The Vacuum Ultraviolet Absorption Spectra of Aniline and Some of Its N-Derivatives

By Katsumi KIMURA,* Hiroshi TSUBOMURA* and Saburo NAGAKURA

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Concerning the effect of substituent groups upon the electronic spectrum of benzene, a number of theoretical and experimental studies have already been carried out.[1-17] This effect may be discussed from two different viewpoints: one of them is the wavelength shift and the intensity change of the bands pertinent to the benzene molecule, and the other is the appearance of an additional new band caused by the charge-transfer interaction between the

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* Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

1) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1949).
2) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
3) S. Nagakura and H. Baba, ibid., **74**, 5693 (1952).
4) I. Fischer, *Ark. Fys.*, **5**, 377 (1952); I. Fischer-Hjalmars, ibid., **21**, 123 (1962).
5) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).
6) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).
7) Y. I'Haya, *J. Am. Chem. Soc.*, **81**, 6120, 6127 (1959).
8) H. Baba, This Bulletin, **34**, 76 (1961).
9) N. Mataga, ibid., **36**, 1607 (1963).
10) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955).
11) J. Tanaka, This Bulletin, **36**, 833 (1963).
12) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).
13) S. Nagakura, *Pure and Applied Chem.*, **7**, 79 (1963); S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectroscopy*, **13**, 174(1964).
14) J. N. Murrell, *Tetrahedron*, **19**, Suppl. **2**, 277 (1963).
15) T. E. Peacock, *Mol. Phys.*, **3**, 453 (1960).
16) J. E. Bloor and F. Peradejordi, *Theoret. Chim. Acta*, **1**, 83 (1962); J. E. Bloor, *Canad. J. Chem.*, **39**, 2256 (1961).
17) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **46**, 1314 (1963).

substituent groups and the benzene ring. The latter band is called an intramolecular charge-transfer or electron-transfer band. Since 1954, the latter phenomenon has been studied by one of the present authors and Tanaka, by Longuet-Higgins and Murrell and by others;[11-15] the intramolecular charge-transfer band has been observed with such substituted benzenes as nitrobenzene, benzoic acid, and *p*-nitroaniline.

Concerning aniline, Nagakura and Tanaka[10] first pointed out the possibility of an intramolecular charge-transfer band for the 235 mμ band. Murrell[12] studied this problem theoretically in detail and assigned the 235 mμ band to an intramolecular charge-transfer band whose transition is accompanied by an electron transfer from the amino group to the benzene ring. In addition, several authors have made quantum mechanical considerations of this problem by various kinds of approximate methods.

Their results are not always consistent with each other in the interpretation of the 235 mμ band of aniline. For instance, some authors interpret this band as the shifted band of the 200 mμ band of benzene. In order to determine which of the two interpretations is correct and, moreover, in order to obtain accurate knowledge about the π-electron structure of aniline, the experimental data of vacunm ultraviolet absorption spectra corresponding to higher-energy transitions are undoubtedly important. In spite of this, only a few experiments of absorption spectra in the vacuum ultraviolet have hitherto been carried out with aniline and its derivatives, although Klevens and Platt have measured absorption spectra for aniline, *N*-methylaniline and *N*, *N*-dimethylaniline in heptane solutions in the 1700~2300 Å region.[18]

Under these circumstances, we undertook to extend absorption measurements down to 1500 Å for aniline and some members of its *N*-derivatives in the vapor phase, using a recording vacuum ultraviolet spectrophotometer. In doing so, we succeeded in finding some new absorption bands in the vacuum ultraviolet region and in confirming the appearance of the intramolecular charge-transfer band. Furthermore, we could obtain more reliable knowledge than before about the π-electron structures of aniline and its derivatives by combining the present experimental results with theoretical considerations.

Experimental

Absorption measurements for aniline and its *N*-derivatives were carried out in the vapor phase at room temperature. A recording vacuum ultraviolet spectrophotometer constructed in our laboratory was used for the measurements in the region from 1500 to 2200 Å, the apparatus using a Bausch and Lomb concave grating with a radius of 995.4 mm. The details of this apparatus have been published elsewhere.[19] Gas cells with paths 10 and 30 mm. long and with lithium fluoride windows were used.

The compounds studied were aniline, *N*-methylaniline, *N*-ethylaniline, *N*, *N*-dimethylaniline, *N*, *N*-diethylaniline, and *N*-*n*-butylaniline. The commercial materials of these compounds were fractionally distilled in a vacuum glass line, and the vapor of the purified samples was transferred through it into the gas cell for absorption measurements. The vapor pressure was measured with an accuracy of ±0.02 mmHg by using a mercury manometer with a travelling microscope attached. Spectra were carefully measured for different vapor pressures under the same optical conditions. Absorption measurements in the quartz region over 1900 Å were also carried out with a Cary spectrophotometer Model 14 M, a gas cell 10 cm. long being used. A comparison between the absorption spectra taken with the two apparatus in the overlap region of wavelength gave us an opportunity to check the accuracy of the intensity measurements made by means of our vacuum ultraviolet spectrophotometer.

The vapor phase spectum of benzene was also taken in the region over 1500 Å; it gives reference data for interpreting the electronic spectra of the anilines reported here. The *N*-*n*-butylaniline spectrum was measured only in the region over 2000 Å, because its vapor pressure at room temperature is too low to measure a vacuum ultraviolet spectrum with the gas cells employed in the vacuum apparatus.

Experimental Results

Our measurement for benzene indicated that the wavelengths of the three absorption peaks in the vapor phase are: 1776 Å (6.98 eV.) for the $^1A_{1g}\rightarrow{}^1E_{1u}$ transition, 2008 Å (6.17 eV.) for the $^1A_{1g}\rightarrow{}^1B_{1u}$ transition, and 2534 Å (4.89 eV.) for the $^1A_{1g}\rightarrow{}^1B_{2u}$ transition,[20] with oscillator strengths of 1.035, 0.126, and 0.01 respectively.

