

TABLE III

R	°C.	B.p.	Mm.	d_{20}^4	n_D^{20}	Nitrogen, %		M.p., °C.	Picrate Nitrogen, %	
						Calcd.	Found		Calcd.	Found
CH ₃	133-134	0.5	1.0464	1.5847	6.22	6.00	210	12.38	12.17	
C ₂ H ₅	141-142	.5	1.0382	1.5797	5.85	5.93	174	12.01	12.08	
C ₃ H ₇	142-143	.5	1.0276	1.5715	5.53	5.26	163	11.61	11.42	
C ₄ H ₉	151-152	.5	1.0104	1.5643	5.24	5.17	172	11.28	11.01	
<i>n</i> -C ₅ N ₁₁	164-165	.5	1.0029	1.5594	4.98	4.95	132	10.98	11.11	

the ketones are given in Table II. *o*-Tolyl-1-diphenylethyl ketimine was refluxed for 48 hours, but no ketone was obtained.

Amines.—A weighed sample of ketimine was added to methanol containing prerduced Adams catalyst and reduced at room temperature and atmospheric pressure. When no more hydrogen was taken up, the total volume required was read from the buret, and the milliliters of hydrogen absorbed per minute per gram of sample was calculated. For the methyl through amyl compounds, in order of in-

creasing molecular weight, these values are 0.222, 0.119, 0.234, 0.065 and 0.066, respectively. Relative rates of reduction, based on these figures are 3.43, 1.84, 3.61, 1.00 and 1.03. The *o*-tolyl- and isoamylketimines absorbed no hydrogen under these conditions even after repurification, cleaning the system used, and preparing fresh catalyst.

The amines were separated from the reduction mixture by filtration of the catalyst and distillation. Physical data derivatives and analyses are given in Table III.

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

The Reactions of Some *p*-Aminotriphenylmethyl Ions with Methanol and Methylate Ion

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It had been observed that the molecular extinction coefficients of the bands of N-dimethyl-*p*-aminotriphenylmethyl ion are markedly less in methanol than in acetic acid.¹ In this paper this phenomenon has been attributed to the formation of a colorless benzenoid ion, (CH₃)₂NHC₆H₄C(C₆H₅)₂OCH₃, in a reversible reaction between the quinoid ion and methanol. That the phenomenon has not been observed with the related ions N-methyl-N-phenyl-*p*-aminotriphenylmethyl ion, N-phenyl-*p*-aminotriphenylmethyl ion and N-diphenyl-*p*-aminotriphenylmethyl ion has been attributed to the stabilization of the quinoid ions by the resonance interaction of the extra phenyl groups in these conjugate systems.

Confirmation of this theory has been found in the restoration of the color by reducing the activity of the methanol with perchloric acid.

An estimate has been made of the molecular extinction coefficient of the pure quinoid ion. This has been used to calculate the quinoid fraction of the ion under different conditions.

The reactions of methylate ion with the four aminotriphenylmethyl ions already mentioned have been given as the equilibrium constants of the reverse reactions, the neutralizations of the methyl ethers to form the quinoid ions. These base strengths were found to decrease with the degree of phenylation, the dimethyl compound being the strongest and the diphenyl one the weakest base. This order of base strengths is the same as that of the parent aromatic amines (dimethylaniline, diphenylamine and triphenylamine). The decrease

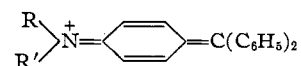
in basicity with the number of phenyl groups of the color base is much less than that of the parent amine. These relationships have been taken as showing that the resonance interactions of the extra phenyl groups in the quinoid ions are less than those of the same groups in the aromatic amines, but that they are strong enough to almost entirely repress the benzenoid ions.

The base strength of 3-carbazyldiphenylmethyl methyl ether to form a quinoid ion was also measured. It proved to be the weakest of the bases.

Reaction with Methanol

Table I shows the molecular extinction coefficients at the peaks of the bands in the spectra of four closely related ions. The measurements are given for solutions in methanol, acetic acid and chloroform. For each ion the positions of the bands in acetic acid and methanol are the same. In chloroform the positions of the bands are shifted a little toward the red. The data are taken from a previous paper by the authors.¹

The related ions all have the general formula



For I, R = CH₃, R' = CH₃; for II, R = CH₃, R' = C₆H₅; for III, R = H, R' = C₆H₅; for IV, R = C₆H₅, R' = C₆H₅. In general we shall use these Roman numerals instead of the names. It is simplest to name them from the formulas of another phase in the resonance. For instance I may be called dimethyl-*p*-aminotriphenylmethyl ion.

