A Configuration Analysis of the Electronic States of Aniline

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The method of configuration analysis has been applied to the interpretation of the ground and the excited electronic states of aniline. The results of full analysis, including all the singly and the doubly excited configurations, is presented. The electronic wave functions analyzed were obtained by a procedure of the Pariser-Parr-Pople type. The first excited singlet state of aniline is assigned to the ^1L_b. The second, the third, and the fourth excited singlet state are assigned to the mixed state of the ^1L_a and $^1CTS1$ states, the ^1CTA, ^1B_b, and ^1L_b states, and the ^1B_a and ^1L_a states respectively. The lowest triplet state of aniline is assigned to the ^3L_a state. The total weights of all the singly excited configurations range from 88% to 95%, except for the ground state. The inclusion of all the doubly excited configurations improves the weights up to 99.6% or more.

The effects of substitution on electronic spectra have been extensively investigated for benzene derivatives.[1-5] Aniline, which is a typical derivative of benzene with an electron-donating group, has received much attention; numerous papers on its semi-empirical calculations have been published.[6-22] From a chemical point of view, the excited states of substituted compounds have been interpreted in terms of locally excited states and charge-transfer states. In accordance with this standpoint, Murrell,[8] Kimura *et al.*,[15] and Godfrey and Murrell[16] determined the assignment of the excited states of aniline by using the localized-orbital or the composite-molecule description. Using the two-step transformation of the wave functions obtained by the Pariser-Parr-Pople method through natural spin orbitals, Fischer-Hjalmars[11] described the excited states of aniline in terms of locally excited and charge-transfer states. There has also been some discussion of the assignment of the second absorption band of aniline. Kimura *et al.*[15] as well as Murrell[8] assigned the band to a charge-transfer transition, whereas Baba[10] and Fischer-Hjalmars[11] assigned it to a locally excited transition.

The present paper will interpret the excited electronic states of aniline in terms of the locally excited states and the charge-transfer states by the application of configuration analysis.[23,24] A full analysis including all the doubly excited configurations will also be given, and contributions from the doubly excited configurations will be discussed.

Method of Calculation

The Pariser-Parr-Pople method with limited configuration interaction was used for the calculation of the π-electronic states of benzene and aniline. The Coulomb repulsion integrals were obtained by means of the following formula:[24,25]

$$\gamma_{pq} = 14.40/[a \exp(-0.3r^2) + r] \text{ eV}$$

where r is the distance in Å units between a pair of atoms, p and q. The parameter, a, is determined by the following formula:

$$a = 14.40 \Big/ \left\{ \frac{1}{2}[(I_p - A_p) + (I_q - A_q)] \right\} \text{ eV}$$

where I_p and A_p are the ionization potential and the electron affinity of an atom, p, respectively.

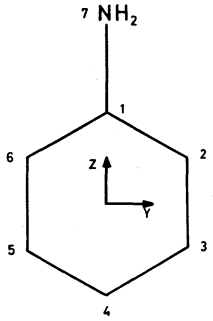

Fig. 1.

The aniline molecule is regarded as being planar and belonging to the C_{2v} symmetry group. The numbering of the atoms and the coordinate axes are shown in Fig. 1. It is assumed that the benzene ring consists of a regular hexagon, with every C–C bond length equal to 1.40 Å, and that the C–N bond length is 1.41 Å. The valence-state ionization potential and the electron affinity for a carbon atom are taken as follows:

$$I_C = 11.16 \text{ eV}, \quad A_C = 0.03 \text{ eV}$$

The resonance integral, β_{CC}, is adjusted to fit the benzene spectrum.

$$\beta_{CC} = -2.48 \text{ eV}$$

In order to discuss the effect of substitution on the electronic spectra, it is reasonable to compare the observed shifts caused by the introduction of a substituent with the calculated shifts, instead of making a direct comparison between the observed and the calculated state energies. From this point of view, the ionization potential, the electron affinity, and the resonance integral related to a nitrogen atom are varied until a satisfactory agreement between the calculated and the observed shifts caused by the introduction of an amino group into benzene is achieved. The best fitted values are as follows:

$$I_N = 26.7 \text{ eV}, \quad A_N = 9.7 \text{ eV}, \quad \beta_{CN} = -1.9 \text{ eV}$$

The SCF MO's are numbered from 1 to 6 for benzene and from 1 to 7 for aniline, in the order of increasing energy. The excited configurations included in the CI calculations are the following one-electron transitions: 2→4, 2→5, 3→4, and 3→5 for benzene and 4→5, 4→6, 3→5, 3→6, 2→5, and 2→6 for aniline.

