A Semi-empirical Theory of the π-Electronic Spectra of Aromatic Derivatives

By Kichisuke NISHIMOTO and Ryoichi FUJISHIRO

(Received October 11, 1961)

In a previous paper[1], we have reported a convenient method (VO method) for calculation of the molecular diagrams of aromatic derivatives. In this paper, a semi-empirical theory of the π-electronic spectra of aromatic derivatives based on the antisymmetrized molecular orbital method (ASMO method) is formularized by the use of the results of the VO method and is applied to calculation of the π-electronic spectra of hydroquinone and phloroglucinol.

Theory

The framework of the present theory is similar to that of Pariser[2] and of our previous paper[3]. The procedure of calculation is as follows:

i) MO's are determined by a simple LCAO MO method based on π-electron approximation, using appropriately chosen parameters.

ii) We give each π-electron a molecular spin orbital (MSO) which is given by the product of a MO and spin function α or β.

iii) Configurational wave functions are built up as antisymmetrized products, or Slater determinants, of these MSO's.

iv) Configurational energies are calculated by a semi-empirical procedure based on zero differential approximation.

v) Electronic state functions and their energies are calculated by the method of the linear combinations of these configurational wave functions.

A) **Calculation of MO's.**—When the molecule contains n 2pπ atomic orbitals (2pπ AO), the MO, ψ_i, is represented by the linear combination of these AO's as follows:

$$\psi_i=\sum_{\mu} C_{i\mu}\phi_\mu \tag{1}$$

where ϕ_μ is the μ-th 2pπ AO and $C_{i\mu}$ is the coefficient to be determined by the variational method. First of all, from the variational theory we obtain the following equations for the coefficients which form the simultaneous equations of n dimensions:

$$\left.\begin{aligned}&\sum_{\mu=1}^{n} C_{i\mu}\left(\int\phi_1 H\phi_\mu \mathrm{d}v-E\delta_{1\mu}\right)=0\\&\quad\vdots\\&\sum_{\mu=1}^{n} C_{i\mu}\left(\int\phi_n H\phi_\mu \mathrm{d}v-E\delta_{n\mu}\right)=0\end{aligned}\right\} \tag{2}$$

where H is an effective one-electron Hamiltonian and $\delta_{\mu\nu}=1$ if $\mu=\nu$, $=0$ otherwise. E is orbital energy defined by H and MO. Now, we assume the matrix elements, $H_{\mu\nu}=\int\phi_\mu H\phi_\nu\,\mathrm{d}v$, as follows:

$$\left.\begin{aligned}&H_{\mu\mu}=\alpha && (\phi_\mu \text{ is carbon 2p}\pi\text{ AO})\\&H_{\mu\mu}=\alpha+\delta_\mu\beta && (\phi_\mu \text{ is heteroatom 2p}\pi\text{ AO})\end{aligned}\right\} \tag{3}$$

$$\left.\begin{aligned}&H_{\mu\nu}=\beta && (\mu \text{ and } \nu \text{ are nearest neighbor carbon atoms})\\&H_{\mu\nu}=k_{\mu\nu}\beta && (\mu \text{ and } \nu \text{ are nearest neighbors, but one or both of them are heteroatom})\\&H_{\mu\nu}=0 && (\mu \text{ and } \nu \text{ are non-neighbors})\end{aligned}\right\} \tag{4}$$

where the numerical values of δ_μ and $k_{\mu\nu}$ are determined by a semi-empirical procedure; e. g., for the case of phenol we have determined these values from the experimental ionization potentials of benzene, methanol and phenol[3]. Energies E_i are obtained as the roots of the following secular determinant:

$$\begin{vmatrix}(H_{11}-E) & H_{12} & \cdots\cdots & H_{1n}\\ H_{21} & (H_{22}-E) & \cdots\cdots & H_{2n}\\ \vdots & & & \\ H_{n1} & H_{n2} & \cdots\cdots & (H_{nn}-E)\end{vmatrix}=0$$

which is defined by Eq. 2. From the secular determinant we obtain the n E_i's. If we substitute the lowest energy E_1 into Eq. 2 and use the normalization condition

$$\int\psi_1^2\mathrm{d}v=\sum_{\mu=1}^{n} C_{1\mu}^2$$

we obtain the coefficients $C_{1\mu}$'s for the lowest MO, ψ_1. In the same way we obtain the MO's, ψ_2, ψ_3, $\cdots\cdots$, ψ_n associated with the energies E_2, E_3, $\cdots\cdots$, E_n respectively. When E is expressed by

