The Electronic Spectra of Aniline and *N*-Methylaniline Adsorbed on Aluminum Chloride. II. The Theoretical Treatment

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(Received March 23, 1965)

In the preceding paper,[1] the electronic spectra of aniline and *N*-methylaniline adsorbed on aluminum chloride were measured and compared with those of gaseous aniline, *N*-methylaniline, toluene and ethylbenzene. In the case of adsorbed *N*-methylaniline, the spectrum was almost the same as that of gaseous ethylbenzene, while in the case of adsorbed aniline, a spectrum with a strong band at 192 mμ and a weak hidden band at about 218 mμ was obtained. The spectra of the adsorbed species were there discussed qualitatively by considering the location of the intramolecular charge-transfer (CT) configurations relative to those of the locally-excited (LE) configurations. In the adsorbed molecules, the former has a higher energy than in gaseous molecules, as a result of the rise of the ionization potential of the electron-donating group. This rise in the ionization potential was attributed to the interaction of the lone-pair electrons in the adsorbed molecule with some electron-accepting center on aluminum chloride, presumably with the vacant sp^3-orbital of the aluminum atom.

In the present paper, the electronic spectra of adsorbed molecules will be studied, by the LCMO treatment, in comparison with those of gaseous molecules. The results can explain satisfactorily the experimental findings mentioned in the preceding paper.[1]

Calculation Procedure

The calculation was carried out according to the intramolecular charge-transfer model, which is based on the idea that the molecules to be treated consist of an electron-accepting group (the benzene ring in this case) and an electron-donating group ($X=NH_2$, $NHCH_3$, CH_3 and C_2H_5 groups). Only π-electrons were taken into account. In the case of aniline or *N*-methylaniline, the lone pair electrons on the nitrogen atom were assumed to belong to the pure 2pπ atomic orbital. For toluene and ethylbenzene, the hyperconjugation was taken into account, and two π-electrons were counted for the methyl- or ethyl-group respectively. For adsorbed aniline and adsorbed *N*-methylaniline, an intermediate situation between gaseous aniline and toluene, and between gaseous *N*-methylaniline and ethylbenzene, respectively, is to be expected, as was discussed in the preceding paper. Hence, in these cases also, two π-electrons may be taken into account for the adsorbed amino-group or the adsorbed *N*-methylamino-group respectively.

After the procedure of Longuet-Higgins and Murrell,[2] configuration interaction was considered among seven electron configurations constructed from the π-electron orbitals of the benzene ring ($\phi_1, \phi_2, \cdots, \phi_6$) and the 2p$\pi$ (or the pseudo-2pπ) orbital on the electron-donating group, X. They include two CT configurations and four LE configurations, besides the ground configuration. Assuming the molecule C_6H_5X to belong to the point group C_{2v}, these configurations can be divided into two symmetry species, A_1 and B_2. The wave functions which are obtained by the linear combination of the orbital wave functions associated with those configurations are:

$$\left.\begin{array}{ll}
A_1: & \psi_G=1/\sqrt{8!}\,|\phi_1\overline{\phi}_1\phi_2\overline{\phi}_2\phi_3\overline{\phi}_3\chi\overline{\chi}| \\
 & \psi_P=1/\sqrt{2}\,\{1/\sqrt{2}\,(\phi_3{}^{-1}\phi_4+\overline{\phi}_3{}^{-1}\overline{\phi}_4) \\
 & \qquad -1/\sqrt{2}\,(\phi_2{}^{-1}\phi_5+\overline{\phi}_2{}^{-1}\overline{\phi}_5)\} \\
 & \psi_{\beta'}=1/\sqrt{2}\,\{1/\sqrt{2}\,(\phi_3{}^{-1}\phi_4+\overline{\phi}_3{}^{-1}\overline{\phi}_4) \\
 & \qquad +1/\sqrt{2}\,(\phi_2{}^{-1}\phi_5+\overline{\phi}_2{}^{-1}\overline{\phi}_5)\} \\
 & \psi_{CT}=1/\sqrt{2}\,(\chi^{-1}\phi_5+\overline{\chi}^{-1}\overline{\phi}_5) \\
B_2: & \psi_\alpha=1/\sqrt{2}\,\{1/\sqrt{2}\,(\phi_2{}^{-1}\phi_4+\overline{\phi}_2{}^{-1}\overline{\phi}_4) \\
 & \qquad -1/\sqrt{2}\,(\phi_3{}^{-1}\phi_5+\overline{\phi}_3{}^{-1}\overline{\phi}_5)\} \\
 & \psi_\beta=1/\sqrt{2}\,\{1/\sqrt{2}\,(\phi_2{}^{-1}\phi_4+\overline{\phi}_2{}^{-1}\overline{\phi}_4) \\
 & \qquad +1/\sqrt{2}\,(\phi_3{}^{-1}\phi_5+\overline{\phi}_3{}^{-1}\overline{\phi}_5)\} \\
 & \psi_{CT'}=1/\sqrt{2}\,(\chi^{-1}\phi_4+\overline{\chi}^{-1}\overline{\phi}_4)
\end{array}\right\} \quad (1)$$