The ground and the excited state functions of aniline thus obtained are submitted to configuration analysis. The procedure for configuration analysis was presented previously.[23,24] The symbols used in the present paper have the same meanings as in Ref. 24, unless otherwise noted. In the present paper, the reference SCF MO's consist of ϕ°_1, ϕ°_2, $\cdots$, ϕ°_6, which are the SCF MO's of benzene, and ϕ°_N, which represents the π-AO of the substituent of aniline.

Results

Table 1 summarizes the observed and the calculated state energies for benzene and aniline, including the f values. The singlet excited state wave functions are denoted by $^1\Psi_I$, $^1\Psi_{II}$, $\cdots$ in the order of increasing energy, while the ground state function is written as $^1\Psi_G$. The triplet excited wave functions are denoted by $^3\Psi_I$, *etc.*

The results of the configuration analysis for the ground and the excited singlet states of aniline are given in Table 2. The results for the triplet states are given in Table 3. In these and the following tables, the reference-state wavefunctions are indicated by a superscript °. The locally excited states are classified by the group theoretical notation and the Platt notation. The charge-transfer configurations arising from the one-electron excitation from $\phi^\circ_N \rightarrow \phi^\circ_4$, $\phi^\circ_N \rightarrow \phi^\circ_5$, and $\phi^\circ_N \rightarrow \phi^\circ_6$ are denoted by Ψ°_{CTS1}, Ψ°_{CTA}, and Ψ°_{CTS2} respectively. The higher excited configurations, which are not included in the CI calculations of benzene, are written as Ψ°_{15}, which means a one-electron excitation configuration from ϕ°_1 to ϕ°_5, *etc.*

Table 1. Excited states of benzene and aniline

Compound	State function	Energy (eV) Calcd	Energy (eV) Obsd[15]	Oscillator strength Calcd	Oscillator strength Obsd[15]
Benzene	$^1\Psi_G$	0	0		
	$^1\Psi_I$	5.014	4.89	0	0.001
	$^1\Psi_{II}$	6.070	6.17	0	0.126
	$^1\Psi_{III}$	6.898	6.98	1.183	1.035
	$^1\Psi_{IV}$	6.898	6.98	1.183	
	$^3\Psi_I$	3.742	3.88[a]		
	$^3\Psi_{II}$	4.378			
	$^3\Psi_{III}$	4.378			
	$^3\Psi_{IV}$	5.014			
Aniline	$^1\Psi_G$	0	0		
	$^1\Psi_I$	4.539	4.40	0.054	0.028
	$^1\Psi_{II}$	5.328	5.39	0.261	0.140
	$^1\Psi_{III}$	6.253	6.40	0.383	0.510
	$^1\Psi_{IV}$	6.611	6.88	0.889	0.570
	$^1\Psi_V$	7.401	7.87	0.696	0.68
	$^1\Psi_{VI}$	7.542		0.192	
	$^3\Psi_I$	3.392	3.56[a]		
	$^3\Psi_{II}$	3.810			
	$^3\Psi_{III}$	4.166			
	$^3\Psi_{IV}$	5.038			
	$^3\Psi_V$	6.058			
	$^3\Psi_{VI}$	6.621			

a) Estimated values from spectral data.

Table 2. Configuration analysis for aniline (singlet state)

$^1A_1$

Reference state	$^1\Psi_G$	$^1\Psi_{II}$	$^1\Psi_{IV}$	$^1\Psi_{VI}$
$^1\Psi^\circ_G$	0.9352	−0.2422	−0.1042	0.1435
$^1\Psi^\circ_{La}$	−0.0392	−0.6422	0.5619	−0.3965
$^1\Psi^\circ_{Ba}$	0.0200	0.1976	0.6587	0.6440
$^1\Psi^\circ_{CTS1}$	0.3040	0.6104	0.3320	−0.4963
$^1\Psi^\circ_{14}$	−0.0235	−0.1051	−0.0948	0.2709
$^1\Psi^\circ_{36}$	−0.0158	0.0037	0.0017	−0.0029
$^1\Psi^\circ_{CTS2}$	0.1613	−0.0414	−0.0178	0.0244
$^1\Psi^\circ_{16}$	−0.0080	0.0020	0.0008	−0.0011
CT weight (%)	11.84	37.43	11.05	24.69
Sum weight (%)	99.58	89.55	88.00	91.29
Assignment	^1G	(^1L_a+^{1}CTS1)	(^1B_a+^1L_a)	(^1B_a)

