π-Electronic Structures of α-Naphthoquinone and Anthraquinone

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The p-quinone type compounds such as p-benzoquinone, α-naphthoquinone, and anthraquinone play an important role as oxidizing reagents in organic chemistry and biochemistry. As for their π-electronic structures, p-benzoquinone has already been studied by many workers but the theoretical work on α-naphthoquinone and anthraquinone is scanty[1]. Therefore, the π-electronic structure of α-naphthoquinone and anthraquinone is studied by the simple MO method.

Method of Calculations.—Because of the great discrepancy from the uniform distribution of π-electron density in quinones, which is due to the existence of electronegative oxygen atoms, it is desirable to use the self-consistent method which was used in our previous paper[2] concerning o- and p-benzoquinones. But the application of this method to α-napthoquinone and anthraquinone is difficult, since these molecules contain too many π-electrons compared with p-benzoquinone.

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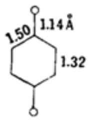
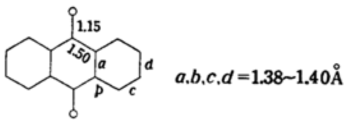
[1] a) D. Hadzi, *Arkiv. Kem.*, **25**, 33 (1953); b) M. L. Josien and J. Deschamps, *J. chim. phys.*, **52**, 213 (1955); c) J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 4567 (1956).

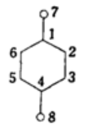
[2] S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 499 (1953); S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954).

Now, as is seen in the following X-ray diffraction data[3], the bond lengths of the C=O bond and the adjacent C—C bond are

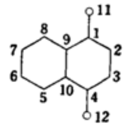




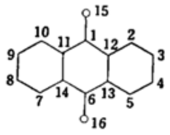
nearly equal in *p*-benzoquinone and anthraquinone, and the structures of the two six-membered carbon rings of anthraquinone are similar to that of the benzene nucleus. In view of these facts, we assumed the coulomb (α_i) and exchange (β_{ij}) integrals for α-naphthoquinone and anthraquinone as follows:



$$\alpha_{C_2}=\alpha_{C_3}=\alpha \quad \alpha_O=\alpha+1.3\beta$$
$$\alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-7}=\beta \quad \beta_{1-2}=0.8\beta$$
$$\beta_{2-3}=1.1\beta$$



$$\alpha_{C_2}=\alpha_{C_{10}}=\alpha_{C_5}=\alpha_{C_6}=\alpha$$
$$\alpha_O=\alpha+1.3\beta \quad \alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-11}=\beta_{9-10}=\beta_{10-5}=\beta_{5-6}$$
$$=\beta_{6-7}=\beta$$
$$\beta_{1-2}=\beta_{1-9}=0.8\beta \quad \beta_{2-3}=1.1\beta$$

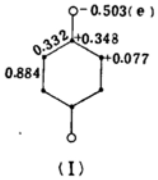


$$\alpha_{C_{12}}=\alpha_{C_2}=\alpha_{C_3}=\alpha$$
$$\alpha_O=\alpha+1.3\beta \quad \alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-15}=\beta_{12-13}=\beta_{12-2}=\beta_{2-3}$$
$$=\beta_{3-4}=\beta \quad \beta_{1-12}=0.8\beta$$

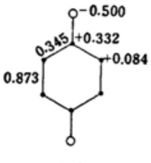
Among these values, those concerning the quinone nuclei were made equal to the values evaluated for *p*-benzoquinone by the SCF method in the previous paper[2].

Results

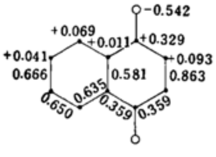
The obtained molecular diagrams and the energy levels are given below.

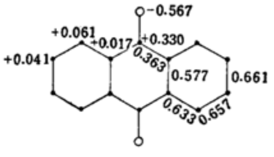


(I)

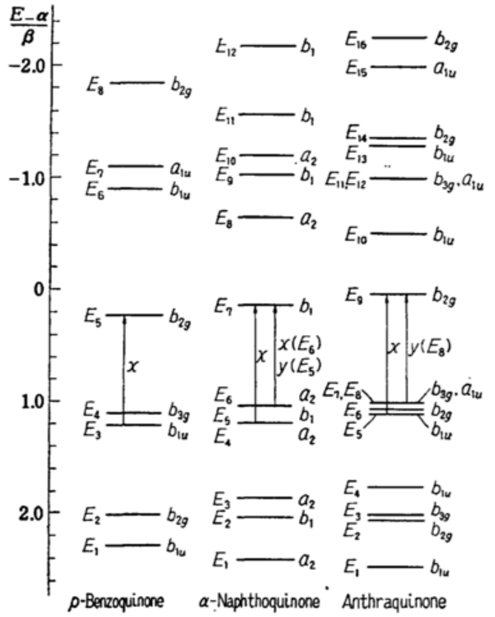


(II)





