

# Self-consistent Field Molecular Orbital Calculations on the Electronic Structure of Mono and Disubstituted Hydroxy (Methoxy) Benzenes

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SCF-LCAO-MO calculations in the Pariser, Parr, Pople approximation including configuration interaction of all singly excited states have been performed on phenol and disubstituted hydroxybenzenes. As far as the effects of hyperconjugation may be neglected the calculations should be applicable also to anisole and dimethoxybenzenes.

The one-electron one and two center integrals pertinent to the C—O bond have been varied. It has been found possible to obtain a set of heteroatom parameters which give a fairly good description of ionization potentials, charge-transfer band energies, dipole moment, nuclear magnetic resonance shielding data of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, and electronic transition energies in the molecules studied.

## INTRODUCTION

Knowledge of the electronic structure of substituted benzenes is of basic importance for a deeper understanding of the reactivities and spectral properties of this important class of compounds. Purely theoretical quantum chemical calculations involving all electrons on molecules of this complexity are at present not conceivable — the numerical work involved is prohibitive even with access to modern high-speed digital computers.

A comparatively large number of calculations on substituted benzenes have been carried out in the Hückel  $\pi$ -electron approximation (*cf.* Refs. 1–3). Although the Hückel method involves many drastic simplifications it has nevertheless proved of great value for the systematization of, in particular, a number of ground state properties. The Hückel method in general gives a less satisfactory picture of the excited states of molecules. The self-consistent field (SCF) molecular orbital (MO) method developed by Pariser, Parr and Pople<sup>4-6</sup> has, however, proved to give a very satisfactory description of both ground state and spectral properties of aromatic and conjugated molecules (*cf.* Ref. 7 and references therein). The degree of complexity of this method

requires the use of electronic computers, but a complete SCF calculation on a moderately large molecule may be performed within a reasonably short period of time.

In the present work we have applied the SCF method due to Pariser, Parr and Pople in an investigation of the electronic structure of phenol and dihydroxybenzenes, and as far as the effects of hyperconjugation may be neglected the calculations should also be applicable to anisole and dimethoxybenzenes. For these molecules nuclear magnetic resonance (NMR) shielding data for both  $^{13}\text{C}$  and  $^1\text{H}$  nuclei are available, which makes possible a comparison of the theoretically calculated electron distributions with those inferred from NMR measurements.

Fischer-Hjalmarsson has recently published a thorough discussion on the evaluation of some one and two center integrals which appear in the Pariser-Parr-Pople SCF method and she has suggested a new and internally consistent method for the evaluation of these integrals.<sup>8</sup> In the present paper we have largely followed her scheme. Since there exists some uncertainty concerning the value of the parameters involving the heteroatom we have made a systematic variation of these parameters in order to examine some of the underlying assumptions by correlation with experimental data. It has been possible to perform a comparatively large number of SCF calculations within a reasonable period of time — including configurational interactions involving all singly excited states as well — thanks to a highly efficient computer program.

## 2. OUTLINE OF THE METHOD AND CHOICE OF PARAMETERS

In the present work the  $\pi$ -electron approximation has been used *i.e.* only the  $\pi$ -electrons are treated explicitly — the  $\sigma$ -electrons and the bare atomic nuclei are considered as a “core” in the field of which the  $\pi$ -electrons move. For a molecule with  $n$  electrons of  $\pi$ -symmetry the Hamiltonian for the  $\pi$ -electrons can be written<sup>7</sup>

$$H = \sum_{i=1}^n H(i)^{\text{core}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} \quad (1)$$

In eqn. (1) the one electron operator  $H(i)^{\text{core}}$  may be written as

$$H(i)^{\text{core}} = T(i) + U(i)^{\text{core}} \quad (2)$$

where  $T(i)$  is the kinetic energy operator of electron  $i$  and  $U(i)^{\text{core}}$  is the potential field operator of the core (atomic nuclei plus  $\sigma$ -electrons).

For the ground state the total wavefunction  $\psi_0$  for the  $n$   $\pi$ -electrons has been written as a Slater determinant of one-electron molecular orbitals  $\varphi_r(i)$ . The molecular orbitals are in turn written as linear combinations of atomic orbitals LCAO

$$\varphi_r(i) = \sum_p C_{rp} \chi_p \quad (3)$$

where  $\chi_p$  is an atomic orbital centered on the atom  $p$ .

Hall<sup>9</sup> and Roothaan<sup>10</sup> have derived the conditions for obtaining the Hartree-Fock self-consistent field (SCF) orbitals for LCAO MO's

$$\sum_r C_{rj} (F_{pr} - \varepsilon_j S_{pr}) = 0 \quad (4)$$

where  $S_{pr}$  is an element of the overlap matrix  $S$

$$S_{pr} = \int \chi_p^* \chi_r d\tau \quad (5)$$

(It has been assumed that  $S_{pr} = \delta_{pr}$ <sup>4-6</sup>).

$F_{pr}$  in eqn. (4) are the matrix elements of the Hartree-Fock operator and the eigenvalues  $\varepsilon_j$  are the roots of the secular equation

$$|F_{pr} - \varepsilon_j \delta_{pr}| = 0$$

For a closed shell configuration in which each occupied space orbital lodges two electrons with opposite spins, the matrix elements  $F_{pr}$  may be written<sup>10</sup>

$$F_{pr} = H_{pr}^{\text{core}} + 2 J_{pr} - K_{pr} \quad (6)$$

where  $H_{pr}^{\text{core}}$  are the matrix elements in the atomic orbital representation of the operator  $H(i)$  in eqn. (1) and  $J_{pr}$  and  $K_{pr}$  are elements defined as

$$J_{pr} = \sum_j (pr/jj) \quad (7)$$

$$K_{pr} = \sum_j (pj/jr) \quad (8)$$

The summations in the two above equations are to be taken over all filled space orbitals  $\varphi_j$ . The right-hand symbols in eqns. (7) and (8) are defined as the following integral

$$(\kappa\lambda/jk) = \iint \varphi_\kappa^*(1) \varphi_\lambda(1) \frac{1}{r_{12}} \varphi_j^*(2) \varphi_k(2) d\tau_1 d\tau_2 \quad (9)$$

where  $\varphi_\kappa$ ,  $\varphi_\lambda$  etc. are LCAO MO's.