---

[1] K. Nishimoto and R. Fujishiro, This Bulletin, **32**, 699 (1959).

[2] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[3] K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).

$$E_i=\alpha-x_i\beta \tag{5}$$

the MO's corresponding to $x_i<0$ are called bonding orbitals, whereas the MO's corresponding to $x_i>0$ are called antibonding orbitals. In the case of a molecule having m π-electrons, the ground state of the molecule is given by the state in which the lower MO's, ψ_1, ψ_2, ……, $\psi_{m/2}$ are used twice. We call the MO's, ψ_1, ψ_2, ……, $\psi_{m/2}$, occupied orbitals, and the other MO's vacant orbitals. Consequently, the π-electron density of the μth atom, q_μ, and π-bond order (or quantity analogous to it) for the $\mu\nu$ atom pair, $p_{\mu\nu}$, in the ground state of the molecule are expressed as follows:

$$\left.\begin{aligned} q_\mu&=2\sum_i^{\text{occ.}}C^2_{i\mu}=2-2\sum_{i'}^{\text{vac.}}C^2_{i'\mu}=2-q^v_\mu \\ p_{\mu\nu}&=2\sum_i^{\text{occ.}}C_{i\mu}C_{i\nu}=-2\sum_{i'}^{\text{vac.}}C_{i'\mu}C_{i'\nu}=-p^v_{\mu\nu} \end{aligned}\right\} \tag{6}$$

where $\sum\limits_i^{\text{occ.}}$ and $\sum\limits_{i'}^{\text{vac.}}$ indicate the sums over occupied orbitals and vacant orbitals respectively. The relations of Eqs. (6) are found in our previous paper[1]. The calculation of q_μ's and $p_{\mu\nu}$'s using vacant orbitals is simple compared with that using occupied orbitals.

B) Reduced Formula for the Calculation of π-Electronic State Energies.—The configurational wave function of the ground state of the molecule, χ_0, is now represented by a Slater determinant having the form of:

$$\chi_0=\frac{1}{\sqrt{m!}}\cdot\begin{vmatrix} (\psi_1\alpha)^1(\psi_1\beta)^1\cdots\cdots(\psi_{m/2}\alpha)^1(\psi_{m/2}\beta)^1 \\ (\psi_1\alpha)^2(\psi_1\beta)^2\cdots\cdots(\psi_{m/2}\alpha)^2(\psi_{m/2}\beta)^2 \\ \vdots \qquad\qquad\qquad \vdots \\ (\psi_1\alpha)^m(\psi_1\beta)^m\cdots(\psi_{m/2}\alpha)^m(\psi_{m/2}\beta)^m \end{vmatrix}$$

$$\equiv(1\,\bar{1}\,2\,\bar{2}\cdots\cdots\tfrac{1}{2}m\tfrac{1}{2}\bar{m})$$

The configurational wave function of the excited state corresponding to the one-electron transition from ψ_i to $\psi_{k'}$, $\chi_{i\to k'}$, is given by:

