as in the other ions indicates that acetylation need not introduce any greatly perturbing factor. Therefore one may conclude that in the acetyl derivatives of V and V′ we have genuine examples of the inversion of the Brooker effect and of the inversion of the hypsochromic effect of the $NH(CH_3)_2^+$ group. The inspiration to look for an inversion of the Brooker effect in *p*-aminotriphenylmethyl ions came from a paper on a similar inversion in the merocyanines, which was presented by Dr. Brooker at the 115th Meeting of the American Chemical Society.

The position of the acetyl derivative of III in the table is anomalous, in that its anilino group is less basic than that of IV in spite of the acetyl radical. The same anomaly is evident in that acetylation of III increases λ_2 by 6 mμ, but acetylation of V increases λ_2 by 14 mμ. This is what would be expected from a strong steric hindrance to the coplanarity of the acetyl group with the rest of the molecule. The steric hindrance of phenyl groups attached to the same atom and being forced into the same plane is relieved by rotation allowing the *o*-hydrogen atoms to get out of each other's way. But the acetyl group is thicker than the hydrogen atoms, and a greater departure from coplanarity is needed for the acetyl group than for the phenyl group to relieve the steric hindrance. In consequence steric hindrance is a more important factor in the acetyl derivative of III than in IV. As already explained steric hindrance does not change the relationship between λ_1 and λ_2, but changes both. Apparently steric hindrance is greater in the ions of the monoamino compounds than in the first ions of the diamino dyes. In the latter Katzenellenbogen and Branch[4] found the acetylphenylanilino group to be less basic than the diphenylanilino group as judged by Brooker effects. This difference is presumably due to the greater degree of double-bondedness between the nitrogen atom and the triphenylmethyl radical in the monoamino than in the diamino compounds.

The lack of steric hindrance in the acetyl derivative of V is due to the bond between the phenyl groups in the carbazyl radical. This enforces coplanarity between the phenyl radicals, reduces the angle between them, and so allows more room for the acetyl group.

Following Katzenellenbogen and Branch,[4] the discrepancy between the calculated and observed values for λ_1 for the acetyl derivative of III′ can be explained by assuming the acetyl derivative of III′ to be the tautomer VI.

The spectrum of VI should be closely related to that of I′. Both are dimethylaminotriphenyl-



VI

methyl ions with a positively charged nitrogen atom on one of the other phenyl radicals. In VI this group ($N{=}C(OH)C_6H_5^+$) extends the conjugate system. This can be compared to the extension of the conjugate system by the phenyl group in II′, and should be bathochromic. But the effect in II′ should be the greater, for in II′ the terminal phenyl group also decreases the Brooker effect. Hence λ_1 of VI should be between that of I′ (450 mμ) and that of II′ (475 mμ). The observed value of 464 mμ is consonant with structure VI.

In VI, the $N^+{=}C$ grouping extends the conjugate system along the y-axis, and should be bathochromic on the second band, to an even greater extent than it is on the first band. The maximum of the second band was found at 355 mμ, which is 33 mμ greater than λ_2 of I′. The λ_3 values of VI and I′ are 360 and 362 mμ, respectively. The spectrum obtained by the above authors agrees better with formula VI than it does with the normal formula $C_6H_5(COCH_3)N^+{=}C_6H_4{=}C(C_6H_5)$-$C_6H_4N^+H(CH_3)_2$.

This latter ion would have the same steric hindrance as the acetyl derivative of III. This steric hindrance is reduced by the shift of the double bond from the triphenylmethyl radical to the acetyl group as in VI, and this might be the explanation for the formation of VI in the place of the normal acetyl derivative. It is significant that the acetyl derivative of III, which has no tautomer corresponding to VI, was formed in low yield. To escape the steric hindrance the acetyl derivative of III must form the benzenoidal ion ($(C_6H_5(COCH_3)$-$N^+HC_6H_4C(OCOCH_3)(C_6H_5)_2)$). This reaction would reduce the extinction coefficient. These are 2×10^4 and 6×10^3 for the first and second bands, respectively, while they are 3.95×10^4 and 1.94×10^4 for the other acetyl derivative.