Under the assumption of zero differential overlap ( $\chi_p^* \chi_q = 0$  for  $p \neq q$ ) adopted in the Pariser-Parr-Pople scheme the calculations of the matrix elements  $J_{kr}$  and  $K_{kr}$  are in the atomic orbital representation reduced to the calculation of integrals of the type ( $pp/qq$ ):

$$(pp/qq) = \iint \chi_p^*(1) \chi_q^*(2) \frac{1}{r_{12}} \chi_p(1) \chi_q(2) d\tau_1 d\tau_2 \quad (10)$$

The matrix elements  $H_{pr}^{\text{core}}$  may be divided into one-center and two-center integrals

$$\alpha_p \equiv H_{pp}^{\text{core}} = \int \chi_p^*(i) H(i) \chi_p(i) d\tau_i \quad (11)$$

$$\beta_{pq} \equiv H_{pq}^{\text{core}} = \int \chi_p^*(i) H(i) \chi_q(i) d\tau_i \quad (12)$$

In conformity with Pariser and Parr<sup>4</sup> it has been assumed that  $\beta_{pq} = 0$  when the atoms  $p$  and  $q$  are non-neighbours.

The Coulomb attraction integrals  $\alpha_q$  may according to the arguments of Goeppert-Mayer and Sklar<sup>12</sup> be written<sup>4</sup>

$$\alpha_p = W_p - \sum_{q \neq p} [(pp/qq) + (q:pp)] - \sum_r (r:pp) \quad (13)$$

where the atoms  $q$  are charged and the atoms  $r$  uncharged in the core;  $(q:pp)$  and  $(r:pp)$  are penetration integrals.<sup>4</sup> (Note that for an atom  $p$  that contributes *two* electrons to the  $\pi$ -electron system the summation shall include also one  $(pp/pp)$  term.)

In eqn. (13)  $W_p$  is equal to

$$W_p = \int \chi_p^*(i) [T(i) + U_p(i)] \chi_p(i) d\tau_i \quad (14)$$

where  $U_p(i)$  is the part of the core potential due to the atomic nucleus  $p$  and all its inner-shell electrons;  $W_p$  is simply the energy of an electron in a  $2p$  atomic orbital of atom  $p$ .

*Excitation energies.* The energy of a singlet state  ${}^1E(i \rightarrow m)$  obtained by exciting an electron from a doubly occupied MO  $\varphi_i$  to an empty MO  $\varphi_m$  has been calculated from the equation<sup>10</sup>

$${}^1E(i \rightarrow m) = E_0 - \varepsilon_i + \varepsilon_m - J(mm/ii) + 2K(mi/mi) \quad (15)$$

where  $E_0$  is the energy of the ground state,  $\varepsilon_i$  and  $\varepsilon_m$  are the Hartree-Fock orbital energies of the MO's  $\varphi_i$  and  $\varphi_m$ .

The energy of the corresponding triplet state  ${}^3E(i \rightarrow m)$  has been calculated according to<sup>10</sup>

$${}^3E(i \rightarrow m) = E_0 - \varepsilon_i + \varepsilon_m - J(mm/ii) \quad (16)$$

When the excited states are described by the superposition of a number of singly excited configurations  ${}^1\psi(i \rightarrow m)$ ,  ${}^1\psi(j \rightarrow n)$  etc. matrix elements of the total  $\pi$ -electron Hamiltonian in eqn. (1) connecting different configurations have to be evaluated. These matrix elements have been calculated from the expressions<sup>11</sup>

$$\int {}^1\psi(i \rightarrow m) H {}^1\psi(j \rightarrow n) d\tau = -J(mn/ij) + 2K(mj/in) \quad (17)$$

$$\int {}^3\psi(i \rightarrow m) H {}^3\psi(j \rightarrow n) d\tau = -J(mn/ij) \quad (18)$$

The oscillator strength  $f$  of an electronic transition from the ground state  $\psi_0$  to an excited state  $\psi(i \rightarrow m)$  has been calculated according to the formula given by Mulliken and Rieke<sup>13</sup>

$$f = 1.085 \times 10^{11} \nu |\bar{Q}|^2 \quad (19)$$

where  $\nu$  is the wave number of the transition in  $\text{cm}^{-1}$  and  $Q$  the transition moment

$$\bar{Q} = \int \psi_0^* \sum_s \bar{r}_s {}^1\psi(i \rightarrow m) d\tau = \sqrt{2} \int \varphi_i^* \bar{r} \varphi_m d\tau \quad (20)$$

where  $r$  is the position vector of the electron.

