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LCAO-MO-SCF-CI Semi-empirical π-Electron Calculations on Heteroaromatic Systems

I. Hydroxy Aromatic Compounds*

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The electronic spectra and structure for phenol, the three dihydroxybenzene isomers, and α- and β-naphthol have been calculated using a modification of the Pariser-Parr-Pople method. Core integrals are defined to be essentially independent of geometry and orthogonalized atomic orbitals are used. The electronic transitions considered involve singlet-singlet and triplet-triplet $\pi \rightarrow \pi^*$ excitations. A limited configuration interaction has been included, involving either single electron excitations or both single and double electron excitations between the two highest occupied and the two lowest unoccupied molecular orbitals. Agreement between calculated and experimental values is good, and calculated values for oscillator strengths are considerably improved when double electron excitations are admitted.

Die Elektronenspektren und Struktur von Phenol, den drei Isomeren des Dihydroxybenzols und α- und β-Naphthol wurden mit einer Modifikation der PPP-Methode berechnet. Die Rumpfintegrale werden so definiert, daß sie im wesentlichen unabhängig von der Geometrie sind; es werden orthogonalisierte Atomorbitale benutzt. Die betrachteten Elektronenübergänge enthalten Singulett-Singulett- und Triplett-Triplett-$\pi \rightarrow \pi^*$-Übergänge. Es wurde eine begrenzte Konfigurationswechselwirkung eingeschlossen, die nur Einelektronen- oder Ein- und Zweielektronenanregung zwischen den beiden höchsten besetzten und den beiden niedrigsten unbesetzten MO's enthält. Es besteht gute Übereinstimmung von berechneten und experimentellen Daten. Die berechneten Werte für Oszillatorenstärken werden erheblich verbessert, wenn man Zweielektronenanregung einbezieht.

Les spectres électroniques et les structures du phénol, des trois dihydroxybenzènes isomères, de l'α et du β naphtol ont été calculé pour une variante de la méthode de Pariser-Parr-Pople. Les intégrales de coeur sont définies de manière à être indépendantes de la géométrie et des orbitales atomiques orthogonalisées sont employées. On considère les transitions électroniques $\pi \rightarrow \pi^*$ singulet-singulet et triplet-triplet. Une interaction de configuration limitée a été effectuée en considérant soit des minoexcitations soit des mono et des diexcitations de la plus haute orbitale occupée aux deux orbitales libres les plus basses. L'accord entre les valeurs calculées et les valeurs expérimentales est bon, et les valeurs calculées des forces oscillatrices sont considérablement améliorées lorsque l'on tient compte des états diexcités.

Introduction

Semi-empirical π-electron calculations based on the Pariser-Parr-Pople method have been extensively applied to conjugated hydrocarbons and less frequently to

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heteroaromatic systems [30—35, 38, 40, 41]. It has been found, however, that a given set of parameters may adequately describe some property of a molecule but fail in another. Recently, ADAMS and MILLER modified the conventional method [2]. They proposed a new way of evaluating core integrals and expressed atomic orbitals on an orthogonalized basis. The results of their calculations on aromatic hydrocarbons and linear conjugated systems showed their method to be an improvement over the Pariser-Parr-Pople approach.

There have been several semi-empirical π-electron investigations on phenol and α- and β-naphthol [3—5, 11, 13, 14, 23, 26—28], but little on the dihydroxybenzenes [13, 24, 25]. In the present investigation, the electronic spectra and structures of these hydroxy aromatic compounds have been calculated. The method of evaluating core integrals suggested by ADAMS and MILLER has been modified to accommodate the heteroatom, and Löwdin orbitals have been used. Singlet-singlet and triplet-triplet electronic transitions have been included and the results are in good agreement with experiment. Values for oscillator strengths are appreciably improved when more configurations are allowed to mix.

Method

Geometry. The geometry adopted is a conventional one. The molecules are assumed to be planar and all bond angles have been set equal to 120°, including the angle the hydroxyl substituent makes with an adjacent C–C bond. The C–C distance has been set equal to 1.396 A [8] and the C–O distance has been taken to be 1.460 A [29]. The latter value was taken from the experimental value for the methoxyl group in methyl acetate.

