a hydroxy group should resonate more with the ring than an alkoxy group. The greater the resonance, the farther toward the visible lies the absorption. The wave lengths of the 0–0 bands lie in the order $OH > OCH_3 < OC_2H_5 < OC_3H_7$. The intensity of absorption also increases with increased resonance. In Fig. 3 are plotted the extinction coefficients as determined in ethyl alcohol. The order of intensity is $OH > OCH_3 \cong OC_2H_5$.

The extent of resonance determines the ortho-para directing powers toward electrophilic substitution. The ordering given in Gilman[21] is also $OH > OCH_3 < OC_2H_5 < OC_3H_7$.

In diphenyl ether each phenyl group could act as a chromophore. The spectrum of diphenyl ether resembles that of other ethers, from which it may be concluded that the two chromophores are not highly coupled. This is due to the high electronegativity of the oxygen atom.

Summary

1. The near ultraviolet absorption spectra in vapor phase and in solution of some O-substituted phenols and of phenol-*d* have been obtained.
2. The shift to smaller wave number of zero-zero band on deuteration of phenol is explained.
3. The position and intensity of the spectra are discussed in terms of the electronic character of the substituents.

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[21] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 204.

[CONTRIBUTION FROM THE UNIVERSITY OF TEXAS]

The Near Ultraviolet Absorption Spectra of N-Substituted Anilines

BY W. W. ROBERTSON AND F. A. MATSEN

The near ultraviolet absorption spectrum of benzene is due to the excitation of a pi electron from the ground state to a low-lying excited state. The low-lying state arises from the delocalization of six pi electrons among six pi orbitals. The substitution of $-NH_2$ introduces two additional pi electrons and an additional pi orbital which interact with the ring resulting in additional delocalization. As a consequence, the excited state is pushed downward with respect to the ground state[1] and the probability of transition from the latter to the former is increased.[2] The aniline spectrum lies 4055 $cm.^{-1}$ farther toward the visible[1] and is twenty times as intense[2] as is the benzene spectrum. An analysis of the aniline spectrum in terms of fundamental vibrations has been published.[3]

It is to be expected that substitution on the nitrogen atom will modify the spectrum by changing the electronegativity of the nitrogen atom or by making available additional orbitals.

The effect of N-methyl substitution on the spectra of Würster salts[4] has been obtained by Michaelis[5] and co-workers and a theoretical discussion has been given by Mayer and McCallum.[6] It was found that N-methyl substitution intensified the spectrum and shifted it toward longer wave lengths. This was attributed to the lowering of the ionization potential of nitrogen[6] and to the hyperconjugation of the methyl groups with the *p*-phenylenediamine[7] system.

Experimental

The amines, Eastman Kodak Co. "white label," were distilled just before use. The vapor phase spectra were obtained on an Eagle-mounted, three-meter, 15,000 line per inch grating, using Eastman 103-0 plates. Only methyl- and ethylaniline yielded spectra discrete enough to measure accurately and for these a Gaertner comparator was used. A mimeographed table of the band positions, relative intensities and probable assignments for methyl- and ethylaniline may be obtained by writing this laboratory. All plates were scanned with a Leeds and Northrup microphotometer (see Fig. 1). Solution data were obtained on a Beckman quartz spectrophotometer (see Fig. 2).

Discussion

The substitution of complex groups on the benzene ring makes the spectrum more diffuse. In the monoalkyl benzenes[8] and in the O-substituted phenols[9] the diffuseness is due to the broadening of each individual band. In the substituted anilines, however, a continuum moves in from the short wave length side, building up the background but apparently not destroying the discreteness of the individual bands (see Fig. 1). This is probably due to a dissociative state which lies relatively high with respect to the excited state, B_1, in aniline and which is pulled closer to B_1 on substitution. For a discussion of these

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[1] Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[2] Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942).

[3] Ginsburg and Matsen, *J. Chem. Phys.*, **13**, 167 (1945).

[4] Radicals obtained by the mild oxidation of *p*-phenylenediamines.

[5] L. Michaelis, M. P. Schubert and S. Granick, THIS JOURNAL, **61**, 1981 (1939); **65**, 1747 (1943).

[6] M. G. Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942).

[7] R. S. Mulliken, *ibid.*, **14**, 257 (1942).

[8] Matsen, Robertson and Chuoke, *Chem. Revs.*, **41**, 273 (1947).

[9] Robertson, Seriff and Matsen, THIS JOURNAL, **72**, 1539 (1950).

