300 ml. (96 mm., 27°) (0.00154 mole, approx. 38% yield) of C_3F_7H.

Stability of N-Bromoperfluorobutyramide to Water.—This was determined by boiling in water several minutes and determining the m.p. It was unchanged after two minutes, and after 30 minutes refluxing had risen only to 83°, indicating that hydrolysis was not yet complete. After refluxing 8 hours perfluorobutyramide was obtained. The results with N-bromotrifluoroacetamide were similar.

Stability of N-Iodoperfluorobutyramide to Water.—The compound was found to be so unstable to water that it could not be handled in humid atmosphere long enough to prepare an infrared sample without decomposing with the production of iodine.

Reaction of Sodium Perfluorobutyrate with Sodium Hydroxide and with Sodium Hypobromite.—In a 50-ml. flask fitted with a reflux condenser whose outlet was connected with a liquid air cooled trap protected by a Drierite trap was placed 5 g. (0.0233 mole) of perfluorobutyric acid and 6.19 mole of 33% aqueous sodium hydroxide (0.07 mole NaOH). The alkaline solution was refluxed for 8 hours. The trap was removed and replaced by a fresh one and an additional 10 ml. of 33% aqueous sodium hydroxide solution added and refluxed an additional 8 hr. Both traps contained *n*-hydroperfluoropropane, C_3F_7H, identified by infrared absorption spectral curve. The yields were low, for example, 50 ml. (78 mm.).

The reaction with sodium hypobromite was carried out in a similar manner except that the bromine was dissolved in cold alkali before addition of the acid. The quantities used were: sodium hydroxide, 7.35 ml. (0.12 mole); bromine, 1.86 g. (0.023) mole); perfluorobutyric acid, 5 g. (0.233 mole). The product was *n*-hydroperfluoropropane. The infrared absorption spectra showed no evidence for the presence of any brominated product.

Acknowledgments.—We are indebted to B. W. Nippoldt and H. Freier for analyses reported in this paper, to A. Duncan for the X-ray data, to D. G. Weiblen and W. Keiser for the infrared data, to B. Oiye for some of the experimental work in the later reaction mechanism work, and to the Minnesota Mining and Manufacturing Company for permission to publish this paper.

ST. PAUL, MINNESOTA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Absorption Spectra of Some *p*-Aminoaryldiazonium Derivatives

BY LEIGH C. ANDERSON AND JOHN W. STEEDLY, JR.[1,2]

RECEIVED MARCH 23, 1954

p-Aminoaryldiazonium salts and some of their derivatives are exceedingly stable compounds when compared to the majority of simple diazonium compounds. Their color, instability to light and coupling properties render them of great value in photochemical reproduction processes. The visible and ultraviolet absorption spectra of *p*-amino-, *p*-methylamino- and *p*-phenylaminophenylenediazoimine, the corresponding diazonium salts as well as the salt of *p*-dimethylaminobenzenediazonium chloride and a number of metal salt complexes of the latter compounds have been studied. A comparison of their absorption spectral curves with those of diphenylquinomethane indicates that these diazonium compounds should be assigned a quinonoid structure.

p-Aminoaryldiazonium salts are a group of exceedingly stable compounds when compared to simple diazonium salts. They are usually yellow or orange in color while the great majority of other diazonium compounds are colorless. The *p*-amino or *p*-monosubstituted aminoaryldiazonium salts are precursors of the *p*-diazoimines which are quite unstable and yet colored like the parent diazonium salts. The unique stability of these *p*-aminoaryldiazonium salts in conjunction with their color prompted this investigation to determine what constitutional differences between these compounds and other diazonium salts are responsible for the observable differences in properties. The *p*-aminoaryldiazonium salts have considerable value in photochemical reproduction processes, because they are decomposed by the long wave ultraviolet light which they absorb whereas the simple colorless diazonium compounds are decomposed very slowly by this radiation. The *p*-diazoimines are characterized by their yellow to orange-red color, relative instability to heat and light with comparatively low explosion temperatures, ready conversion to the *p*-aminoaryldiazonium salts on treatment with mineral acids, and ease of coupling with arylamines and phenols.

