Electronic Structure of Phenol

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Effects of substituents on the electronic structures of reference hydrocarbons are very important from the standpoint of understanding their molecular properties. Hence, much work has been carried out in this domain. As far as the quantitative interpretation of the electronic spectra is concerned, satisfactory results have not yet been obtained, because of the difficulties in calculating the inter-electronic repulsion integrals.

In the previous papers[2], we studied the electronic structures of nitrogen heterocycles by semi-empirical *SCF* method with satisfactory results. In these cases, the repulsion integrals were approximated by the simplified formula.

In this paper, the semi-empirical calculation is applied to the electronic structure of phenol, assuming some further approximations.

Outline of the Method.—The method used is similar to that of Pariser-Parr[3]. It is based on the framework of the method for antisymmetrized products, in *LCAO* approximation, including configuration interaction, with only $2px$ electrons considered explicitly.

The molecular orbitals (*MO*), φ_i, are expressed in the form

$$\varphi_i = \sum_{\mu} c_{\mu i}\phi_{\mu} \tag{1}$$

where ϕ_{μ} is the μ th $2px$ atomic orbital (*AO*), and $c_{\mu i}$ are the coefficients to be determined by the variational method. We give each electron a molecular spin orbital (*MSO*) which is given by the product of coordinate function φ_i and spin function α or β. The configurational wave functions χ_n, for the system are constructed from the antisymmetrized product, or Slater determinant, of these *MSO*'s. A given electronic state function, ϕ_a, is represented by a linear combination of these configurational functions;

$$\phi_a = \sum_n A_{an}\chi_n \tag{2}$$

In the case of excited configuration, χ_n is written as ${}^1\chi_{i\to j}$ or ${}^3\chi_{i\to j}$ which denote a singlet or a triplet excited configuration caused by the excitation of an electron from an occupied orbital φ_i to a vacant orbital φ_j.

The energies of the electronic state are determined by solving a secular determinant

$$\text{Det}\,|H_{mn}-\delta_{mn}E| = 0 \tag{3}$$

and the coefficients A_{an} are obtained by the solution of simultaneous equations

$$\sum_n A_{an}(H_{mn}-\delta_{mn}E) = 0 \tag{4}$$

where

$$H_{mn} = \int \chi_m^* \boldsymbol{H} \chi_n \mathrm{d}v$$

and $\delta_{mn}=1$ if m=n, $=0$ otherwise.

$\boldsymbol{H}$ is the complete electronic Hamiltonian operator determining the motion of the π-electrons, which is expressed in the form

$$\boldsymbol{H} = \sum_i H_{\text{core}}(i) + \frac{1}{2}\sum_{ij}\frac{e^2}{r_{ij}} \tag{5}$$

According to the method described by Mulliken and Rieke[4], oscillator strength, f, associated with a transition between the ground state ϕ_0 and an excited state ϕ_i is calculated as

$$f = 1.085\times10^{11} \times \omega_{0i} \sum_{\gamma=x,y,z} (M^{\gamma}{}_{0i})^2 \tag{6}$$

where ω_{0i} is the frequency of the transition in cm^{-1} and $M^{\gamma}{}_{0i}$ is the transition moment defined by

1) G. W. Wheland and L. Pauling; *J. Am. Chem. Soc.*, **57**, 2086 (1935).
A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).
K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).
F. J. I. López-Vázquez, *An. Soc. Esp. Fis. y Qui.*, (Madrid), **51B**, 203 (1955) etc.

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

3) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); ibid., **23**, 711 (1955).
R. Pariser, ibid., **24**, 250 (1956).

4) R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).

$$M_{0i} = \int \psi_0^* \sum_t e_t \mathbf{r}_t \psi_i \mathrm{d}v \qquad (7)$$

where e_t and $\mathbf{r}_t$ are the charge and the position vector of the t-th charged particle, respectively.

The π-electronic dipole moment, μ_π, is expressed in a similar form:

$$\mu_\pi = \int \psi_0^* \sum_t e_t \mathbf{r}_t \psi_0 \mathrm{d}v \qquad (8)$$

In our calculation, the following approximations are used.

