π-Electronic Structure of Diphenoquinone

By Akira KUBOYAMA

In previous papers the π-electronic structures of p-quinones[1] (p-benzoquinone, α-naphthoquinone and anthraquinone) and o-quinones[2] (o-benzoquinone, β-naphthoquinone and phenanthrenequinone) were studied by the aid of the simple LCAO MO method, with good agreement between the calculated and experimental results concerning the near UV absorption bands of these quinones. In the present paper, it is undertaken to carry out a similar study on the π-electronic structure of diphenoquinone*, the spectroscopic feature of which has never been theoretically studied.
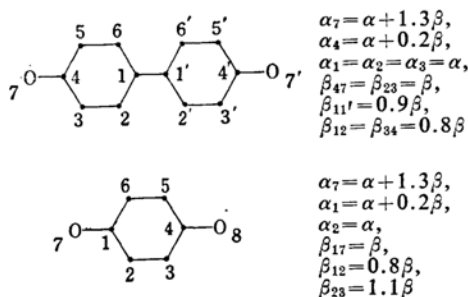
Method of Calculation

As the molecular dimension of diphenoquinone(DQ) has never been known, it is

---

1) A. Kuboyama, This Bulletin, 31, 752 (1958).
2) A. Kuboyama, ibid., 32, 1226 (1959).

---

* C. A. Coulson has studied the bond orders of diphenoquinone [*Trans. Faraday Soc.*, 42, 106 (1946)].

impossible to calculate the overlap integrals necessary for the evaluation of exchange integrals (β_{ij}). Therefore, the values of exchange integrals as well as of Coulomb integrals (α_i) were determined by referring to the corresponding values for p-benzoquinone(BQ)[1]. The values of these integrals eventually used for the present calculation are shown in Chart I. As it was expected that owing to the steric hindrance between hydrogen atoms at the 2, 6-positions and at the 2', 6'-positions, two six-membered rings of DQ are somewhat twisted together around the C_1–$C_{1'}$ bond, the adopted value for $\beta_{11'}$ was a little smaller than that for β_{23}.

Chart I. Values of exchange and Coulomb integrals

$$\alpha_7 = \alpha + 1.3\beta,$$
$$\alpha_4 = \alpha + 0.2\beta,$$
$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha,$$
$$\beta_{47} = \beta_{23} = \beta,$$
$$\beta_{11'} = 0.9\beta,$$
$$\beta_{12} = \beta_{34} = 0.8\beta$$

$$\alpha_7 = \alpha + 1.3\beta,$$
$$\alpha_1 = \alpha + 0.2\beta,$$
$$\alpha_2 = \alpha,$$
$$\beta_{17} = \beta,$$
$$\beta_{12} = 0.8\beta,$$
$$\beta_{23} = 1.1\beta$$

Results

The molecular diagrams are given in Charts II and III, together with those of BQ.
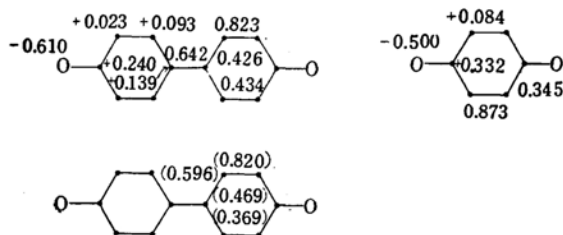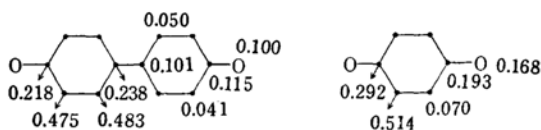
Chart II. Charge densities and bond orders

Chart III. Free valences and unpaired electron densities

In these diagrams, the unpaired electron densities are the squares of the coefficients of atomic orbitals in the lowest unfilled orbital. The bond order values of DQ in parentheses are those obtained by Coulson**. The orbital