$^1B_2$

Reference state	$^1\Psi_I$	$^1\Psi_{III}$	$^1\Psi_V$
$^1\Psi^\circ_{Lb}$	0.7717	0.5172	0.1620
$^1\Psi^\circ_{Bb}$	0.1590	−0.5368	0.7589
$^1\Psi^\circ_{CTA}$	−0.5336	0.5834	0.4825
$^1\Psi^\circ_{15}$	0.0567	−0.1713	−0.2444
$^1\Psi^\circ_{26}$	−0.0003	−0.0004	0.0003
CT weight (%)	28.47	34.04	23.28
Sum weight (%)	90.87	92.54	89.46
Assignment	^1L_b	(^{1}CTA+^1B_b+^1L_b)	^1B_b

Table 3. Configuration analysis for aniline (triplet state)

$^3A_1$

Reference state	$^3\Psi_I$	$^3\Psi_{III}$	$^3\Psi_V$
$^3\Psi^\circ_{La}$	−0.7662	0.4384	−0.3309
$^3\Psi^\circ_{Ba}$	−0.2774	−0.7857	−0.4411
$^3\Psi^\circ_{CTS1}$	0.5230	0.2759	−0.7442
$^3\Psi^\circ_{14}$	−0.0411	−0.0440	0.3059
$^3\Psi^\circ_{36}$	−0.0004	−0.0001	−0.0003
$^3\Psi^\circ_{CTS2}$	0.0003	0.0002	−0.0004
$^3\Psi^\circ_{16}$	0.0000	0.0000	0.0002
CT weight (%)	27.35	7.61	55.38
Sum weight (%)	93.93	88.75	95.16
Assignment	^3L_a	^3B_a	^{3}CTS1

$^3B_2$

Reference state	$^3\Psi_{II}$	$^3\Psi_{IV}$	$^3\Psi_{VI}$
$^3\Psi^\circ_{Bb}$	0.6993	−0.5635	0.2877
$^3\Psi^\circ_{Lb}$	0.3894	0.7520	0.4149
$^3\Psi^\circ_{CTA}$	−0.5089	−0.1924	0.7496
$^3\Psi^\circ_{15}$	0.0320	0.0366	−0.2999
$^3\Psi^\circ_{26}$	0.0001	−0.0006	−0.0001
CT weight (%)	25.90	3.70	56.19
Sum weight (%)	90.07	92.13	90.67
Assignment	(^3B_b)	^3L_b	^{3}CTA

The band assignments are given in Tables 2 and 3. When a single reference state has a weight higher than 50%, the state notation of this state is indicated in the

TABLE 4. CONTRIBUTION FROM DOUBLY EXCITED CONFIGURATIONS (SINGLET STATE)