Here the suffix G denotes the ground configuration; α, P, β and β', the locally-excited configurations, CT and CT$'$, the two charge-transfer configurations respectively. Considering the configuration interaction among these configurations, the energy levels of the molecule

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[1] H. Sato, K. Hirota and S. Nagakura, This Bulletin, **38**, 962 (1965).

[2] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Roy. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).

can be obtained by taking the energy of the ground configuration to be zero. The energies of the LE configurations were taken to be equal to the observed excitation energies of benzene (Kimura and Nagakura[3]), while those of the CT configurations can be evaluated by the following equations:

$$\left.\begin{aligned} H_{\mathrm{CT}} &= I_{\mathrm{X}} - A_{\phi} - C \\ H_{\mathrm{CT}'} &= I_{\mathrm{X}} - A_{\phi} - C' \end{aligned}\right\} \tag{2}$$

where I_{X} and A_{ϕ} are the ionization potential of the electron donating group, X, and the electron affinity of the benzene molecule respectively.

The Coulombic attraction energies, $-C$ or $-C'$, can be calculated by the uniformly-charged sphere model of Pariser and Parr.[4] In order to carry out the calculation, one must know the bond length, C-X. For toluene this length has already been determined to be 1.52Å.[5] For aniline, however, there is no data available so far. The available data on r_{CN} are as follows: 1.35Å (aniline hydrochloride), 1.39Å (*o*-methylaniline hydrochloride), 1.45Å (*p*-tolidine hydrochloride), 1.37Å (*p*-nitroaniline)[6] and 1.407Å (2, 5-dichloroaniline)[7]. In the present calculations, the r_{CN} value of aniline was taken to be 1.37Å. The C-N distance for the adsorbed aniline molecule was assumed, however, to be equal to the C-N single bond length, 1.47Å, because the conjugation between the amino-group and the benzene ring is weakened in this case and, hence, a considerable loss of the double-bond character can be expected. The experimental analysis of molecular structure of *N*-methylaniline and ethylbenzene still has not been made. For these two substances and adsorbed *N*-methylaniline, the C-X distances were assumed to be the same as those of aniline, toluene and adsorbed aniline respectively.

The off-diagonal matrix elements can be determined as follows:

$$\left.\begin{aligned} &H_{\mathrm{G}\cdot\mathrm{CT}} = \sqrt{2}\int \phi_5 H \chi \,\mathrm{d}\tau \\ &H_{\beta'\cdot\mathrm{CT}} = -H_{\mathrm{p}\cdot\mathrm{CT}} = 1/\sqrt{2}\int \phi_2 H \chi \,\mathrm{d}\tau \\ &H_{\mathrm{G}\cdot\beta'} = H_{\mathrm{G}\cdot\mathrm{p}} = H_{\beta'\cdot\mathrm{p}} = 0 \\ &H_{\alpha\cdot\mathrm{CT}} = H_{\beta\cdot\mathrm{CT}} = 1/\sqrt{2}\int \phi_2 H \chi \,\mathrm{d}\tau \\ &H_{\alpha\cdot\beta} = 0 \end{aligned}\right\} \tag{3}$$

In evaluating $\int \phi_5 H \chi \,\mathrm{d}\tau$ and $\int \phi_2 H \chi \,\mathrm{d}\tau$, Kimura's procedure[8] was adopted; i. e., besides the core resonance integral between X and the adjacent carbon atom (β), the corresponding integral between X and the ortho-carbon atom (β') was taken into account. In estimating the values of β and β' for aniline and *N*-methylaniline, their proportionality to the overlap integral was assumed. The obtained values for β (and β') are -1.9 eV. (and -0.3 eV.) for aniline and *N*-methylaniline, and -1.6 eV. (and -0.2 eV.) for adsorbed aniline and adsorbed *N*-methylaniline[9] respectively. For toluene and ethylbenzene, β was equated to 0.7 β_0[10] (β_0 being β_{CC} in benzene), while β' was estimated from this β by assuming its proportionality to the overlap integral. The values of -1.6 eV. and -0.3 eV. were thus obtained for β and β'.