$$\begin{aligned} \chi^1_{i\to k'}&=2^{-1/2}[(1\,\bar{1}\cdots\cdots i\bar{k}'\cdots\cdots\tfrac{1}{2}m\tfrac{1}{2}\bar{m}) \\ &\qquad-(1\,\bar{1}\cdots\cdots k'\bar{i}\cdots\cdots\tfrac{1}{2}m\tfrac{1}{2}\bar{m})] \\ \chi^3_{i\to k'}&=2^{-1/2}[(1\,\bar{1}\cdots\cdots ik'\cdots\cdots\tfrac{1}{2}m\tfrac{1}{2}\bar{m}) \\ &\qquad+(1\,\bar{1}\cdots\cdots\bar{i}\bar{k}'\cdots\cdots\tfrac{1}{2}m\tfrac{1}{2}\bar{m})] \end{aligned}$$

where superscripts 1 and 3 indicate singlet and triplet states, respectively. When we use complete many electron Hamiltonian $\mathscr{H}$ instead of an effective one-electron Hamiltonian, the configurational energies are given by:

$$\mathscr{H}_{i\to k}=\int\chi_{i\to k'}\mathscr{H}\chi_{i\to k'}\,\mathrm{d}v$$

$$\mathscr{H}_{00}=\int\chi_0\mathscr{H}\chi_0\mathrm{d}v$$

where

$$\mathscr{H}=\sum_i H_{\text{core}}(i)+\frac{1}{2}\sum_{ij}\frac{e^2}{r_{ij}}$$

where H_{core} (i) is core Hamiltonian, which consists of the kinetic energy term of the ith π-electron and potential energy terms representing the attraction among the σ-cores and this electron. A rigid core which consists of a nucleus, inner shell electrons and valence electrons except π-electrons, is called a σ-core. Therefore the σ-core of μth atom with q^0_μ π-electrons in its free state has a q^0_μ $|e|$ positive charge. According to Pariser[2], the energy $\Delta E_{ik'}$ associated with a one-electron transition from ψ_i to $\psi_{k'}$ is given by

$$\begin{aligned} \Delta E_{ik'}&=\mathscr{H}_{ik'}-\mathscr{H}_{00} \\ &=I_{k'k'}-I_{ii}+[ii|k'k']\pm[ik'|ik'] \\ &\quad-[ii|ii]-\sum_{f\neq i}\{2[ff|ii]-2[ff|k'k'] \\ &\quad-[fi|fi]+[fk'|fk']\} \end{aligned} \tag{7}$$

where the upper and lower signs are associated with the singlet and triplet configurations respectively. Summation over the index f means that over the occupied MO's in χ_0. The integrals $[ij|kl]$ and I_{ij} are

$$[ij|kl]=\int\psi_i(1)\psi_j(1)\frac{e^2}{r_{12}}\psi_k(2)\psi_l(2)\mathrm{d}v$$

$$I_{ij}=\int\psi_i(1)H_{\text{core}}(1)\psi_j(1)\mathrm{d}v$$

When we define the following quantities:

$$\begin{aligned} \mathscr{H}_{\mu\mu}&=-I_\mu+\frac{1}{2}q_\mu\gamma_{\mu\mu}+\sum_{\nu\neq\mu}(q_\nu-q^0_\nu)\gamma_{\nu\mu} \\ \mathscr{H}_{\mu\nu}&=\beta_{\mu\nu}-\frac{1}{2}p_{\mu\nu}\gamma_{\mu\nu} \\ \bar{\varepsilon}_i&=\sum_{\mu\nu}C_{i\mu}C_{i\nu}\mathscr{H}_{\mu\nu} \end{aligned} \tag{8}$$

where

$$\int\phi^2_\mu(1)\frac{e^2}{r_{12}}\phi^2_\nu(2)\mathrm{d}v=\gamma_{\mu\nu}$$

$$\int\phi_\mu(1)H_{\text{core}}(1)\phi_\mu(1)\mathrm{d}v=I_\mu$$

$$\int\phi_\mu(1)H_{\text{core}}(1)\phi_\nu(1)\mathrm{d}\nu=\beta_{\mu\nu}$$

Equation 7 can be rewritten by these quantities as

$$\Delta E_{i\,k'}^{1,3}=\bar{\varepsilon}_{k'}-\bar{\varepsilon}_i+[ik'|ik']$$
$$-[ii|k'k']\pm[ik'|ik']$$