Configuration	$^1A_1$ $^1\Psi_G$	$^1\Psi_{II}$	$^1\Psi_{IV}$	$^1\Psi_{VI}$	Configuration	$^1B_2$ $^1\Psi_I$	$^1\Psi_{III}$	$^1\Psi_V$
$^1V^\circ_{35,24(1)}$	0.0005	0.0198	−0.0325	0.0024	$^1V^\circ_{35,25}$	−0.0067	0.0001	−0.0067
$^1V^\circ_{35,24(2)}$	−0.0003	−0.0114	0.0188	−0.0014	$^1V^\circ_{35,34}$	−0.0208	0.0004	−0.0206
$^1V^\circ_{35,26(1)}$	0.0002	0.0046	−0.0127	−0.0026	$^1V^\circ_{35,N4(1)}$	0.0207	−0.0226	−0.0187
$^1V^\circ_{35,26(2)}$	−0.0001	−0.0027	0.0073	0.0015	$^1V^\circ_{35,N4(2)}$	0.2020	0.0086	0.2225
$^1V^\circ_{25,25}$	0.0001	0.0046	−0.0125	−0.0025	$^1V^\circ_{35,14(1)}$	−0.0022	0.0066	0.0095
$^1V^\circ_{25,N4(2)}$	−0.0044	−0.1122	0.2753	0.0647	$^1V^\circ_{35,14(2)}$	−0.0152	−0.0035	−0.0218
$^1V^\circ_{25,14(2)}$	0.0003	0.0095	−0.0203	−0.0084	$^1V^\circ_{35,36}$	−0.0079	0.0002	−0.0078
$^1V^\circ_{25,N6(2)}$	−0.0023	−0.0542	0.1489	0.0302	$^1V^\circ_{35,N6(1)}$	0.0078	−0.0086	−0.0071
$^1V^\circ_{25,16(2)}$	0.0001	0.0027	−0.0074	−0.0015	$^1V^\circ_{35,N6(2)}$	0.1090	0.0026	0.1164
$^1V^\circ_{34,34}$	0.0009	0.0268	0.0032	0.0328	$^1V^\circ_{35,16(1)}$	−0.0008	0.0025	0.0036
$^1V^\circ_{34,N4}$	−0.0096	−0.1583	−0.0273	−0.1519	$^1V^\circ_{35,16(2)}$	−0.0052	−0.0013	−0.0076
$^1V^\circ_{34,14}$	0.0007	0.0141	0.0043	0.0044	$^1V^\circ_{25,24}$	0.0044	0.0076	−0.0043
$^1V^\circ_{34,36}$	0.0005	0.0071	0.0008	0.0088	$^1V^\circ_{25,N5}$	0.0055	−0.0060	−0.0049
$^1V^\circ_{34,N6(1)}$	−0.0045	−0.0091	−0.0049	0.0072	$^1V^\circ_{25,15}$	−0.0006	0.0018	0.0025
$^1V^\circ_{34,N6(2)}$	−0.0046	−0.0972	−0.0090	−0.1310	$^1V^\circ_{34,24}$	0.0137	0.0236	−0.0134
$^1V^\circ_{34,16(1)}$	0.0003	0.0016	0.0014	−0.0040	$^1V^\circ_{34,26(1)}$	0.0064	0.0109	−0.0062
$^1V^\circ_{34,16(2)}$	0.0002	0.0042	−0.0002	0.0086	$^1V^\circ_{34,26(2)}$	−0.0037	−0.0063	0.0036
$^1V^\circ_{N4,N4}$	0.0494	0.2112	0.1134	−0.1689	$^1V^\circ_{24,N4}$	−0.0996	−0.1713	0.0970
$^1V^\circ_{N4,14}$	−0.0054	−0.0364	−0.0283	0.0719	$^1V^\circ_{24,14}$	0.0077	0.0132	−0.0075
$^1V^\circ_{N4,N6}$	0.0371	0.0746	0.0405	−0.0606	$^1V^\circ_{24,N6(1)}$	−0.0001	−0.0001	0.0001
$^1V^\circ_{N4,16(1)}$	−0.0035	−0.0157	−0.0142	0.0405	$^1V^\circ_{24,N6(2)}$	−0.0747	−0.1285	0.0728
$^1V^\circ_{N4,16(2)}$	−0.0006	0.0038	0.0053	−0.0191	$^1V^\circ_{24,16(2)}$	0.0037	0.0064	−0.0036
$^1V^\circ_{14,14}$	0.0003	0.0027	0.0024	−0.0068	$^1V^\circ_{N4,N5}$	−0.1227	0.1341	0.1109
$^1V^\circ_{14,16}$	0.0001	0.0006	0.0006	−0.0016	$^1V^\circ_{N4,15(1)}$	0.0116	−0.0127	−0.0105
$^1V^\circ_{36,36}$	0.0001	0.0000	0.0000	0.0000	$^1V^\circ_{N4,15(2)}$	0.0117	−0.0484	−0.0734
$^1V^\circ_{36,N6}$	−0.0019	0.0005	0.0002	−0.0003	$^1V^\circ_{N5,N6}$	−0.0651	0.0712	0.0589
$^1V^\circ_{36,16}$	0.0001	0.0000	0.0000	0.0000	$^1V^\circ_{N5,16(1)}$	0.0085	−0.0256	−0.0365
$^1V^\circ_{N6,N6}$	0.0139	−0.0035	−0.0015	0.0021	$^1V^\circ_{N5,16(2)}$	−0.0003	0.0098	0.0169
$^1V^\circ_{N6,16}$	−0.0010	0.0002	0.0001	−0.0001	$^1V^\circ_{14,15}$	−0.0010	0.0030	0.0043
Sum weight (%)	0.42	10.35	11.66	8.62	$^1V^\circ_{15,16}$	−0.0003	0.0010	0.0015
Total weight (%)	100.00	99.90	99.66	99.91	$^1V^\circ_{N6,26}$	0.0000	−0.0001	0.0000
					Sum weight (%)	8.95	7.39	10.26
					Total weight (%)	99.82	99.93	99.72

