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The Infrared Spectra of Aryldiazonium Salts

By Kermit B. Whetsel, G. F. Hawkins and F. E. Johnson

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The infrared spectra of 30 diazonium salts, diazophenols and closely related compounds derived from 19 different amines were measured with particular attention being given to the 4–6 μ region. The diazonium group is characterized by an absorption band occurring between 4.36 and 4.74 μ. The exact position of the band depends primarily upon the identity of the diazonium cation with shifts of 0.10 μ or less occurring as the anion portion of the salt is changed. Triazenes and the products resulting from the diazotization of an amine group *ortho* to an acetylamino or an N-alkylsulfonamido group do not show characteristic absorption between 4 and 6 μ. The relationship between these results and the structures of the compounds involved is discussed.

In the course of a general investigation of azo dye intermediates, it was observed that the infrared spectrum of a substituted benzenediazonium chloride showed a sharp band of medium intensity at 4.44 μ. Since the carbon–nitrogen triple bond is characterized by a band at 4.43 to 4.52 μ,[1] it seemed reasonable that the 4.44 μ band was due to the nitrogen–nitrogen triple bond in the diazonium salt. A search of the literature, however, produced infrared spectra of only two diazonium salts.[2] These spectra showed strong absorption bands near 4.7 μ but did not show characteristic absorption in the 4.4 μ region.

In order to obtain additional data on the infrared absorption of the diazonium cation, 30 diazonium salts and closely related compounds derived from 19 different amines were prepared and their spectra measured. After the experimental portion of this work was completed, it was reported by Aroney, Le Fèvre and Werner[3] that the diazonium cation is characterized by an absorption band occurring between 4.33 and 4.48 μ. Our results show that the upper wave length limit should be extended somewhat. The relationship between the position of the absorption band and the structure of diazonium compounds is also discussed to some extent in the present paper.

Experimental

Spectra.—All spectra were measured as Nujol mulls using a Baird double beam spectrophotometer equipped with a sodium chloride prism. The wave length scale was calibrated each time a spectrum was run by measuring the spectrum of a capillary film of acetonitrile from 4 to 5 μ before removing the chart from the drum. Values of 4.38 and 4.45 μ were used for the two acetonitrile bands found in this region. On the basis of this calibration, it is believed that the positions of the bands are accurate to ±0.01 μ.

Preparation of the Compounds.—References describing the preparation of many of the compounds are given in Table I. The remaining compounds were prepared by one of the following procedures: 1. Diazonium Chloride of *p*-Aminobiphenyl.—Ethyl nitrite was passed into a mixture of 10 g. of *p*-aminobiphenyl, 25 ml. of concentrated hydrochloric acid and 50 ml. of absolute ethanol at 0°. The diazonium chloride was precipitated by the addition of diethyl ether.

2. Diazonium Chloride of *p*-Aminophenol.—An ethanolic solution of the amine was made acidic with dry hydrogen chloride at 0° and the isolation of the salt carried out as in procedure 1.

3. Diazonium Zinc Chloride Complexes.—The diazotization of *p*-aminobiphenyl, *m*-toluidine and *p*-toluidine were carried out according to procedure 1. Addition of a concentrated solution of zinc chloride caused the salts to precipitate. In the case of *p*-N,N-diethylaminoaniline, the diazotization was carried out in an aqueous hydrochloric acid solution by the addition of sodium nitrite. The ultraviolet spectrum of the product was very similar to that of *p*-N,N-dimethylaminobenzenediazonium chloride[4] (λ_{max} 380 mμ, log ε 4.57 and λ_{max} 246 mμ, log ε 3.57).

4. Diazonium Fluoborate Salts.—Aqueous hydrochloric acid solutions or suspensions of 2,4,6-trichloroaniline and *m*-aminophenol were diazotized with sodium nitrite and the salts precipitated by the addition of a saturated solution of sodium fluoborate. To prepare *p*-aminobenzenediazonium fluoborate, 10 g. of ethyl nitrite was passed into a solution of 100 ml. of ethanol and 20.8 g. of fluoboric acid, followed by a solution of 5.4 g. of *p*-phenylenediamine and 8.8 g. of fluoboric acid in 100 ml. of absolute ethanol. The resulting brown precipitate was filtered and washed with ether.