The *I-A* values were determined by the following procedure, regarding them as parameters. Calculations were carried out for a certain range of *I-A* values, and the "best" *I-A* value was determined by observing the best fit with the observed transition energy of each substance.

Numerical calculations were carried out with a NEAC 2101 computer set up in the Protein Research Institute of Osaka University.

Results and Discussion

The calculated results are shown in Fig. 1 and Table I. The experimental results are plotted in the figure at the position which shows the best fit with the calculated values.

As is shown in Fig. 1, a satisfactory agreement can be obtained between calculated and experimental energy values if we assign 11.0, 11.3, 11.5, 11.8, 11.8 and about 12.5 eV. to the *I-A* values of *N*-methylamino-, amino-, adsorbed amino-, adsorbed *N*-methylamino-, ethyl and methyl groups respectively. In the case of both aniline and *N*-methylaniline, the rise in the ionization potential of the electron-donating group (0.2 eV. and 0.8 eV.) is found to be a result of adsorption on aluminum

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3) K. Kimura and S. Nagakura, *Molecular Physics*, **9**, 117 (1965).

4) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

5) F. A. Keidel, quoted by S. H. Bauer et al., *Ann. Rev. Phys. Chem.*, **4**, 236 (1953).

6) These values are obtained from L. E. Sutton, ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London (1958).

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

8) K. Kimura, H. Tsubomura and S. Nagakura, This Bulletin, **37**, 1336 (1964).

9) The change in hybridization which is possibly effected by adsorption is neglected in the evaluation of these numerals. Such a smaller (in absolute terms) value of the resonance integrals for the adsorbed molecules may be caused by a joint effect of bond elongation and hybridization change.

10) The factor of 0.7 has already been used by several authors in the Hückel MO calculation of toluene: cf. C. A. Coulson and U. A. Crawford, *J. Chem. Soc.*, **1953**, 2052; A. Pullman and J. Metzger, *Bull. soc. chim. France*, **15**, 1021 (1948); B. Pullman, M. Magot and G. Berthier, *J. Chem. Phys.*, **18**, 257 (1950).

TABLE I. CALCULATED ENERGY LEVELS, WAVE FUNCTIONS AND OSCILLATOR STRENGTHS (f) TAKING (I-A) AS A PARAMETER, T, AA AND GA DENOTING TOLUENE-TYPE, ADSORBED ANILINE-TYPE AND GASEOUS ANILINE-TYPE CALCULATION, RESPECTIVELY