The energy levels are classified according to the symmetry properties of the corresponding orbitals in the symmetry group of the molecule (D_{2h} for *p*-benzoquinone and anthraquinone, C_{2v} for α-naphthoquinone), taking the O—O direction as the *x*-axis and the molecular plane as the *xy* plane. The energy difference between the orbitals E_5 and E_6 of α-naphthoquinone is 0.003β. 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. The molecular diagram I for *p*-benzoquinone is the one previously calculated by the SCF method[2] and the diagram II for the same molecule is the one calculated by the present method. The agreement between these two molecular diagrams is satisfactory. Further, the energy levels of *p*-benzoquinone calculated by the two methods mentioned above are also in good agreement with each other. Thus, the results evaluated for α-naphthoquinone and anthraquinone may be thought to be nearly self-consistent.



Discussion

Molecular Diagrams. — The molecular diagrams of the three *p*-quinones are similar in many points. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order *p*-benzoquinone, α-naphthoquinone and anthraquinone. The dipole moment (ca. 2.2 D) of α-naphthoqueinone calculated under

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[3] For *p*-benzoquinone; J. M. Robertson, *Proc. Roy. Soc.*, **150**, 106 (1935). For anthraquinone; S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948).

the assumption that the angle between the two carbonyl bond axes is 180°, is considerably larger than the measured value[4] (1.30 D) in which the contribution (ca. 0.6 D) of the atomic polarisation[5] characteristic of *p*-quinones is contained. Therefore the calculated dipole moment seems too large, though its value is thought to be considerably affected by the angle between the two carbonyl bond axes.

As for bond orders, the value for the C_2—C_3 bond is nearly equal in α-naphthoquinone and *p*-benzoquinone. Furthermore, the above diagrams show that the six-membered carbon rings of α-naphthoquinone and anthraquinone are properly approximated by the benzene nucleus. The bond orders of the two bonds, C_1—C_2, C_1—C_9 of α-naphthoquinone are equal. B. Pullman and J. Deudel[6] also obtained a similar result in their work on 1, 2-benzanthra-3, 4-quinone. From these results, it seems probable that the bond orders of the C—C bonds adjacent to the C—O bonds in quinones can hardly be affected by side carbon atom groups.

Energy Levels.—From the energy levels given above, the following two points are worthy of notice. First, the difference between the highest filled and the lowest vacant orbitals is similar in these *p*-quinones. This result explains a similarity among the π—π transition bands of the three *p*-quinones in the long-wavelength region, that is to say, they have a relatively weak band[*1] near 300 mμ and a strong band near 250 mμ, respectively. The bands near 250 mμ are assigned as $E_3 \to E_5$ (*p*-benzoquinone), $E_4 \to E_7$ (α-naphthoquinone), and $E_5 \to E_9$ (anthraquinone), and the bands near 300 mμ as $E_4 \to E_5$ (*p*-benzoquinone), $E_5, E_6 \to E_7$ (α-naphthoquinone) and $E_6, E_7, E_8 \to E_9$ (anthraquinone). The fact that the intensity of the band near 300 mμ of *p*-benzoquinone is about ten times weaker than that of α-naphthoquinone and of anthraquinone can be explained with the present result that in *p*-benzoquinone alone, the corresponding transition is forbidden.

Second, the energy levels as a whole are a little elevated as the size of the *p*-quinone molecule becomes larger. This result can be anticipated considering the ratios of the number of electronegative oxygen atoms to that of far less electronegative carbon atoms in each *p*-quinone molecule. As a measure of the elevation of the energy levels, the average value of the highest filled and the lowest vacant orbital energies of each *p*-quinone may be adopted. This value has $\alpha+0.665\beta$, $\alpha+0.577\beta$, and $\alpha+0.514\beta$ for *p*-benzoquinone, α-naphthoquinone, and anthraquinone, respectively. Now, the lone-pair orbital energies of the oxygen atoms in the three *p*-quinones are thought to be nearly equal. Then, it may be expected that the *n*-π transition energy becomes greater in the order of *p*-benzoquinone, α-naphthoquinone and anthraquinone. The observed phenomenon[1c,2] agrees satisfactorily with this expectation. It seems sure that the same explanation can be applied to the same phenomenon observed in *o*-quinones[1c,2].

