π-Electronic Energy Levels of *o*-Benzoquinone

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Previously, π-electronic energy levels of quinones have been studied by one[1] of the present authors using the simple MO calculation. In that study, an attempt to explain the electronic spectra of quinones on the basis of calculated results was made. However, in order to clarify the whole aspect of the electronic spectra of quinones, it is desirable that the electronic energy levels of quinones be studied by the MO calculation using a Hamiltonian which includes electronic interaction terms. Among quinones, *p*-benzoquinone alone has been studied by many authors[2] with such a calculation. However, *o*-benzoquinone and anthraquinone are also important compounds among the quinones. We have, therefore, carried out such a calculation concerning *o*-benzoquinone and anthraquinone. In this paper the results obtained for *o*-benzoquinone will be shown.

The Method of Calculation

In the MO calculation of a π-electronic system which contains hetero atoms such as quinones, it is desirable to use the self-consistent field (SCF) technique. In Sidman's work[2d] on carbonyl compounds and *p*-benzoquinone, Pople's SCF MO method[3] was used, but the values of the electron repulsion integrals were obtained according to Pariser-Parr's uniformly-charged sphere approximation[4] instead of Pople's point-charge approximation. The configuration interaction among low-energy excited states were also calculated. This Sidman calculation gives, on the whole, reasonable results. Therefore, our calculation was carried out according to Sidman's method.

The integrals used are shown in Table I. O and C denote oxygen and carbon atoms respectively and, for example, (OO|OO) and (OO|CC) denote the one-center electron repulsion integral of the oxygen atom and the two-center Coulomb repulsion integral over the oxygen and carbon atoms respectively. The values in Table I are those in Sidman's Table except for the formula for (OO|OO) and the values of the core-exchange integrals for the C–C bonds ($\beta_{CC'}$) ($R=1.46$, 1.49Å). The formula for (OO|OO) was obtained from the value of (OO|OO) and the formula for (OO|O′O′) (for $R>2.8$Å) in Sidman's Table.[2d] Sidman regarded the *U*-term in Pople's SCF MO method as the valence-state orbital energy corrected for the fact that the atom is no longer isolated, but is now a part of a molecule. The value of U_{CC} is the same as that used in Hush and Pople's paper.[5] The value of U_{OO} was determined from a comparison of the valence-state ionization potentials of the oxygn and carbon atoms. As will be shown later, the energy levels are not sensitive to the value of U_{OO}. The values of $\beta_{CC'}$ were obtained according to the Pariser-Parr method. The value of β_{CO} is that presented by Parks and Parr.[6]

TABLE I. INTEGRAL VALUES (eV., *R* (INTERATOMIC DISTANCE) IN Å)

(OO|OO)	14.671	U_{OO}	−13.00
(CC|CC)	10.842	U_{CC}	− 9.50
(OO|CC)	$12.757-3.966R_{CO}+0.4169R^2_{CO}$	β_{CO}	− 3.00
		$\beta_{CC'}$	
(CC|CC)	$10.842-2.821R_{CC'}+0.2454R^2_{CC'}$	$R_{CC'}=1.35$	− 2.92
		1.46	− 1.76
(OO|OO)	$14.671-4.748R_{OO'}+0.5012R^2_{OO'}$	1.47	− 1.68
		1.49	− 1.52

In this work an electronic computer (NEAC 2101) was used.[7] SCF calculations were repeated until the coefficients of the symmetry orbitals[8] in the SCF MO's become consistent to three decimal places.

It is assumed that *o*-benzoquinone is planar

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[1] A. Kuboyama, a) This Bulletin, **31**, 752 (1958); b) ibid., **32**, 1226 (1959); c) ibid., **33**, 917 (1960).

[2] H. Kon, ibid., **28**, 275 (1955); b) M. Okuda, *J. Chem. Phys.*, **25**, 1083 (1956); c) T. Anno, I. Matubara and A. Sadô, This Bulletin, **30**, 168 (1957); T. Anno, A. Sadô and I. Matubara, *J. Chem. Phys.*, **26**, 967 (1957); d) J. W. Sidman, ibid., **27**, 429 (1957).

