tion temperature had fallen to 70°; yield 362 g. or 79%, m.p. 243–244° (acid was unchanged by heating at 275° for 4 hr.).

*Anal.* Calcd. for $C_{10}H_{18}O_6S$: C, 45,10; H, 6.81; neut. equiv., 133.1. Found; C, 45.16; H, 7.02; neut. equiv., 132.9.

**Sulfonyldipivalyl Chloride.**—Sulfonyldipivalic acid (30 g.) was refluxed with thionyl chloride (75 g.) for 16 hr. The excess thionyl chloride was removed under reduced pressure and the residue was dissolved in hot benzene (200 ml.). The benzene solution was cooled, then filtered directly into ligroin (500 ml.) at 0° with stirring. The crystals thus precipitated were collected on a filter and dried by suction in a current of dry air; yield 26 g. or 76%, m.p. 103–105°.

*Anal.* Calcd. for $C_{10}H_{16}Cl_2O_4S$: C, 39.65; H, 5.32; Cl, 23.40; neut. equiv., 151.6. Found: C, 39.49; H, 4.98; Cl, 23.57; neut. equiv., 151.3.

**Sulfonyldipivalamide.**—This compound was prepared as described above for thiodipivalamide; yield 85%, m.p. 205–206°.

*Anal.* Calcd. for $C_{10}H_{20}N_2O_4S$: C, 45.40; H, 7.62; N, 10.61. Found: C, 45.52; H, 7.85; N, 10.45.

**N,N′-Di-(*p*-tolyl)-sulfonyldipivalamide.**—This compound was obtained from sulfonyldipivalyl chloride by the standard method previously cited[12]; yield 69%, m.p. 212–213°.

*Anal.* Calcd. for $C_{24}H_{32}N_2O_4S$: C, 64.90; H, 7.27; N, 6.31. Found: C, 64.78; H, 7.62; N, 6.51.

**Dimethyl Sulfonyldipivalate.**—Sulfonyldipivalyl chloride (50 g.) was treated with methanol (400 ml.) in a large beaker. After the vigorous reaction had subsided, practically all excess methanol was removed by evaporation on a steam-bath. The crude ester which remained was recrystallized from a mixture of methanol (150 ml.) and benzene (50 ml.); yield 43.2 g. or 89%, m.p. 90–92°.

*Anal.* Calcd. for $C_{12}H_{22}O_6S$: C, 48.96; H, 8.14. Found: C, 49.06; H, 8.33.

**Diethyl Sulfonyldipivalate.**—This compound was prepared from the acid chloride and ethyl alcohol by the method described for the preparation of the methyl ester. The crude ester was recrystallized from a mixture of ethyl alcohol and ligroin (2:1 by vol.). In this case the solution was allowed to stand overnight at 0°; yield 83%, m.p. 53–54°.

*Anal.* Calcd. for $C_{14}H_{26}O_6S$: C, 52.15; H, 8.14. Found: C, 52.31; H, 8.41.

**Acknowledgment.**—The authors are grateful to Mr. D. C. Sievers and the staff of the analytical section of the Research Laboratories of Tennessee Eastman Co. for all elemental analyses.

KINGSPORT, TENNESSEE

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

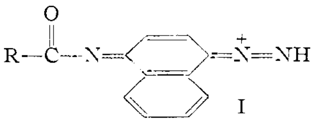
# The Absorption Spectra of Some *p*-Acylaminobenzenediazonium Compounds

BY LEIGH C. ANDERSON AND B. MANNING[1,2]

RECEIVED JUNE 18, 1954

The marked stability of dry *p*-acylaminoaryldiazonium salts as compared to the high instability of simple diazonium compounds leads one to suggest different electronic structures for these two types of compounds. Two *p*-acylaminobenzenediazoimides and seven different *p*-acylaminobenzenediazonium salts and some of their metal complexes have been prepared and their quantitative visible and ultraviolet absorption spectral curves determined. The data indicate that a quinonoid configuration is the chief contributor to the structure of these diazonium compounds.