TABLE 5. CONTRIBUTION FROM DOUBLY EXCITED CONFIGURATIONS (TRIPLET STATE)

Configuration	$^3A_1$ $^3\Psi_I$	$^3\Psi_{III}$	$^3\Psi_V$	Configuration	$^3\Psi_I$	$^3\Psi_{III}$	$^3\Psi_V$
$^3V^\circ_{35,24(1)}$	−0.0126	0.0316	0.0028	$^3V^\circ_{34,14}$	−0.0118	−0.0030	−0.0194
$^3V^\circ_{35,24(2)}$	0.0048	0.0143	0.0078	$^3V^\circ_{34,36}$	−0.0088	−0.0029	−0.0065
$^3V^\circ_{35,24(3)}$	−0.0131	0.0176	−0.0022	$^3V^\circ_{34,N6(1)}$	−0.0967	−0.0308	−0.0872
$^3V^\circ_{35,26(1)}$	−0.0048	0.0120	0.0011	$^3V^\circ_{34,N6(2)}$	0.0759	0.0258	0.0506
$^3V^\circ_{35,26(2)}$	−0.0017	0.0042	0.0004	$^3V^\circ_{34,N6(3)}$	0.0045	0.0024	−0.0062
$^3V^\circ_{35,26(3)}$	−0.0029	0.0073	0.0007	$^3V^\circ_{34,16(1)}$	0.0046	0.0011	0.0081
$^3V^\circ_{25,N4(1)}$	−0.0917	0.2297	0.0207	$^3V^\circ_{34,16(2)}$	−0.0038	−0.0014	−0.0012
$^3V^\circ_{25,N4(2)}$	0.0649	−0.1624	−0.0146	$^3V^\circ_{34,16(3)}$	−0.0004	−0.0004	0.0026
$^3V^\circ_{25,N4(3)}$	−0.0076	−0.0040	0.0108	$^3V^\circ_{N4,14}$	−0.0002	−0.0052	0.0571
$^3V^\circ_{25,14(1)}$	0.0071	−0.0177	−0.0016	$^3V^\circ_{N4,N6}$	−0.0637	−0.0336	0.0907
$^3V^\circ_{25,14(2)}$	−0.0050	0.0125	0.0011	$^3V^\circ_{N4,16(1)}$	0.0021	0.0043	−0.0379
$^3V^\circ_{25,14(3)}$	0.0006	0.0006	−0.0044	$^3V^\circ_{N4,16(2)}$	0.0046	0.0036	−0.0189
$^3V^\circ_{25,N6(1)}$	−0.0487	0.1219	0.0110	$^3V^\circ_{N4,16(3)}$	0.0035	0.0038	−0.0263
$^3V^\circ_{25,N6(2)}$	0.0344	−0.0862	−0.0078	$^3V^\circ_{14,16}$	−0.0002	−0.0003	0.0019
$^3V^\circ_{25,16(1)}$	0.0024	−0.0061	−0.0005	Sum weight (%)	5.97	10.89	4.79
$^3V^\circ_{25,16(2)}$	−0.0017	0.0043	0.0004	Total weight (%)	99.90	99.64	99.95
$^3V^\circ_{34,N4}$	0.1531	0.0477	0.1490				

