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

Spectrophotometric Study of the Reactions of *p*-Aminotriphenylcarbinols with Concentrated Sulfuric Acid

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Many of the *p*-aminotriphenylmethyl ions combine with protons forming carbonium ions on solution in 96% sulfuric acid. Excessive resonance or strongly electronegative groups were found to suppress this reaction. The N-phenyl derivatives of *p*-aminotriphenylmethyl ion sulfonated at room temperature. The spectra of the carbonium ions are compared with those of the quinoidal ions, diphenylmethyl ion and triphenylmethyl ion. The relationships between these spectra are discussed. The effects of sulfonation and solution in sulfuric acid on the spectra of quinoidal ions are discussed.

This paper describes the absorption bands with molal extinction coefficients greater than a hundred from 270 to 750 mμ in the spectra of five *p*-aminotriphenylmethyl ions dissolved in sulfuric acid of density 1.84 g./ml. The solutions were made by dissolving the substance in acetic acid and mixing this solution with the sulfuric acid. The amount of acetic acid was two volumes of acetic in a hundred volumes of solution. In the rest of this paper we shall call this mixture concentrated sulfuric acid.

The aminotriphenylmethyl ions used were *p*-dimethylaminotriphenylmethyl ion (I), *p*-methylphenylaminotriphenylmethyl ion (II), *p*-phenylaminotriphenylmethyl ion (III), *p*-diphenylaminotriphenylmethyl ion (IV) and 3-carbazyldiphenylmethyl ion (V). We shall use the roman numerals given above instead of the names to indicate these compounds. The spectra of all of these compounds in less acidic solvents had been measured previously.[1]

The spectra of diphenylcarbinol, triphenylcarbinol and crystal violet in concentrated sulfuric acid also were measured. The spectrum obtained for triphenylcarbinol differed a little from a previous measurement.[2] Except for quantitative data, any statement in this paper is equally true for the previous and present measurements.

The spectra of some *p*,*p*'-diaminotriphenylcarbinols in concentrated sulfuric acid had been previously measured.[3] In these diamino ions one of the amino groups was similar to an amino group of one of the monoamino compounds discussed in this paper. The other amino group was the dimethylamino group, or a repetition of the first amino group. Comparisons between the results obtained with the mono- and diamino ions will be made.

A *p*-aminotriphenylcarbinol can form three types of ions, which we shall call benzenoidal, quinoidal and carbonium. The benzenoidal ions have four separate groups attached to the central carbon atom. Hence the phenyl groups are insulated from each other and the spectrum is a combination of bands that can be attributed to these parts. Normally, there is no intense band within 100 mμ of the visible. If all the amino groups are neutralized there may be no intense band within 150 mμ of the visible.

The quinoidal ion has three groups attached to the central carbon atom, but only three groups attached to at least one of the nitrogen atoms. The spectra of the quinoidal ions have two intense bands in the visible or near visible and another in the far ultraviolet. The band at the longest wave length has been called the x-band and that next to it the y-band. Usually the x-band is two to five times as intense as the y-band. A separation of 100 to 200 mμ between the bands is normal.

The carbonium ion has three separate groups attached to the central carbon atom and four separate groups to each of the nitrogen atoms. The spectrum is like that of triphenylmethyl ion. There are two intense bands in the visible or near visible. These bands are near each other, the separation being about 60 mμ.

Quinoidal and carbonium ions of *p*-aminotriphenylcarbinols can be recognized by their spectra. This is possible in mixtures of the two ions provided one of them is not greatly in excess. Benzenoidal ions are recognized by the lack of bands in the spectrum. Consequently the presence of a benzenoidal ion is shown by the spectrum only when the ions are predominantly benzenoidal.

The bands observed in freshly prepared solutions in concentrated sulfuric acid are given in Table I. The table includes data for two diaminotriphenylcarbinols in concentrated sulfuric acid. The substances are given as carbinols, actually many were methyl ethers. The trace of methanol introduced in this way can have no appreciable effect.

Carbinols with No Terminal N-Aryl Groups.—In an aminotriphenylmethyl ion the amino group is connected to the central carbon atom by a phenyl group. It may have other aryl groups attached to it. These extra groups we shall call terminal. The compounds without such terminal groups mentioned in Table I are diphenylcarbinol, triphenylcarbinol, I, malachite green and crystal violet. The spectra of none of them showed any evidence of quinoidal ions.

