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Absorption Spectra of Four Naphthalenediols with C_{2v} Symmetry. Interpretation by Means of Configuration Analysis

Tsuneo Fujii and Satoshi Suzuki

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380

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The electronic absorption spectra of four substituted naphthalenes with two electron-donating groups, 1,4-, 1,8-, 2,3-, and 2,7-naphthalenediols, have been investigated by means of configuration analysis, with particular attention paid to the dependence of the spectra on the positions of substitutions 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 excited electronic wave functions of naphthalenediols have been expanded not only in terms of the electronic states of naphthalene, but also in terms of those of naphthol. The present configuration analysis shows that the electronic states of all these four naphthalenediols may reasonably interpreted in terms of locally-excited states of the parent compounds and charge-transfer states from the substituents to the parent compounds. The characteristic spectral changes in the L_b, L_a, and B_b bands caused by substitution are adequately explained in relation to the positions and to the molecular symmetry. The intensification of the L_b band caused by the introduction of the hydroxyl groups is interpreted as due to the mixing between the L_b and B_b bands. The B_b reference state interacts with the L_b and A_g^- reference states in 1,4- and 2,3-naphthalenediols, whereas it interacts with the L_b, B_{1g}^+, and B_{1g}^- reference states in 1,8- and 2,7-naphthalenediols.

The electronic absorption spectra of naphthalene derivatives show characteristic behavior depending on the position and the properties of the substituents. The electronic spectra of monosubstituted naphthalenes are now well understood both theoretically and experimentally.[1-8)]

However, little attention has been directed to the electronic spectra of disubstituted naphthalenes, although some studies have been made from both theoretical and experimental points of view.[4,9-12)]

The present paper will report on the results of configuration analysis (hereafter abbreviated to CA) for four naphthalenediols, 1,4-, 1,8-, 2,3-, and 2,7-naphthalenediols (hereafter abbreviated to 1,4-, 1,8-, 2,3-, and 2,7-diol respectively), based on two different types of reference compounds, naphthalene and naphthols. The 1,4- and 2,3-diols have a symmetry axis along the long(b) axis of the naphthalene ring while the 1,8- and 2,7-diols have a symmetry axis along the short(a) axis. The interaction scheme of the naphthalenediols is expected to be more simple than that of monosubstituted naphthalenes.

Calculation

The method of a semi-empirical LCAO-SCF-CI calculation and the procedure of the CA are the same as has been described previously.[6,7)] It is assumed that the molecules studied have a planar structure and that the naphthalene ring consists of regular hexagons with every C–C bond length equal to 1.40 Å. The parameters, the bond lengths, r, the valence-state ionization potentials, I, the electron affinities, A, and the resonance integrals, β, are the same in a previous paper.[6)] The C–C–O bond angle is assumed to be equal to 120°.

The SCF MO's are numbered in the order of increasing energy. In the CI calculation of 1,4-diol, the following eleven singly excited configurations are included: 7→8, 9, 10, 11; 6→8, 9, 10; 5→8, 9; 4→8, 9. One more configuration is added for the other diols. The added configuration is as follows: for 1,8-diol, 5→10; for the 2,3- and 2,7-diols, 6→11.

Experimental

The 1,4-, 2,3-, and 2,7-diols were purified by treating them with decolorizing carbon and 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(f), and the directions of the transition moments for the lower singlet states of naphthalenediols are presented in Table 1, together with the observed data. The data of naphthalene and naphthols used in the present study were given in a previous paper.[6)] The symbols used in the present paper for denoting the electronic states and absorption bands have the same meaning as the corresponding symbols in that previous paper,[6)] unless otherwise noted. The X-axis and Y-axis are taken along the long and short axes of the naphthalene ring respectively. The newly observed absorption spectra of three naphthalenediols are shown in Figs. 1, 2, and 3. The calculated energies are indicated in the figures by vertical lines, the lengths of which represent the relative values of the oscillator strength.

