The Absorption Spectra of Disubstituted Benzenes. Interpretation by Means of Configuration Analysis

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The method of configuration analysis has been applied to the interpretation of the ground and the excited states of disubstituted benzenes with two electron-donating groups, *o*-, *m*-, and *p*-benzenediols and *o*-, *m*-, and *p*-phenylenediamines, with particular attention paid to the dependence of the spectra on the positions of substitution and on the molecular symmetry. The wave functions calculated by the Pariser-Parr-Pople method are analyzed in terms of locally-excited states and intramolecular charge-transfer states. The characteristic changes in the location of the L_b, L_a, and B_b bands caused by substitution are adequately explained by the analysis. The intensification of the L_b band caused by the introduction of the substituents is interpreted as due to the mixing between the L_b, B_b, and B_a bands for the *o*- and *m*-substituted benzenes and between the L_b and B_b bands for the *p*-disubstituted benzenes. It was found empirically that the magnitudes of the spectral shift from benzene to the derivatives are determined primarily by the extent of charge-transfer contributions.

Although the effects of substitution on the electronic spectra have been extensively investigated for monosubstituted benzenes,1—7) the electronic spectra of disubstituted benzenes have received little attention.8—14) Kiss and Szöke have calculated many disubstituted benzenes, including fluoro, chloro, hydroxyl, amino, formyl, carboxyl, and nitro groups, and have discussed the singlet transition energies as well as the ground-state charge densities and bond orders.

The present paper will report on the results of the configuration analysis (CA) of six disubstituted benzenes: *o*-, *m*-, and *p*-benzenediols (*o*-, *m*-, and *p*-$(OH)_2$) and *o*-, *m*-, and *p*-phenylenediamines (*o*-, *m*-, and *p*-$(NH_2)_2$). The *o*- and *m*-disubstituted benzenes both have the C_{2v} symmetry, but the former have the symmetry axis along the b-axis of the benzene ring, while the latter have the symmetry axis along the a-axis of the benzene ring. The *p*-disubstituted benzenes have the D_{2h} symmetry and have the symmetry axis along the b-axis of the benzene ring.

Calculation

The method of calculation, the procedure, the parameters, and the molecular geometry are the same as have previously been described except for one added substitution.6,7) The geometry of the compounds studied in this paper are shown in Fig. 1. The SCF MO's are numbered in the order of increasing energy. In the CI calculation of all the compounds, the following 10 singly-excited configurations are included: 5→6, 7, 8; 4→6, 7, 8; 3→6, 7; 2→6, 7.

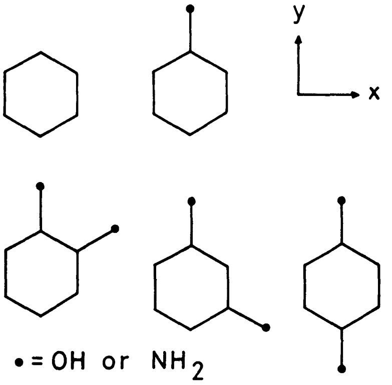

Fig. 1. The molecular geometry of the compounds.

Experimental

o-Benzenediol and phenylenediamines were purified by repeated crystallizations and subsequent sublimation *in vacuo* prior to use. Isooctane (2,2,4-trimethylpentane) was fractionally distilled and then passed through a column of silica gel. The absorption spectra were recorded on a Hitachi EPS-3 recording spectrophotometer.

Results

The calculated energies, the oscillator strengths, and the directions of the transition moments, which are the angles from the x-axis, for the lower singlet states of the six compounds are presented in Table 1, together with the available experimental data. The symbols used in the present paper for denoting the electronic states and absorption bands have the same meaning as the corresponding symbols in previous papers,6,7) unless otherwise noted.

The results of the CA of the six compounds are given in Tables 3—8. The reference MO's employed in the analysis are the SCF MO's of benzene $\phi_1^\circ, \cdots, \phi_6^\circ$, and the 2 MO's of the substituents, ϕ_{X+}° and ϕ_{X-}°, which are the linear combination of the AO's, χ_1 and χ_2, of the substituents:

$$\phi_{X+}^\circ = \frac{1}{\sqrt{2}}(\chi_1+\chi_2),$$

$$\phi_{X-}^\circ = \frac{1}{\sqrt{2}}(\chi_1-\chi_2).$$

The reference states taken into account in the analysis are as follows: the ground and 4 locally-excited states of benzene, Ψ_G°, $\Psi_1^\circ, \cdots$, Ψ_4°: 4 intramolecular charge-transfer reference states, Ψ_{CT4+}°, Ψ_{CT4-}°, Ψ_{CT5+}°, and Ψ_{CT5-}°. The Ψ_{CT4+}° corresponds to a one-electron excitation from ϕ_{X+}° to ϕ_4°, *etc.* The total weight means the sum of the weights of all 9 reference states described above.