The greater the positive charge on the carbonium ion the greater is the tendency for bisulfate ion to combine at the central carbon atom to form a benzenoidal ion. The spectrum of crystal violet showed no bands and hence the carbonium ion, which has four positive charges, must combine almost completely with bisulfate ion to form a benzenoidal ion.

To what extent a similar reaction occurs with the other carbonium ions is not directly shown by the spectra. However the reaction does not occur to a great extent in any of the other substances dealt with in this paper. We know this, because they include carbonium ions with one, two and three

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[1] H. Walba and G. Branch, THIS JOURNAL, **73**, 3341 (1951).

[2] W. R. Orndorff, R. C. Gibbs, S. A. McNulty and C. V. Shapiro, *ibid.*, **49**, 1545 (1927).

[3] G. Branch and B. Tolbert, *ibid.*, **71**, 781 (1949).

TABLE I

SPECTRAL DATA FROM 275 TO 700 Mμ IN CONCENTRATED SULFURIC ACID

Formula of carbinol	Bands[a]	Type of ion[b]
$(C_6H_5)_2CHOH$	442 and 53; 300 and 3	C
$(C_6H_5)_3COH$	428 and 38; 409 and 38; 288 and 1	C
$[p\text{-}(CH_3)_2NC_6H_4](C_6H_5)_2COH$	446 and 33; 385 and 28; 299 and 2	C
$[p\text{-}(CH_3)_2NC_6H_4]_2(C_6H_5)COH$	434 and 32; 388 and 27; 288 and 2	C
$[p\text{-}(CH_3)_2NC_6H_4]_3COH$	No bands	B
$[p\text{-}(CH_3)(C_6H_5)NC_6H_4](C_6H_5)_2COH$	446 and 35; 396 and 29; 283 and 2	C
$(p\text{-}C_6H_5NHC_6H_4)(C_6H_5)_2COH$	446 and 35; 392 and 29; 288 and 3	C
$[p\text{-}(C_6H_5)_2NC_6H_4](C_6H_5)_2COH$	560 and 50; 395 and 14; 280 and 11	Q
(3-Carbazyl)-$(C_6H_5)_2COH$	517 and 50; 395 and 20; 355 and 13	Q
$[p\text{-}(CH_3)_2NC_6H_4][p\text{-}C_6H_5NHC_6H_4](C_6H_5)COH$	490–470; 440 and 20; 410–390; 350–330	C and Q

[a] Bands are given as λ_{max} in mμ and $\epsilon \times 10^{-3}$; shoulders as range in mμ. [b] Q = quinoidal, B = benzenoidal, C = carbonium.

charges, but the total absorption in the region 375 to 475 mμ is much the same for all of them.

The spectra from 375 to 475 mμ of diphenylcarbinol, triphenylcarbinol, I and malachite green are shown in Fig. 1.

In the parts of the spectra not shown the molal extinction coefficients (ε) rapidly go down on the long wave length side and are negligible by 500 mμ and remain so to 750 mμ, which is as far as measurements were made. On the short wave length side ε values go to zero, rise to a small band, return to zero and rise again at 250 to 260 mμ. This latter phase continues to 230 mμ, which is as far into the ultraviolet as measurements were made.

Inspection of Fig. 1 shows (1) that in the range 375 to 475 mμ there is only one band for diphenylmethyl ions, but there are two for all the derivatives of triphenylmethyl ion; (2) that in triphenylmethyl ion itself the third phenyl group is hypsochromic; (3) that the introduction of the first *p*-dimethylaminium ion group, $(CH_3)_2NH^+$, is bathochromic on the first band, but hypsochromic on the second; (4) that a second introduction of this group has the reverse effect, being hypsochromic on the first band, but slightly bathochromic on the second. In the above we have called the band at the longer wave length the first band and the other band the second.