5. Diazonium Silicofluoride from *p*-Aminobiphenyl.—*p*-Aminobiphenyl (5 g.) was added to a solution of 40 ml. of fluosilicic acid (30%) and 100 g. of acetic acid and stirred to form a smooth slurry. Ethyl nitrite was passed in at 0 to 5° until almost complete solution occurred. Addition of isopropyl alcohol and ether caused the separation of an oily layer. The oily layer was separated and added to isopropyl alcohol causing a solid to precipitate. The solid was filtered off and thoroughly washed with isopropyl alcohol and ether.

6. Diazonium Naphthalene Sulfonate from *p*-Aminobiphenyl.—*p*-Aminobiphenyl was diazotized as in procedure 1 and a saturated solution of α-naphthalenesulfonic acid added. An oily precipitate which crystallized upon stirring formed. It was filtered, washed once with water and reslurried in isopropyl alcohol. After filtering again, the solid was washed with ether.

7. Diazonium Salt from *p*-Aminobenzenesulfonic Acid.—About 10 g. of the amine and 6 g. of sodium nitrite were dissolved in water. After cooling the solution, hydrochloric acid was added and the precipitate removed by filtration.

8. Diazophenol from 2-Amino-4-nitrophenol.—An aqueous hydrochloric acid suspension of the amine was diazotized with sodium nitrite and held at 0 to 5° for 1 hr. The yellow precipitate was separated by filtration.

Results

The compounds studied and the positions of the major absorption bands found in the 4 to 5 μ region of their spectra are listed in Table I. The curves shown in Fig. 1 illustrate the general appearance of these bands. With the exception of the triazenes (XIV and XV) and the products resulting from the diazotization of an amine group *ortho* to an N-alkylsulfonamido or an acetylamino group, all of the compounds showed a major absorption band in the 4.36 to 4.74 μ region.

Effect of the Stabilizing Anion.—The spectra of the chloride, fluoborate, fluosilicate, 1-naphthalenesulfonate and zinc chloride diazonium salts derived from *p*-aminobiphenyl showed a strong absorption band between 4.38 and 4.47 μ. The di-

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[1] R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

[2] "Catalogue of Infrared Spectrograms," Samuel P. Sadtler and Sons, Philadelphia 3, Pa., Spectrograms 888, 889 and 1657.

[3] M. Aroney, R. J. W. Le Fèvre and R. L. Werner, *J. Chem. Soc.*, 276 (1955).

[4] L. C. Anderson and J. W. Steedly, This Journal, **76**, 5144 (1954).

TABLE I

ABSORPTION OF ARYLDIAZONIUM SALTS IN THE 4–5 μ REGION

Amine	Anion	λ, μ	Ref.
p-Aminobiphenyl	Cl^-	4.38	[a]
	$ZnCl_4^{=}$	4.46	[a]
	BF_4^-	4.47	[b]
	$SiF_6^{=}$	4.40	[a]
	1-Naphthalenesulfonate	4.40	[a]
Aniline	BF_4^-	4.38 (4.36)[c]	[d]
	$ZnCl_4^{=}$	4.41	[e]
m-Toluidine	BF_4^-	4.37	[d]
	$ZnCl_4^{=}$	4.44	[a]
p-Toluidine	BF_4^-	4.38	[f]
	$ZnCl_4^{=}$	4.43	[a]
2,4,6-Trichloroaniline	BF_4^-	4.41	[a]
p-Nitroaniline	BF_4^-	4.36 (4.33)[c]	[g]
	$SO_4^{=}$	4.36	[h]
m-Aminophenol	BF_4^-	4.37	[a]
p-Aminophenol	Cl^-	4.47	[a]
	(Diazophenol)[j]	4.74	[i]
p-N,N-Diethylaminoaniline	BF_4^-	4.45 weak	[k]
		4.65 strong	
	$ZnCl_4^-$	4.46 weak	[a]
		4.67 strong	
p-N-Ethyl-N-β-hydroxethylaminoaniline	$ZnCl_4^{=}$	4.52 weak	[l]
		4.68 strong	
2-Amino-4-nitrophenol	(Diazophenol)[j]	4.58 strong	[a]
		4.65 strong	
p-Aminobenzenesulfonic acid	(Inner salt)[j]	4.41 (4.38)[c]	[a]
4-Aminoazobenzene	BF_4^-	4.39	[m]
p-Phenylenediamine (one amino group diazotized)	BF_4^-	4.58	[a]
	$SbCl_4^-$	4.65	[n]
2-Amino-3,5-di-nitrobenzene-N-ethylsulfonamide	(Benzothiatriazine)	No band	[o]
2-Aminoacetanilide	(Benzotriazole)[j]	No band	[p]
2-Amino-4-chloroacetanilide	(Benzotriazole)[j]	No band	[q]
1-Phenyl-3-di-phenyltriazene		No band	[r]
1-(*p*-Methylphenyl)-3-diphenyltriazene		No band	[r]