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Table 1. Excited states of disubstituted benzenes

Compound	State function	Energy (eV)		Oscillator strength		Band assignment	Polarization (deg)
		Calcd	Obsd	Calcd	Obsd		
o-Benzenediol(catechol)							
	Ψ_G	0					
	Ψ_1	4.60	4.48	0.048	0.060	I	60
	Ψ_2	5.43	5.78	0.108	0.163	II	−30
	Ψ_3	6.40	6.24	0.848		III	−30
	Ψ_4	6.51		1.183		IV	60
	Ψ_5	7.77		0.008			−30
m-Benzenediol(resorcinol)							
	Ψ_G	0					
	Ψ_1	4.66	4.50[a]	0.030	0.052[a]	I	−60
	Ψ_2	5.56	5.69[a]	0.052	0.163[a]	II	30
	Ψ_3	6.37		0.845		III	30
	Ψ_4	6.49		1.291		IV	−60
	Ψ_5	7.65		0.027			−60
p-Benzenediol(hydroquinone)							
	Ψ_G	0					
	Ψ_1	4.47	4.26[a]	0.105	0.070[a]	I	0
	Ψ_2	5.50	5.54[a]	0.233	0.106[a]	II	90
	Ψ_3	6.69		0.838		III	0
	Ψ_4	6.73		1.215		IV	90
	Ψ_5	7.32		0.000			
o-Phenylenediamine							
	Ψ_G	0					
	Ψ_1	4.30	4.22	0.069	0.038	I	60
	Ψ_2	4.85	5.23	0.163	0.107	II	−30
	Ψ_3	5.84	6.02	0.364	0.662	III	−30
	Ψ_4	5.96		0.885		IV	60
	Ψ_5	7.06		0.032			−30
m-Phenylenediamine							
	Ψ_G	0					
	Ψ_1	4.40	4.19	0.035	0.021	I	−60
	Ψ_2	5.07	5.17	0.091	0.083	II	30
	Ψ_3	5.69	5.79	0.387	0.502	III	−60
	Ψ_4	5.70		0.867		IV	−60
	Ψ_5	6.91		0.228			−60
p-Phenylenediamine							
	Ψ_G	0					
	Ψ_1	4.13	3.89	0.108	0.031	I	0
	Ψ_2	4.90	5.10	0.440	0.180	II	−90
	Ψ_3	5.98		0.000			
	Ψ_4	6.16		0.000			
	Ψ_5	6.41	6.23	0.462	0.559	III	0
	Ψ_6	6.62		0.983		IV	−90
	Ψ_7	7.62		0.000			

[a] Ref. 8.

The band assignments are given in Tables 3—8. When a single reference state has a weight higher than 50%, the state notation of the state is indicated in the column of the band assignments.

Discussion

The calculated band shifts in the transition energies caused by the introduction of hydroxyl and amino groups are compared with the observed band shifts including phenol and aniline in Table 2. There are 4 electronic absorption bands in the ultraviolet region. Although the same parameters are used irrespective of the positions of substitution, the calculated and observed band shifts agree very well except for Band II of the *o*-disubstituted benzenes. The effect of *o*-substitution may perhaps appear in Band II of *o*-disubstituted benzenes. The order of the observed band shifts, ΔE, of the individual absorption band are: $\Delta E(p\text{-})>\Delta E(m\text{-})\approx\Delta E(o\text{-})$ for Band I; $\Delta E(p\text{-})>\Delta E(m\text{-})>\Delta E(o\text{-})$ for

TABLE 2. COMPARISON OF THE CALCULATED AND OBSERVED BAND SHIFTS CAUSED BY THE INTRODUCTION OF THE SUBSTITUENT INTO BENZENE (eV)

