[CONTRIBUTION FROM THE UNIVERSITY OF TEXAS]

The Effect of O-Deuteration and O-Substitution on the Ultraviolet Absorption Spectrum of Phenol

BY W. W. ROBERTSON, A. J. SERIFF[1] AND F. A. MATSEN

The well-known 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[2] of six pi electrons among six pi orbitals. The substitution of –OH introduces two additional pi electrons and an additional pi orbital which interact with the ring, resulting in additional delocalization. As a consequence, it turns out that the excited state is pushed downward with respect to the ground state[3] and the probability of transition from the latter to the former is increased.[4] The phenol spectrum lies 1739 cm.$^{-1}$ farther toward the visible[3] and is about fifteen times as intense[4] as the benzene spectrum. An analysis of the phenol spectrum in terms of fundamental vibrations has been published.[5]

Replacement of hydrogen by deuterium shifts the vibrational frequencies and also the position of the 0–0 band by virtue of changes in the zero point energy. Substitution on the oxygen atom will in addition modify the spectrum by changing the electronegativity of the oxygen atom and/or by making available additional orbitals.

Experimental

The near ultraviolet absorption spectra of the vapors of deuterophenol and the phenyl ethers were taken on a modified Eagle type spectrograph having an inverse linear dispersion of about 2.75 Å./mm. and a theoretical resolving power of 120,000. A 5000-volt, 2.5-kva Hanovia hydrogen discharge tube was the source of continuous radiation. The degree of development of the spectra was controlled by varying the length of the absorption cell and the temperature of the sample in a side-arm reservoir. The vapor spectra were recorded on Eastman 103-0 plates. Solution spectra were obtained with a Beckman quartz spectrophotometer.

The preparation of deuterophenol by an exchange reaction between phenol and heavy water (D_2O) is described in outline by Williams, Hofstadter and Herman.[6] The D_2O, a product of Stuart Oxygen Co., was 99.9% pure. The phenol, a product of the National Aniline and Chemical Company marked "absolutely pure," was distilled in vacuum just before use. Several successive exchanges and separations were carried out in all-glass evacuated systems. Mass spectrographic analysis of the product showed an effective deuteration of approximately 90%, with no apparent ring deuteration.

The anisole, phenetole, *n*-propyl phenyl ether, *n*-butyl phenyl ether, and diphenyl ether were Eastman Kodak Co. "white label" materials and were redistilled in a meter-long packed column.

The frequencies of the bands reported are the critical averages of measurements made on several plates of different degrees of development of the spectra. The comparator measurements of the spectra in phenol-d and anisole were made with the hair-line of the microscope set at the center of the absorption band for narrow bands and against the violet edge of the broader bands. The frequencies of the sharper bands should be accurate to within 0.3 wave number in the phenol-d spectrum and about 0.5 wave number in the more diffuse anisole spectrum.

The diffuse nature of the spectra of phenetole, *n*-propyl phenyl ether, *n*-butyl phenyl ether, and diphenyl ether prohibits accurate determinations of the frequencies of individual bands by comparator measurements on the spectrographic plates. The frequencies that are reported were obtained by locating the centers of the absorption peaks on microphotometer tracings of the spectra. Identical tracings were taken with the iron comparison spectrum lightly superimposed on the absorption spectra and the positions of the centers of the bands located on the first set were transferred to the second set and their wave lengths determined by interpolation between the known wave lengths of the iron lines. The higher frequency bands were more diffuse than those of lower frequencies in such a manner as to suggest predissociation since most of the bands seem to develop unsymmetrically, the development being stronger on the red side, the determination of the frequency of the bands in the above manner might result in consistently low values with respect to the true vibrational frequencies in the molecule.

The bands of phenetole corresponding to ground state frequencies were sharp enough to measure with the comparator and can be taken as accurate within about two wave numbers.

Vibrational Analysis

Deuterophenol.—The substitution of deuterium for the hydrogen atom attached to the oxygen in phenol results in spectroscopic changes that should be associated with the mass change alone, the electronic structure remaining unaffected.

The complete near ultraviolet electronic spectrum of phenol-*d* has been obtained and the vibrational analysis has been carried out.[7] Since the spectrum is very similar to that of phenol, which has been published,[5] only the fundamental frequencies are presented here (Table I).