1) As a set of *LCAO MO*'s, the conventional semi-empirical *MO*'s are chosen.

2) Differential overlap is neglected.

3) Values of some theoretical quantities are estimated by the empirical or semi-empirical procedure.

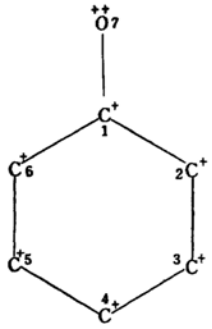

Fig. 1. Core structure of phenol.

4) The core structure of the molecule is shown in Fig. 1. Benzene ring is made up of the hexagone, with all nearest *C–C* distances equal to 1.390 Å. *C–O* distance is taken as 1.460 Å[5] which is the value of methyl acetate.

5) In the calculation of the configuration interaction, only the ground state configuration and the four lowest singly excited configurations are taken into account.

Calculation of Conventional Semi-empirical *MO*'s.—The core field of phenol pictured in Fig. 1 belongs to the symmetry group C_{2v}. It is, therefore, more convenient to express *MO*'s in terms of symmetry orbitals, σ_t, constructed from the *AO*'s according to the symmetry of the molecule;

$$\psi_i = \sum_t c_{ti} \sigma_t$$

σ_t's are written in the form,

$$\sigma_1 = \phi_1 \qquad \sigma_2 = \phi_2 + \phi_6 \qquad \sigma_3 = \phi_3 + \phi_5$$

$$\sigma_4 = \phi_4 \qquad \sigma_5 = \phi_7 \qquad (9)$$

$$\sigma_6 = \phi_2 - \phi_6 \qquad \sigma_7 = \phi_3 - \phi_5 \qquad (10)$$

The orbitals (9) belong to the representation B_1 and the orbitals (10) to A_2. The coefficients, c_{ti}, are determined by minimizing the expression for the energy, ε,

$$\varepsilon = \int \varphi^* H^e \varphi \mathrm{d}v \Big/ \int \varphi^* \varphi \mathrm{d}v$$

where H^e is the total effective Hamiltonian.

The matrix elements are assumed as follows,

i) When μ and ν are both carbon atoms,

$$H^e_{\mu\mu} = \int \phi_\mu^* H^e \phi_\mu \mathrm{d}v = \alpha$$

$$H^e_{\mu\nu} = \int \phi_\mu^* H^e \phi_\nu \mathrm{d}v = \beta \quad (\mu\nu: \text{neighbor})$$

$$H^e_{\mu\nu} = 0 \qquad (\mu\nu: \text{non-neighbor})$$

ii) When μ is an oxygen atom,

$$H^e_{77} = \alpha + \delta\beta$$

δ is determined to be 1.5 by the combination of the ionization potentials of CH_3OH and C_6H_6[6], setting the value of β equal to 3 eV[7].

iii) When μ is an oxygen atom and ν a carbon atom located at the position indicated by 1 in Fig. 1.

$$H^e_{71} = k\beta$$

where the value of k is chosen so as to bring the difference between the calculated energies of the highest occupied orbitals for benzene and phenol close to that between the observed ionization potentials[6] for them. Thus the suitable value is found to be 0.7.

The calculated orbital energies and the corresponding *MO*'s, using above mentioned parameters, are given in Table I.

The four *MO*'s, φ_1, φ_2, φ_3, and φ_4, are occupied by two electrons, respectively, and they form closed shells. The other three are vacant orbitals.

Semi-empirical Evaluation of Some Theoretical Quantities.—Molecular integrals appearing in eqs. 3 and 4 are expanded in terms of atomic integrals which are divided into two groups, one of the type of core integrals and one of the type of repulsion integrals. These quantities are adjusted by the empirical or semi-empirical procedure which is similar to that of Pariser-Parr, but somewhat different.

(1) By the assumption of zero differential overlap, only the two electron

5) J. M. O'Gorman, Jr., W. Shand and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950).

6) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1997).

7) R. S. Mulliken, *Phys. Rev.*, **74**, 736 (1948).