It would seem reasonable that the structure of the *p*-diazoimines would be closely related to that of the analogous diazophenols. Previous investigators have presented evidence for and against the assignment of the quinonoid structure to these latter compounds as well as the corresponding diazonium salts. Anderson and Roedel[3] have presented absorption spectral data indicating that the diazophenols have a quinonoid structure. It would appear, therefore, contrary to the statement of Saunders in 1936[4] regarding the imino compounds, "...and the question as to whether their structure is benzenoid or quinonoid has been settled in favor of the former," that the *p*-diazoimines may have the quinonoid structure as originally proposed by Hantzsch[5] although definite proof has been lacking up to the present time. The formation of metallic salt complexes is reputed to give even greater stability to these diazonium salts in the dry state. No absorption spectral studies of the *p*-diazoimines have been made up to the time of this study.

On Fig. 1 the quantitative absorption spectral curve of a water solution *p*-phenylenediazoimine, $HNC_6H_4N_2$, is compared to that of an ether solution

---

[1] The material presented in this paper represents a portion of a dissertation submitted by John W. Steedly, Jr., to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1949.

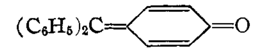
[2] Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April, 1951.

[3] L. C. Anderson and M. J. Roedel, THIS JOURNAL, **67**, 955 (1945).

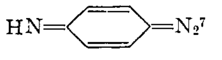
[4] K. H. Saunders, "The Aromatic Diazo Compounds," Arnold and Co., London, 1936, p. 18.

[5] A. Hantzsch, *Ber.*, **35**, 888 (1902).

of diphenylquinomethane.[6] The latter compound was chosen for this comparison because it is representative of a group of compounds known to have the quinonoid structure I



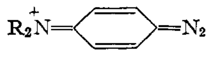
The similarity of the two curves is at once apparent, especially the band at the edge of the visible and ultraviolet regions which in the two curves differs only slightly in intensity and position, indicating that the two systems are conjugated in essentially the same manner and that the structure of the imine can best be indicated as II



Data obtained from quantitative absorption spectral curves of water solutions of N-phenyl-*p*-phenylenediazoimine, *p*-phenylenediazoimine and of N-methyl-*p*-phenylenediazoimine are listed in Table I. The similarity of the absorption spectral curves for N-phenyl-*p*-phenylenediazoimine in ether and in water indicates a similar structure in the two solvents. Since the principal absorption maxima in the three diazoimines appear in approximately the same portion of the spectrum as the principal band of diphenylquinomethane, the conclusion is evident that all of the *p*-diazoimines studied have a similar type of structure. The introduction of a methyl or phenyl group into the amino group produces only a small shift to longer wave length.

Data obtained in this Laboratory as well as some published by Mlle A. Wohl[8] have demonstrated that simple diazonium compounds absorb in the region characteristic of benzene compounds, *i.e.*, they have bands with maxima in the region from 2700–2800 Å. The introduction of alkyl or aryl substituted amino groups in the *para* position of benzenediazonium salts, however, leads to absorption bands which are shifted to the longer wave length region where the diazoimines discussed above show the strongest absorption. This effect is shown in Table I for *para* substituted phenylamino-, amino-, and methylamino- and dimethylaminobenzene derivatives, respectively. In each case, the conversion of the aromatic amine to its salt results in a decreased absorption at shorter wave lengths; on the other hand, the conversion of these amine salts to the diazonium salts leads to an intense absorption band at the edge of the visible region.

p-Dialkylaminobenzene diazonium salts cannot be converted to diazoimines. The similarity of the absorption spectral curve of the salt of the dimethylamino compound with those of the salts of the mono and unsubstituted amino compounds as shown in Table I is so marked, however, that it must be concluded that all possess the same type of structure, III