Calculation of Overlap. The zero differential overlap approximation of Pariser and Parr has been assumed only for orthogonalized orbitals. Overlap between all atomic centers has been calculated from conventional formulas [20]. Values used for effective nuclear charges are listed in Tab. 1.

Evaluation of Repulsion Integrals. One-center repulsion integrals have been calculated from [31]

$$(ii \mid ii) = I_i - A_i \tag{1}$$

where I_i and A_i are the first ionization potential and electron affinity, respectively, for atom i if the atom donates one π electron. In the case of a heteroatom donating

Table 1. *Valence State Data and Effective Nuclear Charges Used for Carbon and Oxygen Atoms*

Quantity	Carbon	Oxygen
First Ionization Potential	11.16[a,b]	17.70[a,c]
Second Ionization Potential		35.146[d]
First Electron Affinity	0.03[a,b]	2.47[a,c]
Second Electron Affinity		17.70
Effective Nuclear Charge	3.25[e]	4.55[e]

[a] See Ref. [12].
[b] For the sp^3 valence state.
[c] For the sp^4 valence state.
[d] See Ref. [18].
[e] See Ref. [42].

two π electrons, a second such integral was calculated using the second ionization potential and electron affinity (first ionization potential). The appropriate valence state data are given in Tab. 1.

Two-center integrals were calculated using the equations of MATAGA and NISHIMOTO given by [17]

$$(ii\,|\,jj) = 14.397/(a + r_{ij})\,, \tag{2}$$

where

$$a = 28.794/(ii\,|\,ii) + (jj\,|\,jj)\,,$$

and r_{ij} is the interatomic distance between centers i and j.

The three-center repulsion integrals over Slater orbitals have been evaluated using the Mulliken approximation [21]

$$(ij\,|\,mm) = S_{ij}/2[(ii\,|\,mm) + (jj\,|\,mm)]\,. \tag{3}$$

Calculation of Core Integrals. ADAMS and MILLER have defined a new empirical parameter, H^0, which contains neutral atom penetration integrals and kinetic and potential energy terms. This new parameter is related to the core integral, H, by the following,

$$H_{ii} = H^0_{ii} - \sum_{\substack{m=1\\ m\neq i}}^{n} (ii\,|\,mm) - \sum_{\substack{q\\ q\neq i}} (ii\,|\,qq)\,, \tag{4}$$

$$H_{ij} = H^0_{ij} - \sum_{\substack{m=1\\ m\neq i,j}}^{n} (ij\,|\,mm) - \sum_{\substack{q\\ q\neq i,j}} (ij\,|\,qq)$$

$$-\tfrac{1}{2}\,[(ij\,|\,ii) + (ij\,|\,jj)] - [\tfrac{1}{2}\,(ij\,|\,qq)]_{q=i,j} \tag{5}$$

where the summations $m = 1, n$ are over all atomic centers except those indicated and the summations involving q extend only over those heteroatoms donating two π electrons. The last term in Eq. (5) is included only if $q = i, j$. Eqs. (4) and (5) are a modification of those given by ADAMS and MILLER for the accomodation of heteroatoms donating two π electrons to the aromatic system.

Calculation of Fock Matrix and Charge Distributions. The Fock matrix elements, F_{ij}, were calculated from the following,

$$F_{ii} = H^\lambda_{ii} + \sum_{k=1}^{\text{nocc}} \left\{ \sum_{\substack{m=1\\ m\neq i}}^{n} 2C^2_{mk}(ii\,|\,mm) + C^2_{ik}(ii\,|\,ii) \right\}, \tag{6}$$

and

$$F_{ij} = H^\lambda_{ij} - \sum_{k=1}^{\text{nocc}} C_{ik}\,C_{jk}(ii\,|\,jj)\,, \tag{7}$$

where k spans the occupied molecular orbitals, m spans the n atomic orbitals and the C's represent eigenvectors, the first subscript representing the atomic orbital and the second, the molecular orbital. The H^λ elements are based on orthogonalized orbitals and are related to the core elements based on Slater orbitals by the transformation [16],

$$H^\lambda = S^{-1/2}\,H S^{-1/2}\,, \tag{8}$$

where H is the matrix containing the elements given by Eqs. (4) and (5), H^λ is the matrix containing core elements based on Löwdin orbitals, and $S^{-1/2}$ is obtained from the overlap matrix, S.