*Parameter values.* As is well known, the use of purely theoretical values of the one center integrals ( $pp/pp$ ) will result in an overestimate of atomic ionization potentials and lead to too high negative electron affinity. Pariser<sup>14</sup> suggested the use of semi-empirical values of the one center integrals and proposed the following relation

$$(pp/pp) = I(p) - EA(p) \quad (21)$$

where  $I(p)$  and  $EA(p)$  are the appropriate valence state ionization potential and electron affinity, respectively. Fischer-Hjalmars<sup>8,15</sup> has recently suggested the use of the theoretical expression

$$(pp/pp) = F_0 + 4F_2 \quad (22)$$

where  $F_0$  and  $F_2$  are the Slater-Condon parameters (*cf.* Ref. 16) — numerical values of which may be obtained from experimental term values in the atomic spectra of the atom under consideration.<sup>15</sup>

In the present calculation we have employed the following values adopted by Fischer-Hjalmars<sup>8</sup>

$$(cc/cc) = 11.76 \text{ eV} = 0.4322 \text{ a.u.}$$

$$(oo/oo) = 18.79 \text{ eV} = 0.6906 \text{ a.u.}$$

A number of methods for the calculation of the two-electron twocenter integrals ( $pp/qq$ ) have been suggested in the literature. In this work we have used the following expression due to Fischer-Hjalmars and based on an estimate of the "remainder energy" in the case of interaction between  $2p$   $\pi$ -electrons<sup>8</sup>

$$(pp/qq) = \frac{1}{2} (\zeta_p + \zeta_q) [8.5742 - 1.4005 \varrho + 0.16724 \varrho^2 - 0.00961 \varrho^3] \text{ (eV)} \quad (23)$$

where  $\zeta_p$  and  $\zeta_q$  are the orbital exponents in the Slater  $2p$   $\pi$ -orbital of the atoms  $p$  and  $q$ , respectively, and  $\varrho$  is a "scaled" radius defined by

$$\varrho = \frac{1}{2} (\zeta_p + \zeta_q) R \quad (24)$$

where  $R$  is the interatomic distance in atomic units.

The following  $\zeta$  values have been used:  $\zeta_c = 1.56$  and  $\zeta_o = 2.275$ .

The relation (23) is valid in the region  $3.0 \leq \varrho \leq 7.5$  a.u. For larger values of  $\varrho$  the integrals ( $pp/qq$ ) have been calculated by using the uniformly charged sphere approximation first introduced by Parr.<sup>17</sup>

The one-electron one-center integrals  $\alpha_p = \langle p | H^{\text{core}} | p \rangle$  may be evaluated from eqns. (14) and (15). In Pariser, Parr, Pople type SCF calculations of hydrocarbon molecules the penetration integrals appearing in eqn. (13) have sometimes been neglected. In most unsaturated hydrocarbons studied in the  $\pi$ -electron approximation each carbon has three nearest neighbour atoms — hydrogen or carbon. With the bond distances commonly encountered in such systems the hydrogen penetration integrals are of the same order of magnitude as the carbon penetration integrals.<sup>8,18</sup> The penetration integrals fall off very rapidly with distance<sup>18,19</sup> and the contributions from atoms other than the nearest neighbours are generally small. This means that in un-

saturated hydrocarbons the contributions to  $\alpha_p$  due to the penetration terms will be approximately constant for all atoms explicitly considered in the calculations.<sup>8</sup> In molecules with heteroatoms it is not necessarily always a good approximation to regard the contributions from the penetration as constant for all atoms. In the present paper we have followed the idea of Fischer-Hjalmar and considered the "effective"  $W_p$ -values  $W_p'$

$$W_p' = W_p - \sum_{q \neq p} (q:pp) - \sum_r (r:pp) \quad (25)$$

as basic semiempirical parameters. The value of  $W_c'$  used in the present work has been determined from the experimental ionization energy of ethylene (10.515 eV)<sup>8</sup>

$$W_c' = -9.59 \text{ eV}$$

For atoms which contribute *two* electrons to the  $\pi$ -electron system it has been suggested that  $-W_p'$  be set equal to the first ionization potential of the aliphatic compound  $C_2H_5X(p)$  where  $X(p) = OH$  for  $W_O$ ,  $X(p) = NH_2$  for  $W_N$  etc.<sup>8</sup> In this suggestion it is implied that the ionization corresponds to the removal of one electron in a lone-pair  $2p$  orbital. This method of evaluating  $W_p'$  has recently been employed by Grabe in SCF calculations on heteroaromatic compounds.<sup>20</sup>

The first ionization potential of  $C_2H_5OH$  has been determined to  $10.65 \pm 0.05$  eV by the electron impact method<sup>21</sup> and  $10.48 \pm 0.05$  eV by the photoionization method.<sup>22</sup> Since the interpretation of the ionization processes is by no means unambiguous we have investigated the influence of the value of  $W_O$  on the calculated molecular properties and employed three different values of  $W_O'$ :  $-10.50$ ;  $-11.50$  and  $-12.50$  eV. The smallest and the largest of these values correspond approximately to the ionization potentials observed for  $C_2H_5OH$  and  $H_2O$ , respectively.

It has been suggested by Fischer-Hjalmar<sup>8</sup> that the one electron two-center integrals  $\beta_{pq} = \int \chi_p(i) H(i) \chi_q(i) d\tau_i$  should be calculated according to

$$\beta_{pq} = S_{pq} \{c_1[(pp/pp) + (qq/qq)] + c_2(pp/qq)\} \quad (26)$$

where  $S_{pq}$  is the overlap integral of the two  $2p\pi$  orbitals centered on atoms  $p$  and  $q$  and the coefficients  $c_1$  and  $c_2$  are dependent on the number of electrons ( $n_p$  and  $n_q$ ) contributed to the  $\pi$ -electron system by the atoms  $p$  and  $q$ .