[a] See Experimental. [b] G. Schiemann and W. Roselius, *Ber.*, 62, 1805 (1929). [c] Values in parentheses reported by Aroney, Le Fèvre and Werner, reference 3. [d] G. Balz and G. Schiemann, *Ber.*, 60B, 1186 (1927). [e] W. E. Hanby and W. A. Waters, *J. Chem. Soc.*, 1029 (1946). [f] E. S. Lewis and E. B. Miller, THIS JOURNAL, 75, 429 (1953). [g] E. B. Starkey, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 225. [h] N. Kornblum, G. D. Cooper and J. E. Taylor, THIS JOURNAL, 72, 3010 (1950). [i] L. C. Anderson and M. J. Roedel, *ibid.*, 67, 955 (1945); the ultraviolet and visible spectrum of our sample matched that shown by Anderson and Roedel. [j] Terms in parentheses are not anions but rather represent the type of compound formed upon diazotization of these amines. [k] G. Schiemann and W. Winkelmuller, *Ber.*, 66B, 727 (1933). [l] Reference 2, spectrogram 889. [m] J. Lichtenberger and R. Thermet. *Bull. soc. chim. France*, 318 (1951). [n] L. C. Anderson and J. W. Steedly, THIS JOURNAL, 76, 5144 (1954). [o] J. G. McNally and J. B. Dickey, U. S. Patent 2,402,611. *Anal.* Calcd. for $C_8H_7N_5O_6S$: C, 31.89; H, 2.34; N, 23.25; S, 10.65. Found: C, 32.18; H, 2.69; N, 22.32; S, 10.52 (see Discussion for proposed structure). [p] T. G. Heafield and L. Hunter, *J. Chem. Soc.*, 420 (1942). [q] Prepared by the procedure used with 2-aminoacetanilide. *Anal.* Calcd. for $C_8H_6N_3Cl$: C, 49.12; H, 3.09; N, 21.48; Cl. 18.13. Found: C, 49.25; H, 3.27; N, 21.28; Cl, 17.77 (see Discussion for proposed structure). [r] K. H. Saunders, "The Aromatic Diazo-compounds and Their Technical Applications," Edward Arnold & Co., London, 1949, p. 159.

azonium bands of the zinc chloride salts derived from aniline, *p*-toluidine, *m*-toluidine and *p*-N,N-diethylaminoaniline occurred at a longer wave length than did those of the corresponding fluoborates, but the largest difference in position was only 0.07 μ. The sulfate and fluoborate salts of diazotized *p*-nitroaniline both exhibited characteristic absorption at 4.36 μ. Thus, it appears that the absorption band of a given diazonium cation does not shift over 0.10 μ as the anion portion of the salt is changed. This conclusion is supported by the work of Aroney, Le Fèvre and Werner,[3] who studied seven complex metallic anions not included in our investigation. Thus, while a classification of diazonium compounds based upon the different types of stabilizing anions[5,6] may be helpful from the preparative or use standpoint, it should not be interpreted as indicating an essential difference in the structure of the diazonium cation. This conclusion is in agreement with that drawn by Anderson and Steedly[4] from ultraviolet data on dilute aqueous solutions of the complex metal salts of *p*-aminoaryldiazonium salts.

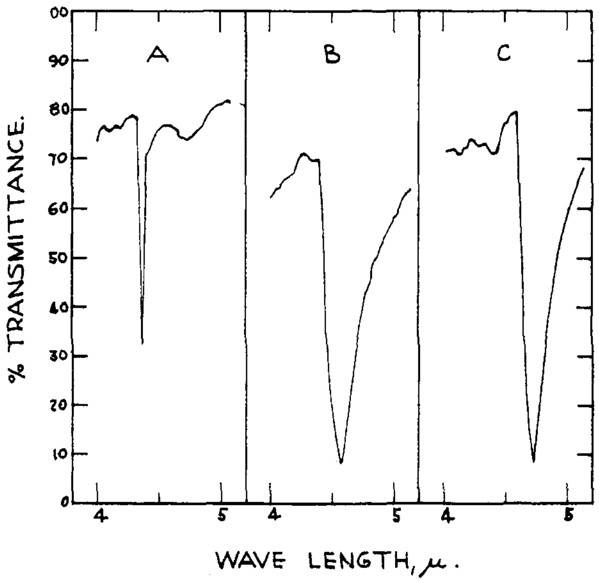

Fig. 1.—Spectra of diazonium salts (Nujol mull spectra with Baird spectrophotometer, NaCl optics): A, *p*-nitrobenzenediazonium fluoborate; B. *p*-aminobenzenediazonium fluoborate; C, *p*-diazophenol.