The quinoidal and carbonium ions of monoaminotriphenylcarbinols, diphenylmethyl ion and triphenylmethyl ion all have the group $(C_6H_5)_2C^+$. The phenyl groups have strong resonance interactions with the central carbon atom in $(C_6H_5)_2C^+$. Where such resonance occurs the interactions between the groups increase on excitation by light, and an absorption band in the visible or near to it is found in the spectrum. Hence all the above mentioned ions should have a band attributable to the chromophore, $(C_6H_5)_2C^+$. In the spectrum of diphenylmethyl ion this band is obviously the band at 442 mμ.

In the language of Lewis and Calvin[4] an absorption band is associated with an axis of polarizability. For a band due to the chromophore, $(C_6H_5)_2C^+$, the axis would be normal to the bond of the third group. This group is therefore not directly concerned in the absorption of light.

The quinoidal ions have two strong bands in the region 340 to 540 mμ. Walba and Branch attributed that at the shorter wave length (y-band) to the chromophore, $(C_6H_5)_2C^+$. They found that the frequencies of these bands varied with the nature of the third group. They attributed the effect of a group normal to the axis to its influence on the amount of positive charge in the chromophore, assuming that the greater this charge the smaller the frequency of the band. Owing to the strong resonance interaction of a *p*-aminophenyl group with a positively charged carbon atom, the charge on the chromophore of a quinoidal ion is less

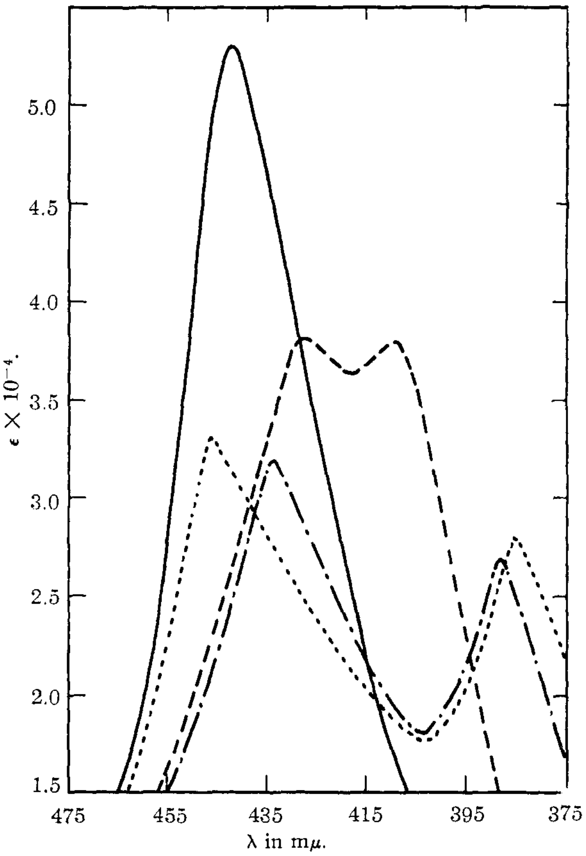

Fig. 1.—Principal bands in spectra of diphenylcarbinol, triphenylcarbinol, I and malachite green in concentrated sulfuric acid: —, diphenylcarbinol; ----, triphenylcarbinol; ...., I; -·-·., malachite green; 1-cm. cells, 10^{-5} *M* solutions, *T* is 20 ±2°.

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(4) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

than that of the chromophore of diphenylmethyl ion. Hence the frequency of the y-band of a quinoidal ion is greater than that of the band of diphenylmethyl ion.

This theory receives support from the observation that the frequencies of the y-bands of the quinoidal ions increase with the basicities of their color bases. The tendency of a base to combine with the central carbon atom of a quinoidal ion depends largely on the positive charge on this atom. This charge also determines the charge on the chromophore. Hence the frequencies of the y-bands should increase with the basicities of the color bases. The relationship is not quantitative, for there are other factors, notably steric hindrance.

The relationship between the basicities of the color bases and the frequencies of the y-bands of the quinoidal ions is shown in Table II. The basicities are given as common logarithms of the equilibrium constants of the reactions of the type

$$\text{color base} + \text{HCl} \rightleftarrows \text{quinoidal ion}$$

These measurements were made in methanol, so the color bases were methyl ethers.[5]

TABLE II

BASICITIES OF COLOR BASES AND FREQUENCIES OF y-BANDS OF QUINOIDAL IONS

Ion	$\bar{\nu}_y$ in mm.$^{-1}$	log K
I	2915	3.85
II	2857	2.79
III	2841	2.71
IV	2770	0.72
V	2688	−0.36

The addition of a proton to the amino group of a quinoidal ion destroys its ability to acquire positive electricity from the chromophore. Further, the proton tends to repel positive charge from the third group to the chromophore. Consequently the frequency of the band due to the $(C_6H_5)_2C^+$ group is much smaller in the carbonium ion than in the quinoidal ion.