In many cases we have a number of configurational wave functions χ_i, belonging to the same symmetry. Therefore, the allowed electronic state function Ψ_a must be given by the linear combination of these χ_i's; that is,

$$\Psi_a=\sum \mathrm{d}_{ai}\chi_i$$

where d_{ai} is a coefficient to be determined by variational procedure. Energies E associated with allowed electronic states are determined by following secular determinant:

$$\begin{vmatrix} (\mathscr{H}_{00}-E) & \mathscr{H}_{01} & \mathscr{H}_{02}\cdots\cdots \\ \mathscr{H}_{10} & (\mathscr{H}_{11}-E) & \mathscr{H}_{12}\cdots\cdots \\ \vdots & & \end{vmatrix}=0$$

Excitation energy $\Delta E_{0\to a}$ associated with a transition from Ψ_0 to Ψ_a is given by:

$$\Delta E_{0\to a}=E_0-E_a$$

General formulas for interconfigurational matrix elements $\mathscr{H}_{ij}$ were given by Pariser[2]. These can be rewritten as follows:

$$[\chi_0|\chi_{i\to k'}^1]=\int\chi_0\mathscr{H}\chi_{i\to k'}^1\mathrm{d}v$$
$$=\sqrt{2}\sum_{\mu\nu}C_{i\mu}C_{k'\nu}\mathscr{H}_{\mu\nu}$$
$$[\chi_{i\to k'}^1|\chi_{j\to l'}^1]=\int\chi_{i\to k'}^1\mathscr{H}\chi_{j\to l'}^1\mathrm{d}v$$
$$=2[ik'|jl']-[ij|k'l']$$
$$[\chi_{i\to k'}^1|\chi_{i\to l'}^1]=\sum_{\mu\nu}C_{k'\mu}C_{l'\nu}\mathscr{H}_{\mu\nu}$$
$$+2[ik'|il']-[ii|k'l']$$
$$[\chi_{i\to k'}^1|\chi_{j\to k'}^1]=-\sum_{\mu\nu}C_{i\mu}C_{j\nu}\mathscr{H}_{\mu\nu}$$
$$+2[ik'|jk']-[ij|k'k']$$
$$[\chi_0|\chi_{i\to k'}^8]=0$$
$$[\chi_{i\to k'}^3|\chi_{j\to l'}^8]=-[ij|k'l']$$
$$[\chi_{i\to k'}^3|\chi_{i\to l'}^3]=[\chi_{i\to k'}^1|\chi_{i\to l'}^1]-2[ik'|il']$$
$$[\chi_{i\to k'}^3|\chi_{j\to k'}^3]=[\chi_{i\to k'}^1|\chi_{j\to k'}^1]-2[ik'|jk']$$

C) Semi-empirical Estimation of Basic Integrals and Semi-empirical Formulation of $\mathscr{H}_{\mu\nu}$ and $\bar{\varepsilon}_i$. — All molecular integrals can be expanded into integrals over AO's which are I_μ, $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$. These basic integrals are estimated by a semi-empirical procedure. The two-center electron repulsion integral, $\gamma_{\mu\nu}$, is calculated from the expression which we found in the previous paper[4]; that is,

$$\gamma_{\mu\nu}=\frac{e^2}{a_{\mu\nu}+r_{\mu\nu}}$$

where $r_{\mu\nu}$ is the interatomic distance between the μ and ν atoms.