An initial set of orthogonalized eigenvectors had been obtained from the Hückel approximation and these were used to calculate the Fock matrix. The latter was then diagonalized by the Jacobi procedure [10] and a new set of eigenvectors was obtained, from which a bond order matrix based on orthogonalized orbitals was constructed. The SCF iteration was contineed until the bond order matrix elements were reproducible to 10^{-4}. Once convergence was attained, the ionization potential was then determined using Koopmans' theorem [15] which states that the energy of the highest occupied molecular orbital in the ground state is a good approximation to the ionization potential of a molecule.

Atom and bond charges were calculated using formulas given by PEACOCK [36], namely,

$$q_{ii} = P_{ii} \tag{9}$$

and

$$q_{ij} = 2 P_{ij} S_{ij} \tag{10}$$

where P_{ij} is the bond order matrix element in terms of Slater orbitals and was calculated from

$$P_{\mathrm{ij}} = \sum_{k=1}^{\mathrm{NCI}} (W_{kv})^2 \sum_{l=1}^{n} Z_{il} Z_{jl} \tag{11}$$

where W_{kv} is the eigenvector for the vth state and Z represents the SCF eigenvector expressed in terms of Slater orbitals. The first summation is over all configurations and the second over all n atomic centers. This type of charge distribution will henceforth be referred to as nonlocalized atom and bond charges or populations.

Alternatively, atom populations were determined from

$$q_i = q_{ii} + \tfrac{1}{2} \sum_{j=1}^{n} q_{ij} \tag{12}$$

and they will henceforth be referred to as localized atom charges or populations.

Localized atom charges were used for calculating the π electron dipole moment (in Debyes). The x and y contributions were determined using

$$\mu_x = 4.8 \sum_{i=1}^{n} x_i (q_i - N_i) \tag{13}$$

$$\mu_y = 4.8 \sum_{i=1}^{n} y_i (q_i - N_i) \tag{14}$$

where N_i indicates the number of π electrons that atomic center i donates to the aromatic system. The total π electron moment is then given by

$$\mu = \sqrt{u_x^2 + u_y^2}\,. \tag{15}$$

Configuration Interaction and Transition Energies. All possible configurations arising from single and double electron excitations between the two highest occupied and the two lowest unoccupied molecular orbitals have been formed and expressed as Slater determinants. For singlet states there are fifteen configurations and for the triplet states there are eleven. Two types of interaction were considered. In method I mixing was allowed only among the singly excited states. In method II mixing was allowed among the ground state and both singly and doubly excited states.

The configuration interaction matrix elements were evaluated in the conventional manner [6, 35]. A Jacobi diagonalization of the resulting matrix gave a series of eigenvalues from which transition energies for singlet and triplet states were determined.

Calculation of Oscillator Strengths. Oscillator strengths, f_V, for the various transitions have been evaluated using [19]

$$f_V = 1.085 \times 10^{-5} \nu_V Q_V^2 \tag{16}$$

where ν_V is the frequency of the transition in wave numbers, and Q_V is the transition moment vector and can be expressed as

$$Q_V^2 = Q_{(x)V}^2 + Q_{(y)V}^2 \, . \tag{17}$$

The transition moment component, $Q_{(x)V}$, was evaluated from

$$Q_{(x)V} = \sum_{i,j=1}^{\mathrm{NCI}} W_{il} W_{jV} \sum_{s,t=1}^{\mathrm{NORM}} N_{is} N_{jt} Q_{(x)st} \tag{18}$$

where W_{il} and W_{jV} are the eigenvectors (obtained from the diagonalization of the configuration interaction matrix) for the ground and excited state, respectively, and N is the sth or tth normalization constant for the ith or jth configuration. The second summation is over all normalization constants together with the product between Slater determinants in the ith and jth configuration. For the evaluation of $Q_{(x)st}$, which is a function of the s and tth Slater determinant, three cases arise for taking the products between the Slater determinants. If the determinants are identical in all spin orbitals, then

$$Q_{(x)st} = \sum_{m} \sum_{k,l=1}^{n} Z_{km} Z_{lm} S_{kl} \tfrac{1}{2}(x_k + x_l) \tag{19}$$

where the first summation is over all molecular orbitals in the Slater determinant s (or t), and the second summation is over all n atomic centers.