In triphenylmethyl ion the third group attached to the central carbon atom of the chromophore is the phenyl group. By virtue of its resonance interaction this group acquires charge from the chromophore. Hence the band due to this chromophore should have a frequency greater than that of the band of diphenylmethyl ion, where the third group is a hydrogen atom. Similarly the frequency of this band should be greater than that of the corresponding band of a carbonium ion of a *p*-aminotriphenylcarbinol. On the other hand the frequency of the band of triphenylmethyl ion should be smaller than that of a quinoidal ion, where the resonance interaction of the phenyl group is enhanced by the basicity of an amino group. Both intense bands of triphenylmethyl ion fulfill these requirements.

Another axis of polarizability is that which passes through the third group and between the phenyl groups of the $(C_6H_5)_2C^+$ group. The frequency of the band associated with this axis decreases with the interaction of the third group with the rest of the molecule. Since a *p*-amino group enhances this interaction and a *p*-aminium ion group diminishes it, the bands associated with this axis should have smaller frequencies in quinoidal ions and larger frequencies in carbonium ions than in triphenylmethyl ion.

Thus the frequency of one of the bands of a carbonium ion of a *p*-aminotriphenylcarbinol is less than that of the corresponding band of the triphenylmethyl ion and that of the other is greater. This enables us to assign the first band of the carbonium ion to an axis normal to the aminated phenyl group and the second band to an axis passing through one of the phenyl groups.

If triphenylmethyl ion had a flat structure with three equivalent phenyl groups, the two bands would have the same frequency. That two bands are obtained shows that at least in one form the three phenyl groups are not equivalent. This arises from the steric hindrance that would result from a flat structure with three equivalent phenyl groups.[6] Lewis and co-workers also assumed two stereoisomers, one in which one of the phenyl groups is thrust out of the way, in the other the phenyl groups are all rotated so as to overlap and form a symmetrical structure. For our argument it is necessary to assume only the unsymmetrical isomer.

Owing to their proximity, the bands of triphenylmethyl ion are closer together than corresponds to the difference of their energies of excitation. This exaggerates the bathochromic and hypsochromic effects of the $(CH_3)_2NH^+$ group on the two bands. However, both effects are real, for though the total absorptions by triphenylmethyl ion and the carbonium ion of I are approximately equal the molal extinction coefficients for the former ion are much less than those for the latter at the peaks of the two bands of the latter ion.

Since there are two positively charged para groups in the carbonium ion of malachite green, one of them must have a hypsochromic effect on the band associated with an axis normal to one of the aminated phenyl groups. Hence this band has a higher frequency than the first band of the carbonium ion of I.

On the other band both $(CH_3)_2NH^+$ groups are hypsochromic. Consequently the frequency is greater than that of the corresponding band of triphenylmethyl ion.

The above theory does not predict whether the frequency of the second band of the carbonium ion of malachite green should be greater or smaller (as found) than the second band of the carbonium ion of I. If we add the gratuitous assumption that the axis passes through the aminated phenyl group in I and between the two aminated phenyl group in malachite green, the band for malachite green would be expected to have the smaller frequency. This assumes that the effects of the groups between which the axis passes should be multiplied by $\sin^2 30$. However, the problem is complicated by the probability that the bands are due to fusions of bands for different axes and even of different isomers.

Carbinols with Terminal N-Phenyl Groups.—Since a terminal N-phenyl group forms part of the

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(5) H. Walba and G. Branch, THIS JOURNAL, **75**, 2149 (1953).