The absorption spectra of the anilines observed in the present work are shown in Fig. 1. The spectra show five characteristic bands near

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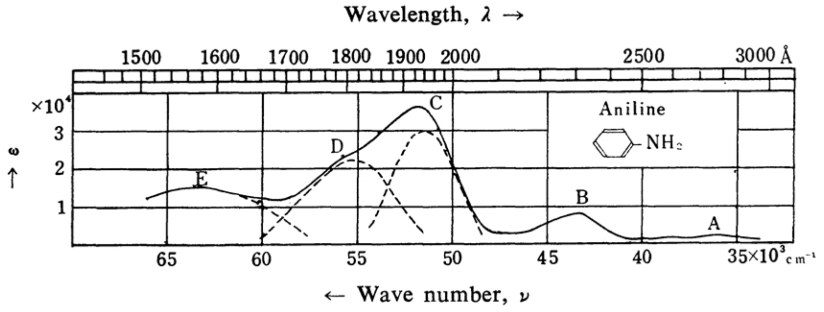
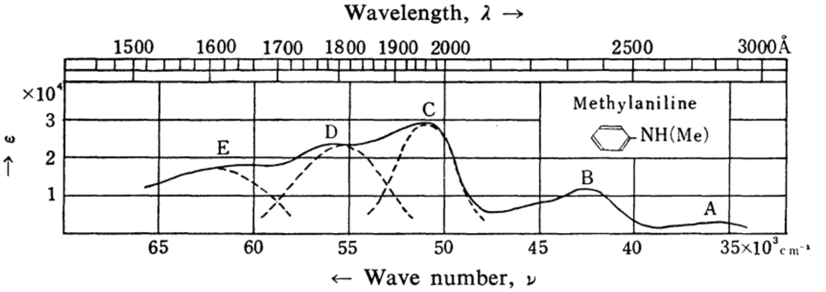
[18] H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, 71, 1714 (1949); Technical Report of the Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago (1954-1955).

[19] H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, 37, 417 (1964).

[20] The $A_{1g}\rightarrow B_{1u}$ and $A_{1g}\rightarrow B_{2u}$ absorptions are accompanied with vibrational structures. The above-mentioned peak wavelength values for these absorptions were taken from the position of the strongest maximum for each absorption. Klevens and Platt[18] determined the $A_{1g}\rightarrow E_{1u}$, $A_{1g}\rightarrow B_{1u}$ and $A_{1g}\rightarrow B_{2u}$ transition energies to be 6.74, 6.14, and 4.89 eV. respectively by measuring the benzene spectrum in a heptane solution.


Wavelength, λ →
1500
1600
1700
1800
1900
2000
2500
3000 Å
×10⁴
3
2
1
ε ↑
Aniline
-NH₂
A
B
C
D
E
65
60
55
50
45
40
35×10³ cm⁻¹
← Wave number, ν


Wavelength, λ →
1500
1600
1700
1800
1900
2000
2500
3000Å
×10⁴
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2
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ε ↑
Methylaniline
-NH(Me)
A
B
C
D
E
65
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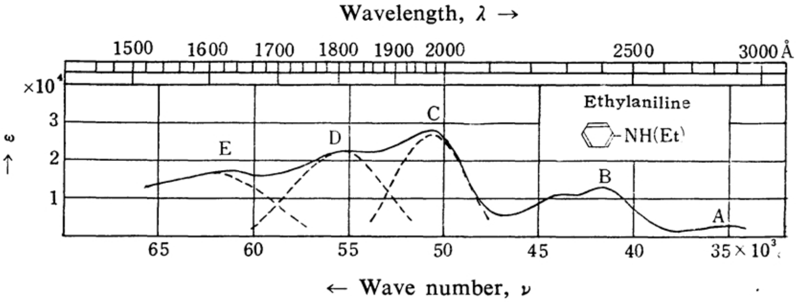
55
50
45
40
35×10³ cm⁻¹
← Wave number, ν


Wavelength, λ →
1500
1600
1700
1800
1900
2000
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3000 Å
×10⁴
3
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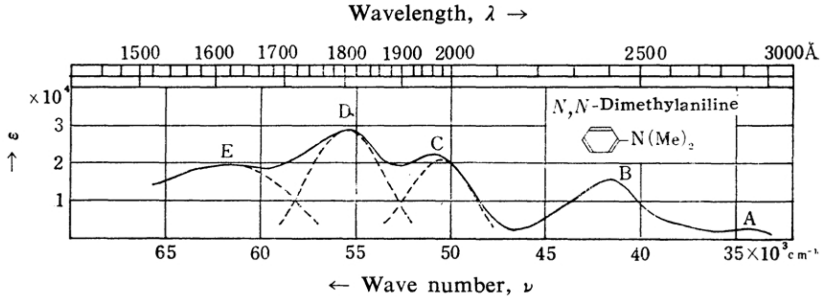
1
ε ↑
Ethylaniline
-NH(Et)
A
B
C
D
E
65
60
55
50
45
40
35×10³
← Wave number, ν


Wavelength, λ →
1500
1600
1700
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1900
2000
2500
3000Å
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3
2
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ε ↑
N,N-Dimethylaniline
-N(Me)₂
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B
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45
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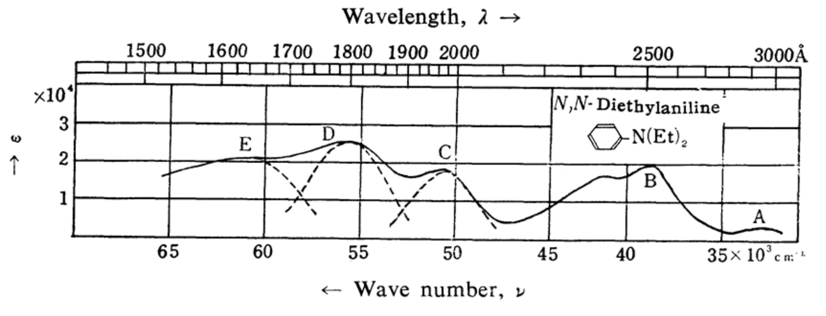
35×10³ cm⁻¹
← Wave number, ν


Wavelength, λ →
1500
1600
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ε ↑
N,N-Diethylaniline
-N(Et)₂
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C
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35×10³ cm⁻¹
← Wave number, ν

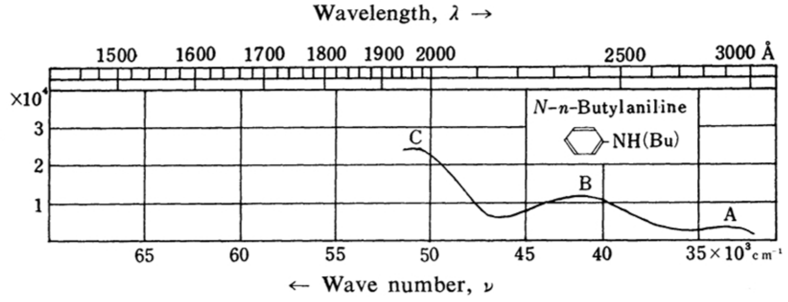

Fig. 1. Ultraviolet absorption spectra of aniline, *N*-methylaniline, *N*-ethylaniline, *N*, *N*-dimethylaniline, *N*, *N*-diethylaniline, and *N*-*n*-butylaniline. The A and B bands of aniline have vibrational structures which are neglected in this figure.