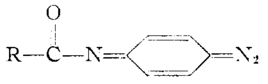
In this investigation, the absorption spectra of solutions of a number of *p*-acylaminobenzenediazonium salts have been compared to those of the benzenoid compounds from which they have been prepared and to those compounds of recognized quinonoid configuration. Hewitt, in 1907,[3] assuming a mobile hydrogen atom on the amide nitrogen, proposed a quinonoid structure for the 4-benzoylamino-1-naphthalenediazonium ion (I) to account for the color of the chloride. Other investigators opposed the assignment of this structure



I

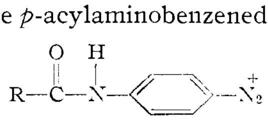
because the corresponding *p*-(alkylacylamino) compounds are colored also. The marked stability of the dry diazonium compound containing the *p*-acylamino group as compared to the high instability of simple diazonium compounds leads one to suggest different electronic structures for these two types of compounds. The imides of the *p*-acylaminobenzenediazonium compounds are colored also, but are quite unstable.

The classical formula for the neutral imide can only be postulated in the quinonoid form II

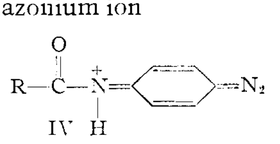


II

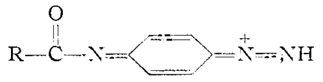
Three structures III, IV and V can be written for the *p*-acylaminobenzenediazonium ion



III



IV



V

Substitution of various acyl groups for a hydrogen atom of an amino group of *p*-phenylenediamine and also substitution of chlorine atoms for one or two of the hydrogen atoms of the benzene nucleus produce marked differences in the ultraviolet absorption spectrum as compared to that of *p*-phenylenediamine (Table I). The absorption of the predominantly benzenoid derivatives of the *p*-phenylenediamine molecules is altered markedly by the introduction of the various acyl groups and the

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[1] The material presented in this paper represents a portion of a dissertation submitted by Bernard Manning to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, June, 1950.

[2] Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society at Boston, Mass., April 5, 1951.

[3] J. T. Hewitt, *Proc. Chem. Soc.*, **23**, 181 (1907).

TABLE I

| Solute | Solvent | Absorption bands Frequency no., mm.$^{-1}$ (log mol. abs. coef.) | | | Color | Decompn. pt., °C. (Ex. = explodes) |
|---|---|---|---|---|---|---|
| *p*-Phenylenediamine | 95% EtOH | | 3230(3.17) | 4180(3.81) | | |
| 4-Aminobenzenediazonium chloride | Water | 2820(4.62) | | 3970(3.71) | Yellow | 155(Ex.) |
| 4-Aminobenzenediazonium chloride + $SbCl_3$ | | | | | Yellow | 179(Ex.) |
| 4-N-Acetylaminoaniline | 95% EtOH | | Infl. 3200(3.15) | 3850(4.26) | | |
| 4-N-Acetylaminoaniline | Dil. HCl | | Infl. 3550(2.55) | 4140(4.09) | | |
| 4-N-Acetylaminobenzenediazonium chloride | Water | 2950(4.48) | | | Colorless | 134(Ex.) |
| 4-N-Acetylaminobenzenediazonium chloride + $SbCl_3$ | Dil. HCl | 2950(4.48) | | | Colorless | 148 |
| 4-N-Acetylaminobenzenediazoimide | Water | 2970(3.98) | | | | |
| 4-(N-Methyl-N-acetylamino)-aniline | Ether | | 3350(3.39) | 4020(4.15) | | |
| 4-(N-Methyl-N-acetylamino)-aniline | Water | | 3570(3.24) | 4190(4.12) | | |
| 4-(N-Methyl-N-acetylamino)-aniline | Dil. HCl | | General from 3600(1.5) to 4300(3.8) | | | |
| 4-(N-Methyl-N-acetylamino)-benzenediazonium chloride | Water | 2940(4.22) | | | Gray | 117(Ex.) |
| 4-(N-Methyl-N-acetylamino)-benzenediazonium chloride + $SbCl_3$ | 7.2% HCl | 2900(4.18) | | | Pale yell. | 119 |
| 4-N-Benzoylaminoaniline | 95% EtOH | | 3400(4.14) | | | |
| 4-N-Benzoylaminoaniline | Dil. HCl | | | 3930(4.27) | | |
| 4-N-Benzoylaminobenzenediazonium chloride | Dil. HCl | 2890(4.62) | | | Yellow | 110, 147(Ex.) |
| 4-N-Benzoylaminobenzenediazonium chloride + $ZnCl_2$ | | | | | Colorless | 146(Ex.) |
| 4-N-Benzoylaminobenzenediazoimide | Abs. EtOH | 2900(4.12) | | | | |
| 4-Acetylamino-2,6-dichloroaniline | 95% EtOH | | 3270(3.36) | | | |
| 4-Acetylamino-2,6-dichlorobenzenediazonium chloride | Water | 2840(4.47) | | 4050(3.95) | Pale yell. | 174–176(Ex.) |
| 4-(*o*-Chlorobenzoylamino)-aniline | 95% EtOH | | 3503(4.20) | | | |
| 4-(*o*-Chlorobenzoylamino)-benzenediazonium chloride | Water | 2960(4.49) | | | Colorless | 143 |
| 4-(*p*-Chlorobenzoylamino)-aniline | 95% EtOH | | 3310(4.14) | | | |
| 4-(*p*-Chlorobenzoylamino)-benzenediazonium chloride | Water | 2910(4.61) | | | Colorless | 149(Ex.) |
| 4-Benzoylamino-2-chloroaniline | 95% EtOH | | 3400(4.12) | | | |
| 4-Benzoylamino-2-chlorobenzenediazonium chloride | Water | 2830(4.59) | | | Pale yell. | 188(Ex.) |