(6) G. N. Lewis, T. T. Magel and D. Lipkin, *ibid.*, **64**, 1774 (1942).

conjugate system in a quinoidal ion, but is insulated from the rest of the molecule in a carbonium ion, it favors the quinoidal ion over the carbonium ion. However the quinoidal ions II and III are almost completely converted to the corresponding carbonium ions by concentrated sulfuric acid. The resonance in the quinoidal ion of V is greater than it is in the quinoidal ion of either II or III. In concentrated sulfuric acid V exists almost completely as the quinoidal ion. In theory, IV should also be chiefly the quinoidal ion in concentrated sulfuric acid. This could not be verified, because IV was sulfonated before the spectrum could be measured.

A terminal N-phenyl group does not affect the frequency of the first band, but it is bathochromic on the second band. This is shown graphically in Fig. 2, which depicts the spectra of II and III and that of I for comparison.

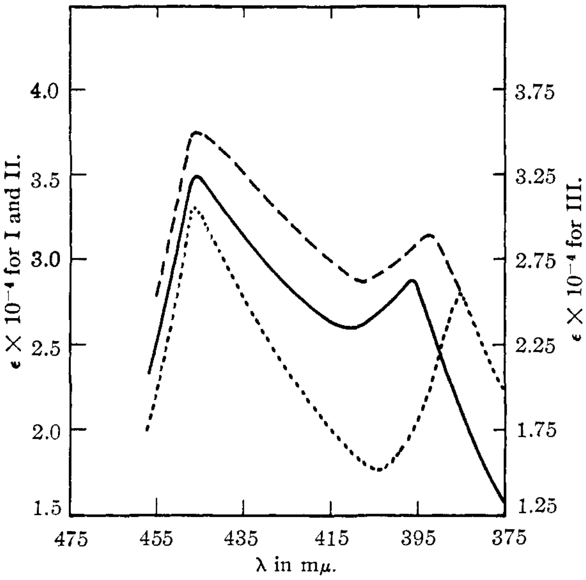

Fig. 2.—Effect of terminal N-phenyl group on spectra of carbonium ions of p-aminotriphenylcarbinols: —, II: ---, III; ....., I; 1-cm. cells, 10^{-5} M solutions, T is 20 ± 2°.

One does not expect any appreciable effect of a terminal N-phenyl group on the frequency of the bands of a carbonium ion, for the terminal group is insulated from the rest of the molecule by a nitrogen atom with four single bonds. However leaks of bathochromic effects of similarly insulated phenyl groups on both x- and y-bands of doubly charged quinoidal ions of p,p'-diaminotriphenylcarbinols have been observed.[7]

The effect of a terminal N-phenyl group on the frequency of the first band of the carbonium ion of a monoaminotriphenylcarbinol is indirect. Further the aminated phenyl group is not activated in the excitation of this band. Consequently the terminal group should have very little effect on the frequency of this band. On the other hand the aminated phenyl group is activated in the excitation of the second band, just as the corresponding group is activated in the excitation of both x- and y-bands of a doubly charged quinoidal ion of a diaminotriphenylcarbinol. Hence the insulated phenyl group should have an effect on the second band of the carbonium ion of a monoaminotriphenylcarbinol similar to its bathochromic effects on the x- and y-bands of the doubly charged quinoidal ion of a diaminotriphenylcarbinol.

One of the aminated phenyl groups of the carbonium ion of a p,p'-diaminotriphenylcarbinol is in the chromophore of the first band. Consequently a terminal N-phenyl group can have a bathochromic effect on the first band of these ions. For instance, $\lambda_{\text{max.}}$ of the first band of the carbonium ion of N-dimethyl-N'-phenyl-p,p'-diaminotriphenylcarbinol is 440 mμ, but that of the carbonium ion of malachite green is 434 mμ (see Table I).

Sulfonation.—The spectra of the carbonium ions of malachite green and of I did not change on standing in concentrated sulfuric acid for two or three weeks. After standing in the concentrated acid and diluting with acetic acid the spectra agreed exactly with those obtained by direct solution in acetic acid containing a little sulfuric acid.

With all of the p,p'-diamino- and p-aminotriphenylcarbinols having one or more terminal N-phenyl groups standing in concentrated sulfuric acid resulted in a reaction. The reactions were observed by the change of the spectrum in concentrated sulfuric acid, or by diluting with acetic acid and comparing the spectrum so obtained with the spectrum of a solution made by dissolving in acetic acid containing the same amount of sulfuric acid.