If the determinants differ by only one spin orbital, say ϕ_s in determinant s in place of ϕ_t in determinant t, then

$$Q_{(x)st} = \sum_{k,l=1}^{n} Z_{ks} Z_{lt} S_{kl} \tfrac{1}{2}(x_k + x_l) \, . \tag{20}$$

If the determinants differ in two or more spin orbitals, then $Q_{(x)st} = 0$. Similar expressions hold for $Q_{(y)V}$ and $Q_{(y)st}$.

In the present calculations, oscillator strengths for singlet excitations are relative to the singlet ground state, while for triplet excitations, they are relative to the lowest triplet state.

Procedure for the Evaluation of the Empirical Parameter H_{ij}^0. Phenol was used as a calibration molecule for determining appropriate values of H_{ij}^0 for the hydroxy aromatic compounds. Initially, a set of values from benzene similar to those given by ADAMS and MILLER were used to construct the H^0 matrix. After the H^λ matrix had been calculated, all elements for non-nearest neighbors were set equal to zero, the Fock matrix calculated, the SCF procedure applied and configuration interaction introduced. The H_{ij}^0 element between carbon and oxygen nearest neighbors was estimated and then varied until the first calculated excitation energy differed from the experimental value by no more than 0.01 eV. The values obtained for the

H^0_{ij} elements between carbon and oxygen neighbors were then used in the remaining hydroxy aromatic compounds.

For each dihydroxybenzene, an additional H^0_{ij} element between oxygen atoms was needed. Initially, a value was guessed and a procedure similar to that for phenol was followed, except that the H^0_{ij} element was not varied. Instead, the H^0_{ij} matrix was calculated from the H^λ matrix after setting all non-nearest neighbor elements equal to zero by appropriate rearrangements of Eqs. (4), (5) and (8). The H^0_{ij} element between oxygen atoms obtained in this way was substituted into Eq. (4) and the calculation repeated.

In the naphthols the H^0_{ij} elements between carbon atoms were taken from naphthalene. Values for the H^0_{ij} elements between oxygen and carbon atoms in the same ring were obtained from phenol and for the matrix elements between oxygen and the carbon atoms in the other ring, a procedure similar to that followed for the dihydroxybenzenes was used to evaluate the four new H^0_{ij} elements.

This procedure for evaluating H^0_{ij} matrix elements had to be employed twice, once for method I and once for method II since the values of the corresponding elements depend upon the amount of configuration mixing included. Values for H^0_{ij} using both methods are given in Tab. 2.

Table 2. *Values for the Empirical Parameter* H^0_{ij}[a]

Molecule	Element	Value	
		Method I	Method II
Phenol	H^0_{11}	-11.597	-11.388
	H^0_{12}	- 4.322	- 3.882
	H^0_{13}	- 0.856	- 0.745
	H^0_{14}	- 0.264	- 0.235
	H^0_{17}	- 5.028	- 4.342
	H^0_{27}	- 0.711	- 0.591
	H^0_{37}	- 0.059	- 0.048
	H^0_{47}	- 0.024	- 0.019
	H^0_{77}	-26.323	-27.178
Catechol	H^0_{78}	- 0.035	- 0.031
Resorcinol	H^0_{78}	0.001	0.001
Hydroquinone	H^0_{78}	0.001	0.001
α-Naphthol	H^0_{15}	- 0.050	- 0.045
	H^0_{16}	- 0.010	- 0.009
	H^0_{26}	- 0.001	- 0.001
	H^0_{36}	- 0.002	- 0.002
	$H^0_{5,11}$	- 0.001	0.000
	$H^0_{6,11}$	- 0.001	- 0.001
	$H^0_{7,11}$	- 0.006	- 0.005
	$H^0_{8,11}$	- 0.106	- 0.096
β-Naphthol	$H^0_{5,11}$	0.001	0.000
	$H^0_{6,11}$	0.000	0.000
	$H^0_{7,11}$	0.000	0.000
	$H^0_{8,11}$	- 0.001	- 0.001

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[a] See Fig. 1 for the numbering scheme.

Results and Discussion

The electronic spectra for the first four singlet-singlet and triplet-triplet π-π^* transitions are given in Tab. 3. Values obtained using both methods I and II are included together with experimental data. Method II gives values for oscillator strengths which are in general a considerable improvement over values obtained using method I, although the results for transition energies are less dramatic.