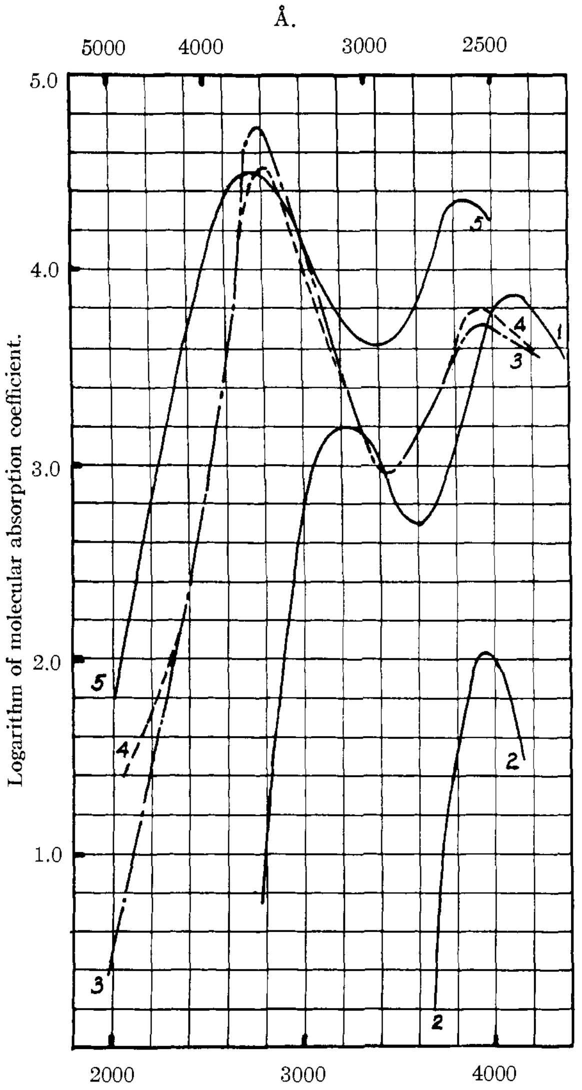


Fig. 1.—1, *p*-Phenylenediamine in alcohol; 2, *p*-phenylenediamine in $^5/_3$ *N* HCl; 3, *p*-aminobenzenediazonium chloride in H_2O; *p*-aminobenzenediazonium chloride·$SbCl_3$ in dilute HCl; *p*-aminobenzenediazonium chloride·$^1/_2ZnCl_2$ in H_2O; 4, *p*-phenylenediazoimine in H_2O; 5, diphenylquinomethane in ether.

In all cases studied, the quantitative absorption spectral curves for the diazonium salts and their complex metal salts were in complete agreement. It must be concluded, therefore, that in the concentrations employed, the metal complex salts of the *p*-aminoaryldiazonium salts have a structure like the uncomplexed aminoaryldiazonium compounds from which they are prepared.

Experimental

p-Aminobenzenediazonium chloride and the N-methyl derivative were prepared by the following series of operations: diazotization of the corresponding acetyl derivatives, isolation of the antimony trichloride double salts, removal of the acetyl group by hydrolysis in dilute acid solution and then precipitation of the antimony as SbOCl by dilution of the acid solutions. Anhydrous *p*-aminobenzenediazonium chloride exploded sharply at 155° after drying in a vacuum desiccator over P_2O_5; the N-methyl compound decomposed

---

[6] L. C. Anderson and M. Gomberg, THIS JOURNAL, **50**, 203 (1928).

[7] The diazo group has been written as $=N_2$ in the formula; it may be $=\ddot{N}-\ddot{N}:$ or $\overset{\oplus}{N}=\overset{..\ominus}{N}:$. In a very acid solution it might be $=\underset{+}{N}=\underset{..}{N}-H$.

[8] A. Wohl, *Bull. soc. chim. France*, **6**, 1319 (1939).