(Table 5, continued) $^3B_2$

Configuration	$^3\Psi_{II}$	$^3\Psi_{IV}$	$^3\Psi_{VI}$	Configuration	$^3\Psi_{II}$	$^3\Psi_{IV}$	$^3\Psi_{VI}$
$^3V^\circ_{35,25}$	0.0079	0.0014	0.0051	$^3V^\circ_{34,26(3)}$	0.0019	−0.0079	−0.0008
$^3V^\circ_{35,34}$	0.0244	0.0042	0.0157	$^3V^\circ_{24,N4}$	−0.0504	0.2138	0.0207
$^3V^\circ_{35,N4(1)}$	0.1857	0.0283	0.1592	$^3V^\circ_{24,14}$	0.0039	−0.0165	−0.0016
$^3V^\circ_{35,N4(2)}$	−0.1511	−0.0275	−0.0836	$^3V^\circ_{24,N6(1)}$	0.0309	−0.1310	−0.0127
$^3V^\circ_{35,N4(3)}$	−0.0114	−0.0043	0.0168	$^3V^\circ_{24,N6(2)}$	−0.0218	0.0925	0.0089
$^3V^\circ_{35,14(1)}$	−0.0146	−0.0014	−0.0211	$^3V^\circ_{24,N6(3)}$	0.0000	0.0001	0.0000
$^3V^\circ_{35,14(2)}$	0.0116	0.0024	0.0033	$^3V^\circ_{24,16(1)}$	−0.0015	0.0065	0.0006
$^3V^\circ_{35,14(3)}$	0.0007	0.0008	−0.0067	$^3V^\circ_{24,16(2)}$	0.0011	−0.0046	−0.0004
$^3V^\circ_{35,36}$	0.0092	0.0016	0.0060	$^3V^\circ_{N4,N5}$	−0.1170	−0.0442	0.1723
$^3V^\circ_{35,N6(1)}$	0.1014	0.0161	0.0803	$^3V^\circ_{N4,15(2)}$	0.0111	0.0042	−0.0163
$^3V^\circ_{35,N6(2)}$	−0.0792	−0.0142	−0.0458	$^3V^\circ_{N4,15(3)}$	0.0040	0.0095	−0.0881
$^3V^\circ_{35,N6(3)}$	−0.0043	−0.0016	0.0064	$^3V^\circ_{N5,N6}$	0.0621	0.0235	−0.0914
$^3V^\circ_{35,16(1)}$	−0.0049	−0.0004	−0.0076	$^3V^\circ_{N5,16(1)}$	−0.0009	−0.0038	0.0370
$^3V^\circ_{35,16(2)}$	0.0040	0.0008	0.0010	$^3V^\circ_{N5,16(2)}$	−0.0041	−0.0028	0.0186
$^3V^\circ_{35,16(3)}$	0.0003	0.0003	−0.0025	$^3V^\circ_{N5,16(3)}$	−0.0028	−0.0032	0.0259
$^3V^\circ_{25,24}$	−0.0022	0.0095	0.0009	$^3V^\circ_{14,15}$	−0.0006	−0.0006	0.0053
$^3V_{25,N5}$	0.0052	0.0020	−0.0077	$^3V_{15,16}$	0.0002	0.0002	−0.0018
$^3V^\circ_{25,15}$	−0.0003	−0.0004	0.0031	$^3V^\circ_{N6,26}$	0.0000	−0.0001	0.0000
$^3V^\circ_{34,24}$	−0.0069	0.0294	0.0028	Sum weight (%)	9.69	7.77	9.13
$^3V^\circ_{34,26(1)}$	0.0030	−0.0129	−0.0012	Total weight (%)	99.76	99.90	99.80
$^3V^\circ_{34,26(2)}$	0.0011	−0.0045	−0.0004				

column of band assignment. If there is no reference state the weight of which singly exceeds 50%, the state notations for the reference states of the most important contribution are indicated in parentheses.

Configuration analysis including all the doubly excited configurations has been performed for both the singlet and the triplet states. All the doubly excited configurations which have a contribution higher than 0.0001 are given in Table 4 for the singlet states and in Table 5 for the triplet states. The notations concerning the doubly excited configurations are the same as in Ref. 24. The total weight means the sum of the weights of all the singly and doubly excited configurations.

Discussion

The calculated shifts in transition energies caused by the introduction of an amino group are compared with the observed shifts in Table 6. The calculated and the observed shifts agree well. Therefore, the electronic wave functions which were subjected to configuration analysis in the present study are appropriate to a discussion of the effect of substitution on the electronic spectra.

The ground state of aniline may safely be assigned to the ground reference state. The charge-transfer reference states have a weight of 11.84% in the ground state. In the first excited state of aniline, the reference state which has the highest contribution to this state is the ^1L_b, the wight of which is 59.55%. The first excited state of aniline may, therefore, be assigned to the locally excited reference state, ^1L_b. The weight of the charge-transfer contributions to this state is 28.47%. The contribution of the ^1B_b to the first excited state is only 2.53%, but the origin of the absorption intensity of the first absorption band in aniline may be explained by the mixing with the ^1B_b.