2850, 2350, 1950, 1800, and 1600 Å ; they are designated as A, B, C, D and E respectively. Among these bands, the C and D bands are superposed to a considerable extent. The resolution of these two bands is made under the assumption that the curves of these bands are approximately of the Gaussian type and that the C bands and the D bands have the same half-widths.

The experimental oscillator strengths, f, were computed from the integral areas under the curves by the following equation:

$$f=4.32\times10^{-9}\int\varepsilon d\nu \qquad (1)$$

where ε is the molar extinction coefficient and ν is the frequency in cm^{-1}. Table I summarizes the experimental results concerning the peak wavelengths, the molar extinction coefficients, the transition energies, and the oscillator strengths for the anilines.

It may be seen from Fig. 1 and Table I that the spectral feature changes in the following order:21)

$$\text{Ph-NH}_2,\ \text{Ph-NH(Me)},\ \text{Ph-NH(Et)},\ \text{Ph-N(Me)}_2,\ \text{Ph-N(Et)}_2 \qquad (2)$$

The A and B bands show red shifts and increasing f values in the above order, from aniline to *N*, *N*-diethylaniline. On the other hand, the C and D bands, roughly speaking, shift to a small extent to longer wavelengths with appreciably decreasing f values and the differences in the absorption intensity between the C and D bands decrease going from aniline to *N*, *N*-diethylaniline. It should also be noticed that the E bands are commonly broad for all the compounds under consideration. This may conceivably show that the E bands are composed of two closely overlapping bands. The above interpretation is supported by the present theoretical consideration, details of which will be described below.

Theoretical

The present method of calculating the π-electron structures of the anilines is essentially based on that presented by Longuet-Higgins and Murrell,12 in particular, on that of the calculation of aniline by Murrell,12) in which the interaction between the two fragments of the benzene ring and the amino group is taken into account by configurational interaction among the ground, charge-transfer and locally excited configurations.

Although no detailed structural data of the anilines, even of the aniline molecule itself, have yet been reported, we assumed in the present theoretical treatment that the molecules are coplanar and belong to the symmetry group C_{2v}. In actual calculations, we took seven electron configurations; that is to say, besides the ground configuration, two charge-transfer configurations and four locally-excited configurations. The wave functions and energies for the locally excited configurations corresponding to the $A_{1g}\rightarrow B_{2u}$, $A_{1g}\rightarrow B_{1u}$, $A_{1g}\rightarrow E_{1u}$ excitations of benzene are as follows:

Wave function	Energy, eV.
$\psi_{B_{1u}}=2^{-1/2}\{(\phi_3{}^{-1}\phi_5)-(\phi_2{}^{-1}\phi_4)\}$	4.89
$\psi_{B_{1u}}=2^{-1/2}\{(\phi_3{}^{-1}\phi_4)+(\phi_2{}^{-1}\phi_5)\}$	6.17
$\psi_{E_{1u}}=2^{-1/2}\{(\phi_3{}^{-1}\phi_5)+(\phi_2{}^{-1}\phi_4)\}$	6.98
$\psi_{E_{1u}'}=2^{-1/2}\{(\phi_3{}^{-1}\phi_5)-(\phi_2{}^{-1}\phi_5)\}$	6.98 (3)

where the ϕ_i's are the molecular orbitals of benzene expressed in terms of the six carbon 2pπ atomic orbitals.22) The energy values given

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21) Ph-NH(*n*-Bu) is located at next to Ph-NH(Et) so far as its spectral data in the quartz region is concerned.

22) The six molecular orbitals of benzene are:

$$\phi_1=6^{-1/2}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)$$
$$\phi_2=12^{-1/2}(2\chi_1+\chi_2-\chi_3-2\chi_4-\chi_5+\chi_6)$$
$$\phi_3=2^{-1}(\chi_2+\chi_3-\chi_5-\chi_6)$$
$$\phi_4=2^{-1}(\chi_2-\chi_3+\chi_5-\chi_6)$$
$$\phi_5=12^{-1/2}(-2\chi_1+\chi_2+\chi_3-2\chi_4+\chi_5+\chi_6)$$
$$\phi_6=6^{-1/2}(\chi_1-\chi_2+\chi_3-\chi_4+\chi_5-\chi_6).$$

TABLE I. EXPERIMENTAL AND THEORETICAL RESULTS FOR ANILINE AND ITS *N*-DERIVATIVES
(Energies are given in eV.)

Aniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2817	1500	4.40	4.72	0.028	0.021	$W_0 \rightarrow W_1$
B	2299	8000	5.39	5.42	0.140	0.174	$W_0 \rightarrow W_2$
C	1938	29800	6.40	6.42	0.510	0.416	$W_0 \rightarrow W_3$
D	1800	23000	6.88	6.86	0.570	0.505	$W_0 \rightarrow W_4$
E	1575	15000	7.87	8.04 8.05	(0.68)	0.745 0.416	$W_0 \rightarrow W_5$ $W_0 \rightarrow W_6$

N-Methylaniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2833	2200	4.37	4.66	0.031	0.024	$W_0 \rightarrow W_1$
B	2380	12000	5.20	5.28	0.190	0.179	$W_0 \rightarrow W_2$
C	1960	28000	6.31	6.32	0.478	0.330	$W_0 \rightarrow W_3$
D	1800	22500	6.88	6.85	0.556	0.440	$W_0 \rightarrow W_4$
E	1587	16000	7.80	7.95 7.97	(0.71)	0.826 0.472	$W_0 \rightarrow W_5$ $W_0 \rightarrow W_6$

N-Ethylaniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2857	2300	4.34	4.63	0.048	0.025	$W_0 \rightarrow W_1$
B	2398	13000	5.17	5.22	0.230	0.181	$W_0 \rightarrow W_2$
C	1972	27000	6.28	6.28	0.450	0.304	$W_0 \rightarrow W_3$
D	1800	22200	6.88	6.85	0.530	0.426	$W_0 \rightarrow W_4$
E	1600	16000	7.75	7.92 7.95	(0.77)	0.850 0.475	$W_0 \rightarrow W_5$ $W_0 \rightarrow W_6$