TABLE I

CONVENTIONAL SEMI-EMPIRICAL *MO*'S OF PHENOL

Orbital energies in β	*MO*
2.1754	$\varphi_1=0.4955\sigma_1+0.3592\sigma_2+0.2860\sigma_3+0.2630\sigma_4+0.5134\sigma_5$
1.6266	$\varphi_2=0.1269\sigma_1-0.1423\sigma_2-0.3584\sigma_3-0.4407\sigma_4+0.7016\sigma_5$
1.0000	$\varphi_3=0.5000\sigma_6+0.5000\sigma_7$
0.7869	$\varphi_4=0.4692\sigma_1+0.3458\sigma_2-0.1971\sigma_3-0.5009\sigma_4-0.4606\sigma_5$
−1.0000	$\varphi_5=-0.5000\sigma_6+0.5000\sigma_7$
−1.0642	$\varphi_6=0.5733\sigma_1-0.2503\sigma_2-0.3070\sigma_3+0.5770\sigma_4-0.1566\sigma_5$
−2.0248	$\varphi_7=0.4353\sigma_1-0.4105\sigma_2+0.3958\sigma_3-0.3909\sigma_4-0.0864\sigma_5$

repulsion integrals of the type $(\mu\mu|\nu\nu)$ may be considered. These are assumed to be as follows,

$$(\mu\mu|\nu\nu)=\int\phi_\mu^*(1)\phi_\nu^*(2)e^2/\mathbf{r}_{12}\phi_\mu(1)\phi_\nu(2)\mathrm{d}v$$
$$=e^2/(a+r_{\mu\nu})$$

where $r_{\mu\nu}$ is the interatomic distance between μ and ν atoms. The parameter a is determined in the following way, using the valence state ionization potential, I_μ, and the electron affinity, A_μ, in the same valence state.

(a) For the case of homonuclear two centers, we put

$$e^2/a=(\mu\mu|\mu\mu)=I_\mu-A_\mu$$

(b) For the case of heteronuclear two centers, i. e., for carbon and oxygen, we take as e^2/a, simple arithmetic mean of e^2/a's for carbon and oxygen.

The values of I_μ and A_μ for carbon are found in the paper of Pritchard-Skinner[8]. For the case of oxygen, I_μ and A_μ may be equal to the second and the first ionization potentials, respectively, because as shown in Fig. 1 the oxygen core has doubly positive charges. Unfortunately, the second ionization potential of oxygen in the valence state has not yet been established. Assuming that the promotion energies from the second ionized state and the first ionized state of oxygen to their valence states are the same, $(I_\mu-A_\mu)$ obtained by the spectroscopic method may be equal to that of the valence state values. The spectroscopic values are found in Ref. (9). Using the above assumption, we find

$$a_{CC}=1.328\ \text{Å}$$
$$a_{CO}=0.889\ \text{Å}$$

For the carbon two centers, in order that our expression for $(\mu\mu|\nu\nu)$ may coincide with one computed by Slater's atomic orbital, the effective nuclear charge, Z, must be put equal to 2.036 at $r_{\mu\nu}=0$[10] and decrease with the increase of $r_{\mu\nu}$.

Since the σ-core is not a point charge, but consists of a nucleus and many electrons surrounding it, it stands to reason that Z approaches to unity with the increase of $r_{\mu\nu}$ considering that the screening of the electrons against the nucleus becomes more and more complete with the increase of $r_{\mu\nu}$. In many papers published hitherto, the effect of the variation of effective nuclear charge has been neglected. Treatment taking such an effect into consideration seems to be desirable.

(2) The core integrals, $H_{\mu\nu}^{\text{core}}$, are given by

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

Pariser-Parr have given the following expressions for $H_{\mu\nu}^{\text{core}}$

$$H_{\mu\mu}^{\text{core}}=-\sum_\nu(\mu\mu|\nu\nu)-A_\mu$$

$$H_{\mu\nu}^{\text{core}}=\beta_{\mu\nu}\qquad(\mu\nu:\text{ neighbor})$$

$$H_{\mu\nu}^{\text{core}}=0\qquad(\mu\nu:\text{ non-neighbor})$$

For the case of an oxygen atom, the value of A_μ is chosen somewhat arbitrarily in the following way. On the calculation of simple *MO*'s, we have taken the value of $\delta=1.5$ for $H^e{}_{77}$. $H^e{}_{\mu\nu}$'s formally correspond to the matrix elements of the Hartree-Fock Hamiltonian, $F_{\mu\nu}$, which are expressed by