$a_{\mu\nu}$ is a characteristic constant which is given by

$$\frac{e^2}{a_{\mu\nu}}=\frac{I_\mu+I_\nu-A_\mu-A_\nu}{2}$$

where I_μ and A_μ are the valence state ionization potential and the electron affinity of the μ atom respectively. The core integrals, I_μ and $\beta_{\mu\nu}$, are estimated in the following manner:

i) In case both ϕ_μ and ϕ_ν are carbon 2pπ AO's, we assume that:

a) I_μ is the valence state ionization potential of the carbon atom

b) $\beta_{\mu\nu}=\beta_{\mathrm{CC}}$ for the $\mu\nu$ bond

c) $\beta_{\mu\nu}=0$, if μ and ν are nonneighbors

In this case, $\mathscr{H}_{\mu\mu}$ and $\mathscr{H}_{\mu\nu}$ can be rewritten as follows:

$$\mathscr{H}_{\mu\mu}=-y_{\mathrm{c}}+\frac{1}{2}(1-q_\mu^v)\gamma_{\mu\mu}$$
$$+\sum_{\nu\neq\mu}(2-q_\nu^0-q_\nu^v)\gamma_{\nu\mu}=-y_{\mathrm{c}}+G_{\mu\mu}$$
$$\mathscr{H}_{\mu\nu}=\beta_{\mathrm{cc}}+\frac{1}{2}p_{\mu\nu}^v\gamma_{\mu\nu}=\beta_{\mathrm{cc}}+G_{\mu\nu}\qquad(9)$$

where y_{c} and q_ν^0 are the valence state electronegativity of the carbon atom and the core charge of the ν atom respectively. By definition,

$$G_{\mu\mu}=\frac{1}{2}(2-q_\mu^0-q_\mu^v)\gamma_{\mu\mu}+\sum_{\mu\neq\nu}(2-q_\nu^0-q_\nu^v)\gamma_{\nu\mu}$$
$$G_{\mu\nu}=\frac{1}{2}p_{\mu\nu}^v\gamma_{\mu\nu}$$

ii) In case either ϕ_μ or ϕ_ν is a heteroatom 2pπ AO, we assume that:

$$\mathscr{H}_{\mu\mu}=-y_{\mathrm{c}}+\delta_\mu\beta_{\mathrm{cc}}+\frac{1}{2}(2-q_\mu^0-q_\mu^v)\gamma_{\mu\mu}$$
$$+\sum_{\nu\neq\mu}(2-q_\nu^0-q_\nu^v)\gamma_{\nu\mu}=-y_{\mathrm{c}}+\delta_\mu\beta_{\mathrm{cc}}+G_{\mu\mu}$$
$$(10)$$
$$\mathscr{H}_{\mu\nu}=k_{\mu\nu}\beta_{\mathrm{cc}}+G_{\mu\nu}$$

where we assign the same values as in Eqs. 3 and 4 for δ_μ and $k_{\mu\nu}$. $(2-q_\mu^0-q_\mu^v)$ gives the net charge of the μ atom. Substituting Eqs. 9 and 10 into Eq. 8, we obtain the following expression:

$$\bar{\varepsilon}_i=-y_{\mathrm{c}}-x_i\beta_{\mathrm{cc}}+\sum_{\mu\nu}C_{i\mu}C_{i\nu}G_{\mu\nu}$$

where x_i has the same value as in Eq. 5. The numerical estimation of β_{cc} is carried out by a semi-empirical procedure to fit the observed spectra.

D) Oscillator Strength. — The oscillator strength, f, associated with a one-electron

---

[4] K. Nishimoto and N. Mataga, *Z. physik. Chem.* [*N. F.*), 12, 335 (1957); N. Mataga and K. Nishimoto, ibid., 13, 140 (1957).

transition from Ψ_a to Ψ_b is given by Mulliken and Rieke[5] as follows:

$$f=1.085\times 10^{11}\tilde{\nu}_{ab}D_{ab}^2$$

where $\tilde{\nu}_{ab}$ is the frequency of the transition in cm^{-1}. D_{ab} is the so-called transition moment which is defined by

$$D_{ab}=\int \Psi_a \sum_i e_i r_i \Psi_b \,\mathrm{d}v$$

where e_i and r_i are the charge and the position vector of the ith charged particle respectively. From the calculation of D_{ab}, we can know the direction of the polarization of the transition. The knowledge of the direction of the transition moment is not only useful for the classification of the electronic state, but also plays an important role in the study of intermolecular interaction[6].

