Electronic Structures of Naphthalenediols. II. β, β′-Naphthalenediols

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To elucidate the molecular properties of naphthalene derivatives with auxochromic substituents, such as methoxy, amino, halogen etc., we have been studying the electronic structures of naphthalenediols. In the previous paper[1], we studied the electronic structures of α, α'-naphthalenediols and pointed out that their molecular properties, such as charge distribution and electronic spectra, depend remarkably upon the type of substitution. These are as follows:

(1) A, A-derivative, in which two hydroxy groups link to the same ring, (A ring in Fig. 1)

(2) A, B-derivatives, in which each hydroxy group bonds with a different ring.

Namely, in the case of 1, 4-diol it is found from the molecular diagram[1] that the substituents have no significant influence upon the B ring, which remains nearly the same as naphthalene, but do produce rather a large effect on the A ring. This fact seems to suggest that the 9—10 bond plays an important role in the conjugation interaction between the ring and the substituents. In the present paper, we will examine this point by calculations based on the perimeter models. It is a well-known fact to organic chemists[2] that the reactivities of naphthalene derivatives with substituents in β-position are peculiar. In the present paper, the theoretical treatment based on the simple MO theory will be applied to the electronic structures of β, β'-naphthalenediols, such as 2, 3-, 2, 6- and 2, 7-diols and

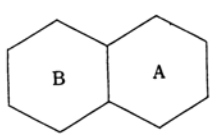


Fig. 1

1) K. Nishimoto and R. Fujishiro, This Bulletin, 32, 445 (1959).

2) a) G. M. Badger, "The Structures and Reactions of the Aromatic Compounds", University Press, Cambridge (1952).

b) L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry", Heath and Company (1950).

we will try to explain the peculiarities in the reactivities of those molecules.

Method of Calculation

The calculation is carried out by means of the simple LCAO MO theory, with only $2p\pi$-electrons considered explicitly. The Coulomb and the resonance integrals used are the same as those in the previous paper[1]. The numbering of the atoms and the symmetry orbitals for the molecules are shown in Fig. 2. The notations of irreducible representations are also the same as those in the previous paper.

Results and Discussion

Vacant MO's and Molecular Diagrams.— The π-MO's of each naphthalenediol are expressed by linear combinations of the twelve $2p\pi$ atomic orbitals. Consequently, there are twelve π-MO's in each diol. According to Pauli's principle, the lowest seven are occupied by fourteen electrons. In the ordinary method

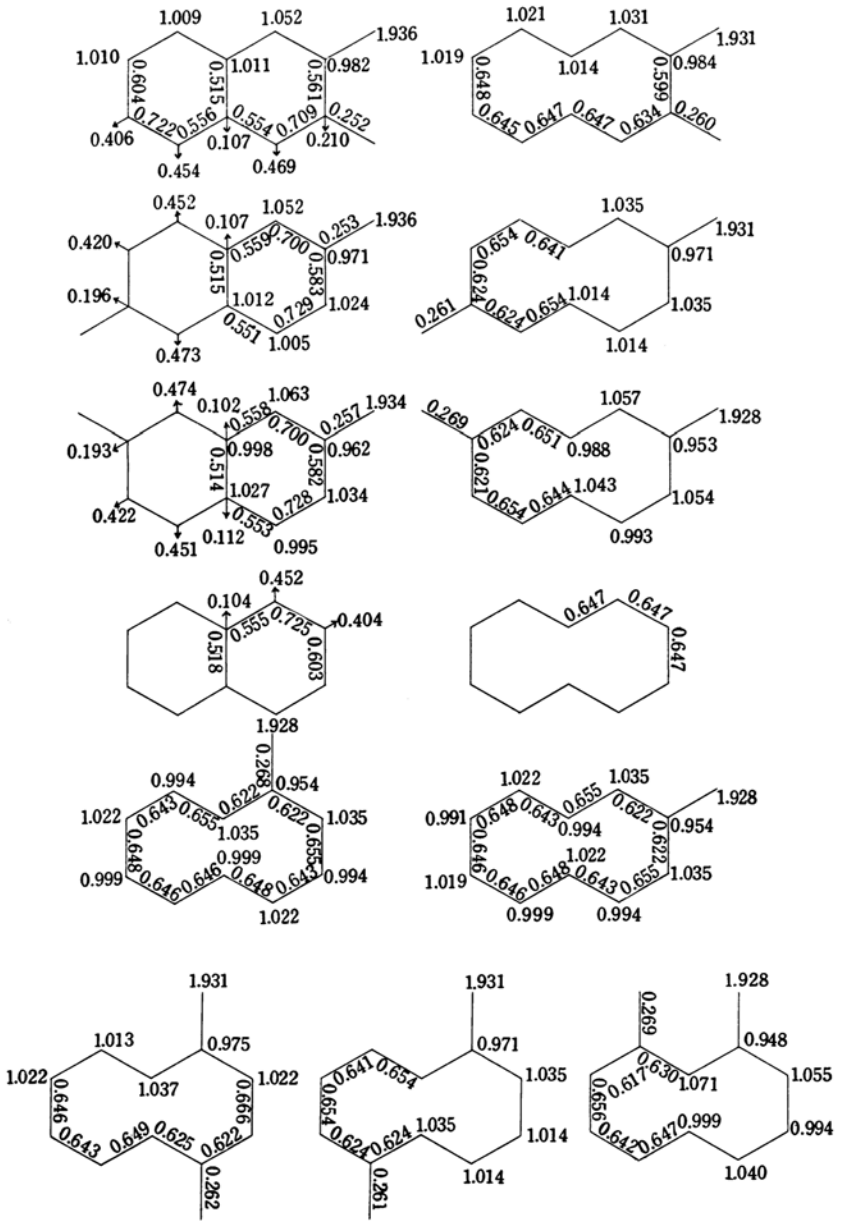


Fig. 2. Molecular diagrams of naphthalene and its hydroxy derivatives.

TABLE I. VACANT MO'S AND MO ENERGIES OF NAPHTHALENEDIOLS

Orbital energy in β	MO
	2,3-Naphthalenediol
−2.3181	$\phi_5^v=0.3063\sigma_7-0.2575\sigma_8+0.2902\sigma_9-0.2202\sigma_{10}-0.4526\sigma_{11}+0.0473\sigma_{12}$
−1.6775	$\phi_4^v=0.2338\sigma_7-0.4468\sigma_8-0.2708\sigma_9+0.3997\sigma_{10}+0.0546\sigma_{11}+0.0984\sigma_{12}$
−1.3143	$\phi_3^v=0.4054\sigma_1-0.1895\sigma_2+0.3891\sigma_3-0.1681\sigma_4-0.3433\sigma_5+0.0473\sigma_6$
−1.0571	$\phi_2^v=-0.0483\sigma_7-0.3589\sigma_8+0.0249\sigma_9-0.4364\sigma_{10}+0.4100\sigma_{11}+0.0983\sigma_{12}$
−0.6518	$\phi_1^v=0.3984\sigma_1-0.2797\sigma_2-0.4315\sigma_3+0.2612\sigma_4+0.0200\sigma_5+0.0908\sigma_5$
	2,6-Naphthalenediol
−2.3173	$\phi_5^v=0.3010\sigma_7-0.2441\sigma_8+0.2332\sigma_9-0.2963\sigma_{10}-0.4535\sigma_{11}+0.0449\sigma_{12}$
−1.6772	$\phi_4^v=0.2761\sigma_1-0.4458\sigma_2+0.4029\sigma_3-0.2299\sigma_4-0.0172\sigma_5+0.0981\sigma_6$
−1.3118	$\phi_3^v=0.3751\sigma_1-0.1485\sigma_2-0.2061\sigma_3+0.4188\sigma_4-0.3435\sigma_5+0.0371\sigma_6$
−1.0686	$\phi_2^v=0.0200\sigma_7-0.4316\sigma_8+0.3589\sigma_9+0.0481\sigma_{10}+0.4103\sigma_{11}+0.1176\sigma_{12}$
−0.6447	$\phi_1^v=0.4075\sigma_7-0.2190\sigma_8-0.3164\sigma_9+0.4230\sigma_{10}-0.0437\sigma_{11}+0.0716\sigma_{12}$
	2,7-Naphthalenediol
−2.3173	$\phi_5^v=0.3020\sigma_1-0.2444\sigma_2+0.2329\sigma_3-0.2953\sigma_4-0.4555\sigma_5+0.4514\sigma_6+0.0449\delta_7$
−1.6766	$\phi_4^v=0.2633\sigma_8-0.4414\sigma_9+0.4086\sigma_{10}-0.2437\sigma_{11}+0.0973\sigma_{12}$
−1.3159	$\phi_3^v=0.3878\sigma_1-0.2151\sigma_2-0.1422\sigma_3-0.4023\sigma_3-0.2952\sigma_5-0.3871\sigma_6+0.0535\sigma_7$
−1.0623	$\phi_2^v=-0.0591\sigma_1-0.3919\sigma_2+0.4005\delta_3-0.0335\sigma_4+0.4547\sigma_5-0.3649\sigma_6+0.1070\sigma_7$
−0.6488	$\phi_1^v=0.3923\sigma_8-0.2545\sigma_9-0.2852\sigma_{10}+0.4395\sigma_{11}+0.0829\sigma_{12}$

it is necessary to use these seven occupied MO's in constructing the molecular diagram. The other five are called "vacant MO's". As we have pointed out in a previous paper[3], the molecular diagram of a diol is obtained from only the five vacant MO's; namely, the π-electron density on the μ-th atom, q_μ, the π-bond order for the μ-ν bond, $p_{\mu\nu}$, and the free valency of the μ-th atom, f_μ, are given by the following relations respectively:

i) $q_\mu=2-2\sum_i^{\text{vac}} C_{\mu i}^2$

ii) $p_{\mu\nu}=-2\sum_i^{\text{vac}} C_{\mu i}C_{\nu i}$

iii) $f_\mu=\sqrt{3}-\sum_\nu p_{\mu\nu}$

(μ and ν are nearest neighbors)

in which $\sum_i^{\text{vac}}$ means the summation over the vacant orbitals and $C_{\mu i}$ is the coefficient of the μ-th $2p\pi$ atomic orbital, ϕ_μ, in the i-th MO, ψ_i.

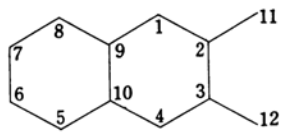
The calculated vacant MO's, ψ_i^v, are given in Table I, and the molecular diagrams are indicated in Fig. 3. A comparison of these diagrams with those of α,α'-diols[1] makes it possible to say that the introduction of substituents into the α-position leads to increases in the bond orders of the 2—3 and 9—10 bonds and to decreases in those of the 1—2, 1—9 and 3—4 bonds. That is, α-substitutions have a tendency to unify the bond orders along the direction of the short molecular axis. Contrary to this, substitutions in the β-positions cause decreases in the bond orders of the 1—2, 2—3 and 9—10 bonds and an increase in that of the 1—9 bond. The same result is reported in the case of α- and β-naphthylamines[4]. In other words, the substitutions in α-positions cause an increase in the mobilities of π-electrons in the direction of the short molecular axis, whereas those in β-positions lead to decreased π-electron mobilities in this direction and to an increase of mobilities in the direction of the long molecular axis. This is an important difference between the α- and β-derivatives, and this remarkable circumstance may be responsible for the distinction between the α- and β-derivatives in their molecular properties, such as reactivities, etc.