In Tab. 4 the molecular ionization potentials are listed together with the only available experimental value, namely, that for phenol. The values are higher with method II than with method I and for phenol the result is somewhat improved using method II. NISHIMOTO and FORSTER [28] have calculated the electronic properties of heteroaromatic systems by the variable β approximation, using singly excited configurations within 3.0 – 3.5 eV of the lowest excited states. For

Table 3. *Transition Energies* (in eV) *and Oscillator Strengths*[a]

Molecule	Singlet States		Exptl.	Triplet States	
	Method I	Method II		Method I	Method II
Phenol	4.59 (0.078)	4.59 (0.025)	4.59[b] (0.0213)[c]	3.17	3.04
	5.75 (0.257)	5.68 (0.079)	5.89[b] (0.103)[c]	3.39 (0.003)	3.60 (0.002)
	6.81 (1.217)	6.61 (0.638)	6.53[c]	3.85 (0.003)	3.81 (0.001)
	6.88 (0.980)	6.64 (0.670)		5.19 (0.012)	4.86 (0.001)
Catechol	4.42 (0.143)	4.35 (0.040)	4.46[d] (0.024)[e]	3.06	2.95
	5.27 (0.242)	5.29 (0.077)	5.78[f]	3.09 (0.000)	3.39 (0.003)
	6.50 (0.826)	6.20 (0.668)		3.77 (0.012)	3.62 (0.007)
	6.55 (1.353)	6.39 (0.623)		4.84 (0.026)	4.60 (0.003)
Resorcinol	4.57 (0.075)	4.43 (0.010)	4.48[g] (0.020)[e]	3.30	3.01
	5.65 (0.062)	5.38 (0.010)	5.63[g]	3.38 (0.000)	3.47 (0.001)
	6.34 (0.907)	6.04 (0.613)		4.00 (0.030)	3.76 (0.007)
	6.43 (1.450)	6.34 (0.816)		4.85 (0.005)	4.62 (0.000)
Hydroquinone	4.09 (0.196)	4.45 (0.066)	4.25[h] (0.030)[e]	2.62	3.00
	5.49 (0.478)	5.67 (0.181)	5.51[h]	2.99 (0.000)	3.18 (0.000)
	6.72 (1.135)	6.67 (0.731)		3.84 (0.000)	3.84 (0.000)
	7.14 (0.854)	6.86 (0.589)		5.80 (0.000)	5.25 (0.000)
α-Naphthol	4.03 (0.359)	3.95 (0.012)	3.86[i] (0.016)	2.48	2.36
	4.18 (0.055)	4.06 (0.186)	4.29 (0.102)	3.48 (0.006)	3.39 (0.002)
	5.62 (1.804)	5.37 (1.260)	5.40 (0.328)	4.24 (0.014)	3.91 (0.000)
	6.52 (0.841)	6.10 (0.543)	5.80 (0.892)	4.37 (0.004)	3.97 (0.002)
β-Naphthol	3.93 (0.205)	3.82 (0.070)	3.78[i] (0.0211)	2.43	2.38
	4.53 (0.100)	4.28 (0.084)	4.54 (0.0811)	3.38 (0.029)	3.29 (0.009)
	5.60 (2.131)	5.36 (1.310)	5.53 (1.06)	3.97 (0.004)	3.73 (0.000)
	6.27 (0.846)	5.86 (0.564)		4.73 (0.003)	4.21 (0.001)

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[a] Values for oscillator strengths are in parenthesis.

[b] See Ref. [9].

[c] See Ref. [3].

[d] See Ref. [13].

[e] See Ref. [39].

[f] See Ref. [7].

[g] See Ref. [22].

[h] See Ref. [1].

[i] All experimental values for α- and β-naphthol have been taken from Ref. [4].