In the second excited state of aniline, there is no reference state which alone has a weight of contribution higher than 50%. The reference state of the highest contribution to this excited states is the ^1L_a; however, the weight of the ^{1}CTS1 state is comparable to, and a little lower than, that of the ^1L_a state. It is reasonable that the second excited state of aniline is assigned to the mixed state of the ^1L_a and the ^{1}CTS1 reference state. The ^1B_a reference state has a weight of 3.90%; the intensity of the second absorption band may be derived from the ^1B_a state. The weight of the ground reference state is 5.87%.

In the third excited state of aniline, the reference state with a maximum wight is the ^{1}CTA state. However, there are two other reference states which have weights comparable to that of the ^{1}CTA, namely, the ^1B_b and ^1L_b states. The third excited state of aniline is, therefore, assigned to the mixed state of the ^{1}CTA, ^1B_b, and ^1L_b states. The ^1B_a reference state makes the highest contribution to the fourth excited state of aniline. The ^1L_a reference state also makes a considerable contribution to this excited state. It is found that the higher excited states of aniline are difficult to explain in terms of a single locally excited state or a single charge-transfer state.

Table 6. Comparison of the band shifts caused by the introduction of an amino group into benzene

Band	Band shift (eV)			
	Obsd	This work	Fischer-Hjalmars	Kimura *et al.*
I	−0.49	−0.475	−0.198	−0.17
II	−0.78	−0.742	−0.619	−0.75
III	−0.58	−0.645	−0.501	−0.56
VI	−0.10	−0.287	−0.336	−0.12

In the first excited triplet state, the ^3L_a state alone has a weight higher than 50%; therefore, the first triplet state of aniline may be assigned to the ^3L_a reference state. The ^{3}CTS1 state and the ^3B_a state have weights of 27.35 and 7.70% respectively. The assignments of the higher triplet states of aniline are given in Table 3. It is of interest that the weights of the charge-transfer reference states in the $^3\Psi_V$ and $^3\Psi_{VI}$ states have values higher than 50%, whereas the charge-transfer reference states make little contribution to the $^3\Psi_{III}$ and $^3\Psi_{IV}$ states. In general, it is found that the reference states in the triplet states are mixed together to a lesser extent than those in the singlet states.

All the contributions from the doubly excited configurations were calculated for both the singlet and the triplet states of aniline. The $^1V^\circ_{25,N4(2)}$ reference configuration has a weight of 7.58% relative to the $^1\Psi_{IV}$ state. The reference configurations which have weights higher than 2% are as follows: $^1V^\circ_{35,N4(2)}$ ($^1\Psi_I$); $^1V^\circ_{N4,N4}$ and $^1V^\circ_{34,N4}$ ($^1\Psi_{II}$); $^1V^\circ_{24,N4}$ ($^1\Psi_{III}$); $^1V^\circ_{25,N4(2)}$ and $^1V^\circ_{25,N6(2)}$ ($^1\Psi_{IV}$); $^1V^\circ_{35,N4(2)}$ ($^1\Psi_V$); $^1V^\circ_{N4,N4}$ and $^1V^\circ_{24,N4}$ ($^1\Psi_{VI}$). All the other reference configurations have weights less than 2% relative to the individual singlet states. The contributions of individual doubly-excited configurations are not important, however, the sum weights from all the doubly excited configurations have values ranging between 7.39 and 11.66%, except for the ground state. The sum weight of all the singly excited states or configurations for the ground state has a value of 99.58%, but the sum weights for the excited singlet states have values of about 90% (from 88.00 to 92.54%). The inclusion of all the doubly excited configurations improves the sum weights of the excited states up to 99.66% or more. It may be said that the "accuracy" of the description of the lower excited electronic states of aniline in terms of the locally excited states and the charge-transfer states within the singly excited configurations is approximately 90%. The inclusion of the doubly excited configurations improves the "accuracy" of the description, but the brevity of the description is lost. When the sum weights of all the singly excited configurations are far from 100%, the selection of reference states or configurations should be reconsidered. If a proper selection of reference states is impossible, one should abandon the description of the excited states in terms of locally excited states and charge-transfer states.