Eqn. (26) has recently been applied by Skancke<sup>23,24</sup> in SCF MO calculations on a number of aromatic hydrocarbons. Excellent agreement between predicted and observed bond distances and ionization potentials were obtained. In the above work the values of the coefficients  $c_1$  and  $c_2$  in eqn. (26) were evaluated by using values of  $\beta_{pq}$  derived from an analysis of the electronic spectra of two reference compounds with different internuclear carbon-carbon distances (benzene and ethylene).

Since the coefficients  $c_1$  and  $c_2$  in eqn. (26) depend on  $n_p$  and  $n_q$  the values of these coefficients derived for  $=C-C=$  bonds are not necessarily also valid for  $=C-\ddot{O}-$  bonds. If one uses the coefficients obtained for carbon-carbon bonds (assuming the values  $\beta = -2.39$  eV for benzene ( $R_{cc} = 1.397$

Å) and  $\beta = -2.85$  eV for ethylene ( $R_{cc} = 1.337$  Å))  $\beta_{C-O}$  for a carbon-oxygen distance of 1.36 Å equals about  $-0.78$  eV and for a distance of 1.22 Å  $\beta_{C-O}$  equals  $-1.56$  eV. These values are very much smaller than  $\beta_{C-O}$  values previously employed by other authors:  $\beta$  values for carbonyl bonds ( $R = 1.22$  Å) around  $-2.9$  to  $-3.0$  eV have been shown to reproduce the  $\pi-\pi^*$  transition energies and the ionization potentials of formaldehyde<sup>25</sup> when similar values of the integrals ( $cc/cc$ ), ( $oo/oo$ ) and ( $cc/oo$ )<sub>1.22 Å</sub> as employed in this work were used.

In view of the difficulty in finding a completely unambiguous method for the calculation of the  $\beta_{C-O}$  integrals we have (without any pretence of completeness) treated these as basic semiempirical parameters and performed the SCF calculations with four values:  $-1.30$ ,  $-1.50$ ,  $-1.70$  and  $-1.90$  eV.

*Structural data.* The  $\pi$ -electron skeleton of all compounds has been assumed to be planar. The carbon-carbon distance in the aromatic rings was assumed to be equal to that in benzene (1.397 Å). The assumption that substituents on aromatic rings do not appreciably affect the geometry of the ring is supported by a careful study of the structure of benzonitrile by Bak *et al.*<sup>92</sup>

The distance between the aromatic carbon and the oxygen in the OH- (or OCH<sub>3</sub>-) groups has been taken equal to 1.36 Å. This latter value is in agreement with X-ray crystallographic studies of resorcinol, phloroglucinol, salicylic acid, 1,4-dimethoxybenzene,<sup>26</sup> and *p*-nitrophenol.<sup>27</sup>

It may be mentioned that the potential barrier for the internal rotation of the OH group and the aromatic ring in phenol has been determined to  $3.1 \pm 0.3$  kcal/mole by microwave spectroscopy by Kojima<sup>28</sup> who also concludes that the molecule is planar in its equilibrium configuration.

### 3. NUMERICAL CALCULATIONS

Core integrals, repulsion integrals and a starting charge and bond order matrix (obtained by a Hückel-type calculation) were calculated by means of an ALGOL-60 program which as an output delivered a deck of punched cards containing all pertinent data for the subsequent SCF calculations. The self-consistent field calculations were then performed by means of a program written in Fortran IV.\*

In connection with the present work a special configuration interaction (CI) program has been developed in which all matrix elements of the secular equation for singlet and triplet states were calculated. Eigenvalues and eigenvectors as well as transition moments and transition frequencies are obtained as output data. The CI program requires instructions as to which states are to be mixed; if *all* possibly singly excited states are to be mixed this can, however, be accomplished by means of a single steering signal.

\* The SCF program was written by Mr. P. Eisenberger and put at our disposal by Prof. I. Fischer-Hjalmars, University of Stockholm.

Table 1a. Results of the SCF-LCAO-MO calculations on the ground state of phenol (anisole).

$W \delta'$ (eV)	$\beta_{C-\delta}$ (eV)	$\rho_1$	$\rho_2$	$\rho_3$	$\rho_4$	$\rho_5$	$\rho_7$	$P_{12}$	$P_{23}$	$P_{34}$	$P_{17}$	$\mu\pi$ (D)	$I$ (eV)
	-1.30	0.9892	1.0173	0.9949	1.0093	1.9771	0.6588	0.6678	0.6660	0.1514	0.285	9.16	
-10.50	-1.50	0.9857	1.0228	0.9933	1.0121	1.9700	0.6564	0.6682	0.6658	0.1737	0.374	9.10	
	-1.70	0.9818	1.0288	0.9916	1.0153	1.9621	0.6535	0.6686	0.6655	0.1956	0.473	9.02	
	-1.90	0.9774	1.0355	0.9897	1.0187	1.9536	0.6504	0.6690	0.6652	0.2171	0.581	8.93	
	-1.30	0.9897	1.0173	0.9949	1.0093	1.9771	0.6568	0.6682	0.6658	0.1701	0.348	9.07	
-11.50	-1.50	0.9864	1.0263	0.9923	1.0142	1.9623	0.6538	0.6686	0.6655	0.1945	0.455	8.98	
	-1.70	0.9826	1.0331	0.9903	1.0178	1.9528	0.6504	0.7791	0.6652	0.2183	0.572	8.89	
	-1.90	0.9784	1.0405	0.9882	1.0218	1.9425	0.6467	0.6697	0.6649	0.2414	0.698	8.80	
	-1.30	0.9909	1.0237	0.9930	1.0131	1.9625	0.6540	0.6686	0.6655	0.1934	0.436	8.90	
-12.50	-1.50	0.9879	1.0308	0.9910	1.0170	1.9517	0.6502	0.6692	0.6651	0.2200	0.565	8.80	
	-1.70	0.9844	1.0386	0.9887	1.0212	1.9400	0.6461	0.6698	0.6647	0.2357	0.704	8.70	
	-1.90	0.9805	1.0469	0.9863	1.0257	1.9275	0.6416	0.6705	0.6643	0.2705	0.851	8.60	

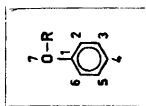
(R = H or CH<sub>3</sub>)



Table 1b. Results of the SCF-LCAO-MO calculations on the ground state of 1,2-dihydroxy (dimethoxy) benzene.