N, *N*-Dimethylaniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2882	2300	4.30	4.61	0.044	0.026	$W_0 \rightarrow W_1$
B	2404	16000	5.15	5.17	0.256	0.182	$W_0 \rightarrow W_2$
C	1980	21000	6.25	6.25	0.350	0.279	$W_0 \rightarrow W_3$
D	1800	28500	6.88	6.85	0.575	0.409	$W_0 \rightarrow W_4$
E	1613	19000	7.68	7.90 7.93	(0.81)	0.875 0.497	$W_0 \rightarrow W_5$ $W_0 \rightarrow W_6$

N, *N*-Diethylaniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2941	4000	4.21	4.55	0.051	0.027	$W_0 \rightarrow W_1$
B	2480	17000	5.00	5.06	0.280	0.186	$W_0 \rightarrow W_2$
C	1980	18200	6.25	6.18	0.318	0.233	$W_0 \rightarrow W_3$
D	1800	25200	6.88	6.84	0.535	0.377	$W_0 \rightarrow W_4$
E	1626	21000	7.62	7.86 7.89	(0.88)	0.920 0.525	$W_0 \rightarrow W_5$ $W_0 \rightarrow W_6$

N-*n*-Butylaniline

	Absorption band		Transition energy		f		Transition
	λ, Å	ε	Obs.	Theoret.	Obs.	Theoret.	
A	2865	4000	4.32	4.63	0.050	0.025	$W_0 \rightarrow W_1$
B	2398	13000	5.17	5.22	0.250	0.181	$W_0 \rightarrow W_2$
C	1975	25000	6.27	6.28	—	0.304	$W_0 \rightarrow W_3$

here are taken from the electronic absorption spectrum data of benzene measured by the present authors. Taking an elelctron from the nonbonding π-orbital of the amino group (θ), and putting it into the lowest vacant orbitals of benzene (ϕ_4 and ϕ_5), we could obtain the two charge-transfer configurations, which might be represented by[23];

$$\phi_{\mathrm{CTa}}=(\theta^{-1}\phi_5) \text{ and } \phi_{\mathrm{CTb}}=(\theta^{-1}\phi_4) \tag{4}$$

the corresponding energies being

$$E_{\mathrm{CTa}}=I-A-Q_1 \text{ and } E_{\mathrm{CTb}}=I-A-Q_2 \tag{5}$$

Here I is the ionization potential of the substituent, A the electron affinity of benzene, Q_1 and Q_2 the electrostatic energies given by;

$$\begin{aligned} Q_1&=1/3\{(\mathrm{C_1C_1/NN})+1/2(\mathrm{C_2C_2/NN}) \\ &\quad+1/2(\mathrm{C_3C_3/NN})+(\mathrm{C_4C_4/NN})\} \\ Q_2&=1/2\{(\mathrm{C_2C_2/NN})+(\mathrm{C_3C_3/NN})\} \end{aligned} \tag{6}$$

The two-center integrals (CC/NN) were calculated by the use of a quadratic equation with the atomic distance r_{CN}:

$$(\mathrm{CC/NN})=0.1922r_{\mathrm{CN}}{}^2-2.502r_{\mathrm{CN}}+10.83 \tag{7}$$

which was derived in the way suggested by Pariser and Parr.[24]** Concerning atomic distances, it was assumed that the C–C distances are the same in benzene (i. e., $r_{\mathrm{CC}}=1.397\,\text{Å}$[25]), and that the distance of the C–N bond is equal to that in 2, 5-dichloroaniline determined recently by an X-ray crystal analysis technique (i. e., $r_{\mathrm{CN}}=1.407$[26]). From this geometry, Q_1 and Q_2 were calculated to be 5.44 and 5.00 eV.

Off-diagonal matrix elements of the total electron Hamiltonian were evaluated by the method of Longuet-Higgins and Murell[12] and also by that of Pople[27] as follows:

$$\begin{aligned} H_{\mathrm{G.CTa}}&=-\frac{2}{\sqrt{6}}(\beta-\beta') \\ H_{\mathrm{CTa.B_{1u}}}&=-\frac{1}{\sqrt{6}}(\beta+\beta') \\ H_{\mathrm{CTa.E_{1u}}}&=\frac{1}{\sqrt{6}}(\beta+\beta') \\ H_{\mathrm{CTb.B_{2u}}}&=\frac{1}{\sqrt{6}}(\beta+\beta') \\ H_{\mathrm{CTb.E_{1u}}'}&=-\frac{1}{\sqrt{6}}(\beta+\beta') \end{aligned} \tag{8}$$

where β is the resonance integral between two atomic orbitals belonging to the nitrogen and adjacent carbon atoms, and β' is that belonging to the nitrogen and ortho-position carbon atoms. The ratio of β' to β was assumed to be equal to that of the corresponding overlap integrals, $\beta'=\beta(S'/S)=0.116\beta$, where S and S' are the overlap integrals corresponding to β and β'. The inclusion of β' is one of the characteristics of the present calculation. This seems to be necessary in order to improve the coincidence between the observed and theoretical transition energies. This point will be discussed later in some detail.

In the present calculations, β and β' were assumed to be parameters common to all the compounds under consideration, and the (I–A) values were regarded as pertinent to the individual molecules. We determined these parameters in such a way that the calculated transition energies fit as well as possible to the experimental values of the anilines reported here by a trial-and-error method. The secular equations were solved by the aid of a Facom 202 electronic computer for various sets of parameters; the β value ranges from -1.4 to -2.6 eV., with an interval of 0.2 eV., and the $(I-A)$ values, from 9.5 to 12.5 eV, with an interval of 0.1 eV. From the systematic comparison, it was found that the best values for β and β' are -1.94 and -0.25 eV. respectively.

The transition energies ΔW evaluated by the use of the above β and β' values are plotted against the $(I-A)$ values in Fig. 2, from which it may be found that the best $(I-A)$ values in eV units are: 11.34 for aniline, 11.04 for *N*-methylaniline, 10.94 for *N*-ethylaniline, 10.84 for *N, N*-dimethylaniline, and 10.64 for *N, N*-diethylaniline. Table II gives the energy levels and wave functions calculated with the best values for β, β' and $(I-A)$. Furthermore, the relation between the electron configurations used in the present calculation and the energy levels finally obtained is shown in Fig. 3, *N, N*-dimethylaniline being taken as an example.