Branch, Tolbert and Lowe[2] have shown that in symmetrical p,p'-diaminotriphenylmethyl ions reduction of basicity of the anilino groups decreases $\bar{\nu}_2 - \bar{\nu}_1$. The obvious explanation is that reduction of the basicity of the anilino groups puts more charge on the phenyl radical, and this is bathochromic on the second band and hypsochromic on the first. In the p-monoaminotriphenylmethyl ions, reduction of the basicity of the anilino group can be either bathochromic or hypsochromic on the first band. It may be expected to increase $\bar{\nu}_2 - \bar{\nu}_1$ when the anilino group is strongly basic and decrease it when the anilino group is weakly basic.

From equation 1 it is easy to express the quantity $\Delta\bar{\nu}$, that is $\bar{\nu}_2 - \bar{\nu}_1$, as a function of $\bar{\nu}_2$ by the equation

$$\Delta\bar{\nu} = \bar{\nu}_2 - k_1(\bar{\nu}_2 - k_2)^2 + k_3(\bar{\nu}_{2\mathrm{I}} - \bar{\nu}_2) - k_4 \quad (3)$$

According to this equation $\Delta\bar{\nu}$ increases to a maximum as the basicity of the anilino group is decreased and decreases with further reduction of the basicity of the group. With the values for the constant already given, the maximum for $\Delta\bar{\nu}$ is reached when $\bar{\nu}_2 = 2780$ mm.$^{-1}$. The calculated and observed values of $\Delta\bar{\nu}$ are shown in Table IV.

TABLE IV

SEPARATION OF FIRST AND SECOND BANDS IN ACETIC ACID

Ion	$\bar{\nu}_2$ in mm.$^{-1}$	$\Delta\bar{\nu}$(obsd.) in mm.$^{-1}$	$\Delta\bar{\nu}$(calcd.) in mm.$^{-1}$
I	2915	750	753
II	2857	799	814
III	2841	804	825
Acetyl III	2793	851	843
IV	2770	854	844
V	2688	798	802
Acetyl V	2591	685	665

The spectra of I to V in methanol are almost identical with those in acetic acid. The only marked difference is that the extinction coefficients of the bands of I are much smaller in methanol than they are in acetic acid. In chloroform both the first and second bands are at longer wave lengths than they are in acetic acid or methanol. This bathochromic effect of chloroform is shown in Table V as $\Delta\bar{\nu}_1$ and $\Delta\bar{\nu}_2$, where the subscripts refer to the first and second bands, and $\Delta\nu$ is ν in acetic acid less ν in chloroform.

Equation 1 should hold in chloroform as well as in acetic acid, provided changes are made in the values of the parameters. There seems to be no reason to change k_1 and k_3. The value of $\nu_{2\mathrm{I}}$ must be changed to 2857 mm.$^{-1}$, the experimental value for chloroform, and changes have to be made in k_2 and k_4. For these two constants the values 2660 mm.$^{-1}$ for k_2 and 1900 mm.$^{-1}$ for k_4 have been chosen, and the calculated and observed values of λ_1 in chloroform have been compared in Table V.

TABLE V

EFFECTS OF CHLOROFORM

Ion	$\Delta\bar{\nu}_1$ in mm.$^{-1}$	$\Delta\bar{\nu}_2$ in mm.$^{-1}$	λ_1(obs.) in mμ	λ_1(calcd.) in mμ
I	64	58	476	478
II	39	40	495	496
III	45	40	502	503
IV	47	53	535	530
V	28	36	537	538

Experimental

The spectra were measured with a Beckman spectrophotometer, using 1 cm. cells and solutions about 10^{-5} M. These conditions do not allow observation of bands with molecular extinctions much below 1000.