In all cases the final spectrum was that of a quinoidal ion. Where, as in III, the original spectrum was that of a carbonium ion the change in the spectrum was very striking. This change of the spectrum with time is shown graphically in Fig. 3.

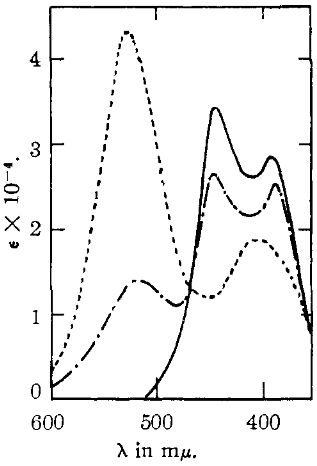

Fig. 3.—Effect of time on the spectrum of III in concentrated sulfuric acid: —, original spectrum; ---., intermediate spectrum; ....., final spectrum; 1-cm. cells, 10^{-5} M solutions, T is 20 ± 2°.

The course of the sulfonation of III was also measured from the molal extinction coefficients at 525 mμ, where the maximum change occurs.

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[7] B. Tolbert and G. Branch, THIS JOURNAL, **69**, 1083 (1947).

The reaction was first order with respect to the solute. The data are shown in Table III. Presumably the reaction is also first order with the other compounds.

TABLE III

VARIATION OF THE MOLAL EXTINCTION COEFFICIENT AT 525 Mμ OF III IN CONCENTRATED SULFURIC ACID, T IS 20 ± 2°

Time, days	$\epsilon \times 10^{-4}$ at 525 mμ	k, days^{-1}
0	0	—
1	1.39	0.34
4	3.49	.32
6	4.30	.36
10	4.88	..
12	4.88	..

The spectral data obtained on standing with sulfuric acid for III, IV and V are shown in Table IV. This table also shows the data when the solutions were diluted after sufficient time to complete the reaction and when the solutions were made in diluted sulfuric acid without any contact with concentrated sulfuric acid.

TABLE IV

SPECTRAL DATA FOR III, IV AND V FROM 350 TO 560 Mμ

Substance	Time, days	Dilution	Bands[a]		
III	0	None	446 and 35;	342 and 29	
III	1	None	519 and 14;	447 and 27;	390 and 26
III	4	None	525 and 35;	450 and 18;	390 and 20
III	6	None	525 and 43;	450 and 14;	405 and 19
III	10	None	525 and 49;	408 and 19	
III	12	None	525 and 49;	408 and 19	
III	12	2-fold	528 and 49;	387 and 12	
III	12	50-fold	514 and 42;	364 and 11	
III	0	50-fold	491 and 37;	352 and 9	
IV	0	None	560 and 50;	395 and 14	
IV	10	None	560 and 50;	395 and 14	
IV	10	2-fold	550 and 44;	374 and 12	
IV	10	5-fold	542 and 40;	368 and 12	
IV	10	50-fold	540 and 40;	365 and 10	
IV	0	50-fold	522 and 39;	361 and 11	
IV	0	5-fold	523 and 40;	360 and 11	
IV	0	2-fold	524 and 41;	361 and 13	
V	0	None	517 and 49;	395 and 20	
V	2	None	505 and 53;	401 and 21	
V	6	None	504 and 58;	403 and 22	
V	8	None	503 and 59;	403 and 22	
V	9	None	503 and 59;	403 and 22	
V	9	2-fold	515 and 52;	395 and 20	
V	9	50-fold	525 and 41;	383 and 18	
V	0	50-fold	529 and 31;	372 and 18	

[a] Bands are given as λ_{max} in mμ and $\epsilon \times 10^{-3}$.

In these experiments IV and V did not show the change from a carbonium ion spectrum to a quinoidal ion spectrum. These compounds are not carbonium ions in concentrated sulfuric acid.

The spectrum obtained with IV as soon as possible after making the solution did not change on standing, but on dilution the spectrum differed from that obtained without contact with concentrated sulfuric acid. Further this latter spectrum changed but little with change in the concentration of the sulfuric acid from 2 to 50%. After contact with concentrated sulfuric acid the spectrum changed considerably when diluted from 50 to 2%. One must conclude that the spectrum obtained a short time after solution in the concentrated acid is that of a sulfonated quinoidal ion. This means that the half time for the sulfonation must be less than five minutes. The half times for III and V are approximately two days and one day, respectively.

