π-*Electronic Structures of o-Quinones*

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Previously⁽¹⁾, we studied the π-electronic structures of *p*-quinones (*p*-benzoquinone, α-naphthoquinone and anthraquinone) by the aid of the simple LCAO MO method and succeeded in explaining the following problems concerning the near UV absorption bands of the *p*-quinones: 1) a similarity among the $\pi-\pi$ transition bands of these *p*-quinones, 2) a relative magnitude of the $n-\pi$ transition energy of *p*-benzoquinone, α-naphthoquinone, and anthraquinone, 3) the effect of the electron-donating group on the $\pi-\pi$ transition bands of α-naphthoquinone and anthraquinone. In the present paper, similar theoretical studies have been extended to absorption spectra of *o*-quinones such as *o*-benzoquinone, β-naphthoquinone, and phenanthrenequinone. The calculations on β-naphthoquinone and phenanthrenequinone by the MO method have never been carried out. The obtained results are now reported.

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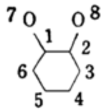
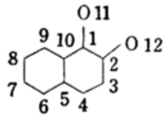
1) A. Kuboyama, This Bulletin, **31**, 752 (1958).

Method of Calculation

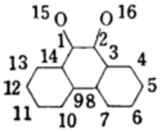
The method employed in the present calculation is exactly the same as that used in the case of *p*-quinones. The coulomb (α_i) and exchange (β_{ij}) integrals were determined on the basis of the same principles as described in the previous paper. They are as follows:



$\alpha_7=\alpha+1.3\beta,\ \alpha_1=\alpha+0.2\beta$
$\alpha_3=\alpha_4=\alpha$
$\beta_{17}=\beta_{34}=\beta,\quad \beta_{12}=0.8\beta$
$\beta_{23}=\beta_{45}=0.9\beta$



$\alpha_{11}=\alpha_{12}=\alpha+1.3\beta$
$\alpha_1=\alpha_2=\alpha+0.2\beta$
$\alpha_3=\alpha_4=\cdots\cdots=\alpha_9=\alpha_{10}=\alpha$
$\beta_{1-11}=\beta_{2-12}=\beta_{34}=\beta_{56}=\beta_{67}$
$=\cdots\cdots=\beta_{9-10}=\beta_{5-10}=\beta$
$\beta_{12}=0.8\beta,$
$\beta_{23}=\beta_{45}=\beta_{1-10}=0.9\beta$



$\alpha_{15}=\alpha+1.3\beta,\ \alpha_1=\alpha+0.2\beta$
$\alpha_3=\alpha_4=\alpha_5=\alpha_6=\alpha_7=\alpha_8=\alpha$
$\beta_{1-15}=\beta_{34}=\beta_{45}=\beta_{56}=\beta_{67}$
$=\beta_{78}=\beta_{38}=\beta$
$\beta_{12}=0.8\beta,\ \beta_{23}=\beta_{89}=0.9\beta$

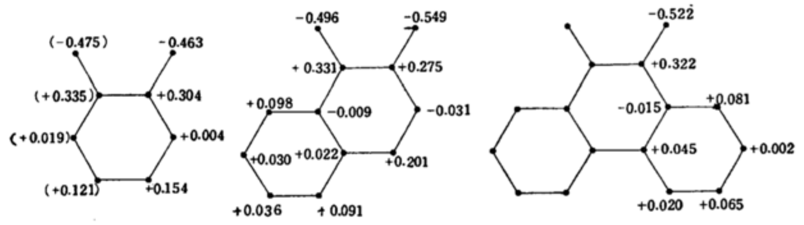
Among these values, those concerning the quinone nuclei were set equal to the values evaluated for *o*-benzoquinone by the self-consistent method[2].

Results

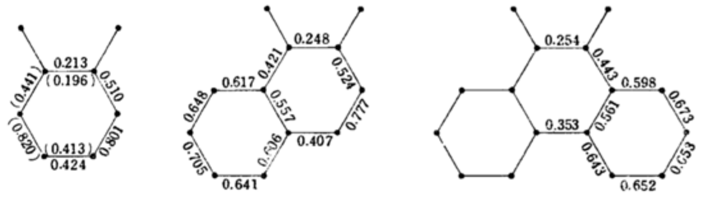
The obtained molecular diagrams are given below.