The reference states included in the calculation by Kimura *et al.*[15] are the ground state, $^1\Psi^\circ_G$, the four locally excited states, $^1\Psi^\circ_{Lb}$, $^1\Psi^\circ_{La}$, $^1\Psi^\circ_{Bb}$, and $^1\Psi^\circ_{Ba}$, and the two charge-transfer states, $^1\Psi^\circ_{CTS1}$ and $^1\Psi^\circ_{CTA}$. The sum weights of these seven reference states in the present configuration analysis are as follows: 90.55% ($^1\Psi_I$), 88.24% ($^1\Psi_{II}$), 89.59% ($^1\Psi_{III}$), 87.07% ($^1\Psi_{IV}$), 83.50% ($^1\Psi_V$), and 83.89% ($^1\Psi_{VI}$). This implies that a portion of the electronic interactions is neglected in the localized-orbital description compared with the Pariser-Parr-Pople method (10—16% in the case of aniline). In other words, the wave functions of locally excited states or charge-transfer states cannot be regarded as the basis functions of rapid convergence in the expansion of excited states of aniline.

Murrell,[8] Kimura *et al.*,[15] and Godfrey and Murrell[16] obtained the electronic wave functions of aniline as the linear combinations of locally excited and charge-transfer state functions by using the localized-orbital method. On the other hand, Fischer-Hjalmars[11] transformed the excited wave functions obtained by the Pariser-Parr-Pople method into locally excited or charge-transfer state functions through natural spin orbitals. In Table 7, the results of the present configuration analysis are compared with those of the other investigations.

Table 7. Comparison of the results

$^1A_1$

Reference state	$^1\Psi_{II}$			$^1\Psi_{IV}$		
	CA[a]	Fischer-Hjalmars	Kimura *et al.*	CA[a]	Fischer-Hjalmars	Kimura *et al.*
$^1\Psi^\circ_G$	6.7		3.7	1.3		0.4
$^1\Psi^\circ_{La}$	46.7	57.5	34.9	36.3	26.1	53.1
$^1\Psi^\circ_{Ba}$	4.4	4.2	11.4	49.8	55.4	37.5
$^1\Psi^\circ_{CTS1}$	42.2	38.3	50.0	12.6	18.7	9.0

$^1B_2$

Reference state	$^1\Psi_I$			$^1\Psi_{III}$		
	CA[a]	Fischer-Hjalmars	Kimura *et al.*	CA[a]	Fischer-Hjalmars	Kimura *et al.*
$^1\Psi^\circ_{Lb}$	65.8	89.5	74.6	29.8	5.7	21.4
$^1\Psi^\circ_{Bb}$	2.8	0.7	2.7	32.2	60.5	39.9
$^1\Psi^\circ_{CTA}$	31.5	9.9	22.6	38.0	33.8	38.7

a) The results of the present work. Weights are normalized to 100% within the states listed in the table.

In the assignment of the first excited state of aniline, a qualitative agreement is found among these results. Kimura *et al.* as well as Murrell assigned the second excited state of aniline to the charge-transfer state, ^{1}CTS1. On the contrary, Baba[10] and Fischer-Hjalmars assigned the band to the locally excited state, ^1L_a. The present study supports the latter assignment rather than the former one, but the weight of the ^1L_a state does not exceed 50%. The third excited singlet state shows a remarkable mixing among the ^1L_b, ^1B_b, and ^{1}CTA states in the present study and in the work of Kimura *et al.*, but it was assigned to the ^1B_b reference state in the work of Fischer-Hjalmars. In the fourth excited state, the result of the present analysis resembles that of Fischer-Hjalmars rather than that of Kimura *et al.* The result obtained by Murrell showed a qualitative resemblance to that obtained by Kimura *et al.*, but the result obtained by Godfrey and Murrell resembled that obtained by Fischer-Hjalmars.

Kimura and Tsubomura[26] calculated the wave functions of the triplet states of substituted benzenes by using the localized-orbital method. They assigned the lowest triplet state of aniline to the ^3L_a, in accordance with the results of the present analysis.

The calculated band shifts caused by the introduction of an amino group into benzene are compared with the

observed shifts as well as the calculated shifts obtained by the other studies in Table 6. Band I of aniline, which was assigned to the locally excited transition of benzene, ^1L_b, shows a considerable red shift compared with Band I of benzene. In the calculation of state energies by the localized-orbital method adopted by Murrell, by Kimura *et al.*, and by Godfrey and Murrell, the observed transition energies of benzene are used as the state energies of the locally excited configurations. Nevertheless, the localized-orbital method can not correctly reproduce the red shift of Band I. The result obtained by Fischer-Hjalmars does not give the red shift of Band I correctly, either. Furthermore, the mixing of the ground state with the excited reference states has been neglected in the work of Fischer-Hjalmars.

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