(R = H or CH<sub>3</sub>)

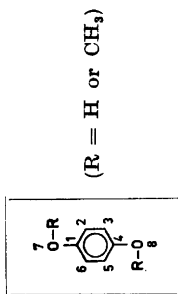
$W\sigma'$ (eV)	$\beta_C-\delta$ (eV)	$\varrho_1$	$\varrho_2$	$\varrho_3$	$\varrho_4$	$\varrho_5$	$\varrho_6$	$\varrho_7$	$p_{12}$	$p_{23}$	$p_{45}$	$p_{56}$	$p_{37}$	$\mu\pi$ (D)	$I$ (eV)
-1.30	1.0170	1.0131	1.0057	1.9642	0.6571	0.6426	0.6667	0.6652	0.1869	0.730	8.64				
-1.50	1.0221	1.0162	1.0073	1.9543	0.6546	0.6358	0.6651	0.2108	0.938	8.47					
-1.70	1.0277	1.0193	1.0091	1.9439	0.6521	0.6285	0.6659	0.2333	1.160	8.30					
-1.90	1.0338	1.0223	1.0109	1.9330	0.6496	0.6208	0.6653	0.2546	1.349	8.14					
-1.30	1.0145	1.0087	1.0046	1.9721	0.6591	0.6478	0.6667	0.6655	0.1654	0.588	8.86				
-1.50	1.0189	1.0110	1.0060	1.9641	0.6571	0.6422	0.6665	0.6654	0.1877	0.762	8.73				
-1.70	1.0238	1.0132	1.0076	1.9554	0.6550	0.6361	0.6662	0.6654	0.2089	0.951	8.58				
-1.90	1.0292	1.0154	1.0092	1.9462	0.6528	0.6295	0.6657	0.6655	0.2292	1.154	8.43				
-1.30	1.0126	1.0058	1.0039	1.9778	0.6606	0.6516	0.6667	0.6658	0.1479	0.484	9.01				
-1.50	1.0165	1.0073	1.0051	1.9712	0.6589	0.6469	0.6666	0.6657	0.1686	0.631	8.90				
-1.70	1.0208	1.0089	1.0064	1.9639	0.6571	0.6418	0.6663	0.6656	0.1884	0.793	8.77				
-1.90	1.0256	1.0104	1.0078	1.9561	0.6552	0.6362	0.6660	0.6657	0.2075	0.969	8.64				

Table 1c. Results of the SCF-LCAO-MO calculations on the ground state of 1,3-dihydroxy (dimethoxy) benzene.

(R = H or CH<sub>3</sub>)

$W'_i$ (eV)	$\beta_{C-O}$ (eV)	$\varrho_1$	$\varrho_2$	$\varrho_3$	$\varrho_4$	$\varrho_7$	$p_{12}$	$p_{23}$	$p_{34}$	$p_{28}$	$\mu\pi$ (D)	$I$ (eV)
-10.50	-1.30	1.0476	0.9842	1.0364	0.9863	1.9625	0.6557	0.6529	0.6674	0.1942	0.435	8.70
	-1.50	1.0618	0.9792	1.0472	0.9823	1.9515	0.6524	0.6486	0.6676	0.2213	0.562	8.55
	-1.70	1.0773	0.9737	1.0589	0.9780	1.9397	0.6488	0.6439	0.6678	0.2474	0.700	8.41
	-1.90	1.0940	0.9678	1.0713	0.9734	1.9272	0.6443	0.6388	0.6681	0.2727	0.846	8.27
-11.50	-1.30	1.0403	0.9839	1.0307	0.9884	1.9710	0.6581	0.6560	0.6671	0.1708	0.348	8.91
	-1.50	1.0528	0.9789	1.0400	0.9849	1.9622	0.6554	0.6526	0.6674	0.1956	0.454	8.78
	-1.70	1.0665	0.9733	1.0504	0.9811	1.9525	0.6525	0.6487	0.6676	0.2198	0.570	8.65
	-1.90	1.0813	0.9672	1.0615	0.9769	1.9421	0.6492	0.6445	0.6678	0.2434	0.695	8.52
-12.50	-1.30	1.0348	0.9842	1.0263	0.9900	1.9770	0.6598	0.6583	0.6671	0.1521	0.285	9.04
	-1.50	1.0458	0.9792	1.0346	0.9869	1.9699	0.6576	0.6555	0.6672	0.1747	0.374	8.93
	-1.70	1.0579	0.9737	1.0437	0.9835	1.9619	0.6551	0.6523	0.6674	0.1969	0.472	8.82
	-1.90	1.0712	0.9676	1.0536	0.9798	1.9533	0.6524	0.6488	0.6676	0.2188	0.580	8.70

Table 1d. Results of the SCF-LCAO-MO calculations on the ground state of 1,4-dihydroxy (dimethoxy) benzene.