In the above diagram, the unpaired electron densities are the ones in the lowest unfilled orbitals[3]. In the molecular diagram for *o*-benzoquinone the values in brackets are the ones previously calculated by the self-consistent method. The agreement between these two molecular diagrams for *o*-benzoquinone is substantially good. Further, the energy levels of *o*-benzoquinone calculated by the two methods mentioned above are in good agreement with each other. The energy levels evaluated with these quinones are given in Fig. 1. Furthermore, the dependence* of the energy levels upon the coulomb integral of the oxygen atom was

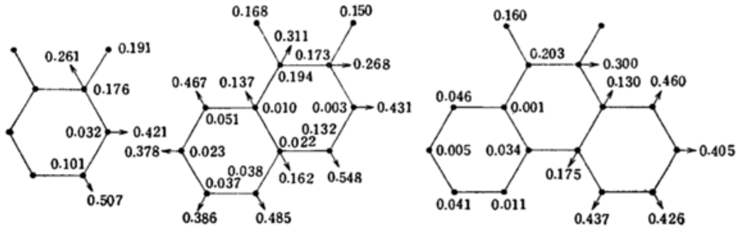
Charge densities



Bond orders



Free valences and unpaired electron densities



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[2] S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 499 (1953); S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954).

[3] H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

* The similar figure for *p*-benzoquinone was given by L. E. Orgel, *Trans. Faraday Soc.*, **52**, 1172 (1956).

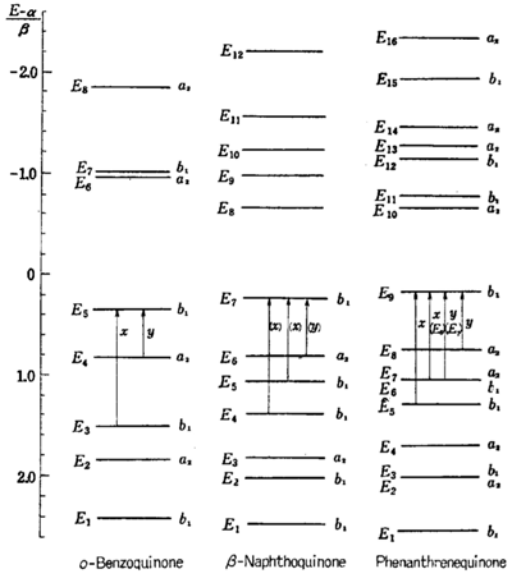

Fig. 1.

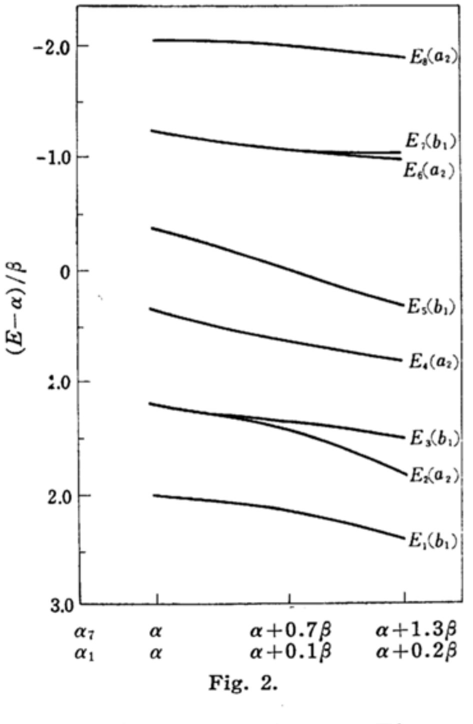

Fig. 2.

studied with *o*-benzoquinone. The result is shown in Fig. 2. The energy levels are classified according to the symmetry properties of the corresponding orbitals in the symmetry groups of these *o*-quinones (C_{2v}), taking the molecular symmetry axis as the *x*-axis and the molecular plane as the *xy* plane. For β-naphthoquinone which has no molecular symmetry axis, the symmetry properties of the orbitals are considered in relation to the quinone nucleus. The letters *x* and *y* attached to the arrow showing the transition between the energy levels denote the directions of the polarization in the allowed transitions. In phenanthrenequinone, the E_2 and E_6 orbital energies are a little lower than the E_3 and E_7 orbital energies, respectively.