Table I shows that the molecular extinction coef-

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

TABLE I

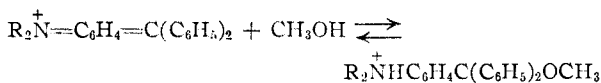
MOLECULAR EXTINCTION COEFFICIENTS OF THE THREE BANDS OF FOUR CLOSELY RELATED MONOAMINOTRIPHENYLMETHYL IONS IN METHANOL, ACETIC ACID AND CHLOROFORM

In the formulas $R = (C_6H_5)_2C$ and it is para to the amino group. In chloroform a standard quantity of trichloroacetic acid was used to neutralize the base. This amount absorbs too strongly in the far ultraviolet to permit measurement of the third band. With II the minimum amount of the acid was used and the third band was measured, its position was within 2 $m\mu$ of that in the other solvents.

Dye No.	Formula	Solvent	Mol. ext. coef. of		
			1st band $\times 10^{-4}$	2nd band $\times 10^{-4}$	3rd band $\times 10^{-4}$
I	$RC_6H_4N(CH_3)_2^+$	CH_3OH	1.52	0.35	0.52
I	$RC_6H_4N(CH_3)_2^+$	CH_3COOH	3.36	.75	1.11
I	$RC_6H_4N(CH_3)_2^+$	$CHCl_3$	3.53	.88	..
II	$RC_6H_4NCH_3C_6H_5^+$	CH_3OH	3.80	.86	1.15
II	$RC_6H_4NCH_3C_6H_5^+$	CH_3COOH	3.78	.90	1.20
II	$RC_6H_4NCH_3C_6H_5^+$	$CHCl_3$	3.74	.92	1.06
III	$RC_6H_4NHC_6H_5^+$	CH_3OH	3.69	.92	1.06
III	$RC_6H_4NHC_6H_5^+$	CH_3COOH	3.69	.93	1.10
III	$RC_6H_4NHC_6H_5^+$	$CHCl_3$	3.65	1.07	..
IV	$RC_6H_4N(C_6H_5)_2^+$	CH_3OH	3.90	1.10	1.17
IV	$RC_6H_4N(C_6H_5)_2^+$	CH_3COOH	3.85	1.12	1.11
IV	$RC_6H_4N(C_6H_5)_2^+$	$CHCl_3$	3.83	1.22	..

coefficients of II, III and IV are the same in methanol and acetic acid, but the bands of I are about twice as intense in acetic acid as in methanol. The relative intensities are not affected by the solvent. Thus the ratios of intensities of the first and third bands are 3.0 in acetic acid and 2.9 in methanol.

The most natural explanation of this anomaly is that the colored ion (I) is partially changed to a colorless ion in methanol, but that the corresponding reactions of I in acetic acid and of II, III and IV in either solvent occur to a much smaller extent. The simplest reaction is the formation of a benzenoid ion by the reaction



This assumption requires reasons for (1) the failure to observe any spectrum for the benzenoid ion, (2) the failure to observe the reaction with II, III and IV and (3) the greater degree of benzoidation with methanol than with acetic acid. Some confirmation may be obtained by showing that (1) the reaction is not instantaneous, (2) the equilibrium is affected by temperature, and (3) the color is regenerated by reducing the activity of the methanol.

The theory that the bleaching of triphenylmethane dyes is due to solvation goes back to the dark ages. The most striking example of an investigation on this reaction is one on the hydration of crystal violet² in which it was shown that the first ion is not measurably hydrated, the second ion somewhat more, and the third ion practically completely, a result readily explained by molecular resonance.

In the benzenoid ion the phenyl groups and the amino group are all insulated from each other. This should prevent the observation of any bands under the conditions of the experiments. These condi-

tions were a Beckman spectrophotometer with 1 cm. cells, λ 600-240 $m\mu$, and 10^{-5} M solutions. Dimethylanilinium ion shows no bands under these conditions.

In a quinoid ion an extra phenyl group has a resonance interaction with the rest of the molecule, it being part of a conjugate system that includes the nitrogen atom, the central carbon atom and all the phenyl groups. In a benzenoid ion an extra phenyl group has no resonance interaction with any other part of the molecule. In consequence the extra phenyl groups of II, III and IV stabilize the quinoid ion with respect to the benzenoid one.