[3] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[4] R. Pariser and R. G. Parr, a) *J. Chem. Phys.*, **21**, 466 (1953); b) ibid., **21**, 767 (1953).

[5] J. M. Parks and R. G. Parr, ibid., **32**, 1657 (1960).

[6] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[7] The program for eigenvalue problem was made by Dr. O. Yamamoto of this institute.

[8] To simplify the calculation, symmetry orbitals were used instead of atomic orbitals.

and that its symmetry group is C_{2v}. Since the molecular dimension of *o*-benzoquinone has never been reported, it was determined as follows. At first, the SCF calculation was carried out with the molecular dimension which has been obtained according to the bond order - bond distance relation[9] from the bond orders previously obtained by the simple MO calculation.[10] From the bond orders obtained by this SCF MO calculation, the molecular dimension which is shown in Fig. 1 was obtained and used in the final SCF MO calculation. The numerals in parentheses in Fig. 1 denote the numbering for the atoms.

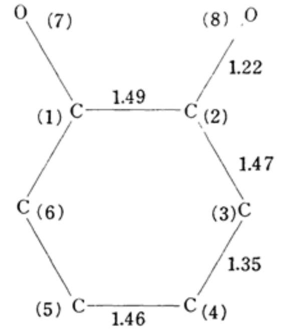

Fig. 1. The assumed molecular dimension (Å).

Results

The molecular orbital (ϕ_i)[11] and their orbital energies (ε_i) are shown in Table II. Among the excitation energies of the excited singlet and triplet configurations,[12] the lower ones are shown in Table III, along with the corresponding Coulomb and exchange integrals and transition dipole strengths (μ^2) from the ground state (for singlet configurations). Configuration interactions among five low energy-excited singlet and triplet configurations in Table III were calculated. The obtained excited state wave functions (${}^{1,3}\Phi_i$), their excitation energies (${}^{1,3}E_i-E_0$), the transition dipole strengths from the ground state and the interconfigurational matrix elements ($\Phi_{i\to j}|H|\Phi_{k\to l}$) are shown in Table IV.

The calculated and observed energy levels[13]

TABLE II. SCF MO'S AND THEIR ENERGIES

Symmetry	SCF MO's	Orbital energies, eV.
b_1	$\phi_1=0.4431(\chi_1+\chi_2)+0.2981(\chi_6+\chi_3)+0.2774(\chi_5+\chi_4)+0.3712(\chi_7+\chi_8)$	−13.588
a_2	$\phi_2=0.3944(\chi_1-\chi_2)+0.3000(\chi_6-\chi_3)+0.1806(\chi_5-\chi_4)+0.4710(\chi_7-\chi_8)$	−11.977
b_1	$\phi_3=0.2567(\chi_1+\chi_2)-0.3195(\chi_6+\chi_3)-0.4844(\chi_5+\chi_4)+0.3120(\chi_7+\chi_8)$	−11.667
a_2	$\phi_4=0.1362(\chi_1-\chi_2)-0.4680(\chi_6-\chi_3)-0.3890(\chi_5-\chi_4)+0.3333(\chi_7-\chi_8)$	− 9.777
b_1	$\phi_5=0.2744(\chi_1+\chi_2)+0.3938(\chi_6+\chi_3)-0.3571(\chi_5+\chi_4)-0.3770(\chi_7+\chi_8)$	0.351
a_2	$\phi_6=0.3492(\chi_1-\chi_2)+0.2788(\chi_6-\chi_3)-0.4636(\chi_5-\chi_4)-0.2923(\chi_7-\chi_8)$	2.449
b_1	$\phi_7=0.4030(\chi_1+\chi_2)-0.3924(\chi_6+\chi_3)+0.2468(\chi_5+\chi_4)-0.3503(\chi_7+\chi_8)$	2.572
a_2	$\phi_8=0.4516(\chi_1-\chi_2)-0.3364(\chi_6-\chi_3)+0.3181(\chi_5-\chi_4)-0.2858(\chi_7-\chi_8)$	4.446