Discussion

Molecular Diagrams. — The molecular diagrams of the three *o*-quinones are also similar in many points as well as those of the *p*-quinones. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order of *o*-benzoquinone < β-naphthoquinone < phenanthrenequinone. In β-naphthoquinone, the carbonyl group (C_1–O_{11}) is relatively electronically more negative than the one (C_2–O_{12}). Positions 3 and 4 of β-naphthoquinone are relatively electronically more negative and positive, respectively, than the corresponding positions of *o*-benzoquinone. The result that position 3 of β-naphthoquinone is electronically somewhat negative explains the remarkable fact[4] that at this position the nitro group substitution reaction occurs. The calculated dipole moments of *o*-benzoquinone, β-naphthoquinone, and phenanthrenequinone are ca. 8.1, 11.0, and 9.9 D, relatively. If the contribution of the inductive effect between two large dipoles belonging to adjacent carbonyl bonds (ca. 1.5 D)** is in every case subtracted from these values, the final values are 6.6, 9.5 and 8.4 D, respectively, which are considerably greater than the experimental values (5.1[2], 5.6[2] and 5.6 D[5], respectively). These differences between the calculated and the experimental values are commonly observed in the simple MO calculations. As for bond orders, in β-naphthoquinone the value for the C_2–C_3 bond is greater than the one for the C_{10}–C_1 bond and the value for the C_3–C_4 bond is nearly equal to the corresponding one of *o*-benzoquinone. The diagrams also show that the six-membered carbon rings attached to the quinone nuclei of β-naphthoquinone and

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[4] L. F. Fieser and M. Fieser, "Organic Chemistry", 2nd Ed. (1950), translated into Japanese, Maruzen Co., Ltd., Tokyo (1957), p. 748.

** The contribution of the inductive effect was calculated by the same method as that described in the following reference: H. M. Smallwood and K. F. Herzfeld, *J. Am. Chem. Soc.*, **52**, 1919 (1930).

[5] C. C. Caldwell and R. J. W. LeFèvre, *J. Chem. Soc.*, **1939**, 1614.

phenanthrenequinone are correctly approximated by the benzene nucleus. Free valence values for position 4 of *o*-benzoquinone and β-naphthoquinone are great, particularly in the case of the latter. The unpaired electron densities in the lowest unfilled orbitals are thought to be roughly equal to the unpaired electron densities in the corresponding semiquinone ions³⁾. In the three *o*-quinones, the parts greater than seventy per cent of the total unpaired electron densities exist at the carbonyl groups. Previously, McConnell³⁾ reported that between the splitting constant, α_i, in the hfs in the electron paramagnetic resonance absorption of semiquinone ions and the unpaired electron density, ρ_i (i denotes the position of a carbon atom to which a proton bonds), the following relationship can be formulated.

$$\alpha_i = 34\,\rho_i \qquad (1)$$

Recently M. Adams⁶⁾ reported the measured values of the splitting constants of various semiquinone ions. In *o*-benzoquinone, the values calculated following formula 1 (3.44 and 1.07 gauss) are in good agreement with the measured values (3.65 and 0.95 gauss). In β-naphthoquinone, the unpaired electron density of position 4 is considerably great and the value calculated by formula 1 is 4.48 gauss. As in β-naphthoquinone the measured values are 1.3 and 0.24 gauss, a doublet with a large splitting constant is probably overlooked. In accordance with the experimental result that in phenanthrenequinone 5 quintets resulting from the two sets of four equivalent protons were found, the calculated results show that the unpaired electron densities at positions 4, 6, 11, 13 and positions 5, 7, 10, 12 are mutually nearly equal in each group, respectively.