** In the calculation*, the adopted integral values are as follows. α_7 and β_{17} are respectively $\alpha + 2\beta$, 2β and the other Coulomb and exchange integrals are all α and β, respectively.
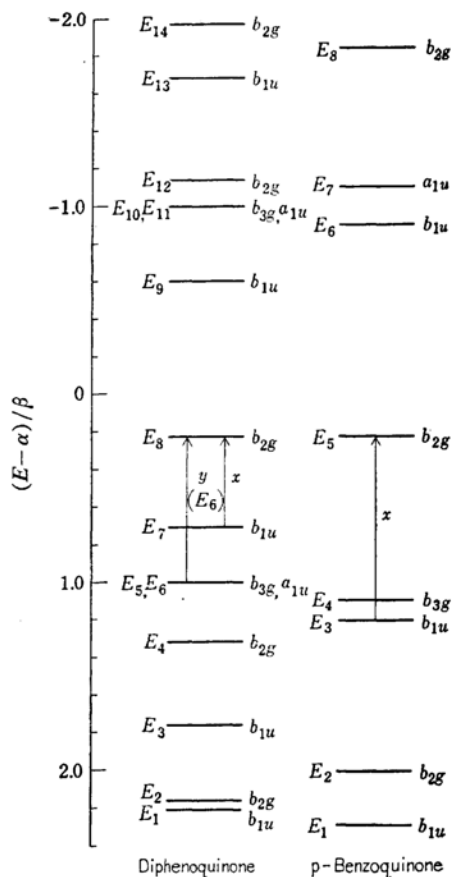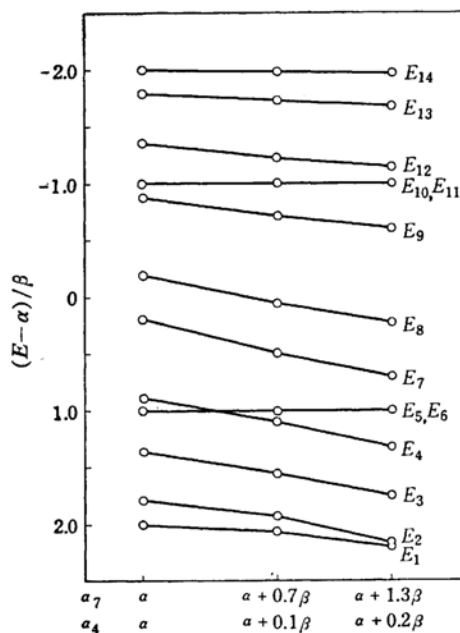

Fig. 1.

Fig. 2.

energies of DQ are given in Fig. 1, together with those of BQ. The dependence of the orbital energies upon the Coulomb integral of the oxygen atoms of DQ is shown in Fig. 2. the molecular orbitals are classified according to their symmetry properties in the symmetry group (D_{2h}), the O–O direction being taken as the x-axis and the molecular plane as the xy plane. The E_5 and E_6 orbitals as well as the E_{10} and E_{11} orbitals are accidentally degenerate. The letter "x" or "y" attached to the arrow showing a transition denotes the direction of polarization in an allowed transition. The filled and the lowest unfilled molecular orbitals of DQ are given below with their energy values. χ_i denotes the $2p\pi$ atomic orbital of the ith atom.

E_1 $0.2100(\chi_1+\chi_{1'})+0.1721(\chi_2+\chi_6+\chi_{2'}+\chi_{6'})$
$+0.2127(\chi_3+\chi_5+\chi_{3'}+\chi_{5'})+0.3726(\chi_4+\chi_{4'})$
$+0.4091(\chi_7+\chi_{7'})$

E_2 $0.0611(\chi_1-\chi_{1'})+0.1169(\chi_2+\chi_6-\chi_{2'}-\chi_{6'})$
$+0.2041(\chi_3+\chi_5-\chi_{3'}-\chi_{5'})+0.4058(\chi_4-\chi_{4'})$
$+0.4701(\chi_7-\chi_{7'})$