Effect of Ring Substituents.—The diazonium fluoborate salts derived from aniline and 10 substituted anilines were studied to determine the effect of the cation upon the diazonium absorption band. The position of the band varied from 4.36 μ for the salt of *p*-nitroaniline to 4.65 μ for the salt of *p*-N,N-diethylaminoaniline. In the case of *p*-diazophenol, the band was shifted still further to 4.74 μ. It is readily apparent that the nature of the parent

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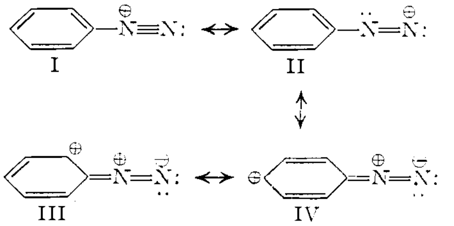
(5) K. Venkataraman, "The Chemistry of Synthetic Dyes," Vol. 1, Academic Press, Inc., New York, N. Y., 1952, p. 223.

(6) K. H. Saunders, "The Aromatic Diazo-compounds and Their Technical Applications," Edward Arnold and Co., London, 1949, p. 71.

amine has a much more pronounced effect upon the position of the characteristic diazonium absorption band than does the identity of the anion portion of the molecule.

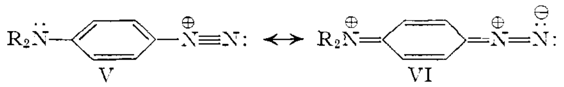
Discussion

Structure of the Diazonium Group.—The diazonium group is sometimes represented simply as structure I, but usually[7,8] structure II is included as a form which contributes to resonance hybrid.[9] Mills[10] has pointed out that contributions of structures III and IV to the resonance hybrid should also be considered. From Raman data on the nitrogen–nitrogen triple bond and infrared data on the nitrile group, one would expect structure I to exhibit characteristic absorption near 4.4 μ. Equal contributions of I and III (or I and IV) to a resonance hybrid would make the system directly analogous to that of covalent azides, in which the forms $\mathrm{R}{-}\overset{\ominus}{\ddot{\mathrm{N}}}{-}\overset{\oplus}{\mathrm{N}}{\equiv}\mathrm{N}{:}$ and $\mathrm{R}{-}\ddot{\mathrm{N}}{=}\overset{\oplus}{\mathrm{N}}{=}\overset{\ominus}{\ddot{\mathrm{N}}}{:}$ contribute equally,[11] and an absorption band should occur near 4.7 μ.[12]


I II III IV

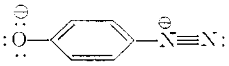
With the exception of the diazophenols and the diazonium salts derived from *p*-phenylenediamine and its N,N-dialkyl derivatives, all of the compounds studied showed an absorption band between 4.36 and 4.47 μ. This absorption is consistent with the diazonium group having essentially the structure represented by formula I. The small shifts in absorption observed with a series of salts having a common anion indicate varying contributions of the other possible resonance forms to the true structure of the diazonium group.

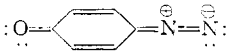
Diazonium salts derived from *p*-N,N-dialkylaminoanilines showed characteristic adsorption between 4.65 and 4.68 μ. This pronounced shift indicates a much larger contribution of a nitrogen–nitrogen double-bonded structure to a resonance hybrid. It appears that the structure of these salts is that resulting from almost complete resonance between structures V and VI. The diazonium band of *p*-aminobenzenediazonium fluoborate was found at 4.58 μ, thus indicating a considerably larger contribution of structure VI to the resonance hybrid than in the case of the analogous N,N-dialkylated salts.[13]

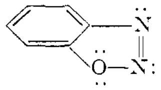

V VI

Although there is definite evidence that an electron-releasing group in the *para* position of benzenediazonium salts causes the diazonium band to shift to longer wave lengths, there is no apparent correlation between the magnitude of the shift and the Hammett σ-value for the substituent group. Such a correlation might be found with solution spectra,[14] but only limited data of this type are available at present.