TABLE I

	Solute	Solvent	Absorption bands Frequency number, mm.$^{-1}$ (log. mol. abs. coef.)			
1	*p*-Phenylenediamine	Alcohol		3210(3.19)		4100(3.86)
2	*p*-Phenylenediamine hydrochloride	5/3 *N* HCl			3960(2.03)	
3	*p*-Phenylenediazoimine	Water	2800(4.50)		3940(3.80)	
4	*p*-Aminobenzenediazonium chloride	Water	2800(4.70)		3930(3.70)	
	+ $SbCl_3$	Dil. HCl				
	+ $ZnCl_2$	Water				
5	N-Methyl-*p*-phenylenediamine	Ether		3040(3.48)		3950(4.16)
6	N-Methyl-*p*-phenylenediamine sulfate	5/3 *N* H_2SO_4			3920(2.32)	
7	N-Methyl-*p*-phenylenediazoimine	Water	2720(4.44)		3860(3.88)	
8	*p*-N-Methylaminobenzenediazonium chloride	Water	2701(4.66)		3860(3.72)	
	+ $SbCl_3$	Dil. HCl				
	+ $ZnCl_2$	Water				
9	*p*-Aminodiphenylamine	Abs. alcohol		3480(4.17)		
10	*p*-Aminodiphenylamine hydrochloride	*N*/6 HCl		3580(4.06)		
11	N-Phenyl-*p*-phenylenediazoimine	Water	2540(4.52)			
12	*p*-Phenylaminobenzenediazoimine	Ether	2800(4.43)			
13	*p*-Phenylaminobenzenediazonium sulfate	Water	2660(4.56)		4040(3.84)	
	+ $HgCl_2$	Water				
	+ $^1/_2ZnCl_2$	Water				
14	*p*-Dimethylaminoaniline	Ether		3040(3.46)		3880(4.24)
15	*p*-Dimethylaminoaniline sulfate	5/3 *N* H_2SO_4			3930(2.35)	
16	*p*-Dimethylaminobenzenediazonium chloride	Water	2620(4.58)		3920(3.72)	
	+ $SbCl_3$	Dil. HCl				
	+ $HgCl_2$	Water				
17	Diphenylquinomethane	Ether	2760(4.50)		3820(4.35)	

suddenly at 153°. Aqueous solutions of the imines of the above diazonium chlorides were prepared by treating solutions of the chlorides with excess calcium hydroxide solution, since decomposition occurred quickly when sodium hydroxide was tried. The concentrations of the imine solutions were calculated from the weights of chloride employed. Because the imine solutions were very sensitive to light and heat, the treatment with lime water was carried out in the dark and at low temperatures. The absorption spectra were ascertained approximately 30 minutes after adding the lime water, a time which was found to be satisfactory both for completeness of conversion to the imine and for minimum decomposition. At the higher dilutions, the solutions could be exposed to ultraviolet light for only a few seconds before decomposition became appreciable. Consequently, tests were made on each compound to determine the maximum exposure allowable. The most dilute solutions of the diazoimines were exposed for five seconds only and the experimental procedure for obtaining the spectral data included the almost continuous replacement of the solution in the absorption cell.

Pure *p*-dimethylaminoaniline hydrochloride was diazotized in alcohol solution with amyl nitrite and the diazonium salt was precipitated by the addition of ether. After repeated recrystallizations and drying over P_2O_5, the salt exploded sharply at 163°.

p-Phenylaminobenzene diazonium chloride was obtained by the diazotization of an aqueous sulfuric acid solution with sodium nitrite. After recrystallization it decomposed at 120°. Aqueous solutions of the imine were prepared by adding ammonium hydroxide to solutions of the diazonium chloride until a *p*H of 11.8 was reached. Ether solutions of the imine were prepared by treating ether suspensions of the sulfate with a few drops of concentrated ammonium hydroxide. The concentration of imine was ascertained by reconversion to the sulfate and spectral determination of the amount of diazonium sulfate in the aqueous layer.

The metal salt complexes were prepared by addition of solutions of the appropriate metal salt to solutions of the diazonium salts. Each of the complexes was repeatedly recrystallized from either water or dilute acid solution before the absorption spectrum was ascertained.

The absorption spectra were obtained with the aid of a Judd–Lewis sector photometer.

ANN ARBOR, MICHIGAN