TABLE III. EXCITATION ENERGIES AND TRANSITION DIPOLE STRENGTHS OF THE CONFIGURATIONS AND ELECTRONIC REPULSION INTEGRALS

$i\to j$	Symmetry	${}^1E_{i\to j}-E_0$, eV.	μ^2, Å^2	${}^3E_{i\to j}-E_0$, eV.	J_{ij}, eV.	K_{ij}, eV.
4→5	$A_1\to B_2$	5.207	0.733	3.803	6.325	0.702
2→5	$A_1\to B_2$	6.930	0.017	5.882	6.446	0.524
4→7	$A_1\to B_2$	6.943	0.036	6.055	6.294	0.444
3→5	$A_1\to A_1$	7.190	1.179	5.716	6.302	0.737
4→6	$A_1\to A_1$	7.263	1.126	5.859	6.367	0.702
3→6	$A_1\to B_2$	8.517		7.643	6.321	0.440
4→8	$A_1\to A_1$	8.782		7.902	6.473	0.437
2→7	$A_1\to B_2$	8.885		7.789	6.232	0.464
3→7	$A_1\to A_1$	8.935		8.007	6.210	0.481
2→6	$A_1\to A_1$	9.178		8.216	6.760	0.548

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9) C. A. Coulson, "Valence," Oxford Univ. Press, Oxford (1952), p. 253.

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

11) χ_i denotes the 2pπ atomic orbital of *i*-atom.

12) Φ_0 and E_0 denote the wave function and the energy of the ground state respectively. ${}^1\Phi_{i\to j}$, ${}^1E_{i\to j}$ and ${}^3\Phi_{i\to j}$, ${}^3E_{i\to j}$ denote the wave functions and the energies of the singlet and triplet configurations, respectively, in which one electron is excited from an occupied orbital χ_i to an unoccupied orbital χ_j. The excitation energy of each excited configuration is given by the following formula.

$$\left.\begin{matrix}{}^1E_{i\to j}\\ {}^3E_{i\to j}\end{matrix}\right\}-E_0=(\varepsilon_j-\varepsilon_i)-(J_{ij}-K_{ij})\begin{cases}+K_{ij}\\ -K_{ij}\end{cases}$$

J_{ij} and K_{ij} denote Coulomb and exchange integrals over Φ_i and Φ_j respectively.

13) S. Goldschmidt and F. Graef, *Ber.*, **61**, 1858 (1928). The $n\to{}^1\pi^*$ band of *o*-benzoquinone is at ca. 600 mμ.

TABLE IV. WAVE FUNCTIONS, EXCITATION ENERGIES AND TRANSITION DIPOLE STRENGTHS OF EXCITED STATES AND INTERCONFIGURATIONAL MATRIX ELEMENTS

(1) Singlet states

Symmetry	$^{1,3}\Phi_i$	$^{1,3}E_i-E_0$, eV.	μ^2, Å^2
$^1B_2$	$^1\Phi_1=0.9880\,^1\Phi_{4\to5}-0.1337\,^1\Phi_{2\to5}-0.0780\,^1\Phi_{4\to7}$	5.171	0.711
$^1B_2$	$^1\Phi_2=0.1494\,^1\Phi_{4\to5}+0.6928\,^1\Phi_{2\to5}+0.7055\,^1\Phi_{4\to7}$	6.615	0.007
$^1A_1$	$^1\Phi_3=0.7522\,^1\Phi_{3\to5}-0.6589\,^1\Phi_{4\to6}$	6.949	0.014
$^1B_2$	$^1\Phi_4=0.0403\,^1\Phi_{4\to5}+0.7086\,^1\Phi_{2\to5}-0.7044\,^1\Phi_{4\to7}$	7.294	0.068
$^1A_1$	$^1\Phi_5=0.6589\,^1\Phi_{3\to5}+0.7522\,^1\Phi_{4\to6}$	7.504	2.290