The results of the CA of naphthalenediols on the basis of the state functions of naphthalene are presented in Tables 2, 4, 6, and 8. The reference MO's employed in the present study are the SCF MO's of naphthalene ϕ_1°, ϕ_2°,……, ϕ_{10}°, and two MO's of the substituents, ϕ_{0+}° and ϕ_{0-}°, which are linear combinations of the two AO's, χ_{01} and χ_{02}, of the substituents:

$$\phi_{0+}^\circ = \frac{1}{\sqrt{2}}(\chi_{01}+\chi_{02}),$$

$$\phi_{0-}^\circ = \frac{1}{\sqrt{2}}(\chi_{01}-\chi_{02}).$$

Table 1. Excited states of naphthalenediols

Compound State function	Energy (eV) calcd	Energy (eV) obsd	Oscillator strength calcd	Oscillator strength obsd	Band assignment	Polarization
1,4-Naphthalenediol						
Ψ_G	0					
Ψ_1	3.87	3.80	0.092	0.082	I	X
Ψ_2	3.87	3.80	0.283		II	Y
Ψ_3	5.09		0.047			
Ψ_4	5.19	5.04	0.484	0.388	III	X
Ψ_5	5.56		0.007			
Ψ_6	5.95	6.39	1.220	0.912	IV	X
Ψ_7	6.32		1.120			Y
1,8-Naphthalenediol						
Ψ_G	0					
Ψ_1	3.99	3.7[a]	0.068		I	X
Ψ_2	4.14	4.2[a]	0.328		II	Y
Ψ_3	5.05		0.014			
Ψ_4	5.34		0.000			
Ψ_5	5.47		0.055			
Ψ_6	5.74	5.6[a]	1.732		III	X
Ψ_7	6.14		0.465			
2,3-Naphthalenediol						
Ψ_G	0					
Ψ_1	3.91	3.84	0.046	0.021	I	X
Ψ_2	4.22	4.43	0.158	0.091	II	Y
Ψ_3	5.27	5.19	0.470		III	X
Ψ_4	5.35		0.028			
Ψ_5	5.66	5.51	0.726	1.256	IV	Y
Ψ_6	5.68		1.583			X
Ψ_7	5.85		0.036			
2,7-Naphthalenediol						
Ψ_G	0					
Ψ_1	3.95	3.85	0.024	0.025	I	X
Ψ_2	4.19	4.41	0.189	0.086	II	Y
Ψ_3	5.24		0.092			
Ψ_4	5.26	5.06	0.558		III	X
Ψ_5	5.59	5.41	1.108	1.461	IV	X
Ψ_6	5.88		0.481			X
Ψ_7	5.96		0.733			Y

a) Estimated for an isooctane solution. See Text.

The reference states which were taken into account in this analysis are as follows: the ground reference state and thirteen excited reference states of naphthalene, Ψ°_G, $\Psi^\circ_1, \cdots\cdots, \Psi^\circ_{13}$; six intramolecular charge-transfer reference states, and $\Psi^\circ_{\mathrm{CTO}\to k+}$ and $\Psi^\circ_{\mathrm{CTO}\to k-}$, which correspond to a one-electron excitation from ϕ°_{0+} and ϕ°_{0-} to ϕ°_k with $k=6$, 7, and 8. Of these nineteen excited reference states, the seven locally excited reference states and six intramolecular charge-transfer reference states are listed in Tables 2, 4, 6, and 8. The total weight means the sum of the weights of all the twenty reference states described above.

The CA of naphthalenediols calculated on the basis of the state functions of 1- or 2-naphthol can also be made in an analogous manner. These results are presented in Tables 3, 5, 7, and 9. In these cases, the reference MO's are the SCF MO's of naphthols $\phi^\circ_1, \phi^\circ_2, \cdots\cdots, \phi^\circ_{11}$, and the π-AO of the substituent, ϕ°_0. In these calculations the reference states are as follows: the ground reference state, Ψ°_G, and the locally excited reference states of naphthol (13 states for 1-naphthol or 14 states for 2-naphthol), and the three intramolecular charge-transfer states, $\Psi^\circ_{\mathrm{CTO}\to k}$, which correspond to a one-electron excitation from ϕ°_0 to ϕ°_k with $k=7$, 8, and 9. The total weight means the sum of the weights of all the seventeen (or eighteen) reference states for 1,4- and 1,8- (or 2,3- and 2,7-) diols.

The band assignments are given in Tables 2—9. When a single reference state has a weight higher than 50%, the state notation of the state is indicated in the columns of the band assignments. The notations given in the columns of the reference absorption bands of Tables 3, 5, 7, and 9 are the same as the band assignments of 1- and 2-naphthols given in a previous paper.[6)]

Discussion

It may be seen in Table 1 that the calculated energies for the naphthalenediols are in good agreement with the observed values.

Naphthalenediols, like monosubstituted naphthalene,[6,7)] show absorption spectra characteristic of the positions of substituents. The first and second absorption bands (L_b and L_a in naphthalene) overlap strongly in 1,8-diol, and coalesce into one band in 1,4-diol. Two absorption bands appear in the region of the B_b band of naphthalene in 1,4-diol, while only one absorption band appears in the B_b band region in 1,8-diol. In contrast to this, the spectra of 2,3- and 2,7-diols resemble the naphthalene spectrum in the first and second absorption bands, although a weak absorption band appears on the lower side of the strong absorption band in the region of the B_b band of naphthalene.

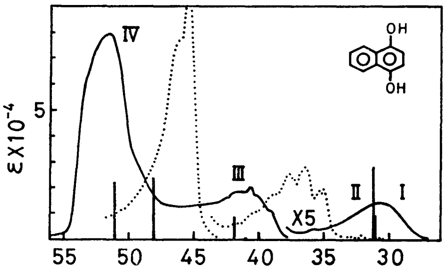

Fig. 1. Absorption spectrum in isooctane solution of 1,4-naphthalenediol. The dotted curve is the spectrum of naphthalene. Vertical lines represent theoretical spectra, with the lengths of lines indicating relative values of oscillator strengths.

1,4-Naphthalenediol. Figure 1 shows the absorption spectrum of 1,4-diol in isooctane, including the calculated data. With reference to the results shown in Tables 1 and 2, Bands I, II, and III may be assigned to the transitions to the Ψ_1, Ψ_2, and Ψ_4 while Band IV is actually composed of two absorption bands related to Ψ_6 and Ψ_7.

Table 2 shows that Bands I and II can reasonably be assigned to the L_b and L_a states respectively. The $\Psi^\circ_{\mathrm{CTO}\to 7+}$ state makes an important weight contribution to the Ψ_1 state (11.4%). The $\Psi^\circ_{\mathrm{CTO}\to 6+}$ state similarly

Table 2. Configuration analysis for 1,4-naphthalenediol from naphthalene (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
			I	II		III		IV	
Wave function[a)]	Symmetry type	Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°	A_g^-	79.4	0.0			0.2		0.0	
Ψ_1°	B_{3u}^-, L_b	0.0	65.3			8.4		0.9	
Ψ_2°	B_{2u}^+, L_a			55.7	0.0		19.1		0.8
Ψ_3°	B_{1g}^+			0.4	57.9		6.7		0.0
Ψ_4°	A_g^-	0.0	0.9			40.3		20.5	
Ψ_5°	B_{3u}^+, B_b	0.0	2.1			15.7		55.8	
Ψ_6°	B_{1g}^-			8.0	5.3		38.3		5.4
Ψ_7°	B_{2u}^+			0.1	1.3		6.9		67.7
$\Psi_{CTO\to 6+}^\circ$				18.1	4.9		6.0		0.0
$\Psi_{CTO\to 7+}^\circ$		0.0	11.4			10.0		0.0	
$\Psi_{CTO\to 8+}^\circ$				0.8	12.8		3.7		1.0
$\Psi_{CTO\to 6-}^\circ$		8.9	0.0			2.7		1.0	
$\Psi_{CTO\to 7-}^\circ$				0.0	0.0		0.3		0.1
$\Psi_{CTO\to 8-}^\circ$		5.1	0.0			0.1		0.0	
Total weight[b)]		93.5	81.0	83.1	84.0	78.8	82.7	80.0	80.6
Assignment[c)]		[G]	[L_b]	[L_a]				[B_b]	[B_{2u}^+]

a), b), and c): See Text for definitions.

makes a large weight contribution to the Ψ_2 state (18.1 %). This large contribution is responsible for the large red shift of Band II. The 1,4-diol has C_{2v} symmetry, so that the L_b state does not interact with the L_a state but interacts with the B_b state, from which the intensity of Band I is derived.

The B_b state interacts with the A_g^- state and splits into two bands, Bands III and IV. The B_{2u}^+ state (Ψ_7) overlaps with the B_b (Ψ_6), yielding Band IV. This interaction is characteristic of the naphthalene derivatives with a substituent at the 1-position.[8)] The $\Psi_{CTO\to 7+}^\circ$ state has a weight of 10.0% in the Ψ_4 state. There are no substantial contributions of charge-transfer states to the Ψ_6 and Ψ_7 states.

It may be seen from Table 3 that Bands I, II, III, and IV can also reasonably be assigned to Bands i, ii, iii, and iv of 1-naphthol. The $\Psi_{CTO\to 7}^\circ$ and $\Psi_{CTO\to 8}^\circ$ states make a important weight contributions to the Ψ_2 and Ψ_1 states (9.7 and 7.0% respectively). The results show that the hydroxyl group still has an electron-donating character with respect to 1-naphthol. The total weights of the individual excited states are about 90%; therefore, the electronic states of 1,4-diol can be well reproduced from the ground and the excited reference states of 1-naphthol and the intramolecular charge-transfer reference states.

1,8-Naphthalenediol. The observed values obtained by other authors between 220 and 350 nm in ethanol are used in the present study.[18)] There are three bands, I, II, and III; their energies are 3.7, 4.1, and 5.5 eV respectively. The band shifts of Bands i, ii, and iii of 1-naphthol on going from an isooctane to an ethanol solution are 150, 750, and 700 cm^{-1} respectively. Provided that the band shifts of 1,8-diol are the same as those of 1-naphthol, the state energies of 1,8-diol in isooctane may be estimated to be 3.7, 4.2, and 5.6 eV

Table 3. Configuration analysis for 1,4-naphthalenediol from 1-naphthol (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
			I	II		III		IV	
Wave function[a)]	Absorption band	Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°		88.9	0.0	1.0	1.5	0.0	0.0	0.0	0.0
Ψ_1°	i	0.0	79.1	1.9	0.1	2.9	0.0	0.1	0.0
Ψ_2°	ii	0.2	1.9	75.3	0.1	0.5	4.4	0.2	0.1
Ψ_3°		0.1	0.0	0.1	67.2	7.9	6.2	0.0	0.0
Ψ_4°	iii	0.0	0.9	0.1	6.9	68.2	0.1	0.7	0.0
Ψ_5°		0.0	0.0	1.7	4.7	0.2	70.9	2.4	0.5
Ψ_6°	iv	0.0	0.2	0.1	0.2	1.0	1.6	81.3	0.2
Ψ_7°		0.0	0.1	0.0	0.1	0.0	0.9	0.1	82.2
$\Psi_{CTO\to 7}^\circ$		4.4	0.0	9.7	1.4	1.6	3.9	0.5	0.0
$\Psi_{CTO\to 8}^\circ$		0.0	7.0	0.0	0.0	6.0	0.1	0.0	0.0
$\Psi_{CTO\to 9}^\circ$		3.5	0.0	0.5	6.9	0.0	2.0	0.0	0.6
Total weight[b)]		97.2	90.3	90.8	90.2	89.1	90.9	89.5	89.6
Assignment[c)]		[G]	[i]	[ii]		[iii]		[iv]	

a), b), and c): See Text for definitions.

TABLE 4. CONFIGURATION ANALYSIS FOR 1,8-NAPHTHALENEDIOL FROM NAPHTHALENE (WEIGHT IN PERCENT)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a)]	Symmetry type		I	II				III	
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°	A_g^-	79.0		2.8		0.0			0.1
Ψ_1°	B_{3u}^-, L_b		72.0		0.2		0.2	4.6	
Ψ_2°	B_{2u}^+, L	0.5		69.9		1.7			0.1
Ψ_3°	B_{1g}^+		0.1		60.9		2.6	0.4	
Ψ_4°	A_g^-	0.0		0.6		60.6			0.0
Ψ_5°	B_{3u}^+, B_b		1.6		0.6		0.6	72.9	
Ψ_6°	B_{1g}^+		0.3		0.6		62.7	0.5	
Ψ_7°	B_{2u}^+	0.0		0.0		0.0			75.0
$\Psi_{CTO\to6+}^\circ$		9.2		8.4		0.7			1.0
$\Psi_{CTO\to7+}^\circ$			7.6		0.0		0.1	4.1	
$\Psi_{CTO\to8+}^\circ$			0.1		4.4		8.1	0.0	
$\Psi_{CTO\to6-}^\circ$			0.0		16.9		9.1	0.3	
$\Psi_{CTO\to7-}^\circ$		0.0		0.1		14.3			0.3
$\Psi_{CTO\to8-}^\circ$		5.1		0.5		0.0			1.9
Total weight[b)]		93.9	81.7	82.5	83.8	79.0	83.4	82.9	79.6
Assignment[c)]		[G]	[L_b]	[L_a]				[B_b]	

a), b), and c): See Text for definitions.

respectively.

According to Table 4, Bands I, II, and III can reasonably be assigned to the L_b, L_a, and B_b states respectively. As in the case of 1,4-diol, the L_b state interacts not with the L_a state, but with the B_b state, because of symmetry. The intensity of Band I is derived from the mixing with the B_b. The $\Psi_{CTO\to7+}^\circ$ and $\Psi_{CTO\to6+}^\circ$ states make weight contributions to the Ψ_1 and Ψ_2 states of 7.6 and 8.4% respectively.

The B_b state interacts not with the A_g^- state, but with the B_{1g}^+ and B_{1g}^- states. Hence, there is no interaction characteristic of naphthalene derivatives with a substituent at the 1-position. It is noteworthy that the interactions of the B_b state with the B_{1g}^+, A_g^-, and B_{1g}^- states are extremely small in extent in 1,8-diol compared with the other diols studied in this paper (see below).

Table 5 shows the results of the CA for 1,8-diol using the state functions composed of 1-naphthol and the OH substituent as the reference state functions. Band i of 1-naphthol contributes to the Ψ_1 state by a weight of 51.5%. Bands II and III have no reference states which singly exceed 50.0%. The total weights of 1,8-diol are smaller than those of 1,4-diol by about 20—30%.

2,3-Naphthalenediol. Figure 2 shows the absorption spectrum of 2,3-diol in isooctane, including the

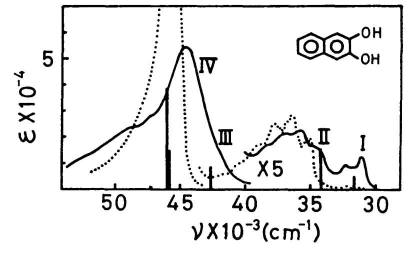

Fig. 2. Absorption spectrum in isooctane solution of 2,3-naphthalenediol. The dotted curve and the lengths of lines have the same meaning as in Fig. 1.

TABLE 5. CONFIGURATION ANALYSIS FOR 1,8-NAPHTHALENEDIOL FROM 1-NAPHTHOL (WEIGHT IN PERCENT)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a)]	Absorption band		I	II				III	
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°		66.6	0.0	3.3	0.6	0.0	0.7	0.0	0.0
Ψ_1°	i	0.1	51.5	0.7	0.3	1.6	0.0	2.5	0.1
Ψ_2°	ii	1.1	1.0	48.3	2.9	0.5	2.8	0.2	0.1
Ψ_3°		1.8	0.1	1.9	45.9	3.4	0.8	0.3	0.4
Ψ_4°	iii	0.1	2.3	0.0	2.5	42.8	0.4	9.7	0.0
Ψ_5°		1.1	0.0	5.6	3.7	0.2	37.3	3.9	4.4
Ψ_6°	iv	0.3	0.0	0.4	0.9	9.5	2.9	47.1	0.0
Ψ_7°		0.0	0.1	0.3	0.0	0.1	3.8	0.2	59.4
$\Psi_{CTO\to7}^\circ$		4.1	0.0	3.9	7.4	0.3	4.7	0.1	0.4
$\Psi_{CTO\to8}^\circ$		0.0	3.4	0.1	0.0	5.1	0.0	1.8	0.1
$\Psi_{CTO\to9}^\circ$		2.3	0.0	0.1	2.8	0.0	2.6	0.0	0.7
Total weight[b)]		85.4	62.5	71.1	69.2	64.7	62.2	69.8	66.7
Assignment[c)]		[G]	[i]						

a), b), and c): See Text for definitions.

Table 6. Configuration analysis for 2,3-naphthalenediol from naphthalene (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a)]	Symmetry type		I	II	III		IV		
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°	A_g^-	80.5	0.3		1.1			1.3	
Ψ_1°	B_{3u}^+, L_b	0.0	68.3		6.7			0.3	
Ψ_2°	B_{2u}^+, L_a			74.7		1.4	0.4		1.1
Ψ_3°	B_{1g}^+			0.5		74.0	1.1		0.0
Ψ_4°	A_g^-	0.0	1.1		45.2			15.4	
Ψ_5°	B_{3u}^+, B_b	0.2	0.6		10.8			54.7	
Ψ_6°	B_{1g}^-			0.2		0.0	1.4		74.3
Ψ_7°	B_{2u}^+			0.2		0.4	48.6		0.8
$\Psi_{CTO\to 6+}^\circ$				5.7		2.4	1.5		2.6
$\Psi_{CTO\to 7+}^\circ$		5.8	2.7		0.1			4.0	
$\Psi_{CTO\to 8+}^\circ$				0.0		2.9	0.0		2.7
$\Psi_{CTO\to 6-}^\circ$		3.9	10.1		8.2			2.0	
$\Psi_{CTO\to 7-}^\circ$				2.0		0.6	21.5		0.6
$\Psi_{CTO\to 8-}^\circ$		1.4	0.2		6.4			3.3	
Total weight[b)]		91.9	83.5	83.5	79.6	82.1	84.1	82.2	82.6
Assignment[c)]		[G]	[L_b]	[L_a]				[B_b]	

a), b) and c): See Text for definitions.

Table 7. Configuration analysis for 2,3-naphthalenediol from 2-naphthol (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a)]	Absorption band		I	II	III		IV		
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ_G°		89.5	0.1	0.7	0.3	0.4	0.8	0.3	0.1
Ψ_1°	i	0.0	75.3	9.2	0.9	0.2	2.5	0.0	0.0
Ψ_2°	ii	0.1	6.5	76.4	1.4	0.7	0.0	0.6	0.2
Ψ_3°		0.0	0.0	0.0	45.8	40.0	2.0	1.1	0.1
Ψ_4°		0.1	0.1	0.2	19.7	39.9	3.3	17.1	0.5
Ψ_5°	iii	0.0	0.4	0.2	9.8	5.5	2.7	47.0	19.7
Ψ_6°		0.0	0.3	0.0	2.5	0.2	13.5	6.0	58.6
Ψ_7°		0.1	0.3	0.1	0.1	0.1	50.0	11.7	6.8
$\Psi_{CTO\to 7}^\circ$		2.8	5.6	2.8	5.0	1.2	0.6	1.8	1.4
$\Psi_{CTO\to 8}^\circ$		2.7	1.6	0.7	0.0	0.2	11.6	2.0	0.2
$\Psi_{CTO\to 9}^\circ$		0.8	0.2	0.0	3.8	1.4	0.0	1.9	1.5
Total weight[b)]		96.2	91.6	90.5	89.9	89.9	91.4	90.9	90.4
Assignment[c)]		[G]	[i]	[ii]					

a), b), and c): See Text for definitions.

calculated data.

From Table 6, the mixing between the B_b and A_g^- states is responsible for the Ψ_3 (Band III) and Ψ_6 (Band IV) states, and Band IV is composed of the two states which correspond to the transitions to the Ψ_5 and Ψ_6 states. Bands I and II are assigned to the L_b and L_a respectively. The $\Psi_{CTO\to 6-}^\circ$ state makes contributions of 10.1 and 8.2% to the Ψ_1 and Ψ_3 states. The $\Psi_{CTO\to 7-}^\circ$ state makes an important weight contribution to the Ψ_5 state of 21.5%.

Table 7 shows the results of the CA for 2,3-diol using the state functions composed of 2-naphthol and the OH substituent as the reference state functions. Bands I and II are assigned to Bands i and ii of 2-naphthol respectively. There is large mixing among the Ψ_3°, Ψ_4°, and Ψ_5° states and among the Ψ_5°, Ψ_6°, and Ψ_7° states. These mixings are responsible for Bands III and IV. The $\Psi_{CTO\to 7}^\circ$ state makes contributions of 5.6, 2.8, and 5.0% to the Ψ_1, Ψ_2, and Ψ_3 states respectively. The $\Psi_{CTO\to 8}^\circ$ state makes a contribution of 11.6% to the Ψ_5 state.

The total weights are about 90%, so that the electronic states of 2,3-diol are well expanded in terms of the electronic states of 2-naphthol and the charge-transfer states from the substituent to 2-naphthol, as in the case of 1,4-diol.

2,7-Naphthalenediol. The absorption spectrum of 2,7-diol in isooctane is shown in Fig. 3, together with the calculated data. Table 1 shows that Band IV is composed of the transitions of the Ψ_5, Ψ_6, and Ψ_7 states. From Table 8, Bands I and II may be assigned to the L_b and L_a states respectively. The Ψ_5 state is made from the interaction among the B_{1g}^+, B_b, and B_{1g}^- states. The $\Psi_{CTO\to 6-}^\circ$ state contributes to the Ψ_1 state by a weight of 10.5% and to the Ψ_4 state by a weight of 6.4%.

Table 9 shows the results of the CA of the 2,7-diol

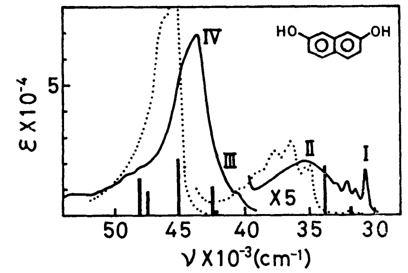

Fig. 3. Absorption spectrum in isooctane solution of 2,7-naphthalenediol. The dotted curve and the lengths of lines have the same meaning as in Fig. 1.

based on 2-naphthol. The results of the CA indicate that Bands I, II, and IV are closely connected with Bands i, ii, and iii of 2-naphthol respectively. The total weights of 2,7-diol are smaller than those of 2,3-diol by about 20—30%. This is analogous to the situation between 1,4- and 1,8-diol.

Remarks and Conclusions. When one chooses 1- or 2-naphthol as the parent compound in the CA, there is a marked difference in the total weight depending on the type of naphthalenediol. The total weights for the 1,4- and 2,3-diols, which have two substituents in the same benzene ring, are slightly larger on the naphthol basis than those on the naphthalene basis, whereas the total weights for 1,8- and 2,7-diols, which have one substituent in every benzene ring, are considerably smaller on the naphthol basis than those on the naphthalene basis. Such a marked difference indicates that the state functions of naphthols are a good basis for the expansion of the state functions of 1,4- and 2,3-diols; however, they are a poor basis for 1,8- and 2,7-diols. This suggests that the interaction between two substituents in diols differs depending on whether or not the two substituents lie on the same benzene ring.

Table 8. Configuration analysis for 2,7-naphthalenediol from naphthalene (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a]	Symmetry type		I	II		III	IV		
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ°_G	A_g^-	79.0		1.9	0.0				2.0
Ψ°_1	B_{3u}^-, L_b		67.3			3.1	0.0	0.0	
Ψ°_2	B_{2u}^+, L_a	0.3		70.9	0.9				0.4
Ψ°_3	B_{1g}^+		1.0			51.4	17.6	2.5	
Ψ°_4	A_g^-	0.0		0.1	53.3				6.5
Ψ°_5	B_{3u}^+, B_b		0.3			13.6	36.0	18.4	
Ψ°_6	B_{1g}^-		0.0			0.8	15.5	55.9	
Ψ°_7	B_{2u}^+	0.2		0.0	3.4				61.2
$\Psi^\circ_{CTO\to 6+}$		3.7		5.3	7.5				0.0
$\Psi^\circ_{CTO\to 7+}$			2.4			3.4	2.4	1.1	
$\Psi^\circ_{CTO\to 8+}$			0.1			2.1	4.0	2.0	
$\Psi^\circ_{CTO\to 6-}$			10.5			6.4	4.0	0.3	
$\Psi^\circ_{CTO\to 7-}$		6.5		0.6	5.6				8.6
$\Psi^\circ_{CTO\to 8-}$		1.3		0.0	7.0				1.4
Total weight[b]		91.1	82.2	79.9	80.3	82.0	80.0	80.9	81.9
Assignment[c]		[G]	[L_b]	[L_a]		[B_{1g}^+]		[B_{1g}^-]	[B_{2u}^+]

a), b), and c) See Text for definitions.

Table 9. Configuration analysis for 2,7-naphthalenediol from 2-naphthol (weight in percent)

Reference state		Absorption band (upper) and state function (lower)							
Wave function[a]	Absorption band		I	II		III	IV		
		Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7
Ψ°_G		70.8	0.3	1.3	0.0	0.0	0.0	0.0	0.4
Ψ°_1	i	0.3	56.5	4.4	0.1	0.0	0.4	0.0	0.3
Ψ°_2	ii	0.0	4.6	55.8	2.0	0.9	0.0	0.0	0.0
Ψ°_3		0.5	0.0	1.0	21.1	30.4	0.5	0.5	2.0
Ψ°_4		0.1	1.6	0.1	27.3	23.7	3.9	0.4	0.2
Ψ°_5	iii	0.3	0.2	0.6	0.7	1.8	51.8	0.5	2.8
Ψ°_6		0.0	0.3	0.1	0.0	0.7	0.5	57.3	6.4
Ψ°_7		0.1	0.4	0.0	0.0	3.5	1.3	7.9	54.5
$\Psi^\circ_{CTO\to 7}$		1.5	4.7	2.7	3.9	2.5	1.4	0.2	0.0
$\Psi^\circ_{CTO\to 8}$		2.8	0.7	0.4	2.1	1.8	1.5	0.4	3.5
$\Psi^\circ_{CTO\to 9}$		0.5	0.0	0.0	2.4	1.1	1.8	1.0	0.8
Total weight[b]		81.3	70.7	67.8	61.8	67.8	65.3	70.4	73.0
Assignment[c]		[G]	[i]	[ii]			[iii]		

a), b), and c) See Text for definitions.

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