TABLE I. PARAMETERS AND INTEGRALS OVER AO'S

$\delta_{\mathrm{O}}=1.5$
$k_{\mathrm{CO}}=0.7$
$\beta_{\mathrm{CC}}=-2.388$ eV. (for benzene and hydroquinone)
$\beta_{\mathrm{CC}}=-2.621$ eV. (for phloroglucinol)
$a_{\mathrm{CC}}=1.328$ Å
$a_{\mathrm{CO}}=0.889$ Å
$a_{\mathrm{OO}}=0.669$ Å
All C-C bond distances are equal to 1.390 Å.
All C-O bond distances are equal to 1.460 Å.
All bond angles are equal to 120°.

Application to the Spectra of Hydroquinone and Phloroglucinol

We have also applied the method to the π-electronic spectra of hydroquinone, phloroglucinol and parent hydrocarbon, benzene. The parameters used are collected in Table I. Many of them are the same as those of phenol[3]. The core structures of the molecules are shown in Fig. 1. The calculated MO's are given in Table II. In the calculation of configuration interaction, the four lowest singly excited singlet configurations, $\chi^1_{1\to 1'}$, $\chi^1_{1\to 2'}$, $\chi^1_{2\to 1'}$ and $\chi^1_{2\to 2'}$, and the ground state, χ_0, are taken into account. The calculated molecular integrals are collected in Table III. Other kinds of integrals not involved in the table be come to zero. The $\bar{\varepsilon}_i$'s correspond formally to the orbital energies in the sence of the self-consistent field method. Therefore, $\bar{\varepsilon}_1$'s are regarded as the calculated apparent first ionization potentials. With same reason $\bar{\varepsilon}_{1'}$'s are regarded as calculated electron affinities. From the table we expect that the magnitudes of first ionization potentials are in the order; benzene > hydroquinone > phloroglucinol. Similarly, the order of electron affinity should be benzene > hydroquinone > phloroglucinol. Unfortunately, experimental data to be compared with our calculated ones are not available. The calculated electronic state energies E_a and the corresponding electronic state functions Ψ_a are given in Table IV. The results in this table show that the calculated excitation

TABLE II. MO'S AND MO ENERGIES

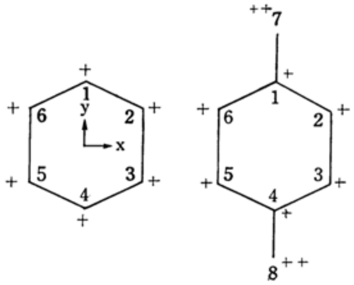
$E-\alpha=-x_1\beta$	MO
	Benzene
-2β	$\phi_{3'}=1/\sqrt{6}\,(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$
$-\beta$	$\phi_{2'}=1/2(-\phi_2+\phi_3-\phi_5+\phi_6)$
$-\beta$	$\phi_{1'}=1/\sqrt{12}(2\phi_1-\phi_2-\phi_3+2\phi_4-\phi_5-\phi_6)$
$+\beta$	$\phi_1=1/\sqrt{12}(2\phi_1+\phi_2-\phi_3-2\phi_4-\phi_5+\phi_6)$
$+\beta$	$\phi_2=1/2(\phi_2+\phi_3-\phi_5-\phi_6)$
	Hydroquinone
-2.0475β	$\phi_{3'}=0.4180(\phi_1-\phi_4)-0.3990(\phi_2-\phi_3-\phi_5+\phi_6)-0.0826(\phi_7-\phi_8)$
-1.1269β	$\phi_{2'}=0.5748(\phi_1+\phi_4)-0.2702(\phi_2+\phi_3+\phi_5+\phi_6)-0.1532(\phi_7+\phi_8)$
-1.0000β	$\phi_{1'}=0.5000(-\phi_2+\phi_3-\phi_5+\phi_6)$
$+0.6440\beta$	$\phi_1=0.4556(\phi_1-\phi_4)+0.2771(\phi_2-\phi_3-\phi_5+\phi_6)-0.3726(\phi_7-\phi_8)$
$+1.0000\beta$	$\phi_2=0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
	Phloroglucinol
-2.0698β	$\phi_{3'}=0.4111(\phi_1+\phi_3+\phi_5)-0.3973(\phi_4+\phi_2+\phi_6)-0.0806(\phi_7+\phi_8+\phi_9)$
-1.0987β	$\phi_{2'}-0.2961(2\phi_1-\phi_3-\phi_5)+0.2695(2\phi_4-\phi_2-\phi_6)-0.0797(2\phi_7-\phi_8-\phi_9)$
-1.0987β	$\phi_{1'}=0.5129(\phi_3-\phi_5)-0.4668(\phi_2-\phi_6)-0.1381(\phi_8-\phi_9)$
$+0.7309\beta$	$\phi_1=0.3676(\phi_3-\phi_5)+0.5029(\phi_2-\phi_6)-0.3347(\phi_8-\phi_9)$
$+0.7309\beta$	$\phi_2=0.2122(2\phi_1-\phi_3-\phi_5)-0.2903(2\phi_4-\phi_2-\phi_6)-0.1932(2\phi_7-\phi_8-\phi_9)$