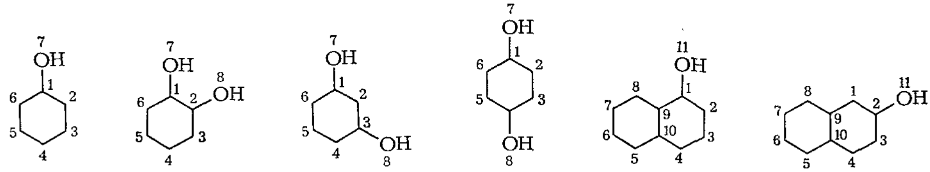
Table 4. *Molecular Ionization Potentials* (in eV)

Molecule	Method I	Method II	Observed
Phenol	8.21	8.35	8.50[a]
Catechol	7.36	7.85	
Resorcinol	7.70	8.00	
Hydroquinone	7.15	7.67	
α-Naphthol	7.60	7.70	
β-Naphthol	7.79	7.84	

[a] See Ref. [43].

the molecular ionization potentials of phenol, hydroquinone, α-naphthol and β-naphthol they obtained values of 8.24, 7.46, 7.78 and 7.92 eV, respectively. The first value agrees well with using method I while the latter three are closer to values obtained using method II.

Localized atom charges are given in Tab. 5. For phenol the values are in line with the experimental fact that electrophilic substitution occurs at the ortho and para positions. For α-naphthol and β-naphthol the calculated atom charges are in agreement with the experimental findings that a strongly activating group in the 1 position in naphthalene tends to direct electrophilic substitution to the 2 and 4 positions, while such a group in the 2 position directs substitution to the 1 position (see Fig. 1 for the numbering scheme).



Phenol Catechol Resorcinol Hydroquinone α-Naphthol β-Naphthol

Fig. 1. Numbering scheme for hydroxy aromatic compounds

The calculated values for the π-electron contribution to the dipole moment in the ground state are listed in Tab. 6. The calculated ground state values in the present work are larger than those obtained by other investigators. For example, NISHIMOTO and FUJISHIRO [23] have calculated a π-electron contribution of 1.04 D for phenol, and FORSTER and NISHIMOTO [11] have obtained values of 1.36 D and 1.40 D for α-naphthol and β-naphthol, respectively. The reason for this is that the value of the parameter, H^0_{ij}, required to give agreement with the electronic spectrum was considerably smaller than the second ionization potential of oxygen to which it is related. This resulted in a greater diffusion of charge from the oxygen atom into the ring system and hence a larger value for the dipole moment.

PEACOCK and WILKINSON [37] have found that for benzene and naphthalene there is approximately 0.2 electron in each bond and about 0.8 electron at each atom center. In the present investigation similar results have been found for the hydroxy aromatic compounds and these are listed in Tab. 7. On the average each

Table 5.[a] *Localized Atom Charges* (q_i)

Molecule		q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}	q_{11}
Phenol	I	0.918	1.117	0.987	1.060	0.987	1.117	1.815	—	—	—	—
	II	0.938	1.079	0.994	1.043	0.994	1.079	1.873	—	—	—	—
Catechol	I	1.007	1.007	1.111	1.043	1.043	1.111	1.839	1.839	—	—	—
	II	1.006	1.006	1.074	1.033	1.033	1.074	1.887	1.887	—	—	—
Resorcinol	I	0.908	1.236	0.980	1.170	0.976	1.170	1.816	1.816	—	—	—
	II	0.931	1.160	0.931	1.120	0.991	1.120	1.874	1.874	—	—	—
Hydroquinone	I	0.965	1.101	1.101	0.965	1.101	1.101	1.832	1.832	—	—	—
	II	0.973	1.072	1.072	0.973	1.072	1.072	1.883	1.883	—	—	—
α-Naphthol	I	0.920	1.146	0.985	1.083	1.014	1.004	1.019	1.028	1.036	0.959	1.805
	II	0.933	1.100	0.989	1.052	1.014	1.006	1.012	1.030	1.025	0.967	1.871
β-Naphthol	I	1.155	0.920	1.091	0.993	1.008	1.024	1.003	1.030	0.956	1.005	1.814
	II	1.108	0.932	1.069	0.999	1.010	1.019	1.003	1.023	0.966	0.997	1.875

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[a] See Fig. 1 for numbering scheme.

Table 6. *Calculated π-Electron Dipole Moment (in Debyes)*

Molecule	π-Electron Dipole Moment	
	Method I	Method II
Phenol	2.62	1.88
Catechol	4.24	3.00
Resorcinol	2.54	1.86
Hydroquinone	0.00	0.00
α-Naphthol	2.83	1.88
β-Naphthol	2.96	2.13

atom is deficient in about 0.2 electron while each bond has a net charge of about 0.2 electron, except for the bond between carbon and oxygen which has a net charge of less than 0.1 electron.