The Effect of the Electron-Donating Substituent on the π—π Transition Bands.—In our previous work[7], the effect of the alkyl groups on the near UV absorption bands of *o*- and *p*-benzoquinones are studied using a modified form of Herzfeld-Nagakura-Baba's formula[8]. In a one-electron transition (*m* orbital → *n* orbital), the shift in wave numbers ($\Delta\nu_{m\to n,i}$) due to a substitution on the *i*th carbon atom in a quinone molecule has the value,

$$\Delta\nu_{m\to n,i}=K_mC_{mi}^2-K_nC_{ni}^2 \qquad (1)$$

Here, the two conditions are required, that *m* and *n* orbitals are non-degenerate and the *m* orbital energy is higher than the substituent's lone-pair orbital energy. C_{mi} and C_{ni} are the coefficients of the *i*th atomic orbital in the LCAO MO, *m* and *n*, respectively. K_m and K_n are nearly constant if the kind of substituent is fixed, and $K_m<K_n<0$. So, if $C_{mi}^2 \gtrsim C_{ni}^2$, $\Delta\nu_{m\to n,i}<0$. Then, 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 is. Thus, considering the C_{mi}^2 and C_{ni}^2 values, the magnitude of the red shift of a band by a substituent can be presumed.

Now, let us apply the above method to α-naphthoquinone and anthraquinone whose data are given in Figs. 1[9], 2[10] and

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[4] B. Eda, Presented at the Symposium on Structural Chemistry, Sendai (1954).

[5] R. J. W. LeFèvre, "Dipole Moments", Methuen & Co. Ltd., London (1948), p. 100.

[6] B. Pullman and J. Daudel, *Compt. rend.*, **238**, 964 (1954).

[*1] In view of the intensity and the solvent effect, this band is thought to be due to π-π transition.

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

[8] K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 72 (1951).

[9] M. O'L Crowe, *J. Biol. Chem.*, **115**, 479 (1936).

[10] R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, **1941**, 159.

Tables I, II. In Figs. 1 and 2, in all cases, the substituent is the hydroxyl group and the solvent ethanol. Since the solvent effect[9] of ethanol on the bands near 250 mμ and 300 mμ of α-naphthoquinone are very small compared with the substitution effect, the former effect may safely be neglected. All the π-orbitals of α-naphthoquinone and anthraquinone are intrinsically non-degenerate and we can reasonably assume that the lone-pair orbital energy of the oxygen atom in the hydroxyl group as a substituent is lower than the E_4(α-naphthoquinone) and E_5(anthraquinone) orbital energies. Thus, the above method can be applied. As the consequence it may be expected that, as for α-naphthoquinone, the band near 250 mμ largely shifts towards longer wave lengths for 2-substitution and remains almost constant for 5-substitution. The data in Table I clearly fit these expectations. On the other hand, the bands near 300 mμ split into the two bands for both 2- and 5-substitutions, and from the data in Table I, the longer-wavelength bands are thought to correspond to the transitions, $E_6 \rightarrow E_7$ (2-substitution) and $E_5 \rightarrow E_7$ (5-substitution), and the shorter wavelength bands to the transitions, $E_5 \rightarrow E_7$ (2-substitution) and $E_6 \rightarrow E_7$ (5-substitution). As for anthraquinone, the band near 250 mμ largely shifts towards longer wavelengths for 3-substitution and scarcely shifts at all for 2-substitution. This fact is clearly explained from eq. (1), and C_{mi}^2 and C_{ni}^2 values given in Table II. It is thought that the band near 300 mμ of unsubstituted anthraquinone is mainly contributed by the transition, $E_8 \rightarrow E_9$, since this transition alone is allowed among the three transitions assigned to this band, but in hydroxy anthraquinone the forbidden transitions come to be allowed to some extent by the perturbation of the substituent group. From the coefficient values in Table 2, it may be induced that the longest wavelength max. of the band near 300 mμ corresponds to the transition $E_8 \rightarrow E_9$ for 2-substitution and $E_7 \rightarrow E_9$ for 3-substitution, respectively. These assignments seem reasonable from the fact that the intensity of the absorption band under consideration is stronger in 2-hydroxy anthraquinone than in 3-hydroxyl derivative (see Fig. 2). Thus, the above theoretical consideration can clearly explain the effect