An interesting feature of the spectra is the split of the 0 + 783 band of phenol (mode 12, symmetry A_1, Wilson notation) into two bands in phenol-*d* of frequencies 0 + 772 and 0 + 789. From Figs. 1 and 2 the relative changes in the intensities of the 0 + 783 phenol band and the two corresponding phenol-*d* bands are seen to be such as to indicate that the intensities of the two phenol-*d* bands are derived from the one phenol band. That the splitting is due to a repulsion between two levels is indicated by the fact that one of the frequencies in phenol-*d* is

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[2] Mulliken, *J. Chem. Phys.*, **7**, 353 (1939).

[3] Herzfeld, *Chem. Rev.*, **41**, 233 (1947).

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

[5] Matsen, Robertson and Ginsburg, *J. Chem. Phys.*, **13**, 309 (1945).

[6] Williams, Hofstadter and Herman, *ibid.*, **7**, 802 (1939).

[7] See Master's Thesis, A. J. Seriff, The University of Texas, 1947. The wave lengths, wave numbers, relative intensities and vibrational assignments of the measurable bands in this spectrum are available in mimeograph form.

TABLE I

(a) EXCITED STATE FREQUENCIES[a]

Suggested normal mode (Wilson's notation)	C_6H_5OH	C_6H_5OD	$C_6H_5OCH_3$	$C_6H_5OC_2H_5$	$C_6H_5OC_3H_7$	$C_6H_5OC_4H_9$	$C_6H_5OC_6H$
	39 s	37 s					
	207 ms			155 w	134 w		
	373 m	370 m	366 w	340 w			
6a	474 vs	471 s					
12	783 vvs	772 vs	758 vs				
		789 vs		760 vs	750 s	744 m	750 s
1	934 vvs	933 vvs	932 vs	940 vs	942 vs	939 vs	910 s
18a	974 s	959 s	952 s				
7a	1272 s	1268 s	1269 m	1255 m	1275 ms	1270 w	1250 m
0–0	36,352.9	36,349.8	36,388.6	36,352 ± 2	36,321 ± 2	36,307 ± 2	36,300 ± 15

(b) GROUND STATE FREQUENCIES[a]

C_6H_5OH	C_6H_5OD	$C_6H_5OCH_3$	$C_6H_5OC_2H_5$
64 vs	51 vs	55 m	49
		64 ms	
224 s	224 s	228 m	
248 m	248 m		345
401 ms	396 m		468
529 ms	522 ms	554 ms	590
814 w	806 w	788 m	801
826 m	821 w		
1002 w	1000 w	999 m	1000

[a] The values given are with respect to the short wave length component of the zero–zero doublet. The intensities are designated as w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, vvs = very very strong. For comparison with frequencies from other monosubstituted benzenes see Ginsburg, Robertson and Matsen, *J. Chem. Phys.*, 14, 511 (1946), and Hirt Howe, *ibid.*, 16, 480 (1948).

higher by 6 cm.$^{-1}$ than the corresponding phenol band. The splitting of the 0 + 783 band could not be the result of the removal of a degeneracy in the vibrational frequencies of phenol by a reduction in the symmetry of the molecule because the deuteration does not affect the symmetry and there are no degenerate representations in the C_{2v} symmetry group, which is the effective symmetry of phenol.[3] The two phenol-*d* bands are not the result of an accidental degeneracy between a fundamental and an overtone of a fundamental of any modes which were detected and assigned.

The splitting probably results from an accidental degeneracy between vibrational mode 12 and either another totally symmetric fundamental or the first overtone of a non-totally symmetric fundamental. Although there has been only one excited state fundamental reported in the neighborhood of 800 for other monosubstituted benzenes, it is recognized that not all the totally symmetric modes are excited in this electronic transition. However, in phenol there are two ground state frequencies 811 and 824, of symmetry A_1, which might possibly become accidentally degenerate in the excited state. Nothing is known about the non-totally symmetric excited state frequencies.

The two bands 0 + 561 and 0 + 1563 were assigned as fundamentals in the phenol spectrum on the basis of intensity considerations,[5] being thought too intense to be the combination bands 0 + 783 − 222 and 0 + 2 × 783. In the phenol-*d* spectrum, however, these bands are double with the same separation as is found for the 783 cm.$^{-1}$ band, indicating that the 561 cm.$^{-1}$ and 1563 cm.$^{-1}$ bands are not fundamentals but are 783 combination bands. The vibrational analysis of the phenol spectrum was thus actually carried out with only seven excited state frequencies rather than the nine that were reported.