(2) Triplet states

Symmetry	$^{1,3}\Phi_i$	$^{1,3}E_i-E_0$, eV.
$^3B_2$	$^3\Phi_1=0.9798\,^3\Phi_{4\to5}-0.0800\,^3\Phi_{2\to5}-0.1831\,^3\Phi_{4\to7}$	3.745
$^3A_1$	$^3\Phi_2=0.7286\,^3\Phi_{3\to5}+0.6849\,^3\Phi_{4\to6}$	4.630
$^3B_2$	$^3\Phi_3=0.1822\,^3\Phi_{4\to5}+0.7336\,^3\Phi_{2\to5}+0.6547\,^3\Phi_{4\to7}$	4.778
$^3A_1$	$^3\Phi_4=0.6849\,^3\Phi_{3\to5}-0.7286\,^3\Phi_{4\to6}$	6.945
$^3B_2$	$^3\Phi_5=0.0820\,^3\Phi_{4\to5}-0.6748\,^3\Phi_{2\to5}+0.7334\,^3\Phi_{4\to7}$	7.217

(3) Interconfigurational matrix elements

	Singlet state eV.	Triplet state eV.
$(\Phi_{4\to5}\|H\|\Phi_{2\to5})$	0.210	−0.054
$(\Phi_{4\to5}\|H\|\Phi_{4\to7})$	0.092	0.332
$(\Phi_{2\to5}\|H\|\Phi_{4\to7})$	−0.354	−1.222
$(\Phi_{3\to5}\|H\|\Phi_{4\to6})$	0.275	−1.155

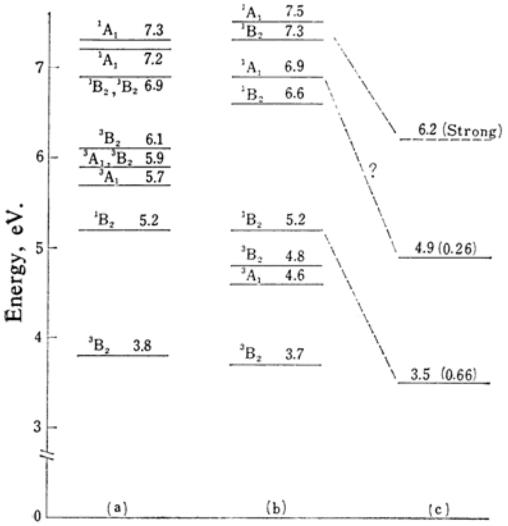

Fig. 2. Energy levels.

(a) Without configuration interaction
(b) With configuration interaction (high triplet levels not described)
(c) Observed

are shown in Fig. 2. In Fig. 2, numerical values on or below the energy levels are the excitation energies rounded to the first decimal in eV., while those in parentheses on the observed levels are the dipole strengths calculated from the observed oscillator strengths. The dipole strength of the 4.9 eV. band is not so accurate because of the overlapping of neighboring bands. As for the observed highest level at 6.2 eV., the corresponding absorption peak has never been observed, but it is certain that an absorption band whose intensity is far greater than the other two observed bands exists near 200 mμ (which corresponds to ca. 6.2 eV.).

Discussion

In *o*-benzoquinone, all singlet π-electronic transitions are allowed and the transitions $^1A_1\to{}^1A_1$ and $^1A_1\to{}^1B_2$ are polarized parallel to and perpendicular to the symmetry axis respectively. In Fig. 2, considering the values of dipole strengths, the two observed levels at 3.5 and 6.2 eV. may reasonably be assigned to the $^1B_2$ level at 5.2 eV. and to the $^1A_1$ level at 7.5 eV. respectively. The calculated and observed dipole strengths for the 3.5 eV. band are in good agreement. It is noticeable that the excited-state wave function of this band ($^1\Phi_1$) consists for the most part of $^1\Phi_{4\to5}$, as may be seen in Table IV. The assignment of the observed level at 4.9 eV. is uncertain. The dipole strengths for the two $^1A_1$ configurations whose energy levels are at 7.2 and 7.3 eV. are large and nearly equal to each other. Therefore, if the mixing of these two configurations differs slightly from that given in Table IV, the dipole strength for the $^1A_1$ level at 6.9 eV. will increase to some extent. Therefore, the observed level at 4.9 eV. may be assigned to the $^1A_1$ level at 6.9 eV.