The oscillator strengths were calculated by the use of the following equation:

$$f_{ih}=1.085\times10^{11}\nu_{ih}D_{ih}{}^2 \tag{9}$$

Where ν_{ih} and D_{ih} are, respectively, the transition energy (in cm^{-1}) and the transition moment (in cm.) for the $i\rightarrow h$ transition. In calculating theoretical oscillator strengths, we took the three following integrals into account:

** In the derivation of Eq. 7, data for the valence state ionization potentials and electron affinities for carbon and nitrogen were taken from the table recently given by G. Pilcher and H. A. Skinner (*J. Inorg. Nucl. Chem.*, **24**, 937 (1962)).

[23] One is symmetric and the other is antisymmetric with regard to the symmetry plane vertical to the molecular plane; they are denoted with the letters "a" and "b" respectively.

[24] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[25] K. Kimura and M. Kubo, ibid., **32**, 1776 (1960).

[26] T. Sakurai, M. Sundaralingam and G. A. Jefferey, *Acta Cryst.*, **16**, 354 (1963).

[27] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

$$\int \psi_{\mathrm{E_{1u}}} \boldsymbol{r} \psi_{\mathrm{CT_a}}\, \mathrm{d}v \approx (Sl/\sqrt{6})\boldsymbol{j}$$

$$\int \psi_{\mathrm{B_{1u}}} \boldsymbol{r} \psi_{\mathrm{CT_b}}\, \mathrm{d}v \approx (Sl/\sqrt{6})\boldsymbol{j} \qquad (10)$$

$$\int \psi_{\mathrm{G}} \boldsymbol{r} \psi_{\mathrm{CT_b}}\, \mathrm{d}v \approx (-2Sl/\sqrt{6})\boldsymbol{j}$$

which have usually been disregarded in such calculations. Here, $\boldsymbol{j}$ is a unit vector along the molecular axis, and l is the destance between the center of the benzene ring and that of the C–N bond. The final results on the transition energies and oscillator strengths are included in Table I where they are compared with the experimental results.

TABLE II. CALCULATED ENERGY LEVELS AND WAVE FUNCTIONS OF ANILINE AND ITS *N*-DERIVATIVES

Aniline

Energy, eV.	Wave function
$W_6 = 7.73$	$\phi_6 = -0.344\phi_{\mathrm{B_{1u}}} + 0.715\phi_{\mathrm{E_{1u}}} - 0.107\phi_{\mathrm{G}} - 0.599\phi_{\mathrm{CTa}}$
$W_5 = 7.72$	$\phi_5 = -0.198\phi_{\mathrm{B_{2u}}} + 0.757\phi_{\mathrm{E_{1u}'}} + 0.622\phi_{\mathrm{CTb}}$
$W_4 = 6.54$	$\phi_4 = 0.729\phi_{\mathrm{B_{1u}}} + 0.612\phi_{\mathrm{E_{1u}}} + 0.063\phi_{\mathrm{G}} + 0.300\phi_{\mathrm{CTa}}$
$W_3 = 6.10$	$\phi_3 = -0.463\phi_{\mathrm{B_{2u}}} - 0.632\phi_{\mathrm{E_{1u}'}} + 0.622\phi_{\mathrm{CTb}}$
$W_2 = 5.10$	$\phi_2 = -0.591\phi_{\mathrm{B_{1u}}} + 0.337\phi_{\mathrm{E_{1u}}} + 0.192\phi_{\mathrm{G}} + 0.707\phi_{\mathrm{CTa}}$
$W_1 = 4.40$	$\phi_1 = 0.864\phi_{\mathrm{B_{2u}}} - 0.165\phi_{\mathrm{E_{1u}'}} + 0.475\phi_{\mathrm{CTb}}$
$W_0 = -0.32$	$\phi_0 = 0.031\phi_{\mathrm{B_{1u}}} - 0.028\phi_{\mathrm{E_{1u}}} + 0.974\phi_{\mathrm{G}} - 0.225\phi_{\mathrm{CTa}}$

N-Methylaniline

Energy, eV.	Wave function
$W_6 = 7.63$	$\phi_6 = -0.338\phi_{\mathrm{B_{1u}}} + 0.756\phi_{\mathrm{E_{1u}}} - 0.100\phi_{\mathrm{G}} - 0.551\phi_{\mathrm{CTa}}$
$W_5 = 7.61$	$\phi_5 = -0.187\phi_{\mathrm{B_{2u}}} + 0.803\phi_{\mathrm{E_{2u}'}} + 0.565\phi_{\mathrm{CTb}}$
$W_4 = 6.51$	$\phi_4 = 0.768\phi_{\mathrm{B_{1u}}} + 0.565\phi_{\mathrm{E_{1u}}} + 0.062\phi_{\mathrm{G}} + 0.294\phi_{\mathrm{CTa}}$
$W_3 = 5.98$	$\phi_3 = -0.524\phi_{\mathrm{B_{2u}}} - 0.568\phi_{\mathrm{E_{2u}'}} + 0.634\phi_{\mathrm{CTb}}$
$W_2 = 4.94$	$\phi_2 = -0.543\phi_{\mathrm{B_{1u}}} + 0.327\phi_{\mathrm{E_{1u}}} + 0.208\phi_{\mathrm{G}} + 0.745\phi_{\mathrm{CTa}}$
$W_1 = 4.32$	$\phi_1 = 0.831\phi_{\mathrm{B_{2u}}} - 0.178\phi_{\mathrm{E_{1u}'}} + 0.527\phi_{\mathrm{CTb}}$
$W_0 = -0.32$	$\phi_0 = 0.032\phi_{\mathrm{B_{1u}}} - 0.029\phi_{\mathrm{E_{1u}}} + 0.971\phi_{\mathrm{G}} - 0.235\phi_{\mathrm{CTa}}$