Compound		Band I	II	III	IV
Phenol	Calcd[a]	−0.24	−0.34	−0.26	−0.17
	Obsd[b]	−0.30	−0.35	−0.28	−0.05
Aniline	Calcd[c]	−0.47	−0.74	−0.65	−0.29
	Obsd[b]	−0.49	−0.78	−0.58	−0.10
o-$(OH)_2$	Calcd	−0.41	−0.64	−0.50	−0.39
	Obsd	−0.40	−0.40		
m-$(OH)_2$	Calcd	−0.35	−0.51	−0.53	−0.41
	Obsd	−0.39	−0.48		
p-$(OH)_2$	Calcd	−0.54	−0.57	−0.21	−0.17
	Obsd	−0.63	−0.63		
$o(NH_2)_2$	Calcd	−0.71	−1.22	−1.06	−0.94
	Obsd	−0.68	−0.94	−0.96	
m-$(NH_2)_2$	Calcd	−0.61	−1.00	−1.21	−1.20
	Obsd	−0.70	−1.00	−1.19	
p-$(NH_2)_2$	Calcd	−0.88	−1.17	−0.50	−0.28
	Obsd	−1.00	−1.07	−0.75	

a) Ref. 6. b) K. Kimura, H. Tsubomura, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **37**, 1336 (1964); K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965); S. Nagakura and K. Kimura, *Nippon Kagaku Zasshi*, **86**, 1 (1965). c) Ref. 7.

Band II; $\Delta E(m\text{-}) > \Delta E(o\text{-}) > \Delta E(p\text{-})$ for Band III.

Band Assignment. Tables 3—5 show the results of the CA of the benzenediols. The first and the second bands of o-, m-, and p-$(OH)_2$ can reasonably be assigned to the L_b and L_a respectively. Since a strong mixing is found to occur between the B_b and B_a reference states in the Ψ_3 and Ψ_4 excited states, one can hardly identify the B_b and B_a bands in the cases of o- and m-$(OH)_2$. On the other hand, Band III and IV, which may be found in the higher energy side of Band II, of p-$(OH)_2$ are assigned to the B_b and B_a respectively. The main charge-transfer reference states to each state are as follows: Ψ°_{CT4-} (Band I), Ψ°_{CT5+} (Band II), Ψ°_{CT4+} (Band III), and Ψ°_{CT4-} (Band IV) in o-$(OH)_2$, Ψ°_{CT4+} (Band I), Ψ°_{CT5-} (Band II), Ψ°_{CT4-} (Band III), and Ψ°_{CT5+} (Band IV) in m-$(OH)_2$, and Ψ°_{CT4+} (Band I), Ψ°_{CT5-} (Band II), Ψ°_{CT4+} (Band III), and Ψ°_{CT5-} (Band IV) in p-$(OH)_2$.

TABLE 3. CONFIGURATION ANALYSIS FOR o-BENZENEDIOL (WEIGHT IN PERCENT)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_3	IV Ψ_4
Ψ_G°		82.2	0.2			3.5
Ψ_1°	L_b	0.0	66.2			7.3
Ψ_2°	L_a			56.2	8.7	
Ψ_3°	B_b	0.0	0.3	2.1	42.3	13.8
Ψ_4°	B_a	0.1	1.0	0.7	14.1	41.5
Ψ°_{CT4+}		2.2	0.7	1.7	8.6	0.9
Ψ°_{CT4-}		2.7	11.1	5.9	2.1	8.5
Ψ°_{CT5+}		0.9	3.7	17.8	6.2	2.8
Ψ°_{CT5-}		6.7	2.0	0.6	2.9	2.7
Total weight[a]		94.8	85.1	85.1	84.9	81.0
Assignment[a]		[G]	[L_b]	[L_a]		

a) See text for definition.

TABLE 4. CONFIGURATION ANALYSIS FOR m-BENZENEDIOL (WEIGHT IN PERCENT)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_3	IV Ψ_4
Ψ_G°		80.0		6.3	0.1	
Ψ_1°	L_b		69.1			2.1
Ψ_2°	L_a	0.6		60.5	0.7	
Ψ_3°	B_b	0.0	0.3	0.7	43.1	13.8
Ψ_4°	B_a	0.0	1.0	0.2	14.4	41.5
Ψ°_{CT4+}		2.5	8.2	2.2	2.1	7.1
Ψ°_{CT4-}		2.6	0.8	2.7	12.0	4.0
Ψ°_{CT5+}		0.9	2.4	0.9	4.0	12.0
Ψ°_{CT5-}		7.5	2.7	6.5	6.2	2.4
Total weight[a]		94.1	84.5	80.0	82.5	82.9
Assignment[a]		[G]	[L_b]	[L_a]		

a) See text for definition.