The greater benzoidation of I in methanol than in acetic acid is not unique. If the second ion of $N-N'$ -tetramethyl- p,p' -diaminotriphenylcarbinol (base of malachite green) is obtained from the green first ion by adding excess acid to a solution of the first ion in methanol a yellow solution is obtained. This solution becomes colorless on standing, but the process can be reversed by partial neutralization or by dilution, when after standing the green color is regenerated and the experiment can be repeated. If this experiment is done in acetic acid solution the yellow color is intense (ϵ 30000) and permanent. If the fading of the color in methanol is attributed to the formation of a benzenoid ion, this ion would be a methyl ether. A corresponding reaction in acetic acid would yield an acetic ester. In this ester the resonance interaction of the carbonyl group with the oxygen atom tends to charge the latter positively, and the electrostatic interaction of this charge with the double positive charge of the ion gives a high energy to the benzenoid ion, and represses its formation. The same effect is present in the acetate benzenoid ion of I, except that it is less marked, as might be expected from there being only one unit of charge on this ion.

A similar difference between the fading of the color of the higher ions of crystal violet in acetic acid and in water has been noted for crystal violet.³

The following experiment showed that the benzoidation is not instantaneous, and that its degree is affected by temperature.

A strongly colored solution of I in acetic acid was made. Equal portions of this solution were added to 10 cc. of acetic acid, and 10 cc. of methanol containing enough acid to prevent the formation of any color base. When first made, the two solutions were approximately the same color, but on standing the solution in methanol faded until it was about half as intense as that in acetic acid. The intensity of the solution in methanol increased on heating in a water-bath, but faded when cooled.

In Table II the molecular extinction coefficients of I at 463 $m\mu$ and 263 $m\mu$ (the locations of the peaks of the first and third bands) are shown under varying conditions of solvent and acid. The object of using both bands is to use the ratio of their extinctions to indicate the presence of any extraneous species, e.g., color base or second ion. The main purpose of the experiments was to observe the effect of an acid ($HClO_4$) that greatly reduces the activity of methanol, but has little tendency to add in the way necessary to form a benzenoid ion.

(2) E. Q. Adams and L. Rosenstein, *THIS JOURNAL*, **36**, 1452 (1914).

(3) J. B. Conant and T. H. Werner, *ibid.*, **52**, 4436 (1930).

TABLE II
VARIATION IN MOLECULAR EXTINCTION COEFFICIENTS OF I
WITH SOLVENT AND ACID

Solvent	Acid	Normality of acid	ϵ_1 $\times 10^{-4}$	ϵ_2 $\times 10^{-4}$	ϵ_1/ϵ_2	Frac- tion of quinoidal ion
CHCl ₃	CCl ₃ CO ₂ H	3.00	3.53	0.96
CHCl ₃	CCl ₃ CO ₂ H	1.50	3.6299
CH ₃ CO ₂ H	CH ₃ CO ₂ H	..	3.36	1.11	3.03	.91
CH ₃ CO ₂ H	HClO ₄	1.5	3.46	1.16	2.98	.94
CH ₃ OH	HClO ₄	7.2×10^{-5}	0.78	1.15	0.68	..
CH ₃ OH	HClO ₄	3.6×10^{-3}	1.52	0.52	2.96	.41
CH ₃ OH	HClO ₄	1.8×10^{-1}	1.59	.57	2.79	.43
CH ₃ OH	HClO ₄	2.43	2.73	.91	3.00	.74
CH ₃ OH	HClO ₄	2.82	3.11	1.07	2.91	.80
CH ₃ OH	HClO ₄	4.50	3.36	1.14	2.95	.91
CH ₃ OH	HCl	6.58×10^{-5}	0.72	1.23	0.59	..
CH ₃ OH	HCl	3.3×10^{-3}	1.52	0.60	2.53	.41
CH ₃ OH	HCl	3.3×10^{-1}	1.01	.36	2.81	.27
CH ₃ OH	HCl	1.04	0.75	.28	2.68	.20

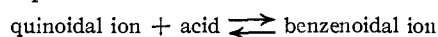
The data also include the effects on the color of HCl in methanol, of reduction of the activity of the solvent by perchloric acid in acetic acid solution, and of varying concentrations of trichloroacetic acid in chloroform solution. The much smaller tendency of the perchlorate ion to add acidic centers than of the chloride ion has long been known.⁴

The experiments with perchloric acid clearly show that reduction of the activity of the methanol decreases the proportion of the colorless ion. Hence this ion is the product of a reaction of the colored ion with methanol. Since a benzenoidal ion might itself add to a quinoidal ion it is theoretically possible that several quinoidal ions to one methanol are involved in the reaction. In view of the great dilution of the solutions ($10^{-5} M$) this seems unlikely, and the formula $(\text{CH}_3)_2\text{NHC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5)_2\text{-OCH}_3$ is probably correct for the benzenoidal ion.