N-Ethylaniline and *N*-*n*-butylaniline

Energy, eV.	Wave function
$W_6 = 7.60$	$\phi_6 = -0.335\phi_{\mathrm{B_{1u}}} + 0.769\phi_{\mathrm{E_{1u}}} - 0.097\phi_{\mathrm{G}} - 0.535\phi_{\mathrm{CTa}}$
$W_5 = 7.58$	$\phi_5 = -0.183\phi_{\mathrm{B_{2u}}} + 0.817\phi_{\mathrm{E_{1u}'}} + 0.547\phi_{\mathrm{CTb}}$
$W_4 = 6.50$	$\phi_4 = 0.780\phi_{\mathrm{B_{1u}}} + 0.550\phi_{\mathrm{E_{1u}}} + 0.062\phi_{\mathrm{G}} + 0.291\phi_{\mathrm{CTa}}$
$W_3 = 5.94$	$\phi_3 = -0.545\phi_{\mathrm{B_{2u}}} - 0.547\phi_{\mathrm{E_{1u}'}} + 0.635\phi_{\mathrm{CTb}}$
$W_2 = 4.88$	$\phi_2 = -0.527\phi_{\mathrm{B_{1u}}} + 0.324\phi_{\mathrm{E_{1u}}} + 0.214\phi_{\mathrm{G}} + 0.756\phi_{\mathrm{CTa}}$
$W_1 = 4.29$	$\phi_1 = 0.818\phi_{\mathrm{B_{2u}}} - 0.182\phi_{\mathrm{E_{1u}'}} + 0.545\phi_{\mathrm{CTb}}$
$W_0 = -0.34$	$\phi_0 = 0.033\phi_{\mathrm{B_{1u}}} - 0.029\phi_{\mathrm{E_{1u}}} + 0.970\phi_{\mathrm{G}} - 0.239\phi_{\mathrm{CTa}}$

N, *N*-Dimethylaniline

Energy, eV.	Wave function
$W_6 = 7.58$	$\phi_6 = -0.332\phi_{\mathrm{B_{1u}}} + 0.782\phi_{\mathrm{E_{1u}}} - 0.095\phi_{\mathrm{G}} - 0.519\phi_{\mathrm{CTa}}$
$W_5 = 7.55$	$\phi_5 = -0.178\phi_{\mathrm{B_{2u}}} + 0.830\phi_{\mathrm{E_{1u}'}} + 0.529\phi_{\mathrm{CTb}}$
$W_4 = 6.50$	$\phi_4 = 0.792\phi_{\mathrm{B_{1u}}} + 0.535\phi_{\mathrm{E_{1u}}} + 0.061\phi_{\mathrm{G}} + 0.288\phi_{\mathrm{CTa}}$
$W_3 = 5.90$	$\phi_3 = -0.566\phi_{\mathrm{B_{2u}}} - 0.526\phi_{\mathrm{E_{1u}'}} + 0.635\phi_{\mathrm{CTb}}$
$W_2 = 4.82$	$\phi_2 = -0.511\phi_{\mathrm{B_{1u}}} + 0.319\phi_{\mathrm{E_{1u}}} + 0.220\phi_{\mathrm{G}} + 0.767\phi_{\mathrm{CTa}}$
$W_1 = 4.26$	$\phi_1 = 0.805\phi_{\mathrm{B_{2u}}} - 0.186\phi_{\mathrm{E_{1u}'}} + 0.564\phi_{\mathrm{CTb}}$
$W_0 = -0.35$	$\phi_0 = 0.033\phi_{\mathrm{B_{1u}}} - 0.030\phi_{\mathrm{E_{1u}}} + 0.969\phi_{\mathrm{G}} - 0.243\phi_{\mathrm{CTa}}$

N, *N*-Diethylaniline

Energy, eV.	Wave function
$W_6 = 7.53$	$\phi_6 = -0.324\phi_{\mathrm{B_{1u}}} + 0.805\phi_{\mathrm{E_{1u}}} - 0.090\phi_{\mathrm{G}} - 0.489\phi_{\mathrm{CTa}}$
$W_5 = 7.50$	$\phi_4 = -0.170\phi_{\mathrm{B_{2u}}} + 0.853\phi_{\mathrm{E_{1u}'}} + 0.494\phi_{\mathrm{CTb}}$
$W_4 = 6.48$	$\phi_4 = 0.814\phi_{\mathrm{B_{1u}}} + 0.505\phi_{\mathrm{E_{1u}}} + 0.060\phi_{\mathrm{G}} + 0.281\phi_{\mathrm{CTa}}$
$W_3 = 5.82$	$\phi_3 = -0.609\phi_{\mathrm{B_{2u}}} - 0.484\phi_{\mathrm{E_{1u}'}} + 0.628\phi_{\mathrm{CTb}}$
$W_2 = 4.70$	$\phi_2 = -0.481\phi_{\mathrm{B_{1u}}} + 0.310\phi_{\mathrm{E_{1u}}} + 0.231\phi_{\mathrm{G}} + 0.787\phi_{\mathrm{CTa}}$
$W_1 = 4.10$	$\phi_1 = 0.775\phi_{\mathrm{B_{2u}}} - 0.194\phi_{\mathrm{E_{1u}'}} + 0.601\phi_{\mathrm{CTb}}$
$W_0 = -0.36$	$\phi_0 = 0.035\phi_{\mathrm{B_{1u}}} - 0.031\phi_{\mathrm{E_{1u}}} + 0.967\phi_{\mathrm{G}} - 0.251\phi_{\mathrm{CTa}}$

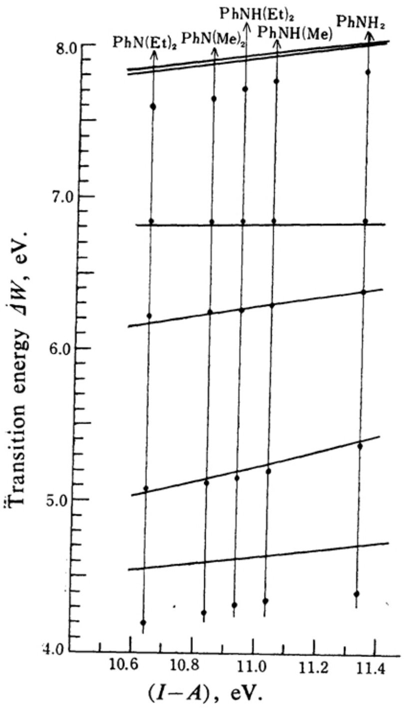

Fig. 2. The calculated best curves of the transition energy ΔW plotted against $(I-A)$ values. The circles show the experimental transition energies obtained from the absorption spectra.