The Energy Levels. — From the energy levels given above, the following two points are noticeable, as in the *p*-quinones. First, the differences between the high filled and the lowest vacant orbitals are similar in these *o*-quinones. In the region 300 ~ 400 mμ, *o*-benzoquinone has one $\pi-\pi$ transition band, and β-naphthoquinone and phenanthrenequinone have two $\pi-\pi$ transition bands and all these bands are relatively weak***. Further, these three *o*-quinones have one $\pi-\pi$ transition band near 250 mμ***. Those of β-naphthoquinone and phenanthrenequinone are strong, and the one of *o*-benzoquinone is relatively weak. In the above energy levels all the transitions are allowed. Now, it is thought that the longest wavelength $\pi-\pi$ bands are assigned as $E_4 \rightarrow E_5$ (*o*-benzoquinone), $E_6 \rightarrow E_7$ (β-naphthoquinone) and $E_8 \rightarrow E_9$ (phenanthrenequinone), and the second long wavelength $\pi-\pi$ transition bands as $E_5 \rightarrow E_7$ (β-naphthoquinone) and $E_6, E_7 \rightarrow E_9$ (phenanthrenequinone), and the bands near 250 mμ as $E_3 \rightarrow E_5$ (*o*-benzoquinone), $E_4 \rightarrow E_7$ (β-naphthoquinone), and $E_5 \rightarrow E_9$ (phenanthrenequinone), respectively. Though there remains a π unfavorable point that the band near 250 mμ of *o*-benzoquinone alone is relatively weak, the above assignments are thought to be reasonable, considering the similarity of the energy levels among the three *o*-quinones. Second, the energy levels are as a whole a little elevated as the size of the *o*-quinone molecule becomes larger. Now, the lone-pair orbital energies of the oxygen atoms in the three *o*-quinones are thought to be nearly equal. Thus, as was previously reported¹⁾, this result explains the fact that the $n-\pi$ transition energy becomes greater as the size of the *o*-quinone molecule becomes larger. The average value of the highest filled and the lowest vacant orbital energies of each *o*-quinone as a measure of the elevation of the energy levels is $\alpha+0.628\beta$, $\alpha+0.514\beta$ and $\alpha+0.469\beta$ for *o*-benzoquinone, β-naphthoquinone and phenanthrenequinone, respectively.

The Effect of the Electron-Donating Substituent on the $\pi-\pi$ Transition Bands. — As was previously reported⁷⁾¹⁾, the greater the C_{mi}^2 value is, and the smaller the C_{ni}^2 value, the greater the extent of the red-shift of the band corresponding to the transition ($m \rightarrow n$) is, and the C_{mi}^2 value has a much greater effect than the C_{ni}^2 value, where C_{mi} and C_{ni} are the coefficients of the i-th atomic orbital in the LCAO MO, m and n, respectively. Now, let us examine this rule for *o*-benzoquinone and β-naphthoquinone. In Figs. 3⁸⁾ and 4⁹⁾, the absorption spectra of some methyl group substituted *o*-benzoquinones and methoxyl group substituted β-naphthoquinones are given, respectively. All the π-orbitals of the three *o*-quinones are intrinsically non-degenerate and we can reasonably assume that the quasi-π-orbital energy of the methyl group and the lone-pair orbital

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6) M. Adams, *J. Chem. Phys.*, **28**, 774 (1958).

*** In view of the intensity and the solvent effect²⁾, these bands are thought to be due to $\pi-\pi$ transition.

7) A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1062 (1956).

8) H. J. Teuber and G. Steiger, *Ber.*, **88**, 802 (1955).

9) H. J. Teuber and N. Götz, ibid., **87**, 1236 (1954).

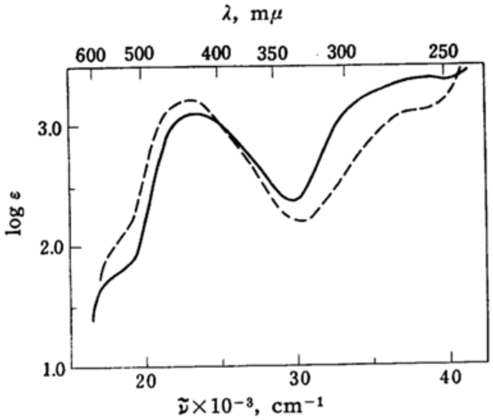

Fig. 3[8]. —— 3,4,5-Trimethyl-*o*-benzoquinone
---- 3,4,6-Trimethyl-*o*-benzoquinone
Solvent, chloroform.

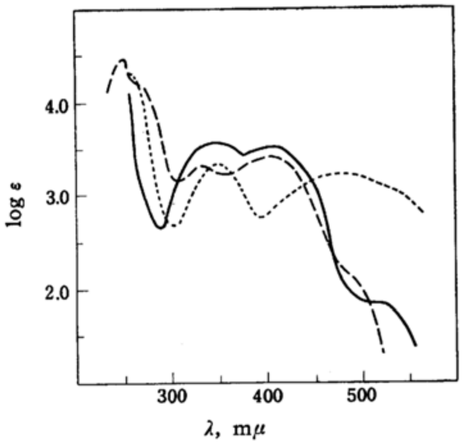

Fig. 4[9]. —— β-Naphthoquinone
------ 3-Methoxy- ″
---- 4-Methoxy- ″
Solvent, chloroform.

TABLE I. THE SQUARE VALUES OF THE COEFFICIENTS IN *o*-BENZOQUINONE
(The numbers in the first row denote the positions of the substitutions)

	3	4
$E_3(b_1)$	0.103	0.290
$E_4(a_2)$	0.296	0.101
$E_5(b_1)$	0.032	0.101

TABLE II. THE SQUARE VALUES OF THE COEFFICIENTS IN β-NAPHTHOQUINONE

	3	4
$E_4(b_1)$	0.113	0.231
$E_5(b_1)$	0.001	0.002
$E_6(a_2)$	0.290	0.074
$E_7(b_1)$	0.003	0.132

energy of the oxygen atom in the methoxyl group as a substituent are lower than the E_3 (*o*-benzoquinone) and the E_4 (β-naphthoquinone) orbital energies, respectively. Thus, the above method can be applied to these cases. In Fig. 3, the longer and the shorter wavelength π−π transition bands of *o*-benzoquinone largely shift toward longer wavelengths for 3- and 4-substitutions, respectively. The data in Table I clearly fit these facts. In Fig. 4, the band near 400 mμ and the band near 250 mμ of β-naphthoquinone largely shift toward longer wavelengths for 3- and 4-substitutions, respectively. The data in Table II clearly explain these facts. In addition, the absorption spectra of some hydroxyl group substituted at the benzene nucleus attached to the quinone nucleus of β-naphthoquinones are also generally explained by the calculated results. Thus, in general, the effect of the electron-donating substituent on the π−π transition bands in the near UV region of *o*-benzoquinone and β-naphthoquinone can be clearly explained by the above method as well as in the case of the *p*-quinones.

The good agreements between the results calculated by the simple MO method and the experimental results, concerning the near UV absorption spectra in the *o*- and the *p*-quinones, are thought to be due to the quinoid field[****], characteristic of quinone compounds, which differs from the round fields, characteristic of the aromatics, presented by J. R. Platt[10].

Summary

Electronic structures of *o*-benzoquinone, β-naphthoquinone and phenanthrenequinone were studied with the simple MO method, using the same integral values as those adopted in the self-consistent MO calculation for *o*-benzoquinone. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order of *o*-benzoquinone, β-naphthoquinone, and phenanthrenequinone. The calculated dipole moments (6.6, 9.5 and 8.4 D for *o*-benzoquinone, β-naphthoquinone and phenanthrenequinone, respectively) seem a little greater than the experimental values. As for bond orders, reasonable results were obtained. The calculated results predict the existence of a doublet with a large splitting constant (ca. 4.5 gauss) in the hfs of the electron paramagnetic resonance absorption of β-naphtho-semiquinone ion. Three problems

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[****] The similar discussion was given in J. W. Sidman's work: *J. Am. Chem. Soc.*, **78**, 4567 (1956).

[10] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

concerning the near UV absorption bands [1) the similarity among the $\pi-\pi$ transition bands of the three *o*-quinones, 2) the relative magnitude of the $n-\pi$ transition energy of *o*-benzoquinone, β-naphthoquinone, and phenanthrenequinone, 3) the effect of the electron-donating group on the $\pi-\pi$ transition bands of *o*-benzoquinone and β-naphthoquinone] can be clearly explained by the calculated results, as in the cases of the *p*-quinones.

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