The reassignment of the 0 + 561 band in phenol is of significance since there are no other unassigned bands in the proper region to correspond to the 6b mode of vibration. The degenerate ϵ_g^+ vibration of D_{6h} symmetry that makes the benzene spectrum allowed divides in C_{2v} symmetry into the totally symmetrical 6a and the non-totally symmetrical 6b vibrations. The 6b vibration was reported in chlorobenzene[8a] and in toluene,[8b] where the mechanism which brought the benzene spectrum into being might be expected to remain of importance due to the relatively low perturbation of the ring by the substituents. In the cases of phenol and anisole (and also possibly in the case of aniline[9]) the much higher perturbing effects of the substituents on the ring results in spectra that have the character of completely allowed spectra and the band corresponding to the 6b mode of vibration in each case does not occur with sufficient intensity to be recognized.

The doublet structure of the phenol-*d* bands seems to be slightly more pronounced than that of the phenol bands. This effect might not be real since there was a difference in density and contrast between the two sets of spectrographic plates.

From Fig. 1 it can be seen that the 1–1 transition listed as 0 + 37 in phenol-*d* is much more intense than the 0 + 39 band in phenol. This effect might be explained in terms of the Franck–

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(8) (a) Sponer and Wollman, *J. Chem. Phys.*, **9**, 816 (1941); (b) Ginsburg, Robertson and Matsen, *ibid.*, **14**, 511 (1946).

(9) Ginsburg and Matsen, *ibid.*, **13**, 167 (1945).

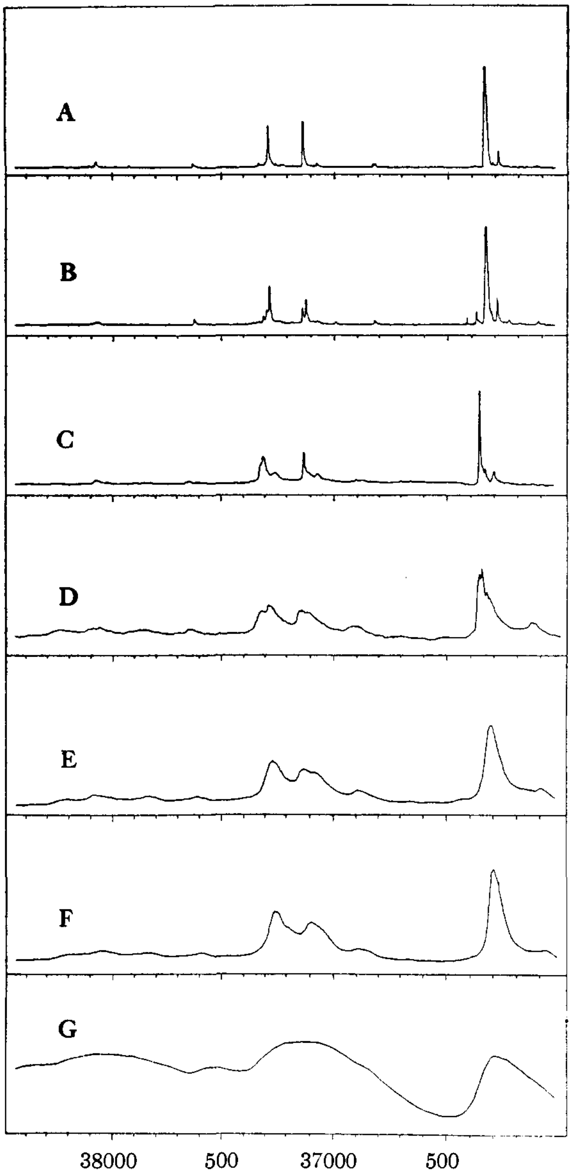

Fig. 1.—Microphotometer tracings of the near ultraviolet absorption spectra of the vapors of (A) phenol, (B) phenol-*d*, (C) anisole, (D) phenetole, (E) *n*-propyl phenyl ether, (F) *n*-butyl phenyl ether and (G) diphenyl ether. The scale is in wave numbers.

Condon principle, the shifts of the vibrational levels involved in the ground and excited states producing a better alignment of turning points and a consequent higher transition probability.

Anisole.—About 150 bands have been measured in the near ultraviolet absorption spectrum of anisole.[7] The strongest band of the spectrum, a well-resolved doublet at 36385.8 and 36388.6 cm.$^{-1}$, was designated as the 0–0 band. The fundamental frequencies were chosen on the basis of intensity and combining power.