Reactivity.—It is a well-known fact[2a] that in all naphthalene derivatives with substituents in β-positions the 1-position is found to be reactive and the 3-position to be inert, or nearly so in the case of electrophilic substitution reactions.

In the electrophilic substitution reaction, π-electron density at the positions which are attacked by the reagent is a measure of reactivity. From the standpoint of this situation, it may be expected that their 1-positions in any β-substituted naphthalene derivatives are the first point to be attacked by any reagent. In a similar way, the 3-positions in α-derivatives may become less active. It is a well-known fact that the frontier electron

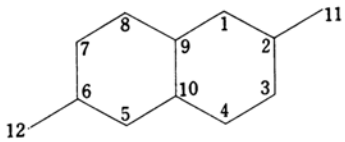
3) K. Nishimoto and R. Fujishiro, This Bulletin, 32, 699 (1959).

4) H. Baba and S. Suzuki, ibid., 34, 82 (1961).



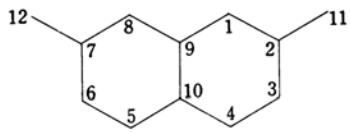
2,3-Naphthalenediol

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



2,6-Naphthalenediol

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



2,7-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. 3. Numbering of atoms and symmetry orbitals of naphthalenediols.

theory proposed by Fukui et al.[5] provides powerful information for chemical reactions, such as electrophilic, nucleophilic and radical reactions. Frontier electron densities in occupied highest orbitals, which are responsible for electrophilic substitutions, are collected in Table II. As is seen from this table, the 3-positions in any naphthalene derivatives with auxochromic substituents should be inactive for this type of reaction. This expectation is consistent with the experimental facts[2b]. For example, 2,7-diol couples at positions 1 and 8, but if these positions are blocked by alkyl groups, no coupling occurs. The molecular diagrams of A, A-derivatives show that their A rings are

5) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid, **22**, 1433 (1954).

Table II. Frontier eletron density distributions in the occupied highest orbitals of naphthalenediols

	Position	π-Electron density
1,4-Naphthalenediol	2	0.1784
	7	0.0934
	8	0.1918
1,5-Naphthalenediol	2	0.1682
	3	0.1118
	4	0.3176
1,8-Naphthalenediol	2	0.2156
	3	0.0768
	4	0.3524
2,3-Naphthalenediol	1	0.3196
	7	0.1492
	8	0.3616
2,6-Naphthalenediol	1	0.3596
	3	0.0160
	4	0.2792
2,7-Naphthalenediol	1	0.4468
	3	0.0800
	4	0.2690
Naphthalene	1, 4	0.3618
	2, 3	0.1382

reactive and their B rings less reactive than the A rings. By a simple extension of this result, it would be expected that even in the ecas of α- and β-naphthol the A ring would be more active than the B ring. This expectation has been supported by many experiments in connection with substitution reactions. For example, in α-naphthol the 4-position is the first point of attack, and also in β-naphthol the point of first attack is the activated 1-position. Of course, in the case of A, B-derivatives, the reactivities of the two rings are not different from each other.

Molecular Diagrams based on Perimeter Model.—As mentioned above, the B rings in A, A-derivatives are scarcely influenced by the substitution. This result seems to suggest that the 9—10 bond in the derivatives may play an important role in the motion of the $2p\pi$ electrons in the molecules. When the 9—10 bond in the naphthalene is absent, the reactivity at any position and the bond order of any bond in the molecule may be nearly equivalent. Therefore, the presence of the 9—10 bond may be the main reason for the appreciable difference in the reactivity from one position to another. In order to examine the effect of the 9—10 bond on the electronic structures of the diols, we carried out calculations based on the perimeter model. In this model it is assumed that the π-electrons are moving in the perimeter potential field. Our method of calculation is based on the simple LCAO MO theory. The parameters used were the same as in the above calculation, except

that the 9—10 bond was neglected, that is, the value of resonance integral $\int\phi_9 H\phi_{10}d\tau$ was put at zero. The molecular diagrams obtained on the basis of this model are shown in Fig. 3. We can see from the diagrams that the 9—10 bond has the following effects on the electronic structures of these molecules:

1) It breaks the uniformity of the bond order in the case of naphthalene, which means a decrease in the mobilities of the π-electrons.