The effect of excess of hydrochloric acid was the reverse of that of perchloric acid. Hydrochloric acid reduces the activity of methanol. Hence the reduction of the color indicates the addition of hydrochloric acid to form a benzenoidal ion, probably $(\text{CH}_3)_2\text{NHC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5)_2\text{Cl}$.

Since perchloric acid increased the color in acetic acid to a greater extent than would be expected from experimental error, one must assume that in acetic acid some benzenoidal ion was present.

In chloroform solution trichloroacetic acid was used to neutralize the color base. The extinction coefficient was found to be smaller with 3.0 *N* acid than with 1.5 *N* acid. This indicates the formation of the benzenoidal ion, $(\text{CH}_3)_2\text{NHC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5)_2\text{-OCOCCl}_3$. Assuming constancy for the concentration equilibrium constant for the reaction



one can obtain the equation

$$\epsilon_0 = R\epsilon_1/(\epsilon_1 - R\epsilon_2) = 36600$$

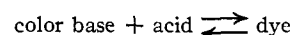
where *R* is the ratio of the concentrations of the acid in the two experiments and ϵ_0 , ϵ_1 and ϵ_2 are, respectively, the molecular extinction coefficients of the pure quinoidal ion and of the equilibrium mixture of ions in the two experiments. Since this method is equivalent to an extrapolation from 36200 to 36600 no appreciable error could have been in-

troduced by the neglect of the variation of activity coefficients in the two experiments.

Reference to Table I shows that ϵ_1 values of II, III and IV in chloroform are between 1 and 2% lower than they are in methanol and acetic acid, so that an estimate of 37000 for the molecular extinction coefficients of the pure quinoidal ion of I in methanol and acetic acid should be fairly accurate. We have used this estimate and the value 36600 in chloroform to calculate the fractions of the ions that are quinoidal and have given these values in the last column of Table II.

Reactions with Methylate Ion

The effective base strengths of the methyl ethers are given by the concentration equilibrium constants of the reaction



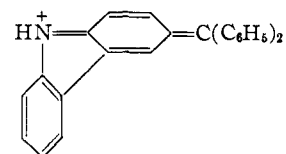
in methanol. It makes no difference whether the color base is added as the carbinol or the methyl ether, as it would be all changed to the latter by the time equilibrium is achieved.

These equilibria constants were obtained by measuring the apparent molecular extinction coefficients in partially and completely neutralized methanol solutions, using chiefly hydrochloric acid. Then $K = \epsilon/A(\epsilon_0 - \epsilon)$, where ϵ and ϵ_0 are extinction coefficients for incomplete and complete neutralization, and *A* is the acid concentration. Since these measurements were done at dye concentrations of the order of $10^{-5} M$, *A* is practically the concentration of acid added. Where the acid is also very dilute the concentration of dye must be taken from the concentration of acid added to obtain *A*.

These equilibrium constants are not thermodynamic equilibrium constants, since they were not corrected for variation of activity coefficients. However, for individual dyes they were constant over the two- to tenfold variations made in the concentration of dye and acid. The reason for such constancy is that the acid and dye are both salts and the ratio of their activity coefficients is less variable than the activity coefficient of either. The constancy of the values of *K* with change in concentrations of dye indicates that neither color base nor dye is appreciably polymerized in $10^{-5} M$ solutions.

The measurements were not made with a thermostat, but in a room of fairly constant temperature. This temperature was $28 \pm 0.5^\circ$. An accuracy that would make 5% errors rare was sought.

The dyes measured were the four mentioned in the previous section and 3-carbazylidiphenylmethyl ion (V), whose formula in the quinoidal phase is



An inconveniently high concentration of hydrochloric acid is needed for the complete neutralization of the color base of this dye in methanol, and ϵ_0 in methanol was not measured. The molecular extinction coefficient in acetic acid with enough sul-