Energy, eV.	Wave function	f
T, I-A=12.5 eV.		
0.00	$\psi_1=0.9900\psi_G-0.0169\psi_p+0.0150\psi_{\beta'}+0.1390\psi_{CT}$	—
5.92	$\psi_2=0.0799\psi_G+0.8521\psi_p-0.2787\psi_{\beta'}-0.4357\psi_{CT}$	0.16
6.85	$\psi_3=-0.0478\psi_G+0.4360\psi_p+0.8461\psi_{\beta'}+0.3027\psi_{CT}$	0.99
8.55	$\psi_4=-0.1055\psi_G+0.2890\psi_p-0.4540\psi_{\beta'}+0.8362\psi_{CT}$	0.06
4.85	$\psi_5=0.9668\psi_\alpha+0.0817\psi_\beta+0.2423\psi_{CT'}$	0.0054
6.79	$\psi_6=-0.1762\psi_\alpha+0.8994\psi_\beta+0.4000\psi_{CT'}$	0.91
8.71	$\psi_7=-0.1852\psi_\alpha-0.4294\psi_\beta+0.8839\psi_{CT'}$	0.27
T, I-A=12.0 eV.		
0.00	$\psi_1=0.9886\psi_G-0.0180\psi_p+0.0160\psi_{\beta'}+0.1484\psi_{CT}$	—
5.82	$\psi_2=0.0977\psi_G+0.7907\psi_p-0.3048\psi_{\beta'}-0.5218\psi_{CT}$	0.21
6.81	$\psi_3=-0.0527\psi_G+0.5261\psi_p+0.7817\psi_{\beta'}+0.3307\psi_{CT}$	0.88
8.23	$\psi_4=-0.1014\psi_G+0.3125\psi_p-0.5438\psi_{\beta'}+0.7722\psi_{CT}$	0.12
4.82	$\psi_5=0.9550\psi_\alpha+0.0936\psi_\beta+0.2816\psi_{CT'}$	0.0070
6.70	$\psi_6=-0.2254\psi_\alpha+0.8460\psi_\beta+0.4832\psi_{CT'}$	0.79
8.36	$\psi_7=-0.1930\psi_\alpha-0.5249\psi_\beta+0.8290\psi_{CT'}$	0.38
AA, I-A=12.0 eV.		
0.00	$\psi_1=0.9860\psi_G-0.0190\psi_p+0.0168\psi_{\beta'}+0.1648\psi_{CT}$	—
5.82	$\psi_2=0.1134\psi_G+0.7620\psi_p-0.3039\psi_{\beta'}-0.5605\psi_{CT}$	0.23
6.82	$\psi_3=-0.0612\psi_G+0.5664\psi_p+0.7406\psi_{\beta'}+0.3561\psi_{CT}$	0.83
8.06	$\psi_4=-0.1057\psi_G+0.3133\psi_p-0.5990\psi_{\beta'}+0.7293\psi_{CT}$	0.16
4.87	$\psi_5=0.9565\psi_\alpha+0.0882\psi_\beta+0.2781\psi_{CT'}$	0.0062
6.73	$\psi_6=-0.2237\psi_\alpha+0.8336\psi_\beta+0.5050\psi_{CT'}$	0.77
8.26	$\psi_7=-0.1873\psi_\alpha-0.5452\psi_\beta+0.8171\psi_{CT'}$	0.40
AA, I-A=11.5 eV.		
0.00	$\psi_1=0.9838\psi_G-0.0203\psi_p+0.0180\psi_{\beta'}+0.1770\psi_{CT}$	—
5.65	$\psi_2=-0.1385\psi_G-0.6665\psi_p+0.3147\psi_{\beta'}+0.6614\psi_{CT}$	0.29
6.77	$\psi_3=-0.0632\psi_G+0.6756\psi_p+0.6380\psi_{\beta'}+0.3641\psi_{CT}$	0.66
7.84	$\psi_4=0.0943\psi_G-0.3144\psi_p+0.7026\psi_{\beta'}-0.6314\psi_{CT}$	0.28
4.84	$\psi_5=0.9376\psi_\alpha+0.1032\psi_\beta+0.3320\psi_{CT'}$	0.0084
6.59	$\psi_6=-0.2955\psi_\alpha+0.7398\psi_\beta+0.6045\psi_{CT'}$	0.59
7.98	$\psi_7=-0.1832\psi_\alpha-0.6649\psi_\beta+0.7241\psi_{CT'}$	0.58
GA, I-A=11.5 eV.		
0.00	$\psi_1=0.9775\psi_G+0.0287\psi_p+0.0255\psi_{\beta'}+0.2075\psi_{CT}$	—
5.45	$\psi_2=0.1733\psi_G-0.6158\psi_p-0.3397\psi_{\beta'}-0.6895\psi_{CT}$	0.34
6.83	$\psi_3=-0.0604\psi_G-0.7079\psi_p+0.6344\psi_{\beta'}+0.3045\psi_{CT}$	0.64
8.05	$\psi_4=0.1042\psi_G+0.3447\psi_p+0.6939\psi_{\beta'}-0.6235\psi_{CT}$	0.24
4.84	$\psi_5=0.9033\psi_\alpha+0.1445\psi_\beta+0.4040\psi_{CT'}$	0.016
6.51	$\psi_6=-0.3751\psi_\alpha+0.7231\psi_\beta+0.5800\psi_{CT'}$	0.62
8.16	$\psi_7=-0.2083\psi_\alpha-0.6755\psi_\beta+0.7073\psi_{CT'}$	0.60
GA, I-A=11.0 eV.		
0.00	$\psi_1=0.9737\psi_G-0.0308\psi_p+0.0274\psi_{\beta'}+0.2241\psi_{CT}$	—
5.21	$\psi_2=-0.1998\psi_G-0.5338\psi_p+0.3248\psi_{\beta'}+0.7548\psi_{CT}$	0.37
6.80	$\psi_3=-0.0588\psi_G+0.7759\psi_p+0.5549\psi_{\beta'}+0.2944\psi_{CT}$	0.52
7.91	$\psi_4=0.0926\psi_G-0.3348\psi_p+0.7654\psi_{\beta'}-0.5417\psi_{CT}$	0.34
4.69	$\psi_5=0.8618\psi_\alpha+0.1651\psi_\beta+0.4797\psi_{CT'}$	0.020
6.38	$\psi_6=-0.4684\psi_\alpha+0.6220\psi_\beta+0.6275\psi_{CT'}$	0.40
7.99	$\psi_7=-0.1947\psi_\alpha-0.7654\psi_\beta+0.6134\psi_{CT'}$	0.75