TABLE 5. CONFIGURATION ANALYSIS FOR p-BENZENEDIOL (WEIGHT IN PERCENT)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_3	IV Ψ_4
Ψ_G°		81.5				
Ψ_1°	L_b		61.0		16.1	
Ψ_2°	L_a			60.3		3.4
Ψ_3°	B_b		4.7		62.4	
Ψ_4°	B_a			4.9		66.2
Ψ°_{CT4+}			17.8		8.5	
Ψ°_{CT4-}						
Ψ°_{CT5+}		12.6				
Ψ°_{CT5-}				22.4		5.4
Total weight[a]		94.0	83.4	87.6	86.9	82.9
Assignment[a]		[G]	[L_b]	[L_a]	[B_b]	[B_a]

a) See text for definition.

Since the amino group is known to be a strong electron donor, charge-transfer configurations are mixed effectively with locally-excited states of benzene of a lower energy, as is seen in Tables 6—8. Accordingly, the amino-substitution has a greater influence on the electronic structure of benzene than does the hydroxy-substitution.

The most important reference states in the excited states of phenylenediamines are the charge-transfer reference states. Indeed, Ψ°_{CT4+} in the Ψ_3 of o-$(NH_2)_2$ and in the Ψ_1 of p-$(NH_2)_2$, Ψ°_{CT4-} in the Ψ_3 of m-$(NH_2)_2$, Ψ°_{CT5+} in the Ψ_2 of o-$(NH_2)_2$ and in the Ψ_4 of m-$(NH_2)_2$, and Ψ°_{CT5-} in the Ψ_2 of p-$(NH_2)_2$ are the most important reference states in the states of phenylenediamines.

The L_b reference state does not interact with the L_a reference state, but interacts with the B_b and B_a for the o- and m-$(OH)_2$ and the B_b for the p-$(OH)_2$, from which the intensity of Band I is derived.

Table 6. Configuration analysis for *o*-phenylenediamine (weight in percent)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a)]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_3	IV Ψ_4
$\Psi_G{}^\circ$		78.9	0.5			9.8
$\Psi_1{}^\circ$	L_b	0.0	48.8			11.3
$\Psi_2{}^\circ$	L_a			30.4	8.5	
$\Psi_3{}^\circ$	B_b	0.0	0.4	2.2	18.5	5.4
$\Psi_4{}^\circ$	B_a	0.1	1.1	0.7	6.2	16.2
Ψ°_{CT4+}		2.7	1.2	2.6	32.6	3.5
Ψ°_{CT4-}		3.2	20.2	11.3	2.1	12.1
Ψ°_{CT5+}		1.1	6.7	33.8	6.4	4.1
Ψ°_{CT5-}		8.0	3.5	0.9	10.9	10.6
Total weight[a)]		94.0	82.3	81.9	85.1	74.7
Assignment[a)]		[G]				

a) See text for definition.

Table 7. Configuration analysis for *m*-phenylenediamine (weight in percent)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a)]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_3	IV Ψ_4
$\Psi_G{}^\circ$		76.3		12.9	0.0	
$\Psi_1{}^\circ$	L_b		54.0			0.6
$\Psi_2{}^\circ$	L_a	0.7		35.3	0.0	
$\Psi_3{}^\circ$	B_b	0.0	0.3	0.6	17.9	4.0
$\Psi_4{}^\circ$	B_a	0.0	0.9	0.2	6.1	11.5
Ψ°_{CT4+}		3.0	16.0	3.8	4.0	11.3
Ψ°_{CT4-}		3.2	1.5	6.4	30.5	11.2
Ψ°_{CT5+}		1.1	4.4	2.2	9.8	34.7
Ψ°_{CT5-}		9.0	5.4	11.6	12.1	3.6
Total weight[a)]		93.1	82.4	73.0	80.6	77.0
Assignment[a)]		[G]	[L_b]			

a) See text for definition.

Table 8. Configuration analysis for *p*-phenylenediamine (weight in percent)

Reference state		Absorption band (upper) and state function (lower)				
Wave function[a)]	State notation	Ψ_G	I Ψ_1	II Ψ_2	III Ψ_5	IV Ψ_6
$\Psi_G{}^\circ$		78.1				
$\Psi_1{}^\circ$	L_b		42.9		33.2	
$\Psi_2{}^\circ$	L_a			32.8		28.8
$\Psi_3{}^\circ$	B_b		4.3		33.7	
$\Psi_4{}^\circ$	B_a			4.9		42.9
Ψ°_{CT4+}			33.1		17.7	
Ψ°_{CT4-}						
Ψ°_{CT5+}		15.1				
Ψ°_{CT5-}				46.5		6.5
Total weight[a)]		93.3	80.3	84.2	84.6	78.2
Assignment[a)]		[G]				

a) See text for definition.