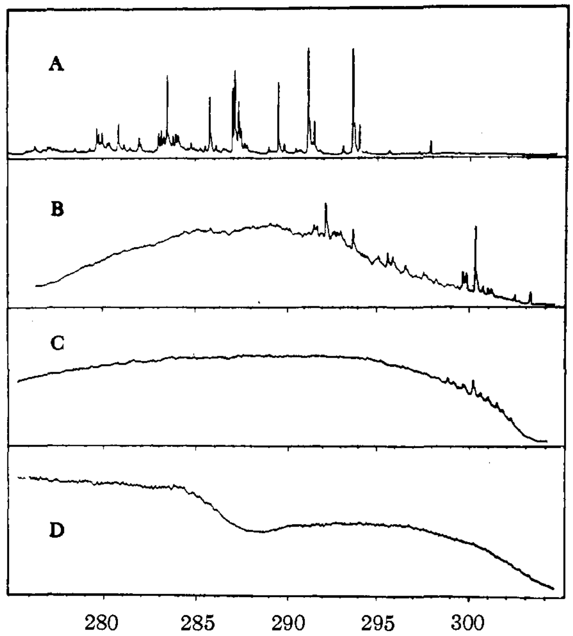

Fig. 1.—Microphotometer tracings of the near ultraviolet absorption spectra of the vapors of (A) aniline, (B) monomethylaniline, (C) ethylaniline, and (D) dimethylaniline.

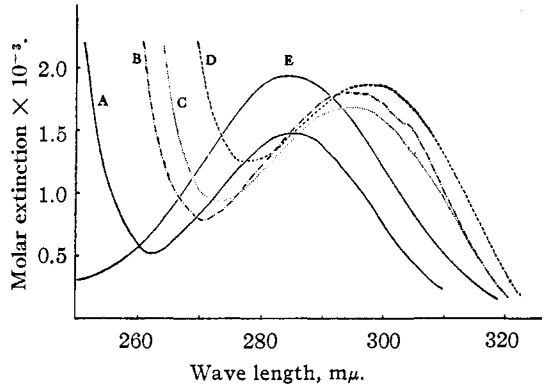

Fig. 2.—Solution absorption spectra of (A) aniline, (B) monomethylaniline, (C) ethylaniline, (D) dimethylaniline, and (E) diphenylamine. The ordinate of the curve for diphenylamine is "molar extinction × 10^{-4}."

higher excited states see reference 10. The solution data (Fig. 2) and work by Platt and Klevens[11] show a rather clean break in the absorption between the 2600 and 2000 Å. region. This may indicate that the dissociative state is stabilized less in solution than is the B_1 state for the equilibrium internuclear distances of the latter. In an attempt to bridge the gap between the solution and the vapor data, the spectrum of dimethylaniline vapor was obtained in the presence of one atmosphere of inert gas and was found to be almost identical with the ordinary vapor data. Equipment was not available to carry out the experiment at higher pressures.

In Table I are given the positions of the zero-zero bands, from the vapor data, and the positions of the maxima of absorption and the value of the maxima from solution data.

TABLE I

Compound	Zero-zero band cm.$^{-1}$	Absorption maximum, mμ	Maximum molar extinction
Aniline	34,032	285	1.5 × 10^3
Ethylaniline	33,300	295	1.7
Methylaniline	33,292	295	1.8
Dimethylaniline	....	298	1.9
Diphenylamine	....	285	19.0

It has been shown that alkyl groups when substituted on the benzene ring produce typical resonance effects (hyperconjugation) and that the methyl group is a more effective hyperconjugator than is the ethyl group.[8] Table I shows that alkyl groups have qualitatively the same effect when substituted on aniline. In the preceding paper[9] it is shown that when alkyl groups are substituted on phenol, the order of resonance is $OH > OCH_3 < OC_2H_5$. It is believed that the lower electronegativity of the nitrogen atom as compared to oxygen permits the alkyl group orbitals to couple with the aniline states to a greater extent than with the phenol states.

Diphenylamine, while having a very high extinction coefficient, lies at shorter wave lengths than do the other substituted anilines. Since diphenylamine contains two chromophoric groups which are coupled to some extent because of the low electronegativity of nitrogen, it seems probable that a different kind of excited state is involved in the diphenylaniline spectrum[12] than in that of aniline.

Summary

1. The vapor and solution spectra of some N-substituted anilines have been obtained.

2. Evidence is presented for a low-lying dissociative state in N-substituted anilines.

3. The ability of N to pass hyperconjugation and 1st order conjugation effects is demonstrated.

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(10) Nordheim, Sponer and Teller, *J. Chem. Phys.*, **8**, 455 (1940).

(10) Klevens and Platt, THIS JOURNAL, **71**, 1714 (1949).

(12) It was at first believed that this band corresponded to the 2000 Å. band in the monophenyl systems and which had moved into the 2600 Å. region for the diphenyl compounds. This concept was abandoned when no absorption could be detected at longer wave lengths even with high pressures or high concentrations.