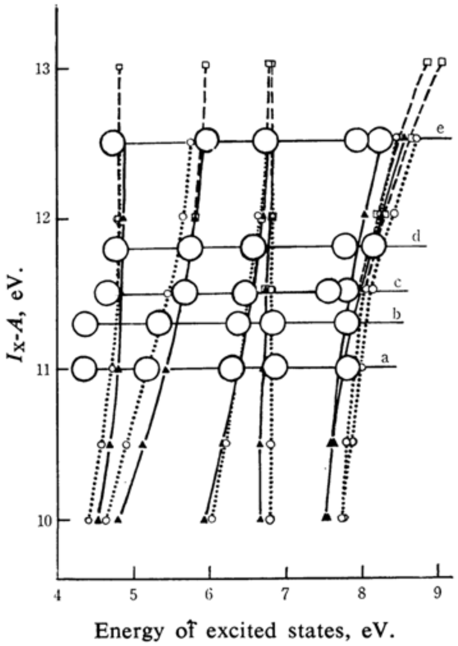

Fig. 1. Calculated and observed energies of excited states.
······ Calcd. for gaseous aniline and N-methylaniline
—— Calcd. for adsorbed aniline and N-methylaniline
---- Calcd. for toluene and ethylbenzene
○ Observed
a) N-Methylaniline b) Aniline
c) Adsorbed aniline
d) Ethylbenzene and adsorbed N-methylaniline e) Toluene

chloride, if the change in the electron affinity of benzene ring can be disregarded.

In the calculated results one can find a general tendency for bands to shift and intensities to change with an increase in the I-A values. The band corresponding to the $2A_1$ state (hereafter abbreviated to "$2A_1$") shifts to a shorter wavelength with a decrease in the intensity. The "$2B_2$" and "$3A_1$" bands approach each other with an increase in the intensity. For adsorbed N-methylaniline, ethylbenzene and toluene, these bands nearly overlap, forming a band corresponding to the degenerate β and β' bands of benzene. The "$4A_1$" and "$3B_2$" bands show a tendency to separate from each other with a decrease in the intensity. These general trends are just the same as those observed in the spectra of N-methylaniline, aniline, adsorbed aniline, adsorbed N-methylaniline, ethylbenzene and toluene, according to this order. Such being the case, adsorbed aniline and N-methylaniline clearly show intermediate spectra between aniline and toluene, and between N-methylaniline and ethylbenzene, respectively.

In the spectra of toluene and ethylbenzene reported by Hammond et al.,$^{11)}$ more than two bands are found near 150—160 mμ. They assigned them as Rydberg bands. In the light of the present calculations, however, it may be, rather, possible to assign two of these bands as CT bands. In the spectrum of adsorbed aniline,$^{1)}$ two peaks are found near 160 mμ, though they are weak and less-resolved than other peaks. These bands may also have much of a CT character.

Why the spectra of adsorbed aniline and adsorbed N-methylaniline become nearer to those of toluene and ethylbenzene is a difficult question to answer. It may result from the interaction of the lone pair electrons on the nitrogen atom of the adsorbate molecule and a vacant sp^3 orbital of the aluminum atom.

Summary

The electronic spectra of aniline and N-methylaniline adsorbed on aluminum chloride have been examined by the LCMO method and have been compared with those of gaseous aniline, N-methylaniline, toluene and ethylbenzene. All of these molecules can be treated by the intramolecular charge-transfer model. In order for us to be able to interpret the spectra from the LCMO point of view, the ionization potential of the electron donating group in aniline and N-methylaniline molecules should rise upon adsorption on aluminum chloride.

The authors would like to express their gratitude to Dr. Katsumi Kimura, Faculty of Engineering Science, Osaka University, for his helpful discussions. The authors are also indebted to Professor Tatsuo Miyazawa, The Protein Research Institute of Osaka University, for numerical calculations with a NEAC 2101 computer.

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Note Added in Proof

The details of Terenin's work referred in the part I of this paper (∗2 in p. 962) was published in *Acta Phys. Chem. URSS*, **18**, 210 (1943) (in English).

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11) V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Discussions Faraday Soc.*, **9**, 53 (1950).