$$F_{\mu\nu}=\int\phi_\mu^*\boldsymbol{F}\phi_\nu\mathrm{d}v$$

where $\boldsymbol{F}$ is the Hartree-Fock Hamiltonian which is composed of the core operator, $\boldsymbol{H}$, and an operator concerned with the electron interaction, $\boldsymbol{G}$. If we put $F_{77}=\langle F_{CC}\rangle+1.5\langle F_{12}\rangle$ and calculate, using the approximated formula proposed by

8) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

9) C. E. Moore, "Atomic Energy Levels" Vol. 1 (1949), The National Bureau of Standards, Washington.

10) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948).

Pople[11], A_μ amounts to 11.649 eV, where $<>$ means the simple arithmetic average about the relating matrix elements. In a similar way, if we put $H_{17}=0.7<F_{12}>$, it is found to be $\beta_{CO}=-2.115$ eV. The value of β_{CC} is the same as in the previous papers.

Results and Discussion

In the calculation of configuration interaction, the four lowest singly excited configurations, $\chi_{4\to5}$, $\chi_{4\to6}$, $\chi_{3\to5}$, and $\chi_{3\to6}$, and ground state χ_0 are taken into account. $\chi_{4\to5}$ and $\chi_{3\to6}$ belong to the irreducible representation B_2 and the other three to A_1. According to the symmetry consideration, the secular determinant of 5th degree is factorized into two determinants, one degree and one of 3rd degree. The computed energies of configurations and the interconfigurational matrix elements, using the above described semi-empirical quantities are given inTable II.

TABLE II
VALUES OF THE ENERGIES OF CONFIGURATIONS AND THE INTERCONFIGURATIONAL MATRIX ELEMENTS IN eV UNITS

$E(\chi_0)$	0	$(^1\chi_{3\to5}\|\boldsymbol{H}\|\chi_0)$	0.020
$E(^1\chi_{3\to5})$	6.556	$(^1\chi_{4\to6}\|\boldsymbol{H}\|\chi_0)$	0.049
$E(^1\chi_{3\to6})$	6.018	$(^1\chi_{3\to5}\|\boldsymbol{H}\|^1\chi_{4\to6})$	−0.313
$E(^1\chi_{4\to5})$	5.264	$(^1\chi_{4\to5}\|\boldsymbol{H}\|^1\chi_{3\to6})$	0.927
$E(^1\chi_{4\to6})$	5.770	$(^3\chi_{3\to5}\|\boldsymbol{H}\|^3\chi_{4\to6})$	−0.375
$E(^3\chi_{3\to5})$	3.610	$(^3\chi_{4\to5}\|\boldsymbol{H}\|^3\chi_{3\to6})$	−0.375
$E(^3\chi_{3\to6})$	4.638		
$E(^3\chi_{4\to5})$	3.914		
$E(^3\chi_{4\to6})$	3.280		

The calculated excitation energies and oscillator strengths are presented in Table III, in comparison with the observed values, and the corresponding electronic state wave functions are collected in Table IV.

TABLE III
CALCULATED AND OBSERVED EXCITATION ENERGIES (IN eV) AND OSCILLATOR STRENGTHS

	Excitation energies		Oscillator Strengths	
	Calcd.	Obsd.	Calcd.	Obsd.
$^1B_2^-$	4.640	4.59[a]	0.022	0.02[b]
$^1A_1$	5.662	5.89[a]	0.251	—
$^1B_2^+$	6.642	—	0.987	—
$^1A_1$	6.667	—	0.971	—
$^3A_1^+$	3.035	—	0	—
$^3B_2^+$	3.755	—	0	—
$^3A_1^-$	3.855	—	0	—
$^3B_2^-$	4.797	—	0	—

a) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).
b) R. S. Mulliken, Ref. 4).