Structure of Diazophenols.—The long controversy over the structure of *o*- and *p*-diazophenols and diazonaphthols has been summarized by Saunders.[15] At present the discussion centers over whether the structure of these compounds is best represented by structure VII, structure VIII or a resonance hybrid of the two. Similar structures can be written for the *ortho* compounds, and structure IX must also be considered. On the basis of ultraviolet and visible absorption spectra, Anderson and Roedel[16] concluded that *p*-diazophenol and *o*- and *p*-diazonaphthols exist in ether solution as structure VIII. *p*-Diazophenol showed a strong absorption band at 4.74 μ, thus indicating essentially complete resonance between structures VII and VIII in the solid state. In the case of 4-nitro-1,2-diazophenol, the benzenoid form is of considerably greater importance as evidenced by the diazonium band being shifted to 4.58–4.65 μ.[17] The presence of this strong band also eliminates IX as a possible structure for this *o*-diazophenol.


VII


VIII

IX


Structure of Diazotized *p*-Aminobenzenesulfonic Acid.—When *p*-aminobenzenesulfonic acid is diazotized, an insoluble product is obtained which is described as an inner salt and represented by formula X. The diazonium band of this com-

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[7] Reference 5, p. 412.

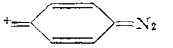
[8] H. A. Lubs, "The Chemistry of Synthetic Dyes and Pigments," ACS Monograph No. 127, Reinhold Publishing Corp., New York, N. Y., 1955, p. 104.

[9] One of the referees has pointed out that contribution of **11** to a resonance hybrid would be very small since the $\mathrm{C}{-}\overset{\oplus}{\mathrm{N}}{\equiv}\mathrm{N}{:}$ system is linear whereas the $\mathrm{C}{-}\ddot{\mathrm{N}}{=}\overset{\oplus}{\mathrm{N}}{:}$ system is bent.

[10] W. H. Mills, *J. Chem. Soc.*, 349 (1944).

[11] L. Pauling, "The Nature of The Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 200.

[12] J. H. Bover, This Journal, **73**, 5248 (1951).

[13] L. C. Anderson and J. W. Steedly, Jr., This Journal, **76**, 5144 (1954), assigned the structure  to the *p*-amino, *p*-N-methylamino and *p*-N,N-dimethylaminobenzenediazonium salts on the basis of ultraviolet and visible absorption data. These authors do not discuss this point, but an increased amount of quinoid character in *p*-N,N-dimethylaminobenzenediazonium salts, compared with *p*-aminobenzenediazonium salts, is indicated by the fact that the long wave length absorption band of the dialkylamino compound occurs at 382 mμ while that of the unsubstituted amino compound is at 357 mμ.

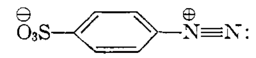
[14] A plot of the carbonyl frequency of substituted acetophenones *vs.* σ yields a straight line when the spectra are measured using dilute solutions in carbon tetrachloride (N. Fuson, M. L. Josien and E. M. Shelton, This Journal, **76**, 2526 (1954)), but not when the spectra are measured as Nujol mulls (A. H. Soloway and S. L. Friess, This Journal, **73**, 5000 (1951)).

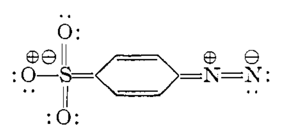
[15] Reference 6, pp. 28–35.

[16] L. C. Anderson and M. J. Roedel, This Journal, **67**, 955 (1945).

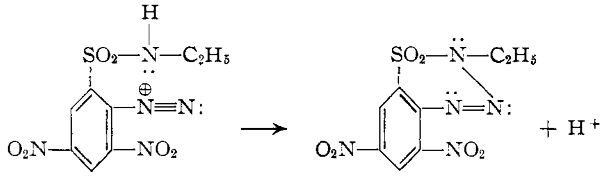
[17] R. J. W. Le Fèvre, J. B. Sousa and R. L. Werner, *J. Chem. Soc.*, 4886 (1954), reported that both *o*- and *p*-diazonaphthols show characteristic absorption at 4.94 μ. Thus, these compounds appear to have more quinoid character than do diazophenols

pound was found at 4.41 μ indicating some contribution of a quinoid structure such as XI.