(4) A. Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

TABLE III
 EQUILIBRIUM CONSTANTS FOR FORMATION OF QUINOIDAL IONS FROM COLOR BASES IN METHANOL AT 28°

Color base	Color base added in mole/liter	Acid added in mole/liter	$\epsilon_0 \times 10^{-4}$	$\epsilon \times 10^{-4}$	α	K_q
I	2.64×10^{-5}	$6.58 \times 10^{-3}(\text{HCl})$	1.52	0.72	0.41	6.9×10^3
I	2.64×10^{-5}	$7.28 \times 10^{-3}(\text{HClO}_4)$	1.52	0.78	0.41	7.3×10^3
						Av. 7.1×10^3
II	2×10^{-5}	$2.67 \times 10^{-3}(\text{HCl})$	3.80	2.38	1	6.3×10^2
II	1.25×10^{-5}	$1.34 \times 10^{-3}(\text{HCl})$	3.80	1.71	1	6.1×10^2
II	3.0×10^{-5}	$1.07 \times 10^{-3}(\text{HCl})$	3.80	1.49	1	6.1×10^2
II	5.0×10^{-5}	$2.5 \times 10^{-3}(\text{HCl})$	3.80	2.32	1	6.3×10^2
II	2.5×10^{-5}	$1.25 \times 10^{-3}(\text{HCl})$	3.80	1.64	1	6.1×10^2
						Av. 6.2×10^2
III	1.42×10^{-5}	$6.74 \times 10^{-3}(\text{HCl})$	3.69	2.89	1	5.3×10^2
III	9.5×10^{-6}	$6.49 \times 10^{-3}(\text{HCl})$	3.69	2.53	1	4.9×10^2
III	2.79×10^{-5}	$5.45 \times 10^{-4}(\text{HCl})$	3.69	0.79	1	5.1×10^2
III	2.84×10^{-5}	$1.39 \times 10^{-3}(\text{HCl})$	3.69	1.52	1	5.1×10^2
						Av. 5.1×10^2
IV	4.6×10^{-6}	$5.2 \times 10^{-4}(\text{HCl})$	3.90	2.86	1	5.3
IV	4.6×10^{-6}	$3.12 \times 10^{-4}(\text{HCl})$	3.90	2.38	1	5.0
IV	2.3×10^{-6}	$1.56 \times 10^{-4}(\text{HCl})$	3.90	1.78	1	5.4
IV	2.3×10^{-6}	$3.30 \times 10^{-4}(\text{HCl})$	3.90	2.49	1	5.3
						Av. 5.25
V	1.02×10^{-4}	$2.78 \times 10^{-4}(\text{HCl})$	3.12	0.324	1	4.2×10^{-1}
V	2.04×10^{-4}	$2.08 \times 10^{-4}(\text{HCl})$	3.12	.265	1	4.5×10^{-1}
V	1.13×10^{-4}	$1.16 \times 10^{-4}(\text{HCl})$	3.12	.156	1	4.5×10^{-1}
						Av. 4.4×10^{-1}

furic acid for complete neutralization has been used instead.

The base constants obtained are over-all constants, since both quinoidal and benzenoidal ions may be obtained. The K_q and K_b for the formation of quinoidal or benzenoidal ions, respectively, are connected to the over-all constant by the equations

$$K = K_q + K_b, K_b = \alpha K \text{ and } K_b = (1 - \alpha)K$$

where α is the quinoidal fraction of the ion. This fraction is unity for II, III, IV and V, for I the value 0.41 for α given in the previous section is probably fairly accurate. The results are given as K_q , which is K for II, III, IV and V. For I the over-all constants were measured as 1.68×10^4 and 1.78×10^4 . These give $K_q = 7 \times 10^3$ and $K_b = 1 \times 10^4$. The K_q values are an inverse measure of the tendency of methylate ion to combine with the quinoidal ion.

The color bases I, II, III, IV and V are derived from dimethylaniline, methyldiphenylamine, diphenylamine, triphenylamine, and carbazole, respectively. The K_q values show a correlation with the base strengths of the parent amines, K_q being greater for the more basic parent amine. In the quinoidal ion an extra phenyl group extends the conjugate system and so interacts with the rest of the molecule. In the color base the extra phenyl group interacts with the unshared pair of electrons

of the nitrogen atom, in the same way that it does in the parent amine. The effects of these interactions on K_q are opposed, so the data indicate that the latter interaction is the greater. However, the K_q values vary to a much less extent than the base strengths of the parent amines. This indicates that the resonance interaction of the extra phenyl group in the quinoidal ion is enough to repress the benzenoidal ion.

A quantitative analysis shows that if the ratio of quinoidal ion to benzenoidal ion is $2/3$ in I, as previously estimated, the amount of benzenoidal ion in the other dyes would not have been detected in measuring the spectra. The relative K_b values would be approximately the same as the relative base strengths of the parent amines. Dimethylamine, the parent of I, is about 10^4 times as strong as diphenylamine, but K_q of I is only fourteen times that of III. This gives the ratio of quinoidal to benzenoidal ion in III as $2 \times 10000/3 \times 14 = 476$. It would need a tenfold error in this estimation to permit the spotting of the benzenoidal ion of III from an anomalously low extinction in methanol. Similarly the thousandfold relationship between K_q for I and IV is trivial when compared with the relative strengths of dimethylaniline and triphenylamine and hence the amount of benzenoidal ion of IV must be negligible at equilibrium.

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