In the results described above, it is noticeable that the calcluated singlet excited levels are much higher than the observed ones. In the case of *o*-benzoquinone studied by Sidman,

TABLE V. EXCITATION ENERGIES OF THE CONFIGURATION ($^1\Phi_{4\to5}$) IN VARIOUS CASES

	a	b	c	d	e	f	g	h	obs.
$^1E_{4\to5}-E_0$, eV.	5.21	4.98	5.12	5.13	4.94	4.57	4.14	4.60	3.5

a) The value in Table III.
b) The two center Coulomb repulsion integrals obtained by the Mataga-Nishimoto's method(14) were used.
c) The value (−14.00 eV.) for U_{OO} was used.
d) The value (−10.00 eV.) for U_{CC} of the carbonyl carbon atoms was used.
e) β's obtained by Kon's method(2a) were used.
f) For β's of the conventional double and single bonds, the values (−2.7 and −1.9 eV. respectively) were used.
g) For β's of the conventional double and single bonds, the values (−2.5 and −2.0 eV. respectively) were used.
h) For β's the values smaller than those in the case a by the factor (0.8) were used.

TABLE VI. SIMPLE MO'S AND THEIR ENERGIES

Symmetry	Simple MO's	Orbital energies
b_1	$\phi_1=0.4655(\chi_1+\chi_2)+0.2820(\chi_6+\chi_3)+0.2419(\chi_5+\chi_4)+0.3811(\chi_7+\chi_8)$	$(\alpha+)\ 1.7657\beta$
a_2	$\phi_2=0.4114(\chi_1-\chi_2)+0.2801(\chi_6-\chi_3)+0.1454(\chi_5-\chi_4)+0.4808(\chi_7-\chi_8)$	1.3268β
b_1	$\phi_3=0.2231(\chi_1+\chi_2)-0.3197(\chi_6+\chi_3)-0.5136(\chi_5+\chi_4)+0.2902(\chi_7+\chi_8)$	1.2226β
a_2	$\phi_4=0.0990(\chi_1-\chi_2)-0.4908(\chi_6-\chi_3)-0.3852(\chi_5-\chi_4)+0.3177(\chi_7-\chi_8)$	0.6740β
b_1	$\phi_5=0.2682(\chi_1+\chi_2)+0.3889(\chi_6+\chi_3)-0.3484(\chi_5+\chi_4)-0.3943(\chi_7+\chi_8)$	-0.5164β
a_2	$\phi_6=0.3640(\chi_1-\chi_2)+0.2374(\chi_6-\chi_3)-0.4641(\chi_5-\chi_4)-0.3095(\chi_7-\chi_8)$	-1.1115β
b_1	$\phi_7=0.4020(\chi_1+\chi_2)-0.4086(\chi_6+\chi_3)+0.2373(\chi_5+\chi_4)-0.3393(\chi_7+\chi_3)$	-1.1218β
a_2	$\phi_8=0.4341(\chi_1-\chi_2)-0.3526(\chi_6-\chi_3)+0.3393(\chi_5-\chi_4)-0.2686(\chi_7-\chi_8)$	-1.1693β

a similar trend was observed. We examined the lowering of the calculated singlet excited levels by using modified values of various kinds of integrals. Since the $^1B_2$ level at 5.2 eV. is much lower than the other singlet excited levels, and since its state almost entirely consists of the configuration ($^1\Phi_{4\to5}$), as is mentioned above, the energy level of this configuration is thought to be reasonably usable as a measure of the lowering of the calculated singlet excited levels. The calculated energy levels of that configuration in various cases where the values of one of the three kinds of integrals (two-center Coulomb repulsion integrals, U and β) are modified are shown in Table V. As may be seen in Table V, the lowering of that level is small except for the cases (f, g, h) where modified values of β are used. From the results in Table V, it may be concluded that a satisfactory lowering of the calculated singlet excited levels cannot be expected unless values of β are used which are much modified from those generally used. This disagreement between the calculated singlet energy levels and the observed ones may be attributed to a peculiar electronic structure of quinones, one different from those of usual aromatic compounds.