Band Shift. The contributions of charge-transfer configurations to the individual excited states of substituted benzenes are expected to be the principal source of the spectral changes.[15)] In order to ascertain the dependence of the spectral shifts on the contribution of charge-transfer states of substituted benzenes, the calculated state energies, E_{calcd}, for Bands I, II, III, and IV are plotted against the total charge-transfer weights, W_{CT}, including the corresponding values of phenol and aniline. The calculated state energies of benzene are also plotted on the axis of the ordinate in Fig. 2.

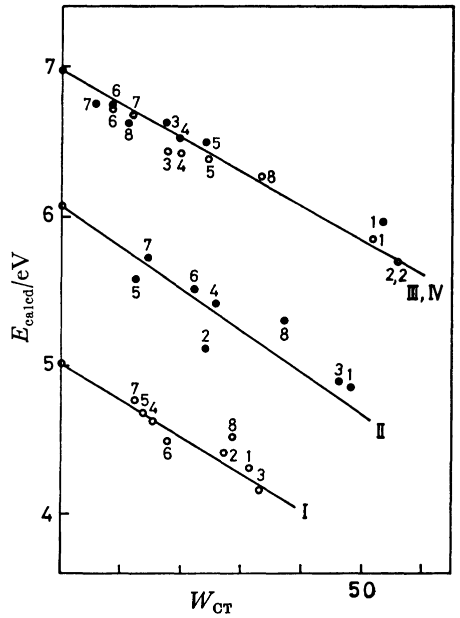

Fig. 2. The plots of E_{calcd} against W_{CT}. 1: *o*-Diaminobenzene, 2: *m*-diaminobenzene, 3: *p*-diaminobenzene, 4: *o*-dihydroxybenzene, 5: *m*-dihydroxybenzene, 6: *p*-dihydroxybenzene, 7: phenol, 8: aniline. The calculated state energies of benzene are plotted on the axis of ordinate. Band I: ○; Band II: ●; Band III: ○; Band IV: ●. Band III and IV lie on the same line.

It may be seen from Fig. 2 that approximately linear relationships exist between E_{calcd} and W_{CT} for individual bands of benzene derivatives including phenol and aniline. The plots of E_{calcd} against W_{CT} for Band I intersect the ordinate axis at the point corresponding to the L_b-state energy of benzene. The plot for Band II may be approximated by a straight line, and the point of intersection of the ordinate for Band II is the point representing the L_a-state energy of benzene. The plots for Bands III and IV also have an approximately linear relation and lie on the same straight line. It is to be noted that the gradients for the individual bands have approximately the same values. It is concluded that the plots of E_{calcd} against W_{CT} are approximately linear and that the extrapolations of the plots for each band to zero total weight give the corresponding state energies of benzene.

The plots for the observed state energies, E_{obsd}, against the total charge-transfer weights, W_{CT}, are presented in Fig. 3. Although the observed data are

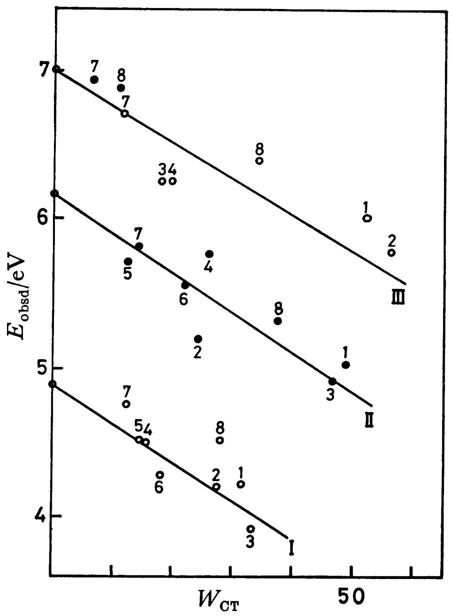

Fig. 3. The plots of E_{obsd} against W_{CT}. The numberings are the same as in Fig. 2. The observed state energies of benzene are plotted on the axis of ordinate.

not so many, approximately linear relationships also exist between E_{obsd} and W_{CT}. As is the case of E_{calcd} *vs.* W_{CT}, the gradients of the individual bands have nearly the same values.

Although the contribution of the charge-transfer configurations to individual bands is expected to increase with the decrease in molecular size, the total weight of the charge-transfer configurations is closely correlated with the spectral shifts on going from benzene to its derivatives, as in the case of naphthalene derivatives.[15] This shows that the total charge-transfer contributions determine the spectral shifts on going from parent compounds to their derivatives.

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