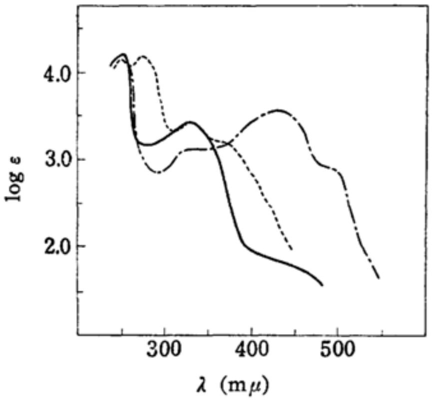

Fig. 1. ——, 1, 4 Naphthoquinone;
- - - -, 2-Hydroxy- 〃 ;
—-—, 5-Hydroxy- 〃 ;
Solvent, Ethanol.

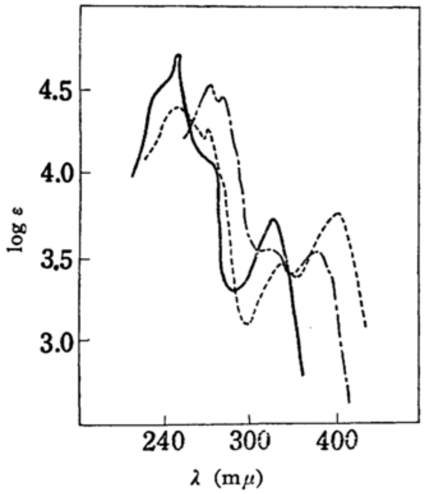

Fig. 2. ——, Anthraquinone;
- - - -, 2-Hydroxy- 〃 ;
—-—, 3-Hydroxy- 〃 ;
Solvent, Ethanol.

TABLE I

THE SQUARE VALUES OF THE COEFFICIENTS IN α-NAPHTHOQUINONE (THE NUMBERS IN THE FIRST ROW DENOTE THE POSITIONS OF THE SUBSTITUTIONS)

	2	5	6
$E_4(a_2)$	0.270	0.001	0.017
$E_5(b_1)$	0.000	0.298	0.073
$E_6(a_2)$	0.085	0.000	0.207
$E_7(b_1)$	0.082	0.036	0.028

TABLE II

THE SQUARE VALUES OF THE COEFFICIENTS IN ANTHRAQUINONE

	2	3
$E_5(b_{1u})$	0.001	0.098
$E_6(b_{2g})$	0.136	0.032
$E_7(b_{3g})$	0.000	0.125
$E_8(a_{1u})$	0.167	0.042
$E_9(b_{2g})$	0.032	0.031

of the electrondonating substituent on the $\pi-\pi$ transition bands in the near UV region of α-naphthoquinone and anthraquinone.

In addition, as for the report[11] that in the α-naphthosemiquinone ion the probability of finding the unpaired electron in a $p_z\pi$ orbital centered on the 2nd carbon atom is ca. ten times greater than that in a $p_z\pi$ orbital centered on the 5th or 6th carbon atoms, the probabilities are thought to be approximately parallel to the $C_{7i}{}^2$ values and the result in Table I is unsatisfactory in comparison with the experimental result, but a similar trend is seen for the o-benzosemiquinone ion[11b,*2].

Summary

Electronic structures of p-benzoquinone, α-naphthoquinone, and anthraquinone were studied with the simple MO method, using the same integral values as adopted in the SCF MO calculation for p-benzoquinone. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order p-benzoquinone, α-naphthoquinone and anthraquinone. The calculated dipole moment (2.2 D) of α-naphthoquinone seems too large. As for bond orders, the reasonable results were obtained. Two problems concerning the near UV absorption bands (1. a similarity among the $\pi-\pi$ transition bands of the three p-quinones, 2. a relative magnitude of the $n-\pi$ transition energy in the order of p-benzoquinone, α-naphthoquinone and anthraquinone) can be clearly explained with the calculated results. Especially, the effect of the electrondonating group on the $\pi-\pi$ transition bands of α-naphthoquinone and anthraquinone can also be favourably explained, according to the modified Herzfeld-Nagakura-Baba's formula, with the calculated results. It seems sure that for the o-quinone type compounds the similar result can be obtained with the same method as used for the p-quinone type compounds.

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[11] a) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **24**. 479 (1956); b) H. M. McConnell, ibid., **24**, 632 (1956).

[*2] In our previous calculation[2], the similar result to 11b) was obtained.