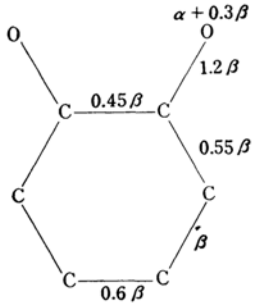

Fig. 3. Integral values in the simple Mo method.

The Coulomb and exchange integrals in the simple MO method appropriate to simulate the simple MO's to the SCF MO's obtained here for *o*-benzoquinone were searched for with the trial-and-error method. The integral values obtained are shown in Fig. 3. The Coulomb integral of the oxygen atoms and the exchange integrals of the conventional single bonds are far smaller (in β units) than those generally used. Similar results have been reported by other authors.(14,15) The MO's of *o*-benzoquinone obtained using these integral values are shown in Table VI. The molecular diagrams of the SCF and simple MO's are shown in Fig. 4. The charge densities of the oxygen atoms and the carbonyl carbon atoms in Fig. 4a are similar to those (−0.149e and +0.131e) of *p*-benzoquinone calculated with Sidman's SCF MO's.(2d) The dipole moment

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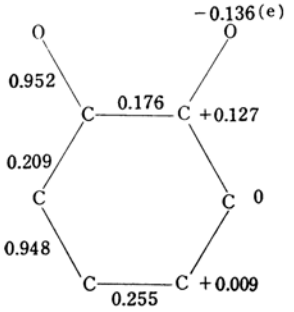
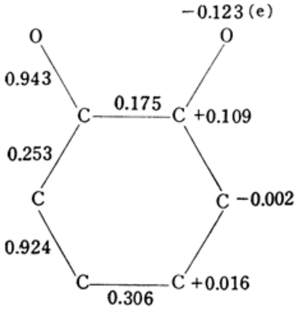
14) N. Mataga and K. Nishimoto, *Z. physik. Chem. N. F.*, **12**, 335 (1957).

15) a) R. Mcweeny and T. E. Peacock, *Proc. Phys. Soc.*, **A69**, 41 (1957); b) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).



(a) SCF MO



(b) Simple MO

Fig. 4. Molecular diagrams (charge densities and bond orders).

calculated from the charge densities in Fig. 4a is 1.56 D. The observed dipole moment of *o*-benzoquinone in benzene is 5.1 D.[10] In *o*-benzoquinone, the lone-pair moment of two oxygen atoms and the σ-moment cannot be estimated with certainty, but the former[16] may be quite large. Even considering this, the π-moment obtained here seems too small.

Summary

The π-electronic energy levels of *o*-benzoquinone have been obtained by using Pople's SCF MO method, while the electron repulsion integrals have been obtained by the Pariser-Parr method. The absorption band near 360 mμ and the strong band which is thought to exist near 200 mμ have unambiguously been assigned to the first $^1A_1 \rightarrow {}^1B_2$ and the second $^1A_1 \rightarrow {}^1A_1$ transitions respectively. The calculated singlet excited energy levels are much higher than the observed levels. The reason for this has been examined by SCF MO calculations using modified values of various kinds of electron repulsion integrals and core integrals. It has been concluded that a satisfactory lowering of the calculated singlet excited energy levels cannot be expected unless values of the core resonance integrals (β) are used which are much modified from those generally used. Simple MO parameters for *o*-benzoquinone adequate to simulate the simple MO's to the SCF MO's have been obtained.

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[16] The lone-pair moments of sp- and sp^2-hybridized oxygen atoms are 1.6 D and 1.5 D respectively.