p-Dimethylaminotriphenylcarbinol.—p-Dimethylaminobenzophenone (0.063 mole) in 100 ml. of dry benzene was added to 0.129 mole of phenylmagnesium bromide in 60 ml. of ether. After refluxing for half an hour, and standing for 12 hours, a saturated solution of ammonium chloride in water was added slowly until the solution changed from red to a pale orange. The organic layer was steam distilled off. The residual tar was extracted with ether. The ethereal extract was decolorized with charcoal and filtered. Three volumes of petroleum ether were added to the filtrate, and the crude carbinol precipitated on standing. The carbinol was repeatedly crystallized from ether–petroleum ether mixtures. Large colorless needles were obtained, m.p. 88–89°. Clarke and Patch,[5] who used the same method found 92–93° for the melting point. Recrystallization from acetone–petroleum mixtures did not change the melting point.

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.1; H, 6.98; N, 4.62. Found: C, 82.8; H, 7.10; N, 4.56.

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[5] L. Clarke and R. H. Patch, THIS JOURNAL, **34**, 917 (1912).

_p_-Methylphenylaminotriphenylmethyl Perchlorate.—Two methods were used in this preparation as far as the carbinol. Thereafter the same method was used in both cases. In the first method the previously described procedure was used, except that _p_-methylphenylaminobenzophenone was substituted for _p_-dimethylaminobenzophenone. The resulting carbinol did not crystallize. The oily product was dissolved in ether and added to a 1 _M_ aqueous solution of perchloric acid. On standing a brick-red precipitate was formed. This precipitate was dissolved in acetone converted to the carbinol, which came out of the acetone solution as an oil by addition of water. This was again transformed to the perchlorate, as described above. The perchlorate came out as brick-red needles. The perchlorate was recrystallized from chloroform-ether mixtures, and acetone–petroleum ether mixtures.

Anal. Calcd. for $C_{26}H_{22}O_4NCl$: C, 69.9; H, 4.95; N, 3.16; Cl, 7.92. Found: C, 69.8; H, 5.03; N, 3.22; Cl, 7.97.

This substance was also prepared by a different method. Since the same method was used in the last three preparations, we shall refer to it later as method 2. The general principle of this method is to condense α,β-dichlorodiphenylmethane with an aromatic amine by a procedure that keeps an excess of the aromatic amine during the reaction.

A solution of α,α-dichlorodiphenylmethane dissolved in carbon disulfide (0.1 mole in 100 ml.) was slowly added to a boiling solution of excess of methyldiphenylamine (0.2 mole) in 100 ml. of carbon disulfide and 0.2 mole of aluminum chloride. Constant stirring was maintained during the addition, which took about an hour and a half. Boiling and stirring were continued for about two hours after the addition. While warm, the reaction mixture was poured slowly onto cracked ice and perchloric acid. The salt was taken up in chloroform and precipitated with ether. The perchlorate was changed to the carbinol from an acetone solution as in the first method. Purification failed to crystallize the carbinol.

The carbinol was again changed to the perchlorate and recrystallized as in the first method. The perchlorate prepared by this method gave the same spectrum as that prepared by the previous one.

_n_-Phenylaminotriphenylmethyl Methyl Ether.—The perchlorate of this color base was prepared by method 2, using diphenylamine instead of methyldiphenylamine. The crystals were blue and the solution red. The perchlorate was dissolved in hot methanol, and a dilute solution of sodium methylate in methanol was added until the solution was colorless. The methanol was evaporated off, and the residue was extracted with ether. After removal of the ether, the residual solid was recrystallized several times with methanol. The final product was in the form of colorless prisms melting at 127–128°. This compound had been previously prepared by Baeyer and Villiger,[6] who obtained a melting point of 127°.