The spectrum can be fairly completely analyzed on the basis of the four ground state frequencies 229, 554, 788 and 999 (corresponding to the Raman frequencies 210, 530, 783 and 991 cm.$^{-1}$)[10] the three excited state frequencies 758, 952 and 1269, and the two difference frequencies 0–64 and 0–228. All of these bands occur strongly and combine well.

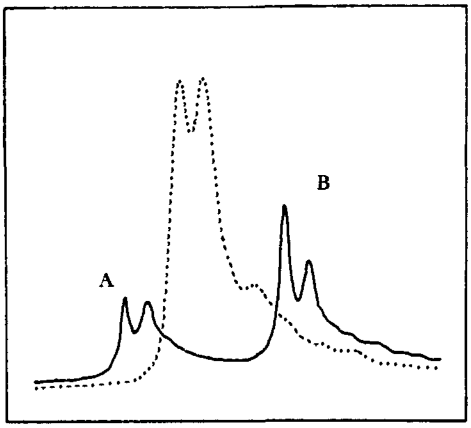

Fig. 2.—Microphotometer tracings of the 0 + 783 band of phenol and of the 0 + 772 (B) and 0 + 789 (A) bands of phenol-*d*.

The two additional excited state frequencies 0 + 366 and 0 + 932 are designated as fundamentals. The 0 + 366 band is considerably stronger than any other band in its region of the spectrum, it cannot be explained as a combination of the above listed fundamentals, and it corresponds well to the fundamentals 0 + 373 in phenol and 0 + 370 in phenol-*d*. The corresponding ground state frequency might be the weak band 0–441 corresponding to the Raman frequency 441.[10] The 0 + 366 band is therefore listed as a fundamental even though it does not occur in combination with the other fundamentals.

The three strong bands at 0 + 929, 0 + 932, and 0 + 936 appear to be components of a single band. Corresponding triplet bands are found in aniline (950, 953, 957),[9] toluene (929, 931, 933)[8b] phenol (931, 934, 937),[5] and phenol-*d* (931, 933, 938), where the bands occur strongly and combine well. This band in toluene was assigned as the normal mode 1. It would be expected that the same assignment would hold in the other compounds listed above. However, in anisole no combination of this band with any of the other fundamentals occurs. No explanation for the absence of combination bands is offered, but on the basis of the discussion above, the band is listed as the fundamental 0 + 932.

From Fig. 1 it will be seen that the spectra of the remaining compounds become less discrete as the substituent becomes more complex. Because of this, precise measurements could not be made nor detailed analysis carried out for the higher members of the series.

(10) Kohlrausch and Pongratz, *Monatsh.*, **65**, 6 (1934).

Position of 0–0 Bands.—Listings of the 0–0 bands and the identified and tentatively identified fundamentals and important difference frequencies are given in Table I.

All 0–0 electronic bands contain a contribution from zero point energy differences in the excited and ground states.

$$\nu_{00} = \frac{\Delta E}{hc} + \frac{1}{2}\sum_{i=1}^{n} (\nu_i' - \nu_i'')$$

where ΔE is the energy difference between the two electronic levels and ν' and ν'' are the frequencies of mode i in the excited and ground states. The summation extends over the n normal modes. The location of the zero–zero bands may be discussed in terms of a mass effect and an electronic effect:

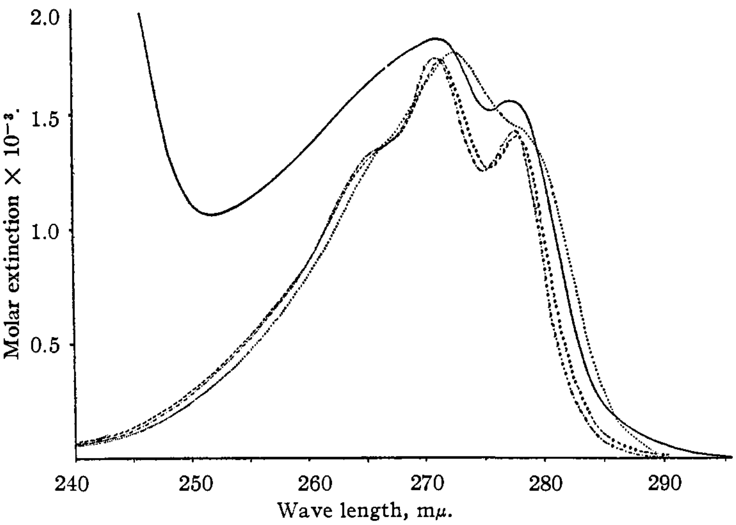

Fig. 3.—Solution absorption spectra of diphenyl ether, ——; phenol, ...; anisole, –·–·–; and phenetole, ------.