Spectra of Sulfonated Quinoidal Ions.—In all cases sulfonation was found to be bathochromic on the y-band of a quinoidal ion. Sulfonation introduces a strongly electronegative group on a terminal N-phenyl group. This tends to increase the charge on the $(C_6H_5)_2C^+$ group, and consequently is bathochromic.

The terminal group has been chosen for the location of the sulfonation, because sulfonation does not occur in the absence of such a group, and because there are more locations for the complementary positive charge when a negative charge is induced on an ortho or para position of the terminal group than when a negative charge is induced anywhere else in the quinoidal ion.

As a solvent sulfuric acid was found to be bathochromic on the y-bands of all the sulfonated ions. This suggests that the protons or other positive poles of the strong acid act on the oxygen atoms of the sulfonic acid or sulfone group and so transmit positive charge to the chromophore of the y-band. It must also be assumed that this action does not produce different molecular species whose absorption bands are resolved, for as the concentration of sulfuric acid is increased one does not observe difference bands changing in their relative intensities, but a shift of the band. Examples of a change in the proportions of two molecular species producing a shift of one band instead of a change in the relative intensities of two bands are known.

On the x-band, sulfonation is bathochromic with III and IV, but hypsochromic with V. As a solvent sulfuric acid is bathochromic on the x-band of the sulfonated quinoidal ion of IV, at first bathochromic, but at higher concentrations hypsochromic, on the x-band of the sulfonated quinoidal ion of III, but hypsochromic at all concentrations on the x-band of the sulfonated quinoidal ion of V.

The charge in a quinoidal ion is concentrated about the amino group (the most basic part of the molecule). This produces a hypsochromic Brooker effect.[8] A change that reduces the basicity of the amino group is consequently bathochromic. But when the basicity is sufficiently reduced the Brooker effect is inverted and further reduction of the basicity becomes hypsochromic. The contradictions in the effects of sulfonation and sulfuric acid on the x-bands are chiefly due to this inversion of the Brooker effect.

From the above it follows that λ_{max} of the x-band tends to increase with λ_{max} of the y-band to a maximum and thereafter decrease. Since there are other factors governing λ_{max} values for x- and y-bands the relationship cannot be exact, more especially where changes of solvent are involved. Both the relationship and the deviations are illustrated in Fig. 4.

In Fig. 4 the points for the quinoidal ions of I,

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

II, III, IV, V, the N-acetyl derivatives of III and V and the sulfonated products of III, IV and V in acetic acid, chloroform, concentrated sulfuric acid and a 50% by volume solution of sulfuric acid in acetic acid are shown in a plot of λ_x against λ_y. A parabola has been drawn through the points for acetic acid solutions, neglecting that for sulfonated IV. These points fall fairly well on the parabola.

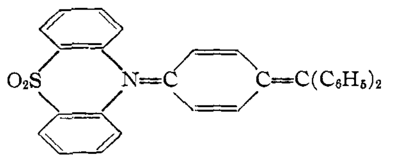
A simple solvent variation is shown by two cases (IV and V) in chloroform solution. The points for these compounds are well above the parabola. The spectra of I, II, III, have also been measured in chloroform. The points for these measurements and those for IV and V in chloroform fall fairly well on a parabola, but the parabola is narrower and taller than that shown in the Fig. 4. This is an example of a solvent effect that is not due to a change in the charge on the $(C_6H_5)_2C^+$ group.

Sulfuric acid should have a similar solvent effect in addition to that due to an increase in the charge on the $(C_6H_5)_2C^+$ group, and the points for sulfuric acid should vary from the parabola suitable to acetic acid solutions. But the points in sulfuric acid do not fall on a parabola of their own. For instance the points for V and its sulfonated derivative in sulfuric acid are not very distant from the parabola shown in Fig. 4, but that for the sulfonated derivative of III (λ_x 425 mμ, λ_y 408 mμ) is far to the right of the parabola. That is, sulfuric acid has a specific bathochromic effect on the y-band of this ion.