_n_-Diphenylaminotriphenylcarbinol.—This compound was prepared by method 2, except that longer times and room temperature were used, and the chloride instead of the perchlorate was made. The chloride was changed to the carbinol, and the chloride reformed from the carbinol in carbon tetrachloride with dry hydrochloric acid gas. After two such transformations, the carbinol was taken up in ether. The ether solution was dried and treated with charcoal. After filtration the ether was evaporated off, and the resulting residue repeatedly crystallized from acetone–water mixtures. Colorless prisms, m.p. 141–142°, were obtained.

Anal. Calcd. for $C_{31}H_{25}NO$: C, 87.1; H, 5.89; N, 3.26. Found: C, 86.7; H, 5.87; N, 3.15.

3-Carbazyldiphenylcarbinol.—This color base was made by method 2, using about a threefold excess of carbazole. The perchlorate was obtained by addition of the reaction product to 6 _M_ perchloric acid. The salt was extracted with chloroform, from which it was precipitated with ether. This was dissolved in acetone, and the carbinol precipitated with water. This carbinol is so weak a base that no alkali is needed to obtain it from its salts. The carbinol was dissolved in acetone and treated with charcoal. The solution was filtered and petroleum ether was added. The resulting precipitate was crystallized several times from benzene, and finally from an acetone–petroleum ether mixture. The final product was obtained as colorless prisms, m.p. 217°.

Anal. Calcd. for $C_{25}H_{14}ON$: C, 86.1; H, 5.48; N, 4.01. Found: C, 86.1; H, 5.72; N, 3.81.

In general the salts of these compounds are soluble in acetone, methanol and chloroform, and insoluble in ether, carbon tetrachloride, benzene, petroleum ether and water. The color bases are soluble in acetone, chloroform, carbon tetrachloride, benzene and ether, somewhat less soluble in methanol, and insoluble in petroleum ether and water. The carbinol of the carbazyl compound is anomalous in that it is difficultly soluble in benzene and chloroform. Its solubility in carbon tetrachloride was not tried; but it was freely soluble in acetone, and fairly soluble in ether.

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[6] A. Baeyer and V. Villiger, _Ber._, **37**, 2837 (1904).

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

The Vapor Pressure of Water over Phosphoric Acids

BY B. J. FONTANA

The vapor pressure of water over phosphoric acids has been measured over a range of compositions representing from 86.5% orthophosphoric acid to almost pure pyrophosphoric acid. Temperature dependence of the vapor pressure measured in the region of about 35 to 280° can be expressed in the usual form of log $P = -A/T + B$. The variation in heat of vaporization calculated from the vapor pressures appears to agree qualitatively with analytical and phase studies of the composition of phosphoric acids.

Phosphoric acid is used as a polymerization catalyst at compositions in the region of, and exceeding, that corresponding to 100% orthophosphoric acid.[1] Process control requires appropriate data on the variation of water partial pressure as a function of temperature and phosphoric acid composition.

The old data of Balareff[2] on the "formation temperatures" of pyro- and metaphosphoric acids should correspond to the water partial pressures over the pure ortho- and pyrophosphoric acids, respectively. However, the values thus obtained are completely erroneous.

The only data in the literature in the region of interest are those correlated by Striplin.[3] This author found the available data, consisting of (1) a nomograph by Perry and Duus[4] covering the range of 75 to 95% orthophosphoric acid at temperatures between 25 and 35°, (2) data by Kablukov and Zagvozdkin[5] up to a maximum composition of 87.1% orthophosphoric acid and

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[1] G. E. Langlois and J. E. Walkey, presented before the Third World Petroleum Congress, The Hague, May 28–June 6, 1951.

[2] D. Balareff, _Z. anorg. Chem._, **67**, 234 (1910).

[3] M. Striplin, Jr., _Ind. Eng. Chem._, **33**, 910 (1941).

[4] J. H. Perry and H. C. Duus, _Chem. Met. Eng._, **41**, 74 (1934).

[5] I. A. Kablukov and K. I. Zagvozdkin, _Z. anorg. Chem._, **224**, 315 (1935).