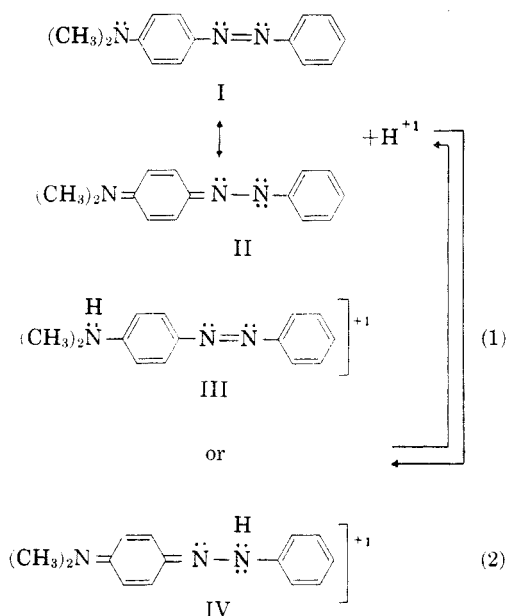


## The Structure of Protonated Molecules of Aminoazobenzene Derivatives

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The protonic equilibria of aminoazobenzene and its derivatives have been studied for many years.<sup>1-4</sup> Two viewpoints exist in regard to the structures of the participating ions. For 4-dimethylaminoazobenzene in acid solution formulas I and II show the

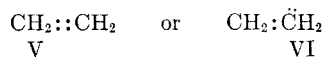


structures contributing to the resultant hybrid and addition of a proton could lead to III or IV.

The literature shows a preference for the quinonoid structure IV based on early spectroscopic studies.<sup>5</sup> In 1952 we obtained the ultraviolet absorption data shown in Figures 1 and 2, which would indicate that the benzenoid structure III and not the quinonoid structure IV exists in the presence of strong acids. Other recent studies<sup>6</sup> also confirm this structure. Considering the greater basicity<sup>7</sup> of the dimethylamino group compared to the lesser basicity of the azo group it would seem that III should be the more likely and predominating structure of the acid form.

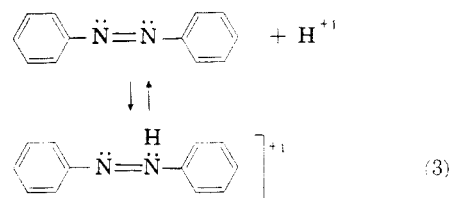
## DISCUSSION OF RESULTS

Current electronic theories indicate that covalent bonds may have either homopolar (V) or polar (VI) electronic arrangements:



When molecules are placed in an alternating electromagnetic field having large wavelengths compared to the sizes of the molecules, the induced oscillations of the electrons will be proportional to the polarizability of the molecules. In the electronically excited states produced by the absorption of light energy, there are oscillations within the molecule of the same character as shown in VI. The light absorption of the molecules causes them to change from a ground state to an ionic, electronically excited state. Ultraviolet light absorption spectra of compounds can serve as a basis for comparing the electronic displacements and structures of their molecules.

The similarities of absorption curves I and IV seem to prove the relatively weak basicity of the azo group. Curve I shows the ultraviolet absorption of azobenzene in 95% ethanol and curve IV the absorption of azobenzene that has been dissolved in 95% ethanol saturated with gaseous HCl. Comparison of the curves would seem to indicate practically no reaction between the azobenzene and the HCl. Since the absorption curves are so much alike, the same electronic oscillations must be present in both samples and apparently, under these conditions, the following reaction does not take place:



The absorption curves of 4-dimethylaminoazobenzene (curve II) and methyl orange (curve III) dissolved in 95% ethanol are very much alike. These curves differ from the azobenzene curves, however (Figure 1), because the electronic oscillations are different. The unshared pair of electrons on the dimethylamino nitrogen can aid in forming a quinonoid structure (VIII and X) with the ring:

- (1) Stieglitz, *J. Am. Chem. Soc.*, **25**, 1117 (1903).
- (2) Hantzsch, *Ber.*, **46**, 1545 (1913).
- (3) Hantzsch and Vogt, *Ber.*, **62**, 968 (1929).
- (4) Brooker, *J. Chem. Educ.*, **18**, 245 (1941).
- (5) Hantzsch and Hilscher, *Ber.*, **41**, 1171 (1908).
- (6) Klotz, Fiess, Ho, and Melody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).
- (7) Luder and Zuffanti, *Electronic Theory of Acids and Bases*, John Wiley, New York, 1946.