(a) Mass Effect.—To a good approximation ΔE does not change on deuteration. Then the isotopic shift of the zero–zero band becomes

$$\nu_{00} - \nu_{00}^{\mathrm{D}} = {}^1/_2 \sum_{i=1}^{n} [(\nu_i' - \nu_i'^{\mathrm{D}}) - (\nu_i'' - \nu_i''^{\mathrm{D}})] = \frac{1}{2}\sum_{i=1}^{n} \Delta_i$$

Sponer and Teller[11] state that as a general rule isotopic substitution moves the zero–zero band to higher frequencies, *i. e.*, $\nu_{00} - \nu_{00}^{\mathrm{D}}$ negative. For comparison

$\nu_{00}(C_6H_6) - \nu_{00}(C_6D_6) = -202$ cm.$^{-1}$ [12]
$\nu_{00}(C_6H_6) - \nu_{00}(C_6H_5D) = -34$ cm.$^{-1}$ [13]
$\nu_{00}(C_6H_5CH_3) - \nu_{00}(C_6H_4DCH_3$ – ortho$) = -35$[14]
$\nu_{00}(C_6H_5CH_3) - \nu_{00}(C_6H_4DCH_3$ – meta$) = -33$
$\nu_{00}(C_6H_5CH_3) - \nu_{00}(C_6H_4DCH_3$ – para$) = -33$
$\nu_{00}(C_6H_5CH_3) - \nu_{00}(C_6H_5CH_2D) = -9$

While from this research

$$\nu_{00}(C_6H_5OH) - \nu_{00}(C_6H_5OD) = +3$$

which indicates that some of the Δ_i must be positive.

It must be concluded that one (or more) of the force constants in the molecule has increased on electronic excitation. An increase in force constant on electronic excitation has recently been demonstrated.[15] It was shown that the C–H stretching constant in benzene increased from 5.06 to 5.35 × 10^5 dynes per centimeter. On electronic excitation, this increase makes the zero point energy contributions of the C–H stretching modes greater in the excited state than in the ground state and yields positive Δ_i's. It appears that in phenol-*d* positive Δ_i's must predominate.

It is to be expected that the mass effect of the other types of substituents considered in this paper will also be small. In previous studies on alkyl[16] and chloroalkyl[17] benzenes a small increase in wave length with increase in mass of substituent has been noted. This shift is of opposite sign to the $C_6H_5CH_3$–$C_6H_5CH_2D$ shift quoted earlier. Work on substituent deuterated alkyl benzenes now in progress in this Laboratory may give more information on this point.

(b) Electronic Effect.—The variations in ΔE in the above equation depend primarily on the variations in the resonance interaction of the substituent with the ring. For the compounds studied in this paper the interaction involves the unshared pair of electrons in the O-atom of the substituent.

The shifts in the series studied here are such as to indicate that the oxygen atom does not transmit hyperconjugation effects to the ring. This is believed to be due to the relative high electro-negativity of the oxygen atom. Brode[18] has referred to oxygen as an insulator toward resonance effects. Nitrogen, with a lower electronegatvity, does transmit these effects.[19] The effects which are found in the phenol series are small and correlate with available information on bond moments.

The bond moment of an OH bond is 1.5*D* (33% ionic character) while that of an OC bond is 0.8*D* (12% ionic character).[20] This indicates that the oxygen has a higher electron density when a hydrogen is attached than when an alkyl group is attached. It would seem probable that

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(11) Sponer and Teller, *Rev. Mod. Phys.*, **13**, 106 (1941).

(12) Sponer, *J. Chem. Phys.*, **8**, 705 (1940).

(13) Beck and Sponer, *ibid.*, **10**, 575 (1942).

(14) Choppin and Smith, THIS JOURNAL, **70**, 577 (1948).

(15) Garforth, Ingold and Poole, *J. Chem. Soc.*, 491 (1948).

(16) Matsen, Robertson and Chuoke, *Chem. Rev.*, **41**, 273 (1947).

(17) Hamner and Matsen, THIS JOURNAL, **70**, 2482 (1948).

(18) Brode, "Chemical Spectroscopy," John Wiley and Sons, New York, N. Y.

(19) Robertson and Matsen THIS JOURNAL, **72**, 1543 (1950).

(20) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 22.

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

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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).