Conclusion

The new method for evaluating core integrals suggested by ADAMS and MILLER has been modified to accomodate the heteroatom in hydroxy aromatic compounds. A set of empirical parameters, H^0_{ij}, has been obtained which when transferred from one molecule to another successfully describes the electronic properties of these molecules. Hence, the method proposed by ADAMS and MILLER is not only an improvement of the conventional Pariser-Parr-Pople approach for aromatic hydrocarbons and linear conjugated polyenes, but also for heteroaromatic systems. In the next two papers in this series, it will be shown that this method can be applied to other heteroaromatic systems with good results.

Appendix

The computer program used for the present calculations was written in Fortran and can be used for either conjugated hydrocarbons or heteroaromatic systems. Computations were performed on the Control Data Corporation G-20 electronic digital computer. Charge distributions are calculated for singlet and triplet states, although only ground state values are reported.

A flow chart for the calculation scheme in shown in Fig. 2. Input values include (1) atomic valence state ionization potentials, electron affinities, and effective nuclear charges; (2) an initial set of H^0_{ij} parameters; and (3) a starting set of eigenvectors obtained from a Hückel solution for the molecule under investigation. Using the calculation procedures previously described, the molecular ionization potential, dipole moment, charge densities, and oscillator strengths are calculated as shown.

Provisions have been included in the program for varying the empirical parameter H^0_{ij}. This is usually done for a calibration molecule and the parameter is varied until the first calculated excitation energy is within a certain tolerance of the experimental value, this tolerance being left to the discretion of the investigator. When the desired convergence is obtained, these parameters are transferred to analogous molecules and are not further varied.

Whenever matrix elements between Slater determinants are evaluated, the orbitals in each must be in maximum alignment in both space and spin parts. Therefore, in constructing the program, a technique had to be devised for rearranging any out-of-place orbitals and it was decided that a special array would be set up which would contain the subscripts of the orbitals, and that a negative number would represent a subscript of an orbital of β spin, and a positive number, one of α spin. The program contains provisions for this rearranging whereby it scans the subscripts of one of the determinants comparing them with those in the other determinant, rearranges where necessary, and also changes the sign of the normalization constant each time two subscripts are interchanged. This procedure is carried out in two parts

Table 7. *Nonlocalized Atom and Bond Charges* (q_{ij})[a]

Molecule	Method											
		q_{11}	q_{22}	q_{33}	q_{44}	q_{77}	q_{12}	q_{23}	q_{34}	q_{17}		
Phenol	I	0.674	0.905	0.754	0.836	1.776	0.205	0.244	0.239	0.094		
	II	0.704	0.874	0.776	0.827	1.845	0.209	0.226	0.229	0.066		
		q_{11}	q_{33}	q_{44}	q_{77}	q_{12}	q_{23}	q_{34}	q_{45}	q_{17}		
Catechol	I	0.775	0.897	0.818	1.807	0.182	0.225	0.227	0.250	0.078		
	II	0.781	0.886	0.816	1.864	0.189	0.218	0.221	0.237	0.056		
		q_{11}	q_{22}	q_{44}	q_{55}	q_{77}	q_{12}	q_{34}	q_{45}	q_{17}		
Resorcinol	I	0.663	1.044	0.996	0.742	1.776	0.208	0.201	0.242	0.094		
	II	0.696	0.964	0.916	0.768	1.847	0.210	0.208	0.231	0.067		
		q_{11}	q_{22}	q_{77}	q_{12}	q_{23}	q_{17}					
Hydroquinone	I	0.725	0.980	1.797	0.211	0.235	0.084					
	II	0.742	0.867	1.858	0.212	0.220	0.060					
		q_{11}	q_{22}	q_{33}	q_{44}	q_{55}	q_{66}	q_{77}	q_{88}	q_{99}	$q_{10,10}$	$q_{11,11}$
α-Naphthol	I	0.688	0.939	0.753	0.875	0.798	0.773	0.791	0.809	0.791	0.700	1.765
	II	0.703	0.889	0.762	0.842	0.800	0.780	0.788	0.815	0.780	0.712	1.844
		q_{12}	q_{23}	q_{34}	$q_{4,10}$	$q_{5,10}$	q_{56}	q_{67}	q_{78}	q_{89}	q_{18}	$q_{1,11}$
	I	0.238	0.204	0.276	0.179	0.181	0.277	0.203	0.276	0.187	0.151	0.095
	II	0.252	0.196	0.275	0.178	0.179	0.274	0.196	0.273	0.181	0.161	0.067
		q_{11}	q_{22}	q_{33}	q_{44}	q_{55}	q_{66}	q_{77}	q_{88}	q_{99}	$q_{10,10}$	$q_{11,11}$
β-Naphthol	I	0.961	0.677	0.877	0.774	0.790	0.796	0.772	0.815	0.696	0.751	1.774
	II	0.909	0.692	0.854	0.784	0.796	0.794	0.777	0.810	0.710	0.745	1.847
		q_{12}	q_{23}	q_{34}	$q_{4,10}$	$q_{5,10}$	q_{56}	q_{67}	q_{78}	q_{89}	q_{19}	$q_{2,11}$
	I	0.239	0.168	0.283	0.178	0.182	0.278	0.201	0.279	0.179	0.183	0.094
	II	0.251	0.178	0.275	0.177	0.179	0.274	0.197	0.274	0.178	0.179	0.067