$W\bar{O}'$ (eV)	$\beta_{C-\bar{O}}$ (eV)	$e_1$	$e_2$	$e_7$	$p_{12}$	$p_{23}$	$p_{17}$	$I$ (eV)
-10.50	-1.30	1.0029	1.0168	1.9638	0.6634	0.6702	0.1890	
	-1.50	1.0033	1.0217	1.9536	0.6498	0.6710	0.2139	8.33
	-1.70	1.0034	1.0271	1.9428	0.6458	0.6717	0.2375	8.15
	-1.90	1.0032	1.0328	1.9315	0.6417	0.6723	0.2599	7.97
-11.50	-1.30	0.9998	1.0143	1.9718	0.6563	0.6694	0.1671	
	-1.50	0.9994	1.0187	1.9636	0.6533	0.6700	0.1901	8.60
	-1.70	0.9989	1.0234	1.9546	0.6501	0.6707	0.2122	8.43
	-1.90	0.9981	1.0286	1.9451	0.6466	0.6712	0.2335	8.28
-12.50	-1.30	0.9978	1.0124	1.9776	0.6584	0.6689	0.1493	
	-1.50	0.9970	1.0163	1.9708	0.6559	0.6694	0.1705	8.78
	-1.70	0.9959	1.0205	1.9633	0.6532	0.6699	0.1911	8.65
	-1.90	0.9947	1.0251	1.9553	0.6503	0.6704	0.2111	8.52

## 4. RESULTS AND DISCUSSION

In the following section the results of the SCF-LCAO-MO calculations will be presented. The discussion has been divided into two parts: first, a number of molecular quantities best characterized as ground state properties are considered and secondly the electronic transition energies are discussed. Experimental data for both phenols and methoxybenzenes will be concurrently examined.

## 4.1. Ground state properties

The results of the SCF-LCAO-MO calculations on the ground states of phenol and the three dihydroxybenzenes (or the corresponding methoxy-compounds if hyperconjugative effects are neglected) are summarized in Table 1. The symbols used are:  $q_i$  = the gross atomic population<sup>29</sup> or charge density of atom  $i$ ,  $p_{ij}$  = the bond order between atoms  $i$  and  $j$ ,  $\mu^\pi$  = the dipole moment due to the  $\pi$ -electrons in Debye units and  $I$  = the ionization potential in eV calculated from the energy of the highest occupied MO by the use of Koopmans' theorem (see below).

*Ionization potentials.* Ionization potentials are defined as  $E_{\text{ion}} - E_0$  where  $E_{\text{ion}}$  and  $E_0$  are the total energies of the ionized and ground states respectively. According to Koopmans' theorem<sup>10,30</sup> this difference may be approximated with the negative of the Hartree-Fock orbital energy in the ground state for the electron removed. Ionization potentials calculated by the application of Koopmans' theorem may consequently be considered as ground state properties.

From an experimental point of view two types of ionization potential are usually recognized. Ionization potentials determined by the photoionization method developed by Watanabe *et al.*<sup>31</sup> refer to the ionized molecule in its lowest vibrational state and are sometimes referred to as "adiabatic" ionization potentials. Values determined by the electron impact method are on the other hand regarded as "vertical" as a consequence of the Franck-Condon principle. "Adiabatic" and "vertical" ionization potentials differ frequently by a few tenths of an electron volt, the adiabatic photoionization values being the lowest.

The validity of Koopmans' theorem has recently been discussed by several authors.<sup>32-34</sup> Birss and Laidlaw have studied the helium, lithium, and beryllium atoms as well as the pyridine molecule. SCF calculations were performed both on the neutral and the ionized states. Good agreement was found between ionization potentials calculated as differences between energies of the ions and the corresponding neutral parents on the one hand and ionization potentials calculated by Koopmans' theorem on the other hand. The latter values were actually found to be in better agreement with the experimental ionization potentials. The authors conclude that Koopmans' theorem is valid when the ionization energy is a small fraction of the total electronic energy of the parent molecular or atomic system. In contrast, Hoyland and Goodman have concluded that Koopmans' theorem when applied to aromatic hydrocarbons leads to ionization potentials in excess of the experimental values by 2 to 4 eV. In recent SCF-LCAO-MO calculations by Skancke<sup>23,24</sup> on the aromatic hydro-

carbons naphthalene, anthracene, biphenylene, phenanthrene, chrysene, and perylene, however, good agreement was obtained between experimental ionization potentials and theoretical values obtained by Koopmans' theorem.

It appears that the particular choice of  $W_c'$  employed by Skancke ( $-9.59$  eV, *i.e.* the same value as used in this work) and which is based upon the ionization potential of ethylene is very suitable for ionization potential calculations.

Only a limited number of experimental ionization potentials are available for phenols and methoxybenzenes. For phenol two relatively congruous values determined by the electron impact method are available:  $9.01 \pm 0.05$  eV,<sup>35</sup> and  $9.03$  eV.<sup>35</sup> For the same compound the ionization potential has also been determined by Watanabe *et al.* by the photoionization technique to be  $8.50$  eV.<sup>37</sup>

For anisole the ionization potential has been determined to be  $8.83$  eV by the electron impact method.<sup>38</sup> For the other compounds ionization data have not been found in the literature. As can be seen from Table 1a the calculated ionization potentials for phenol (anisole) are of the same order as the experimental values. In particular the almost perfect agreement between the electron impact values for phenol and the theoretical values obtained with  $W_{\delta'} = -10.50$  and  $\beta_{C-\delta} = -1.70$  eV may be noted.