E_3 $0.4604(\chi_1+\chi_{1'})+0.2465(\chi_2+\chi_6+\chi_{2'}+\chi_{6'})$
$+0.0650(\chi_3+\chi_5+\chi_{3'}+\chi_{5'})-0.1654(\chi_4+\chi_{4'})$
$-0.3616(\chi_7+\chi_{7'})$

E_4 $0.2255(\chi_1-\chi_{1'})+0.3128(\chi_2+\chi_6-\chi_{2'}-\chi_{6'})$
$+0.2325(\chi_3+\chi_5-\chi_{3'}-\chi_{5'})-0.0075(\chi_4-\chi_{4'})$
$-0.3804(\chi_7-\chi_{7'})$

E_5 $0.3535(\chi_2+\chi_3-\chi_5-\chi_6+\chi_{2'}+\chi_{3'}-\chi_{5'}-\chi_{6'})$

E_6 $0.3535(\chi_2+\chi_3-\chi_5-\chi_6-\chi_{2'}-\chi_{3'}+\chi_{5'}+\chi_{6'})$

E_7 $0.3459(\chi_1+\chi_{1'})-0.0406(\chi_2+\chi_6+\chi_{2'}+\chi_{6'})$
$-0.3056(\chi_3+\chi_5+\chi_{3'}+\chi_{5'})-0.2211(\chi_4+\chi_{4'})$
$+0.3759(\chi_7+\chi_{7'})$

E_8 $0.3185(\chi_1-\chi_{1'})+0.2246(\chi_2+\chi_6-\chi_{2'}-\chi_{6'})$
$-0.2015(\chi_3+\chi_5-\chi_{3'}-\chi_{5'})-0.3388(\chi_4-\chi_{4'})$
$+0.3161(\chi_7-\chi_{7'})$

$E_1(b_{1u})$	$\alpha+2.21098\beta$	$E_8(b_{2g})$	$\alpha+0.22822\beta$
$E_2(b_{2g})$	$\alpha+2.16326\beta$	$E_9(b_{1u})$	$\alpha-0.60266\beta$
$E_3(b_{1u})$	$\alpha+1.75738\beta$	$E_{10}(b_{3g})$	$\alpha-\beta$
$E_4(b_{2g})$	$\alpha+1.31977\beta$	$E_{11}(a_{1u})$	$\alpha-\beta$
$E_5(b_{3g})$	$\alpha+\beta$	$E_{12}(b_{2g})$	$\alpha-1.13941\beta$
$E_6(a_{1u})$	$\alpha+\beta$	$E_{13}(b_{1u})$	$\alpha-1.67736\beta$
$E_7(b_{1u})$	$\alpha+0.71165\beta$	$E_{14}(b_{2g})$	$\alpha-1.97184\beta$

Discussion

Molecular Diagram.—As for charge distribution, the negative charge of the oxygen atom of DQ is a little larger than that of BQ and of anthraquinone (0.567 e). As for bond orders, the general feature of DQ is in qualitative agreement with the one obtained by Coulson. The bond order of the C_2–C_3 bond of DQ is nearly as large as that of the C_2–C_3 bond of BQ, and the bond orders of the C_1–C_2 and C_3–C_4 bonds of DQ are nearly equal. The bond order obtained by Coulson is considerably smaller in the C_3–C_4 bond than in the C_1–C_2 bond. The free valences of DQ are in general nearly equal to those of BQ. In DQ the free valency value of the C_1 atom is almost the same as that of the C_4 atom. As for the unpaired electron densities, in o- and p-quinones previously studied, the part larger than sixty percent of the total unpaired electron density exists at the two carbonyl groups, while in DQ the part smaller than fifty percent of the total unpaired electron density exists at the two carbonyl groups. The relatively large unpaired electron density value for the C_1 atom of DQ is noticeable. Unfortunately, in DQ the hfs of the electron paramagnetic resonance absorption of the semiquinone ion has never been measured due to the unstability of the ion, but for 3, 5, 3', 5'-tetramethyl-DQ Matsunaga*** obtained the splitting constant (0.78 gauss) of the hfs due to ring protons. This value is considerably smaller than the one (1.39 gauss) calculated from the combination of the obtained unpaired electron density with McConnell's formula[3].