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[a] See Fig. 1 for the numbering scheme.

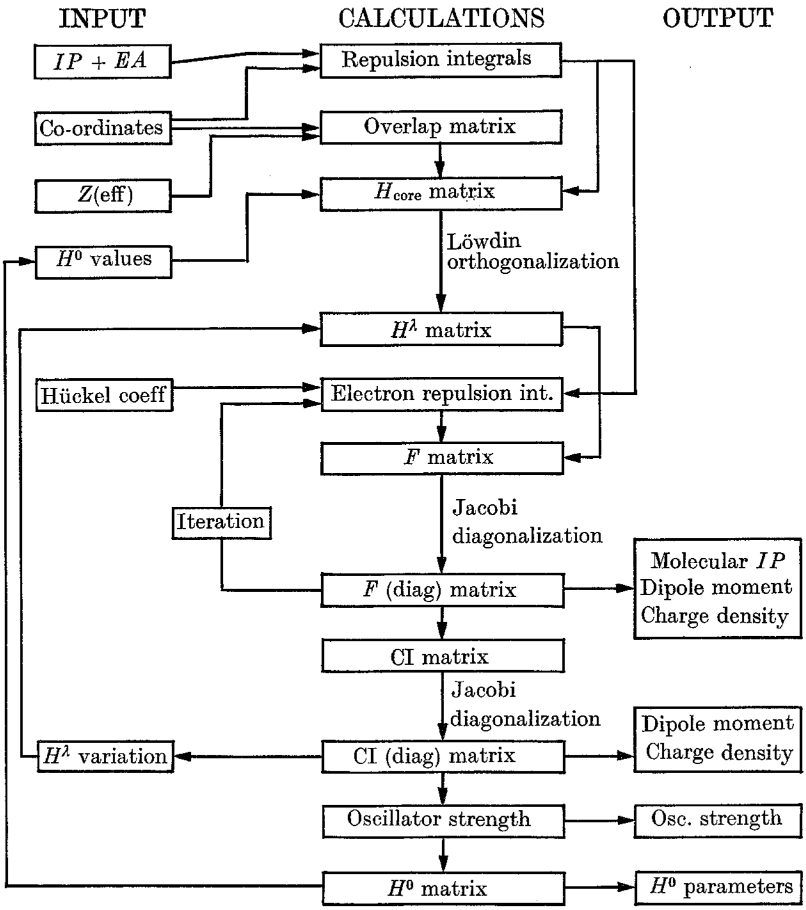

Fig. 2. Flow chart

of the program; in the evaluation of the configuration interaction matrix and also in the calculation of oscillator strengths.

The time required to perform all the calculations for each molecule was dependent on the size of the molecule and the method employed. For phenol and the dihydroxybenzenes, calculations using method I about 4 or 5 min, while for method II the time increased to between 30 and 50 min per molecule. The naphthols took the longest time, approximately 8 min using method I and 90 min per molecule for method II. The major contribution to the greater amount of time used in going from method I to method II is the larger size of the configuration interaction matrix; there are only four singlet functions and four triplet functions to be considered in method I, while the numbers increase to 15 and 11, respectively, for method II.

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