---

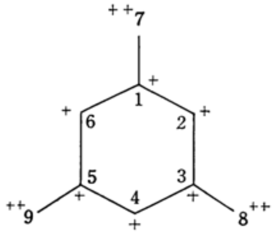
[5] R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

[6] For example, M. A. El-Bayoumi, Thesis, Florida State Univ. (1961).

energies agree satisfactorily with the observed ones. It is natural results that β_{cc}'s have different values for various molecules, because the π-electron distribution varies from molecule to molecule. From the calculation of transition moment, $D_{0\to a}$, we can show that all Ψ_1's given in the table have the polarization in the direction of x axis, whereas all Ψ_2's have the polarization in the direction of y axis. This fact means that the Ψ_1's of hydroquinone and of phloroglucinol may be regarded as modified Ψ_1 of benzene, on the other hand, the Ψ_2's of them may be regarded as modified Ψ_2 of benzene. This situation is shown in Fig. 2.



Benzene Hydroquinone



Phloroglucinol

Fig. 1 Numbering of atoms.

TABLE III. CALCULATED MOLECULAR INTEGRALS in eV.

	Benzene	Hydro-quinone	Phloro-glucinol
$\overline{\varepsilon}_{2'}+y_c$	4.738	5.195	5.488
$\overline{\varepsilon}_{1'}+y_c$	4.738	4.777	5.488
$\overline{\varepsilon}_1+y_c$	−4.738	−3.611	−3.502
$\overline{\varepsilon}_2+y_c$	−4.738	−4.709	−3.502
$[11\|1'1']$	5.874	4.731	5.460
$[11\|2'2']$	5.009	5.393	4.715
$[22\|1'1']$	5.009	5.874	4.715
$[22\|2'2']$	5.874	4.913	5.460
$[11'\|11']$	1.473	0.674	1.221
$[12'\|12']$	0.731	1.196	0.610
$[21'\|21']$	0.731	1.473	0.610
$[22'\|22']$	1.473	0.641	1.221
$[11'\|22']$	0.010	0.657	−0.001
$[12'\|21']$	0.731	−0.004	0.610
$[12\|1'2']$	0.433	0.389	0.370
$[\chi_0\|\chi_{1\to 1'}]$	0	0	0.124
$[\chi_0\|\chi_{2\to 2'}]$	0	0	0.124