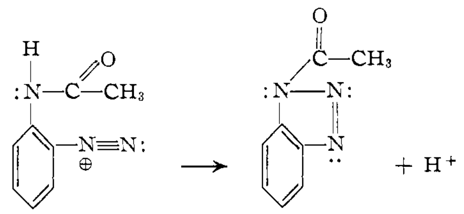

X


XI

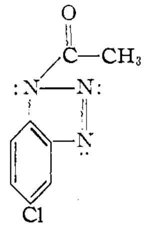
Diazonium Compound from 2-Amino-3,5-dinitrobenzene-N-ethylsulfonamide.—The product resulting from the diazotization of 2-amino-3,5-dinitrobenzene-N-ethylsulfonamide did not show an absorption band between 4 and 6 μ. The absence of the band characteristic of a nitrogen–nitrogen triple bond provides direct evidence that the diazonium ion cyclizes to form a benzothiatriazine by elimination of a proton.[18] Elemental analyses of the product agreed very closely with the theoretical values for the cyclic product and clearly showed that the compound was not a diazonium sulfate. Since the equilibrium would be shifted to the left to some extent in acidic solutions, the infrared spectrum of an acetic acid solution of the benzothiatriazine was measured in an attempt to observe the characteristic diazonium band. No trace of the band could be found, thus indicating that under these conditions the equilibrium is still far to the right. This conclusion is in agreement with the fact that in an acetic acid medium the diazonium compound couples very slowly with amines.[19]

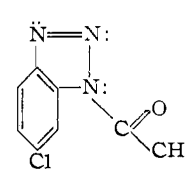


Diazonium Compounds from *o*-Aminoacetanilides.—It is well established that diazotization of *o*-aminoacetanilides results in the formation of 1,2,3-benzotriazoles[20] according to the equation

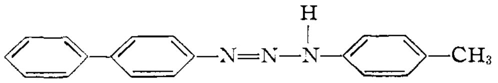


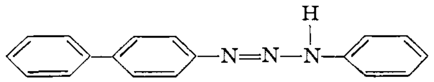
The infrared spectra of the products resulting from the diazotization of 2-aminoacetanilide and 2-amino-4-chloroacetanilide were consistent with this structure in that no characteristic diazonium band was observed. Elemental analyses of the product from 2-amino-4-chloroacetanilide were in agreement with those calculated for the triazole. The absence of sulfur showed that the compound was not a diazonium sulfate. No attempt was made to determine whether this product was the 1- or the 3-acetylbenzotriazole (XII and XIII) or a mixture of the two.[20]


XII


XIII

Triazenes.—The spectra of two diaryltriazenes XIV and XV, were measured.


XIV


XV

As expected, neither of those compounds showed characteristic absorption in the 4 to 6 μ region.

KINGSPORT, TENN.

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(18) Reference 6, p. 253.

(19) Unpublished data obtained in this Laboratory.

(20) Reference 6, pp. 247–250.

[JOINT CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO, AND THE CHEMISTRY DEPARTMENT, ACTON TECHNICAL COLLEGE]

Absorption Spectra of Azo- and Related Compounds. II.[1] Substituted Phenylnitrones

BY OWEN H. WHEELER[2a] AND PETER H. GORE[2b]

RECEIVED FEBRUARY 10, 1956

The ultraviolet absorption of a number of substituted phenylnitrones (N-phenylbenzaldoximes) has been measured, and the spectra are discussed with reference to the electronic and steric properties of the substituents. Comparison is made with the spectra of azoxybenzenes.

The ultraviolet absorption of a number of phenylnitrones[3a] and other nitrones[3b,c] has been reported very generally. No systematic study of substituent effects in the spectra of phenylnitrones has been made. This paper records the absorption (Table I) of a number of phenylnitrones, some of them new compounds, and an interpretation of the data.

The spectra fall into three distinct regions (at *ca.* 230, 280 and 320 mμ). Each of the bands is of high intensity ($\epsilon > 5{,}000$) and, therefore, due to

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(1) Part I, THIS JOURNAL, **78**, 2160 (1956).

(2) (a) Universidad Nacional Autónoma de Mexico, México, D. F. (b) Acton Technical College, London.

(3) (a) P. Grammaticakis, *Bull. soc. chim. France*, 965 (1951); (b) 664 (1947); (c) G. von Fodor and P. Csokán, *Ann.*, **535**, 284 (1938).