The other notable anomalies are the points for the sulfonated ion of IV. These are shown as squares in the figure. They all fall well above the parabola. That is, sulfonation of IV has a specific bathochromic effect on the x-band.

Discussion of the above two anomalies must be speculative in so far as structures must be assumed for the products of sulfonation. If III is sulfonated at the ortho position of the terminal group on the side opposite to the proton on the nitrogen atom, the sulfonic acid group is not far from one of the phenyl groups of the chromophore for the y-band. A sulfuric acid molecule solvating the sulfonic acid group would be in close contact with this chromophore and would have an exalted solvent effect on the y-band. This effect would not exist in the sulfonated ion of V, for whether the sulfonation were at the ortho or para position of the terminal group, the sulfonic acid group would be distant from the chromophore.

The extra bathochromic effect on the x-band on sulfonating IV can be explained by assuming the formation of a cyclic sulfone of high polarizability. The formula of this sulfone would be



This assumption suggests a reason for the anomalously fast sulfonation of IV. When a sulfuric acid molecule is caught by its sulfur atom between the two terminal groups of IV, its escape is difficult. Consequently a proton escapes, with consequent sulfonation, more often than would be the case were the sulfuric acid caught by only one phenyl group. The assumption here is that when the sulfur atom of sulfuric acid is bonded or partly bonded to a benzene ring the benzene resonance is restored more often by the loss of the sulfuric acid than of a proton attached to the ring. Only the latter event results in sulfonation.

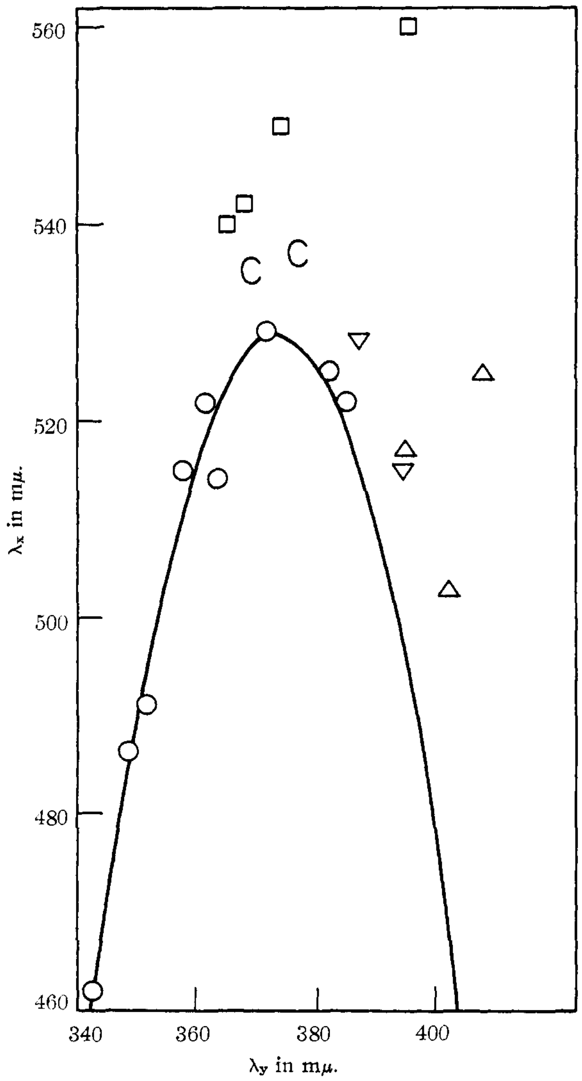


Fig. 4.—Plot of λ_x against λ_y of quinoidal ions in various solvents: ○, in acetic acid; △, in concentrated sulfuric acid; ▽, in fifty–fifty mixture of sulfuric acid and acetic acid; C, in chloroform; □, sulfonated IV in various mixtures of sulfuric acid–acetic acid. The curve is a parabola drawn through the points in acetic acid.

Experimental

The preparation and purification of the *p*-aminotriphenylmethyl compounds used are described in reference 1. The diphenylcarbinol, triphenylcarbinol and crystal violet were high grade commercial products further purified by recrystallization.

The spectra were measured with a Beckman spectrophotometer, using 1-cm. cells and 10^{-5} *M* solutions.

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