As shown in Table III, the agreement between the calculated and the observed values is satisfactory and further improvement will be expected by including other excited configurations and adjusting the core parameters. It may be reasonable to interpret the spectra of phenol in the near-ultraviolet region as those of benzene perturbed by mobile lone pair electrons of the substituent. As shown in our calculation, this correspondence will be explained by considering only four excited configurations. It is interesting to note that in the case of benzene the state energies of $^3B_{2u}^-$ and $^1B_{2u}^-$ which is the radiation emitting state are the same, while in phenol the latter is higher than the former by 0.157 eV which is greater compared with kT. It may be regarded as the principal reason for the appearance of intense fluorescence of phenol, because the radiationless,

TABLE IV
ELECTRONIC STATE WAVE FUNCTIONS AND THEIR ENERGIES

Symmetry	State energy (in eV)	Wave function
A_1	−0.001	$^1\psi_0=\chi_0-0.0092\ ^1\chi_{4\to6}-0.0038\ ^1\chi_{3\to5}$
B_2	4.640	$^1\psi_1=0.8298\ ^1\chi_{4\to5}-0.5581\ ^1\chi_{3\to6}$
A_1	5.661	$^1\psi_2=0.0092\chi_0+0.9439\ ^1\chi_{4\to6}+0.3301\ ^1\chi_{3\to5}$
B_2	6.642	$^1\psi_3=0.5581\ ^1\chi_{4\to5}+0.8298\ ^1\chi_{3\to6}$
A_1	6.666	$^1\psi_4=0.0038\chi_0-0.3301\ ^1\chi_{4\to6}+0.9439\ ^1\chi_{3\to5}$
A_1	3.035	$^3\psi_1=0.8372\ ^3\chi_{4\to6}+0.5469\ ^3\chi_{3\to5}$
B_2	3.755	$^3\psi_2=0.9204\ ^3\chi_{4\to5}+0.3909\ ^3\chi_{3\to6}$
A_1	3.855	$^3\psi_3=0.5469\ ^3\chi_{4\to6}-0.8372\ ^3\chi_{3\to5}$
B_2	4.797	$^3\psi_4=0.3909\ ^3\chi_{4\to5}-0.9204\ ^3\chi_{3\to6}$

11) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

or thermal, transition is inhibited. The fact that the values of interconfigurational matrix elements among the ground configuration and the excited configurations are small gives us to understand that the calculated conventional semi-empirical *MO*'s are fairly close to the self-consistent field *MO*'s. The π-electronic dipole moment, invoking the assumption of neglect of differential overlap, is calculated as

$$\mu = 1.04\,\mathrm{D}$$

The π-electronic dipole moment should be obtained by subtracting vectorially the σ-electronic dipole moment from the total moment determined experimentally. Unfortunately, the σ-electronic dipole moment has not been estimated, because the information about the σ-electronic states, especially for the substituent, is not enough and, moreover, the σ-core is not rigid, but is affected by the π-electronic state. Hence, we will not discuss this further.

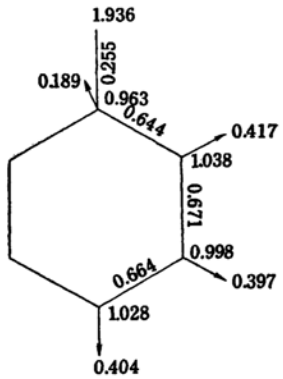

Fig. 2. Molecular diagram of phenol

The molecular diagram calculated by present treatment is shown in Fig. 2. From this diagram it may be expected that;

(i) In the electrophilic reactions, *o-p* substitution takes place.

(ii) The radical reactions take place preferentially at the *o*-positions.

(iii) The C—C bond distances are $C_1—C_2 > C_3—C_4 > C_2—C_3$.

(i) agrees with the experimental facts generally recognized. The information compared with (ii) or (iii) are not available. In the case of anisol which is similar to phenol in the π-electronic configuration, Suehiro[12] reported the order $o > p > m$ in the radical reactivities.

Summary

The electronic structure and spectra of phenol was studied from the semi-empirical point of view, using the *LCAO-ASP-CI-MO* method. The excitation energies and oscillator strengths of transitions to lower excited states were calculated. The agreement between the calculated and the observed values is very good. The charge distribution, bond orders and the π-electronic dipole moment are also calculated.

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12) T. Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 301 (1951).