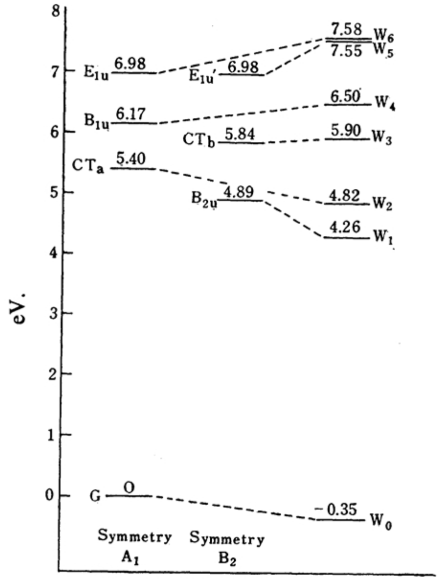

Fig. 3. Energy levels of *N, N*-dimethylaniline. The energy levels before and after the configuration interactions are shown, and the correlations are denoted with the broken lines.

TABLE III. COMPARISON OF THE PRESENT RESULTS OF ANILINE WITH THOSE BY OTHER AUTHORS (Transition energies, $E-E_0$, are given in eV.)

Symmetry of the excited state	Present work				Klevens and Platt[18]		Mataga[9]	
	Obs. (gas)		Theoret.		Obs. (heptane solution)		Theoret.	
	$(E-E_0)$	f	$(E-E_0)$	f	$(E-E_0)$	$\log\varepsilon_{max}$	$(E-E_0)$	f
B_2	4.40	0.028	4.72	0.021	4.32	3.1	4.5324	0.05
A_1	5.39	0.144	5.42	0.174	5.31	3.9	5.4652	0.31
B_2	6.40	0.510	6.42	0.416	6.32	4.3	6.5656	0.84
A_1	6.88	0.570	6.86	0.505	7.06	4.5	6.7248	1.04
B_2	7.87	(0.68)	8.04	0.745				
A_1			8.05	0.416				

Fischer-Hjalmars[4]		Bloor and Peradejordi[16]		Baba[8]		Peacock[15]	Murrell[12]
Theoret.		Theoret.		Theoret.		Theoret.	Theoret.
$(E-E_0)$	f	$(E-E_0)$	f	$(E-E_0)$	f	$(E-E_0)$	$(E-E_0)$
4.699	0.015	4.24	0.09	4.28	0.091	4.3	4.91
5.581	0.19	5.29	0.44	5.38	0.289	4.3	5.16
6.503	0.55	6.57		6.53	0.773	6.1	6.34
6.668	0.68	6.61		6.59	1.051	7.6	6.67
7.496	0.61					8.3	7.58
7.396	0.41					10.1	7.39

Discussion

As may be seen in Table I, we obtained an excellent agreement in the transition energies and oscillator strength values between the theoretical and the experimental results. It is interesting that the changes in the absorption spectra of the compounds can be well interpreted in terms of the change in the $(I-A)$ values or the energies of the charge-transfer configurations on the assumption that β and β' are constant for the series of compounds under consideration. The resuls on aniline obtained by other authors are compared with the present results in Table III. The results by Fischer-Hjalmars and by Murrell are similar to ours, although their results are somewhat different from ours in that the calculated transition energies for the three higher frequency transitions are considerably smaller than the observed values.

The most important point of our experimental results is that the five absorption bands were found in the wavelength region of 160 mμ to 300 mμ. On the basis of the absorption intensity and the shape of absorption curve, these bands can safely be assigned to the $\pi \rightarrow \pi^*$ transition bands. This means that some additional bands appear in the absorption spectra of the anilines, in addition to the shifted bands of the 180, 200 and 260 mμ bands of benzene. According to our interpretation, the additional bands are intramolecular charge-transfer bands caused by the interaction between the electron donor (NH_2, NHMe, etc.) and the electron acceptor (the benzene ring). The additional bands of this kind could not observed with phenol and toluene, as will be mentioned in a following paper. In other words, the absorption bands of these two compounds can be interpreted as the shifted bands of benzene. In this point the absorption spectra of the anilines exhibit a striking contrast to those of phenol and toluene. At any rate, it may be said that theoretical treatment[1-3,8] in which the substituent effect is considered to be only a weak perturbation to the energy levels of benzene itself, can not be applied to the anilines.

The transitions to the lowest excited states (W_1) which give rise to the A bands correspond mainly to the transition to the B_{2u} state of benzene. The contributions from the charge-transfer configuration in the W_1 state are 22% for aniline, 36% for N,N-diethylaniline, and so on. There is no doubt that the B bands appearing around 240 mμ, which are called intramolecular charge-transfer bands, are to be assigned to the transitions to the W_2 states to which the charge-transfer configurations are mainly contributed; for instance, their contributions are, respectively, 50% and 62% for aniline and N,N-diethylaniline.

According to the present experimental results, going from aniline to N,N-diethylaniline, the C and D bands show very small red shifts and the oscillator strengths of the C bands decrease appreciably. These phenomena can be well explaind by the present theoretical study. The decrease in the intensity of the C band may be due to the decreasing contributions of the E_{1u} locally excited configuration, going from aniline to N,N-diethylaniline.

The shortest wavelength band for each compound is most likely to be attributed to two transitions, $W_0 \rightarrow W_5$ and $W_0 \rightarrow W_6$, whose transition energies are almost equal to each other. This seems to be a reason for the broadness of the band. As is shown in Table II, the calculated results show that, going from aniline to N,N-diethylaniline, the fifth and the sixth bands both shift toward the longer wavelengths and, at the same time, their f values increase, with increasing contributions from the E_{1u} locally excited configuration of benzene. These features derived by the theoretical calculations agree well with those of the observed E bands.

As can be seen in Table II, the contributions of the charge-transfer configurations to the ground states are 5% for aniline, 6% for N,N-diethylaniline, and so on, while the calculated stabilization energies due to conjugation are 7.37 kcal./mol. for aniline, 8.29 kcal./mol. for N,N-diethylaniline, and so on. The conjugation energy of aniline coincides well with the extra resonance energy estimated empirically (6 kcal./mol.)[28]. This seems to establish that the present theoretical results on the conjugation effect in the ground states are reasonable.

As may be easily seen from Fig. 2, the present calculations indicate that the $(I-A)$ values decrease in the order of aniline>N-methylaniline > N-ethylaniline > dimethylaniline > N,N-diethylaniline. The changes in the $(I-A)$ values should be attributed to those in the ionization potentials of the substituents. In Fig. 4, the $(I-A)$ values of aniline, N-methylaniline and N,N-dimethylaniline are compared with the ionization potentials of ammonia and amines. It may be said that the differences in the $(I-A)$ values obtained for the anilines reflect a general tendency in th effect of methyl and ethyl substituents upon the ionization potential of ammonia.