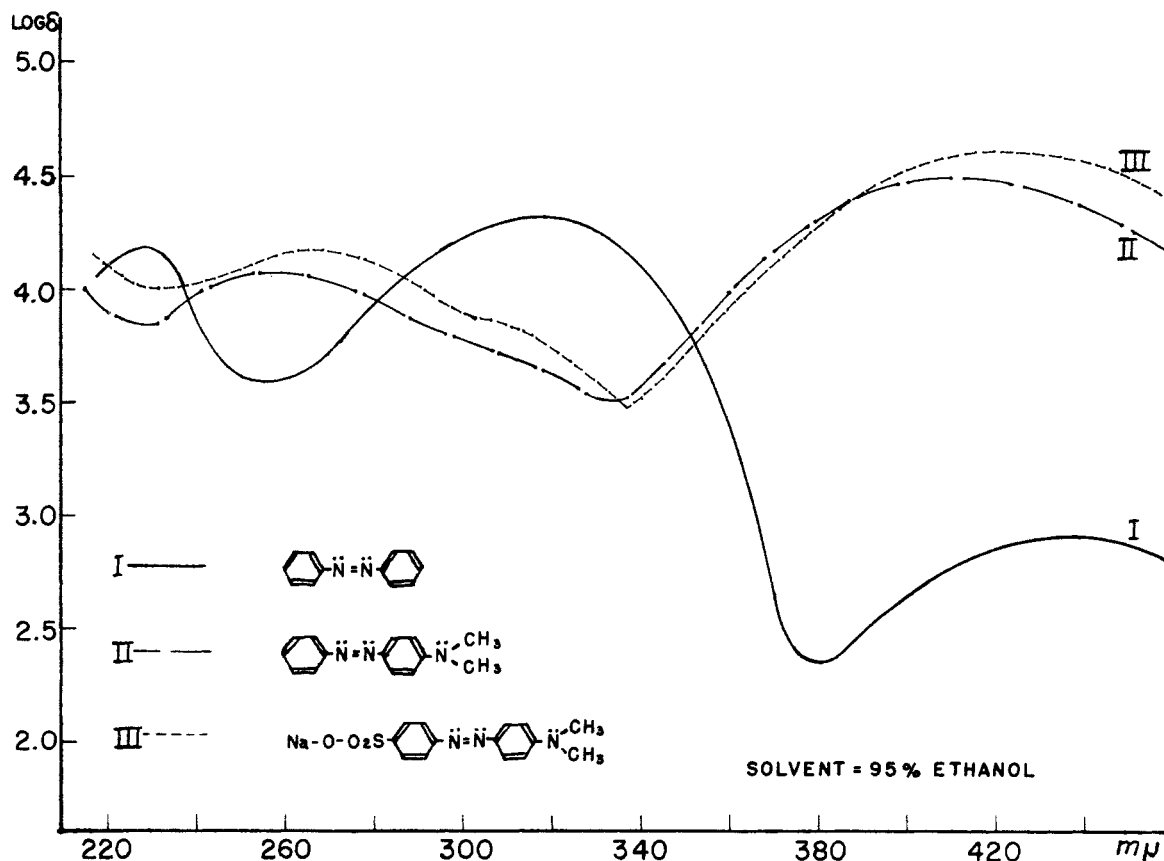
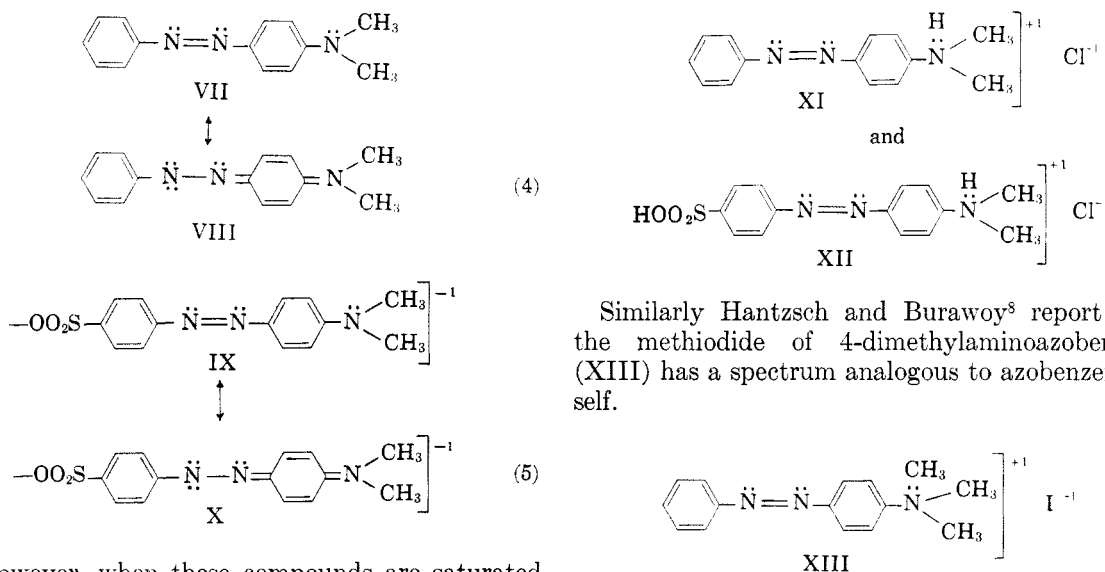
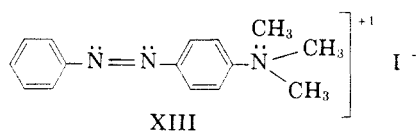


FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA OF AMINOAZOBENZENE DERIVATIVES IN 95% ETHANOL SOLUTION.



Similarly Hantzsch and Burawoy<sup>8</sup> report that the methiodide of 4-dimethylaminoazobenzene (XIII) has a spectrum analogous to azobenzene itself.



However, when these compounds are saturated with HCl and dissolved in 95% ethanol saturated with HCl, the ultraviolet absorption curves (curves V and VI) resemble those of azobenzene itself (Figure 2). A probable explanation is that the proton of the HCl coordinates on the electron pair of the dimethylamino nitrogen (XI and XII) and thus prevents it from forming a quinonoid structure such as VIII and X. These compounds thus would be expected to show light absorption similar to azobenzene.

Here again the resemblance to azobenzene is probably caused by the methyl group of the methyl iodide coordinating with the electron pair of the dimethylamino nitrogen and thus preventing the formation of a quinonoid structure. It would, therefore, be expected that XIII would resemble closely the light absorption of azobenzene.

(8) Hantzsch and Burawoy, *Ber.*, **63**, 1760 (1930).

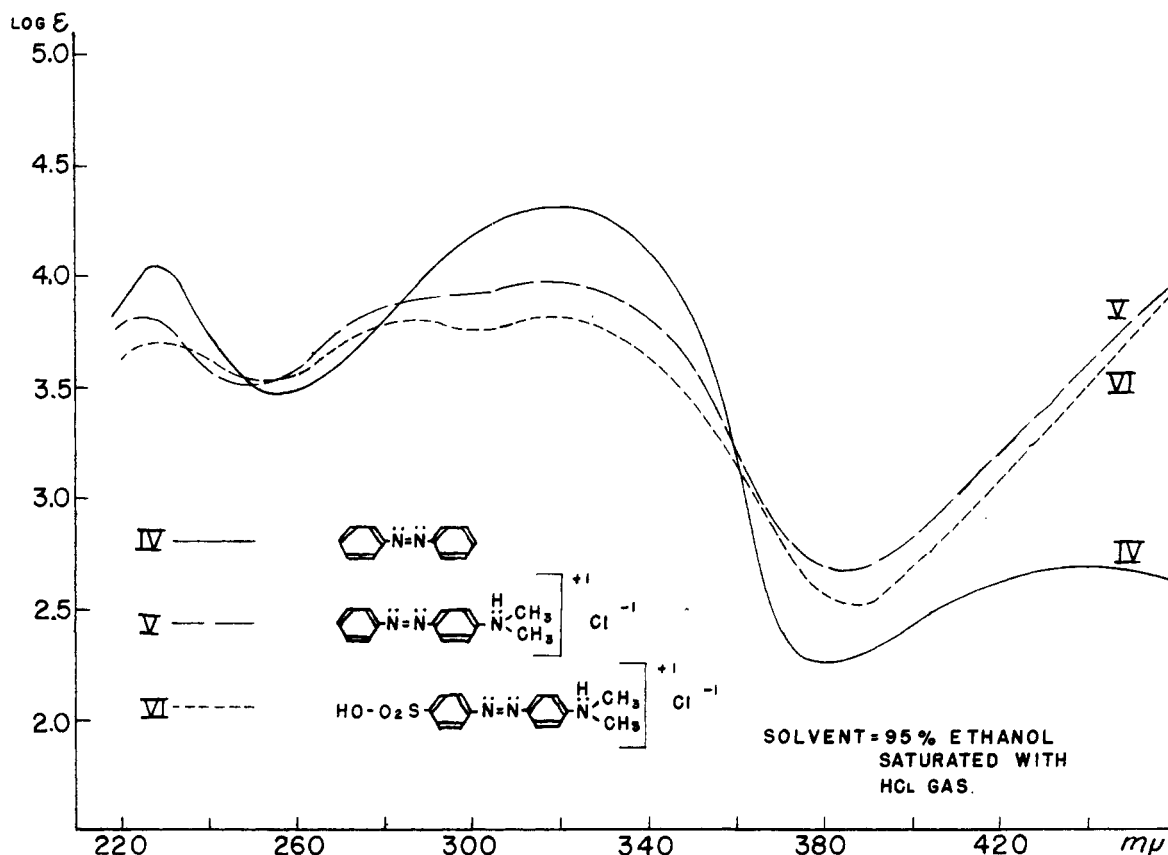


FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRA OF AMINOAZOBENZENE DERIVATIVES IN 95% ETHANOL SATURATED WITH HCl GAS.

In view of (1) the greater basicity of the dimethylamino group as compared to an azo group, and (2) the spectroscopic data furnished, it seems highly probable that when acids react with such aminoazobenzene derivatives, the acid takes a position on the dimethylamino group and not the azo group. Thus, quinonoid structures such as IV are highly unlikely in the presence of strong acids. The reaction of an acid with these dyes should be written as in equation 1 to show the predominating change that occurs.

#### EXPERIMENTAL

*Ultraviolet absorption spectra.* All ultraviolet absorption data were obtained with a Beckman quartz spectrophotometer, model DU, using a 1-cm. quartz cell. A hydrogen discharge tube was used as the ultraviolet source and a tungsten lamp was employed in the visible range. The solvents used

were 95% ethanol and 95% ethanol saturated with gaseous HCl. In using the latter solvent the aminoazobenzene derivatives were first converted to their hydrochlorides before dissolving in the 95% ethanol saturated with HCl. This was necessary to ensure an excess of the HCl.

*Materials.* The azobenzene, 4-dimethylaminoazobenzene, and the methyl orange were purchased from Eastman Kodak Company, catalog numbers 704, 338, and 432 respectively. All compounds were purified by recrystallization.

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