TABLE IV. ELECTRONIC STATE FUNCTIONS AND ELECTRONIC STATE ENERGIES

Electronic state function	Electronic state energy in eV.	Calculated oscillator strength	Observed excitation energy in eV.	Observed oscillator strength
Benzene				
$\Psi_0=\chi_0$	0	Ref.	Ref.	Ref.
$\Psi_1=1/\sqrt{2}\,(\chi^1{}_{1\to 2'}-\chi^1{}_{2\to 1'})$	4.900	0	4.9[a]	0
$\Psi_2=1/\sqrt{2}\,(\chi^1{}_{1\to 1'}+\chi^1{}_{2\to 2'})$	6.135	0	6.0[a]	0.1
$\Psi_3-1/\sqrt{2}\,(\chi^1{}_{1\to 1'}-\chi^1{}_{2\to 2'})$	6.958	2.353	7.0[a]	0.69
$\Psi_4=1/\sqrt{2}\,(\chi^1{}_{1\to 2'}+\chi^1{}_{2\to 1'})$				
Hydroquinone				
$\Psi_0=\chi_0$	0	Ref.	Ref.	Ref.
$\Psi_1=0.8847\chi^1{}_{1\to 1'}-0.4893\chi^1{}_{2\to 2'}$	4.518	0.058	4.25[b]	—
$\Psi_2=0.9192\chi^1{}_{1\to 2'}+0.3938\chi^1{}_{2\to 1'}$	5.634	0.250	5.51[b]	—
$\Psi_3=0.3938\chi^1{}_{1\to 2'}-0.9192\chi^1{}_{2\to 1'}$	6.727	1.112	—	—
$\Psi_4=0.4893\chi^1{}_{1\to 1'}+0.8847\chi^1{}_{2\to 2'}$	6.760	0.962	—	—
Phloroglucinol				
$\Psi_0=0.9995\chi_0-0.0223(\chi^1{}_{1\to 1'}+\chi^1{}_{2\to 2'})$	−0.005	Ref.	Ref.	Ref.
$\Psi_1=1\sqrt{2}\,(\chi^1{}_{1\to 2'}-\chi^1{}_{2\to 1'})$	4.645	0	4.65[c]	—
$\Psi_2=0.7068(\chi^1{}_{1\to 1'}+\chi^1{}_{2\to 2'})+0.0316\chi_0$	5.605	0	5.52[c]	—
$\Psi_3=1/\sqrt{2}\,(\chi^1{}_{1\to 1'}-\chi^1{}_{2\to 2'})$	6.351	2.302	—	—
$\Psi_4=1/\sqrt{2}\,(\chi^1{}_{1\to 2'}+\chi^1{}_{2\to 1'})$				

[a] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
[b] R. Adams and J. C. Anderson, *J. Am. Chem. Soc.*, **72**, 5154 (1950).
[c] H. Köhler and G. Scheibe, *Z. anorg. u. allgem. Chem.*, **285**, 221 (1956).

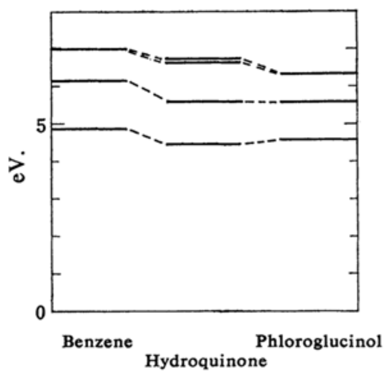


Fig. 2. Electronic state energies of benzene, hydroquinone and phloroglucinol.

Summary

A semi-empirical theory of the π-electronic spectra of aromatic derivatives based on antisymmetrized molecular orbital method is given and is applied to the calculations of the singlet π-electronic states of hydroquinone and of phloroglucinol. In the theory the core integrals over AO's of heteroatoms are expressed as the functions of the core integrals over carbon atom $2p\pi$ AO's. The calculated excitation energies for these molecules agree satisfactorily with the observed ones. In addition, our calculations give some informations with respect to the nature of their electronic state and their first ionization potentials.

The authors express their gratitude to Dr. Noboru Mataga for his helpful discussion.

Department of Chemistry
Faculty of Science
Osaka City University
Sumiyoshi-ku Osaka