Taking the value of I as equal to the ionization potential of ammonia, 10.25 eV., we can

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[28] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca (1960), p. 208.

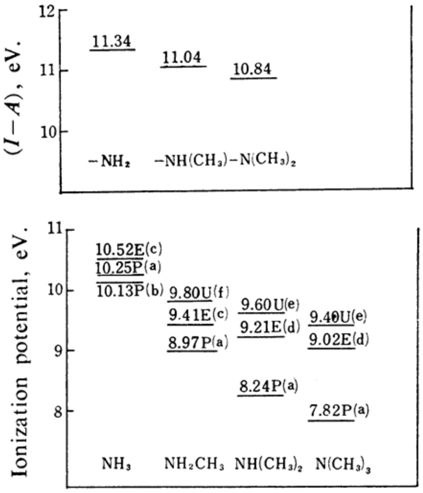

Fig. 4. The upper diagram shows the $(I-A)$ values for aniline, *N*-methylaniline, and *N, N*-dimethylaniline. The lower one shows the ionization potentials of ammonia and amines; NH_3, $NH_2(CH_3)$, $NH(CH_3)_2$, and $M(CH_3)_3$.
(a) K. Watanabe, *J. Chem. Phys.*, **22**, 1564 (1954); **26**, 542 (1957). (b) E. C. Y. Inn, *Phys. Rev.*, **91**, 1154, 1194 (1953). (c) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). (d) I. Ohmura, K. Higasi and H. Baba, This Bulletin, **29**, 504 (1956). (e) T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 372 (1941). (f) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).
E: Electron impact P: Photo-ionization
U: Ultraviolet

estimate the electron affinity of benzene to be $A=-1.00$ eV. from the $(I-A)$ value of 11.25 eV. obtained for aniline. We have a few theoretical data on the electron affinity of benzene available for comparison with the present data; one is the −1.63 eV. given by Hedges and Matsen,[29] and the other, the −0.54 eV. given by Pople and Hush.[30] From the comparison of these values, it may be said that the present electron affinity value of benzene seems to be reasonable. Similar attempts to estimate the electron affinity of benzene from the $(I-A)$ values obtained for the aniline derivatives have been unsuccessful because of the large fluctuations among the experimental ionization potential data for amines (see Fig. 4.)

The present values of $\beta(CN)=-1.94$ eV. may be compared with the other data used in the theoretical calculations of aniline by several other authors. Murrell[12] has used $\beta(CN)=-1.60$ eV., and Fischer-Hjalmars[4] has used $\beta(CN)=-1.452$ eV. in her calculation using the Pariser-Parr-Pople method, while Bloor and Peradejordi's value[16] was $\beta(CN)=-2.74$ eV.

In the present calculations, it should be emphasized that taking β' (the resonance integral for the N⋯C(ortho) atom pair) into account leads to considerably better results than when it is disregarded. As can be seen from Eq. 8, β' $(=0.116\beta)$ makes the off-diagonal term, $H_{G.CTa}$, smaller by about 12%, while it makes all the other terms in Eq. 8 greater by about 12%. This effect brings about a lower transition energy value for the longest wavelength band; consequently, a good agreement between the theoretical and experimental results was obtained.

Furhermore, we checked the effect of the other electron configurations with higher energies upon the transition energies,[31] although we could well reproduce the observed spectra of the anilines by the above-mentioned calculation, taking the seven electron configurations into account. The results show that the effect is not important.

Extra peaks appearing at about 230 mμ for *N*-methylaniline, *N*-ethylaniline, and *N*-butylaniline, and at about 250 mμ for *N, N*-diethylaniline may be attributed to the n → σ* transitions, since the ultraviolet absorption measurements with saturated amines have indicated that a relatively weak absorption band due to an n → σ* transition appears around 200 mμ; for instance, for trimethylamine it appears at 212 mμ.[19]

Summary

The vacuum ultraviolet absorption spectra of anilne, *N*-methylaniline, *N*-ethylaniline, *N, N*-dimethylaniline, *N, N*-diethylaniline and *N-n*-butylaniline have been measured in the vapor phase by a recording vacuum ultraviolet spectrophotometer, with which the absorption measurements have been extended down to

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29) R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).

30) J. A. Pople and N. S. Hush, *Trans. Faraday Soc.*, **51**, 600 (1955).

31) We checked how the other electron configurations with higher energies affect the calculated results. In order to check this point, we tried to calculate by including several additional higher energy configurations of the following types:
$(\phi_2^{-1}\phi_6)$, $(\phi_3^{-1}\phi_6)$, $(\theta^{-1}\phi_6)$, $(\theta^{-1}w)$, $(\phi_2^{-1}w)$ and $(\phi_3^{-1}w)$ which correpond to transitions to the highest vacant orbital of benzene (ϕ_6) and to the 3pπ atomic orbatal of nitrogen (w). Assuming roughly that all the diagonal elements of the new configurations are 9.0 eV., and that the resonance integral between the nitrogen 3pπ orbital and the adjacent carbon 2pπ orbital is −2.0 eV., we obtaind transition energies by solving 5th- and 8th-order secular equations built up with the thirteen configurations. The resulting transition energies (in eV.) for seven original configurations were found to be 4.97 (4.72) for the $W_0 \rightarrow W_1$ transition, 5.53 (5.42) for the $W_0 \rightarrow W_2$, 6.65 (6.42) for the $W_0 \rightarrow W_3$, 7.04 (6.86) for the $W_0 \rightarrow W_4$, 7.81 (8.04) for the $W_0 \rightarrow W_5$, and 8.18 (8.05) for the $W_0 \rightarrow W_6$; the values in parentheses indicate the corresponding energies listed in Table I.

1500 Å. Some new bands have been found in the vacuum ultraviolet region, and in total five $\pi \rightarrow \pi^*$ transtion bands with molar extinction coefficients larger than 1500 have been observed commonly for the anilines. In order to clarify the nature of these bands, a theoretical treatment has been made by considering the configuration interaction among the ground, locally excited and charge-transfer configurations. An excellent agreement has been obtained between the experimental and the calculated results. It has been concluded that the anilines studied here exhibit intramolecular charge-transfer bands characteristic of the electron transfer interaction between the substituents and the benzene ring.

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo