Electronic Structures of Naphthalenediols. I. α,α'-Naphthalenediols

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While the electronic structures of substituted benzenes have been studied by many authors, the theoretical investigations of those of substituted naphthalenes have been scarcely ever made[1-4], because of difficulties of the calculation due to low symmetry of these molecules and the presence of many π-electrons to be considered. The spectra of naphthalene mono-derivatives show[5] in general two kinds of characteristic picture depending upon the position of substitution, either β or α positions. In the di-derivatives, two substituents are bonded with rings in two ways, that is, both with the same

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[1] H. Baba and T. Suzuki, Symposium on the Electronic Structures of Molecules, held at Kyoto, 1958.

[2] R. Daudel and M. Martin, *Bull. soc. chim. France*, **1948**, 559; ibid., **1949**, 83.

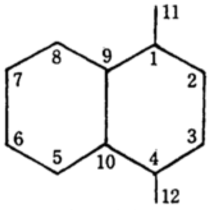
[3] D. Peters, *J. Chem. Soc.*, **1957**, 646, 1993.

[4] B. Pullman, *Bull. soc. chim. France*, **1948**, 533.

[5] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", Jone Wiley and Sons, New York, (1951).

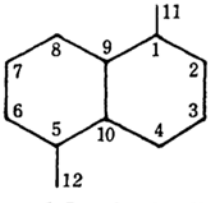
ring and each with the different rings. This seems to lead additional effects on their molecular properties. De Laszlo[6] showed that fourteen isomeric dichloronaphthalenes could be classified spectroscopically as aa, ab and bb compounds. But as pointed out by Daglish[7] in the case of naphthalene di-derivatives having strongly conjugating substituents, such as hydroxyl, amine etc., this classification is an over-simplification of the problem. In the present paper theoretical treatments based on the simple MO theory will be applied to the electronic structures of α, α'-naphthalenediols, such as 1-4, 1-5 and 1-8 diols, in order to establish the effects of substituents on their molecular properties. The electronic structures of β, β'-naphthalenediols will be considered in the next paper.

Method of Calculation.—The method is based on the simple LCAO MO theory with only fourteen $2p\pi$ electrons considered explicitly. The Coulomb and the exchange integrals used are the same as those in the previous paper[8], where the electronic structure of phenol was discussed. All the Coulomb integrals for carbon atoms are taken as equal to α. When the non-uniformity of charge distribution is small, the above assumption may be approximately held. In order to simplify the calculation we make this approximation. The numbering of atoms and the symmetry orbitals for the moleclues are shown in Fig. 1. A, B, A_2 and B_1 in the figure express the irreducible representations, to which each symmetry orbital belongs.



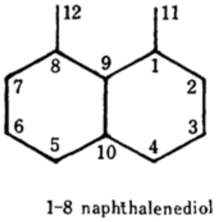
1-4 naphthalenediol

B_1 $\sigma_1=\phi_1+\phi_4$ A_2 $\sigma_7=\phi_1-\phi_4$
$\sigma_2=\phi_2+\phi_3$ $\sigma_8=\phi_2-\phi_3$
$\sigma_3=\phi_5+\phi_8$ $\sigma_9=\phi_5-\phi_8$
$\sigma_4=\phi_6+\phi_7$ $\sigma_{10}=\phi_6-\phi_7$
$\sigma_5=\phi_9+\phi_{10}$ $\sigma_{11}=\phi_9-\phi_{10}$
$\sigma_6=\phi_{11}+\phi_{12}$ $\sigma_{12}=\phi_{11}-\phi_{12}$



1-5 naphthalenediol

A $\sigma_1=\phi_1+\phi_5$ B $\sigma_7=\phi_1-\phi_5$
$\sigma_2=\phi_2+\phi_6$ $\sigma_8=\phi_2-\phi_6$
$\sigma_3=\phi_3+\phi_7$ $\sigma_9=\phi_3-\phi_7$
$\sigma_4=\phi_4+\phi_8$ $\sigma_{10}=\phi_4-\phi_8$
$\sigma_5=\phi_9+\phi_{10}$ $\sigma_{11}=\phi_9-\phi_{10}$
$\sigma_6=\phi_{11}+\phi_{12}$ $\sigma_{12}=\phi_{11}-\phi_{12}$



1-8 naphthalenediol

B_1 $\sigma_1=\phi_1+\phi_8$ A_2 $\sigma_8=\phi_1-\phi_8$
$\sigma_2=\phi_2+\phi_7$ $\sigma_9=\phi_2-\phi_7$
$\sigma_3=\phi_3+\phi_6$ $\sigma_{10}=\phi_3-\phi_6$
$\sigma_4=\phi_4+\phi_5$ $\sigma_{11}=\phi_4-\phi_5$
$\sigma_5=\phi_9$ $\sigma_{12}=\phi_{11}-\phi_{12}$
$\sigma_6=\phi_{10}$
$\sigma_7=\phi_{11}+\phi_{12}$

Fig. 1. Numbering of atoms and symmetry orbitals.

Results and Discussion

(A) MO's and their Polarization.—The calculated MO's and their energies for the naphthalenediols are summarized in Table I.

The comparison of the MO's of the naphthalene[9] and those of diols obtained here makes it clear that the signs of the coefficients at each carbon AO in each MO are unchanged by the introduction of the hydroxy groups. Thus, so far as the mono- and di-derivatives are concerned, it is not too much to say that the effect of substitution brings about some modification of the MO's of parent hydrocarbon, but the extent of these modifications is not so large as to destroy their orbital characteristics. This situation will give a basis to the assumption that in many cases the perturbation theory supplies qualitatively useful results, even if the effect of the substitution amounts to considerable extent. In the naphthalene molecule, φ_1 is totally symmetric for the symmetry operation with respects to the principal axis and has no node of the wave function. For the naphthalenediols, φ_1's of them have still no node, but they are strongly polarized along the direction toward the substituents in a regular manner. If we try to measure the degree of polarization by the value of $C_{1\mu}/C_{1\mu_0}$, where the $C_{1\mu}$ is the square of coefficient at μ-th carbon AO in φ_1 of the diol and the $C_{1\mu_0}$ is that of naphthalene, these values are the greatest at the carbon atoms bonded with a hydroxy group and decrease with the increase in the distance between the μ-th carbon atom and the substituent. For the case of 1-8 diol, the values at the carbon atoms numbered by 1, 2, 3 and 4 in Fig. 1 are 1.367, 0.925, 0.656 and 0.591, respectively. This polarization is similar to the inductive effect which is usually regarded as the polarization of σ-cores

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[6] H. de Laszlo, *J. Am. Chem. Soc.*, **50**, 892 (1928).

[7] C. Daglish, ibid., **72**, 4859 (1950).

[8] K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).

[9] B. Pullman and A. Pullman, "Les Theories electroniques de la Chimie organique", Masson et Cie, Paris, (1952), p. 199.

TABLE I. MO'S AND MO ENERGIES

Symmetry	Orbital energy in β	MO
		1-4-naphthalenediol
B_1	2.4227	$\varphi_1=0.3452\sigma_1+0.2426\sigma_2+0.2386\sigma_3+0.1677\sigma_4+0.4103\sigma_5+0.2619\sigma_6$
A_2	1.9264	$\varphi_2=0.3498\sigma_7+0.1195\sigma_8-0.0962\sigma_9-0.0329\sigma_{10}+0.1524\sigma_{11}+0.5742\sigma_{12}$
B_1	1.8058	$\varphi_3=0.1695\sigma_1+0.2103\sigma_2-0.3111\sigma_3-0.3860\sigma_4-0.1757\sigma_5+0.3877\sigma_6$
B_1	1.3271	$\varphi_4=0.1246\sigma_1+0.381\sigma_2-0.0796\sigma_3-0.2433\sigma_4+0.1377\sigma_5-0.5048\sigma_6$
A_2	1.1082	$\varphi_5=0.1631\sigma_7+0.0774\sigma_8-0.4849\sigma_9-0.2300\sigma_{10}+0.3074\sigma_{11}-0.2914\sigma_{12}$
B_1	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_4-\sigma_5)$
A_2	0.4321	$\varphi_7=0.4276\sigma_7+0.2986\sigma_8+0.3096\sigma_9+0.2162\sigma_{10}+0.0824\sigma_{11}-0.2803\sigma_{12}$
B_1	−0.6922	$\varphi_8=0.3818\sigma_1-0.2256\sigma_2-0.4607\sigma_3+0.2722\sigma_4+0.0466\sigma_5-0.1219\sigma_6$
A_2	−1.0000	$\varphi_9=-0.4083(\sigma_8-\sigma_{10}-\sigma_{11})$
B_1	−1.3635	$\varphi_{10}=0.4369\sigma_1-0.1846\sigma_2+0.3574\sigma_3-0.1512\sigma_4-0.3361\sigma_5-0.1069\sigma_6$
A_2	−1.6396	$\varphi_{11}=0.2616\sigma_7-0.4090\sigma_8+0.2750\sigma_9-0.4299\sigma_{10}+0.0209\sigma_{11}-0.0584\sigma_{12}$
A_2	−2.3271	$\varphi_{12}=0.3158\sigma_7-0.2379\sigma_8-0.2901\sigma_9+0.2186\sigma_{10}-0.4565\sigma_{11}-0.0578\sigma_{12}$
		1-5-naphthalenediol
A	2.4190	$\varphi_1=0.3362\sigma_1+0.2195\sigma_2+0.1949\sigma_3+0.2519\sigma_4+0.4144\sigma_5+0.2561\sigma_6$
B	1.9945	$\varphi_2=0.3687\sigma_7+0.2472\sigma_8+0.1243\sigma_9+0.0007\sigma_{10}+0.1229\sigma_{11}+0.5219_{12}$
A	1.6212	$\varphi_3=0.1038\sigma_1-0.0407\sigma_2-0.1698\sigma_3-0.2346\sigma_4-0.2106\sigma_5+0.5994\sigma_6$
B	1.5296	$\varphi_4=-0.0084\sigma_7+0.2853\sigma_8+0.4447\sigma_9+0.3951\sigma_{10}-0.1594\sigma_{11}-0.1981\sigma_{12}$
B	1.0034	$\varphi_5=0.2897\sigma_7+0.2877\sigma_8-0.0010\sigma_9-0.2887\sigma_{10}+0.2887\sigma_{11}-0.4082\sigma_{12}$
A	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_3-\sigma_5)$
A	0.4590	$\varphi_7=0.3696\sigma_1+0.2900\sigma_2-0.2365\sigma_3-0.3985\sigma_4+0.0535\sigma_5-0.2484\sigma_6$
B	−0.7005	$\varphi_8=0.4268\sigma_7-0.2336\sigma_8-0.2632\sigma_9+0.4180\sigma_{10}+0.0296\sigma_{11}-0.1357\sigma_{12}$
B	−1.0000	$\varphi_9=-0.4083(\sigma_8-\sigma_9-\sigma_{11})$
A	−1.3550	$\varphi_{10}=0.3739\sigma_1-0.1062\sigma_2-0.2300\sigma_3+0.4178\sigma_4-0.3362\sigma_5-0.0917\sigma_6$
A	−1.6442	$\varphi_{11}=0.3159\sigma_1-0.4337\sigma_2+0.3972\sigma_3-0.2194\sigma_4-0.0365\sigma_5-0.0703\sigma_6$
B	−2.3269	$\varphi_{12}=0.3129\sigma_7-0.2313\sigma_8+0.2254\sigma_9-0.2931\sigma_{10}-0.4567\sigma_{11}-0.0572\sigma_{12}$
		1-8-naphthalenediol
B_1	2.4249	$\varphi_1=0.3513\sigma_1+0.2219(\sigma_2+2\sigma_5)+0.1868(\sigma_3+2\sigma_6)+0.2312\sigma_4+0.2659\sigma_7$
A_2	1.9360	$\varphi_2=0.3278\sigma_8+0.2662\sigma_9+0.1875\sigma_{10}+0.0969\sigma_{11}+0.5264\sigma_{12}$
B_1	1.7562	$\varphi_3=0.1794\sigma_1-0.0094(\sigma_2+2\sigma_5)-0.1959(\sigma_3+2\sigma_6)-0.3346\sigma_4+0.4903\sigma_7$
A_2	1.4410	$\varphi_4=0.0319\sigma_8+0.3116\sigma_9+0.4172\sigma_{10}+0.2895\sigma_{11}-0.3795\sigma_{12}$
B_1	1.0035	$\varphi_5=0.2977\sigma_1+0.1975(\sigma_2+2\sigma_5)-0.0995(\sigma_3+2\sigma_6)-0.2973\sigma_4-0.4198\sigma_7$
B_1	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_3-\sigma_5-\sigma_6)$
A_2	0.4666	$\varphi_7=0.3490\sigma_8+0.3283\sigma_9-0.1958\sigma_{10}-0.4197\sigma_{11}-0.2364\sigma_{12}$
A_2	−0.7020	$\varphi_8=0.4332\sigma_8-0.2077\sigma_9-0.2874\sigma_{10}+0.4094\sigma_{11}-0.1378\sigma_{12}$
B_1	−1.0000	$\varphi_9=-0.4083(\sigma_2-\sigma_3-\sigma_5+\sigma_6)$
B_1	−1.3573	$\varphi_{10}=0.3939\sigma_1-0.1557(\sigma_2+2\sigma_5)-0.1826(\sigma_3+2\sigma_6)+0.4035\sigma_4-0.0965\sigma_7$
A_2	−1.6416	$\varphi_{11}=0.2864\sigma_8-0.4255\sigma_9+0.4121\sigma_{10}-0.2511\sigma_{11}-0.0637\sigma_{12}$
B_1	−2.3273	$\varphi_{12}=0.3172\sigma_1-0.2325(\sigma_2+2\sigma_5)+0.2240(\sigma_3+2\sigma_6)-0.2887\sigma_4-0.0581\sigma_7$

caused by the introduction of the polar group into the molecule. But, when we take $\beta_{CO}=0$, this polarization is absent, so far as invoking the simple theory, since the interactions between the 2pπ electrons of the substituents and of the naphthalene ring are impossible in this case. If the polarizations of φ_1's are inductive, it is expected that the value of C_{11}/C_{11_0} for 1–8-diols is the greatest and the smallest for 1–5-diol. Actually, their values are 1,367, 1,319 and 1.251 for 1–8, 1–4 and 1–5-diols, respectively. Although the all MO's for the diols have the same numbers of nodes as those for the corresponding naphthalene MO's, the regular polarizations are not recognized in them except φ_1's. In the light of the above fact, we may except that when the overlap between the electronic cloud of conjugated molecule and that of the attacking molecule is present, the lowest π-orbital of the former will be most sensitive to the influence of the latter. The occupied lowest π-orbital will, therefore, play the most important role for the rearrangement of charge distribution of the molecule produced by the approach of the reagent.

(B) Absorption Spectra. — It is well known that the introduction of the hydroxy group into the α-position of naphthalene causes a very large bathochromic shift in the p-band with some distortion of the fine structure and a rather small shift in the α-band. As mentioned by Daglish⁷⁾ and Spruit¹⁰⁾, the spectra of α, α'-diols also have those characteristic features, but these bathochromic shifts in the p-bands are larger in 1-4 derivative and slightly larger in 1-5 compound than that in α-naphthol. Comparison of the energy level diagrams given in Fig. 2 makes it possible to expect that the spectra of 1-8 diol may be very close to that of 1-5 diol, since the spacing of their levels concerned with the electronic transitions in the near ultraviolet region are very similar to each other. This is the case of Hochstein et al.¹¹⁾, who reported that the spectroscopic distinction between them was difficult. The energy level diagram of α-naphthol which is calculated by using the same parameters for diols is also given in Fig. 2. The numerical values given in Fig. 2 express the orbital energy differences between φ_7 and φ_8 for the corresponding compounds in the units of β, respectively. The comparison of these values suggests that the wave lengths of absorption corresponding to the $\varphi_7 \rightarrow \varphi_8$ transitions which are closely related to the p-band are in following order; 1-4 diol$>$1-5 diol$\simeq$1-8 diol$\simeq\alpha$-naphthol.

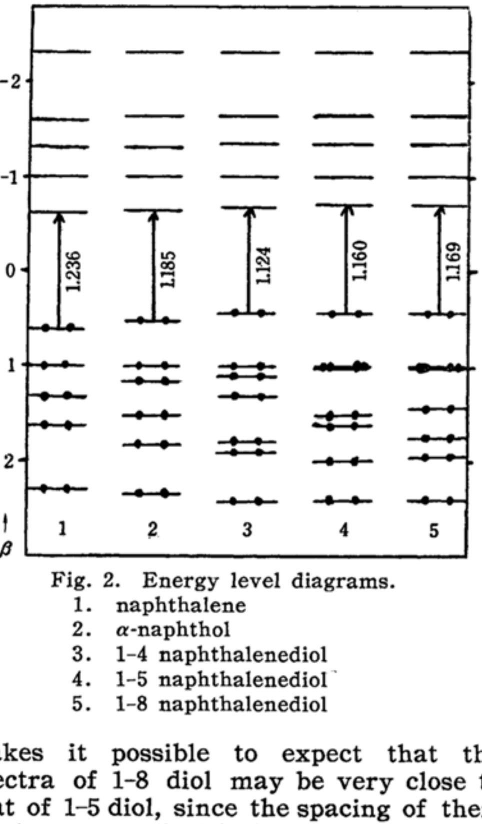

Fig. 2. Energy level diagrams.
1. naphthalene
2. α-naphthol
3. 1-4 naphthalenediol
4. 1-5 naphthalenediol
5. 1-8 naphthalenediol

The fact that the orbitals having orbital energies of $\pm\beta$ are not affected by the substitution in the α-positions of naphthalene may provide a determining factor for the discussion of electronic transitions concerned with α-bands of α-compounds, because these orbitals are closely connected with them. Experimentally observed distortion of the fine-structure in the p-band will be reasonably attributable to the anharmonicity produced by the ununiform charge distribution and the alteration of the bond orders. The full discussion about the electronic transitions on the ground of the method involving the electronic interaction will be desirable. Here, we will try no further discussion about this problem.

(C) Extra Delocalization Energies and Molecular Diagrams.—Delocalization of the 2pπ-electrons of substituents into the naphthalene ring brings the excess of stabilization energies (extra delocalization energies) for the molecule as a whole. These values per one hydroxy group are evaluated to be 0.1807, 0.1851 and 0.1866β for the 1-4, 1-5 and 1-8 diols, respectively. A naive consideration will give larger extra delocalization energy for greater charge migration. Actually, if we plot these values against the magnitudes of the charge migrations from the hydroxy

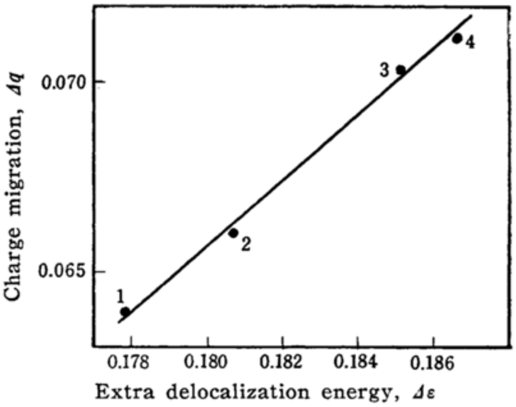

Fig. 3. Relation between the extra delocalization energy of diols and the charge migration in them.
1. phenol
2. 1-4 naphthalenediol
3. 1-5 naphthalenediol
4. 1-8 naphthalenediol

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10) C. J. P. Spruit, *Rec. trav. chim.*, **68**, 309 (1949).

11) F. A. Hochstein et al., *J. Am. Chem. Soc.*, **75**, 5457 (1953).

group into the naphthalene ring, a linear relationship is obtained as shown in Fig. 3. It is surprising that a point corresponding to the phenol, which is obtained from our previous paper[9], is also located on this line. This fact gives us an interesting suggestion that the degree of charge migration will be estimated by only the calculation of orbital energies of the molecule. This seems to give a theoretical background to a well-known conception of the electronic theory in organic chemistry that the acidity of the aromatic hydroxy derivatives is closely connected with the magnitude of charge migration. In the case of α-naphthol, the value of extra-delocalization energy is $0.1862\,\beta$. Its magnitude of charge density at the hydroxy group will be, therefore, expected to be comparable with that of 1–8 diol.

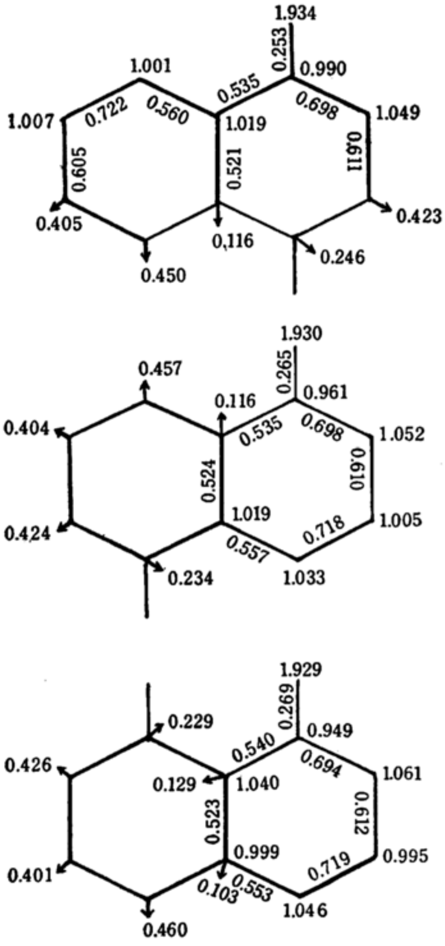

Fig. 4. Molecular diagram.

As seen from the molecular diagrams given in Fig. 4 the charge distributions in the molecules show a sharp difference according to the type of substitution, either two hydroxy groups bonded with the same ring or not. Namely, in the case of 1–4 diol the migrated charges are, for the most part, localized within one ring whereas in those of 1–5 and 1–8 diols they are equally distributed into both rings. In the discussion of the molecular properties, such as reactivity, of the naphthalene di-derivatives this characteristic charge distribution will supply a useful information.

Summary

The simple LCAO MO method was applied to the electronic structures of α,α'-naphthalenediols, using the same parameters as those of phenol based on the ASPMO calculation. The theory proved that

(a) the lowest π-orbital of the molecule would be the most sensitive to the influence of the external molecular field,

(b) the absorption spectra of diols were satisfactorily correlated with their energy level diagrams, and

(c) the extra delocalization energies produced by the charge migrations from the hydroxy groups into the naphthalene ring increased linearly with the increment of the magnitude of charge migrations.

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