2) It suppresses the effect of substituents on the B ring in the case of A, A-derivatives. This circumstance may probably be expected in the cases of mono- and polysubstitution.

3) It restrains the conjugation interactions among the ring and substituents to some extent. We will consider this point in the next section.

4) It makes the distinction of positions, i. e., the α-position or β-position, in naphthalene necessary.

From the above results, the differences among the molecular properties of α-, β-, α,α'-, β,β'-, α,β-, A, A- and A, B-naphthalene derivatives should be attributable to the presence of the 9—10 bond in these molecules.

Extradelocalization Energies.—Extradelocalization energy is defined as the stabilization energy of the molecule due to substitution. By using the VO method[3], the extradelocalization energy, $\Delta\varepsilon$, of a naphthalene derivative with auxochromic substituents can be obtained from five vacant orbital energies, ε_i, using the following equation:

$$\Delta\varepsilon = -2(\sum_i^{\text{vac}}\varepsilon_i - \sum_i^{\text{vac}}\varepsilon_i^\circ)$$

In this equation, the ε_i°'s are those of naphthalene. They are -2.3028, -1.6180, -1.3028, -1.0000 and -0.6180 in β respectively. Therefore, $\sum_i^{\text{vac}}\varepsilon_i^\circ$ amounts to $-6.8416\ \beta$. In the case of the perimeter model, $\sum_i^{\text{vac}}\varepsilon_i^\circ = -6.4720\ \beta$. The calculated $\Delta\varepsilon$'s are given in Table III. The table also contains those values of α- and β-naphthol calculated by using the same parameters as those of the diols.

Table III. Extradelocalization energies of naphthalene hydroxy derivatives

	$\Delta\varepsilon$ in β	
	With 9—10 bond	Without 9—10 bond
α-Naphthol	0.1862	0.1888
β-Naphthol	0.1792	0.1888
1,4-Naphthalenediol	0.3618	0.3720
1,5-Naphthalenediol	0.3700	0.3722
1,8-Naphthalenediol	0.3730	0.3790
2,3-Naphthalenediol	0.3544	0.3706
2,6-Naphthalenediol	0.3560	0.3722
2,7-Naphthalenediol	0.3586	0.3780

From this table we obtain the following results;

1) The α-derivatives are more stable than the β-derivatives.

2) The effect of the insertion of the 9—10 bond in the perimeter model is to decrease the extradelocalization energies. This effect is remarkable in the case of β-, β,β'- and A, A-derivatives, but rather small in that of α-derivatives.

3) The $\Delta\varepsilon$'s of diols are nearly equal to double that of the corresponding naphthol; for example, those of α,α'-diols are nearly equal to twice that of α-naphthol.

Summary

The molecular diagrams and extradelocalization energies of the 2, 3-, 2, 6- and 2, 7-naphthalenediols were calculated by using the LCAO MO method. To elucidate the effect of the 9—10 bond on the molecular properties of naphthalene derivatives, we carried out calculations of the electronic structures of naphthalene hydroxy derivatives based on the perimeter model. These calculations proved that:

1) The 3-position in the naphthalene derivatives in less reative than the other positions.

2) The α-derivatives are more stable than the β-derivatives.

3) The insertion of the 9—10 bond in the perimeter model causes a decrease in the degree of conjugation interactions among the ring and the substituents.

4) In the cases of A, A-derivatives, the substituents have no significant influence on the unsubstituted ring, but produce rather a large effect on the substituted rings.

5) α-Substitutions cause an increase in the mobilities of π-electrons in the direction of the short molecular axis, but the β-substitutions lead to an increase in the direction of the long molecular axis.

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