Energy Levels.—Concerning the energy levels given above, two points should be mentioned. First, the lowest unfilled orbital(E_8) is far lower than the other unfilled orbitals, as was previously obtained with o- and p-quinones, and is near the orbital(E_5) of BQ. Second, the highest filled orbital(E_7) is considerably higher than the ones of the p-quinones. The electronic spectrum of DQ in dioxanë obtained by Hartmann and Lorenz[4] is given in Fig. 3. As is seen in Fig. 3, DQ has three adsorption bands at about 500, 390 and 260 mμ. Now these absorption bands are reasonably attributed to the transitions from the rather higher filled
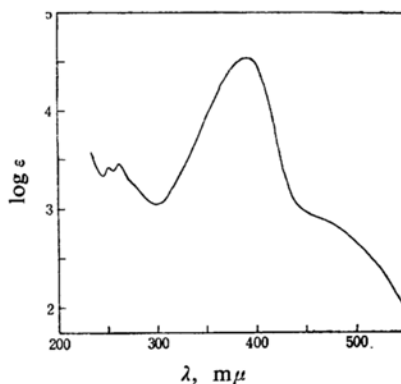

Fig. 3[4]. Electronic spectrum of diphenoquinone, solvent dioxane.

*** Unpublished data.
3) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).
4) H. Hartmann and E. Lorenz, *Z. Naturforsch.*, **7a**, 360 (1952).

orbitals to the lowest unfilled orbital (E_8) of DQ. The transitions $E_4 \rightarrow E_8$, $E_5 \rightarrow E_8$ are forbidden. The dipole strengths, calculated with Mulliken's approximation[5], are 0.0014 (Å^2) and 5.97 (Å^2) for the transitions $E_6 \rightarrow E_8$ and $E_7 \rightarrow E_8$, respectively. Thus, the strong band near 390 mμ is unambiguously assigned to the transition $E_7 \rightarrow E_8(A_{1g} \rightarrow B_{3u})$. This transition corresponds to the transition $E_3 \rightarrow E_5(A_{1g} \rightarrow B_{3u})$ of BQ. For the $A_{1g} \rightarrow B_{3u}$ transition bands, the calculated transition energies (0.979β for BQ, 0.483β for DQ) are reasonable in comparison with the observed ones (ca. 5.0 e. V. for BQ, ca. 3.2 e. V. for DQ). The weak band near 500 mμ may be assigned to the transition $E_6 \rightarrow E_8(A_{1g} \rightarrow B_{2u})$ or $E_5 \rightarrow E_8(A_{1g} \rightarrow B_{1g})$, but the transition energy (0.772β) seems too great for this assignment. This band may tentatively be due to the n-π^* transition. The intensity of this band seems considerably great compared with the n-π^* transition band of other quinones but is nearly equal to that of the n-π^* transition band of *trans*-azobenzene[6]. The band near 260 mμ is tentatively assigned to the transition $E_4 \rightarrow E_g(A_{1g} \rightarrow A_{1g})$.

Summary

The electronic structure of diphenoquinone was studied with the simple MO method using the similar integral values as adopted in our previous work on p-quinones. The obtained result was discussed in comparison with the previously obtained one for p-benzoquinone. As for energy levels, the lowest unfilled orbital (b_{2g}) of diphenoquinone is far lower than the other unfilled orbitals as was obtained with the p-quinones The highest filled orbital (b_{1u}) of diphenoquinone is considerably higher than the ones of the p-quinones. From the calculated result the intense absorption band near 390 mμ was unambiguously assigned to the $A_{1g} \rightarrow B_{3u}$ transition.

Government Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo

5) R. S. Mulliken, *J. Chem. Phys.*, 7, 20 (1939).
6) P. P. Birnbaum, J. H. Linford and D. W. G. Style, *Trans. Faraday Soc.*, 49, 735 (1953).