chlorine atoms, but there is no uniform change; conversion to the salt produces a strong hypsochromic effect.

In contrast to the varied alterations of absorption just mentioned, conversion of the amine salt to the diazonium salts produces a strong bathochromic effect and the spectra of the diazonium salts are very similar to one another and to the absorption spectrum of *p*-aminobenzenediazonium chloride. The maxima of the absorption bands in the spectra of all of the diazonium salts investigated are located at the edge of the visible and ultraviolet region at frequency numbers (waves per millimeter) between 2800 and 3000, and at values of the logarithm of the molecular absorption coefficient between 4.2 and 4.6.

The similarity of the absorption spectra of these diazonium salts indicates that they all have nearly the same predominating electronic structure and, because of the differences between the spectra of the diazonium salts and the salts of the parent amines, the structure is not benzenoid. Since neither (a) variation of the acyl group, (b) replacement of the hydrogen of the *p*-acylamino group, nor (c) substitution of one or two chlorine atoms for the hydrogen atoms of the phenyl ring, results in any major variations of the absorption spectra, the absorption band near the visible in the spectra of these diazonium salts must be associated with that portion of the molecule which is common to all these salts, namely, the *p*-aminobenzenediazonium fragment.

Anderson and Steedly[4] have shown *p*-amino- and *p*-alkylaminobenzenediazonium salts to be quinoidal on the basis of the resemblance of their spectra to that of fuchsone, Inasmuch as the spectra of the *p*-acylaminobenzenediazonium salts including *p*-N-methyl-N-acetylaminobenzenediazonium chloride, are similar to the *p*-amino compounds, it is concluded that the chief contributor to the structure of a *p*-acylaminobenzenediazonium ion must be similar to formula IV in spite of the fact that one might expect the presence of the acyl group to reduce the probability of structure IV contributing much to the final structure.

## Experimental

The general procedure for preparing the acyl derivatives of *p*-phenylenediamine involved acylation of *p*-nitroaniline or appropriate derivative and reduction of the nitro group with iron and acetic or formic acid. The diazotizations were carried out according to standard procedures using alcohol or aqueous acid as solvent and either amyl nitrite or sodium nitrite, respectively. In most cases the antimony chloride double salt of the diazonium compound was isolated and analyzed and the metal-free diazonium salt was separated after hydrolysis of the antimony complex. The acyl-*p*-benzenediazoimides were synthesized by diazotization of the amine in acetone solution with nitrogen trioxide and were precipitated by the addition of ether. Because the diazoimides decompose readily, it was not possible to purify them by recrystallization. All steps in obtaining the absorption spectra of the diazoimides were carried out as rapidly as possible in diffused light in order to prevent decomposition due to exposure to light and to air.

The compounds whose absorption spectral curves are included in this paper were prepared in the pure dry state. The salts were dried in vacuum desiccators over phosphorus pentoxide and were protected from light. Previous investigators have prepared some of the metallic salt complexes discussed here and those which had not been prepared previously were analyzed and tested for purity. The color and decomposition points of the diazonium chlorides and metal salt complexes are also given in Table I.

Considerable experimental difficulty was entailed in obtaining the data for the absorption curves since these diazonium compounds are very sensitive to ultraviolet light. It was necessary to replace the solutions after only a few seconds exposure in order to avoid having enough decomposition products in the solution to vitiate the results. The spectral data were obtained with the aid of a Judd–Lewis sector photometer.

ANN ARBOR, MICHIGAN

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(4) L. C. Anderson and J. W. Steedly, Jr., THIS JOURNAL, **76**, 5144 (1954).