*Intermolecular charge-transfer transition energies.* The methoxy derivatives of benzene form charge transfer complexes with a number of molecules with pronounced acceptor properties such as tetracyanoethylene (TCNE), 1,2,4,5-tetracyanobenzene (TCNB), *p*-chloroanil (PCA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDPQ). The charge-transfer spectra of these complexes have been determined by Zweig *et al.*<sup>40,41</sup> who have also interpreted the experimental results within the theoretical framework of Hückel-type MO calculations. The experimental transition energies for the charge-transfer complexes are summarized in Table 2.

In the first approximation the energy  $\Delta E_{CT}$  connected with an intermolecular charge-transfer transition may be taken<sup>42,43</sup> as

$$\Delta E_{CT} = I_D - EA_A - C \quad (27)$$

where  $I_D$  is the ionization potential of the donor molecule,  $EA_A$  is the electron affinity of the acceptor molecule and  $C$  is the Coulomb interaction energy between the oppositely charged donor and acceptor molecules. The latter energy is difficult to calculate since an accurate evaluation would require

Table 2. Charge-transfer transition energies of methoxybenzene complexes.<sup>40,41</sup>

Donor compound	Acceptor compound			
	tetracyano- ethylene (eV)	1,2,4,5- tetracyano- benzene (eV)	<i>p</i> -chloroanil (eV)	2,3-dichloro-5,6- dicyano- <i>p</i> - benzoquinone (eV)
anisole	2.44	3.37	2.76	2.22
1,2-dimethoxybenzene	2.10	2.97	2.42	1.92
1,3-dimethoxybenzene	2.25	—	—	1.98
1,4-dimethoxybenzene	2.00	2.82	2.28	1.74

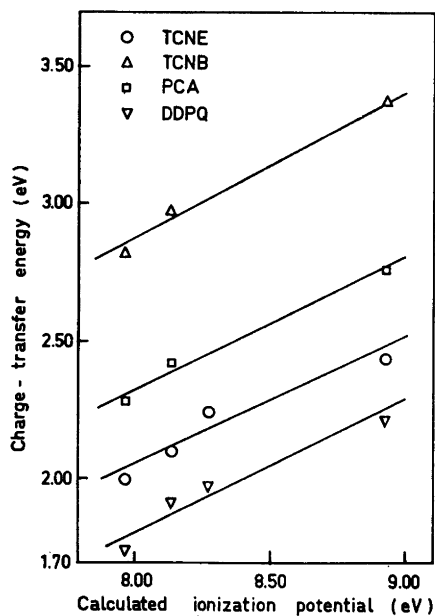


Fig. 1. A graph of energies of experimental charge-transfer absorption bands in anisole and dimethoxy benzene complexes versus theoretical ionization potentials calculated using the parameter values  $W_{\delta'} = -10.50$  eV and  $\beta_{C-O} = -1.90$  eV. The abbreviations of the acceptor compounds are: TCNE = tetracyanoethylene, TCNB = 1,2,4,5-tetracyanobenzene, PCA = *p*-chloroanil and DDPQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Experimental data are due to Zweig *et al.*<sup>40,41</sup>

a detailed knowledge of the structure of the charge-transfer complex. Furthermore, precise electron affinity data are known only for a few acceptor molecules. However, if one restricts oneself to the study of a series of charge-transfer complexes with a common acceptor molecule and if the Coulomb interaction energy is reasonably constant in the series one would according to eqn. (27) expect a linear correlation between the ionization potential of the donor and the transition energy of the charge-transfer band. Linear correlations of this kind have in fact been found for a number of charge-transfer complexes.<sup>44,46</sup> It appears that the Coulomb term in eqn. (27) is either fairly constant when the complexes studied are closely related structurally, or that the Coulomb term varies in an approximately regular manner with the ionization potentials.

A comparison of the theoretical ionization potentials listed in Tables 1a-d and the energies of the observed charged-transfer transitions in Table 2 shows that good correlation is obtained with data calculated using  $W_{\delta'} = -10.50$  eV — the correlation is less good for the data obtained using  $W_{\delta'} = -11.50$  and with  $W_{\delta'} = -12.50$  eV the correlation is very poor. A graph showing the correlation between  $\Delta E_{CT}$  and  $I$  calculated using  $\beta_{C-O} = -1.90$  eV is shown in Fig. 1. The slopes of the correlation lines are nearly the same for all four acceptors involved. The changes in the transition energies are slightly less than can be accounted for on the basis of changes in ionization potentials. This fact has also been noted for charge-transfer complexes where experimental ionization potentials have been available.

*Dipole moments.* If the dipole moment due to the  $\pi$ -electrons in a substituted benzene were a directly measurable molecular property, this would give a strong clue to the  $\pi$ -electron distribution in the molecule. The "mesomeric"

$\pi$ -moments must, however, be estimated from the total molecular dipole moments using several assumptions of sometimes questionable validity.

The total dipole moments of hydroxy and methoxybenzenes have been measured and discussed by several workers.<sup>47,57</sup> The dipole moments of the hydroxybenzenes seem in general to be less accurate presumably due to effects of hydrogen bonding.<sup>48</sup>

One of the most pronounced difficulties involved in the calculation of mesomeric moments from a comparison of dipole moments of aromatic and aliphatic compounds with the same substituent X, is the estimate of the change of the  $\sigma$ -moment in the C—X bond. It was first pointed out by Walsh<sup>58</sup> that if one varies the hybridization of the carbon atom in a C—X bond the effective electronegativity of the carbon atom should increase with increasing *s*-character in the orbital used by the carbon to form the C—X bond. Accordingly, the polarity of a  $C_{sp^s}$ -X bond should be quite different from that of a  $C_{sp^s}$ -X bond if the hybridization of the X-atom remains essentially the same in the both cases (*cf.* also Ref. 59). This hybridization-dependent electronegativity of carbon is experimentally apparent in the case of C—H bonds as the increasing acidity of the C—H group in the series ethane < ethylene < acetylene. Also studies of the absolute intensity of infra-red absorption bands associated with C—H bending vibrations in these and analogous compounds indicate different polarity in the C—H bonds (*cf.* discussion in Ref. 60).

In the earliest work on mesomeric moments in substituted benzenes done by Sutton<sup>61</sup> and Groves and Sugden<sup>62</sup> the hybridization effects on bond electronegativity were not recognized. Lumbroso *et al.*<sup>50,56</sup> have reinvestigated the mesomeric moments of phenol and anisole taking into consideration the hybridization effects on the C—O bond moment. The values of the  $\pi$ -electron moment,  $\mu^\pi$ , given by Lumbroso and Dumas are: phenol  $0.8 \pm 0.1$  D and anisole  $0.9 \pm 0.1$  D. These two values seem indeed very high and constitute a considerable fraction of the total dipole moments (*ca.* 1.36 D for phenol and *ca.* 1.26 D for anisole).

One of the few substituted benzenes for which the mesomeric moment is known with reasonable accuracy is aniline. From measurements of the total dipole moment of aniline, N,N-dimethylaniline and derivatives with bulky substituents in the 2- and 6-positions — which will force the N,N-dimethyl group out of the plane of the benzene ring and retrench the conjugative interaction — the mesomeric moment was calculated by Fischer<sup>63</sup> to be 0.7 D. Since a number of chemical and physical data (for example the <sup>1</sup>H and <sup>13</sup>C chemical shifts<sup>80</sup>) indicates that the distorting effects of an -OH or -OCH<sub>3</sub> substituent on the  $\pi$ -electron distribution in a benzene ring is less pronounced than that of an -NH<sub>2</sub> or -N(CH<sub>3</sub>)<sub>2</sub> group it would appear that the values of  $\mu^\pi$  for phenol and anisole given by Lumbroso and Dumas are too high. Values of  $\mu^\pi$  somewhat less than 0.6 D seem more likely to us.

As can be inferred from Table 1a the theoretical values of  $\mu^\pi$  are very reasonable. In particular, the parameters which give good values of the ionization potential of phenol and which correlate well with the charge-transfer band energies also give mesomeric moments close to the estimated values (0.4—0.6 D).

No attempts have been made to estimate the mesomeric dipole moments of the 1,2- and 1,3-disubstituted benzenes since the configurations of the substituents in these compounds are somewhat uncertain (*cf.* Ref. 55).

*Nuclear magnetic resonance shielding constants of  $^{13}\text{C}$  and  $^1\text{H}$  nuclei.* The nuclear magnetic shielding constant ( $\sigma$ ) is a molecular quantity which is dependent upon the electronic environment of the nuclei.<sup>64</sup> It is convenient to consider the total shielding ( $\sigma_t$ ) as the sum of three subterms

$$\sigma_t = \sigma_d + \sigma_p + \sigma_s \quad (28)$$

where  $\sigma_d$  is the Lamb diamagnetic contribution related to the electron density in the vicinity of the nucleus,  $\sigma_p$  is a paramagnetic contribution which allows for mixing of excited states into the electronic wave function of the ground state, and  $\sigma_s$ , finally, is a term which includes all contributions due to distant electronic distributions. This last term is commonly further divided into intramolecular contributions due to diamagnetic anisotropy effects of neighbouring groups, to electric field effects arising from molecular dipoles, and to intermolecular interactions.

Investigations on a number of aromatic hydrocarbons, aromatic carbonium ions and carbon ions — where the charge distributions are obtained directly from the molecular symmetry — have indicated that there exists a close correlation between the shielding constants ( $\sigma_i$ ) of the hydrogen atom  $i$  and the  $\pi$ -electron charge density ( $\rho_i$ ) on the contiguous carbon atom.<sup>65-67</sup> From the experimental results as well as by theoretical reasoning<sup>65,68</sup> the following relationship between the proton shielding constant ( $\sigma_i$ ) and the  $\pi$ -electron density ( $\rho_i$ ) was suggested

$$\Delta\sigma_i = K \times (\rho_i - 1) \quad (29)$$

The proportionality constant  $K$  in eqn. 29 is generally agreed to be in the range 6–10 ppm/electron — the actual value preferred by different authors depends on how corrections are applied for variations in induced “ring currents” and also for solvent effects.<sup>65-69</sup>

For a number of substituted benzenes relatively good correlations between proton shielding data and  $\pi$ -electron densities calculated with the Hückel MO method have been found.<sup>70-73</sup> In monosubstituted benzenes the best correlations are generally obtained for the hydrogens *para* to the substituent — for certain substituents the observed proton shieldings in the *ortho* and *meta* positions may deviate considerably from the values expected on the basis of the charge densities as calculated by the Hückel method.<sup>72</sup> It appears likely that a considerable part of the “anomalous” *ortho* shieldings have their root in diamagnetic anisotropy effects and in electric field effects in the case of the most polar substituents. In the particular case of carbonyl groups a considerable number of experimental proton magnetic resonance data on compounds with known conformation indicate that the resonance frequency of protons located in a conical region above or below the trigonal  $\text{>C=O}$  plane is shifted to higher field, whereas the resonance frequency of protons located in the  $\text{>C=O}$  plane is shifted to lower fields (for recent data see Refs. 74–76). For a few aromatic and heteroaromatic aldehydes it has also



been possible to "freeze in" two rotational isomers and directly determine the different shielding for protons "ortho" to the aldehyde group when the C=O bond is "cis" and "trans" to the *ortho* C-H bond.<sup>77-79</sup> The observed shielding differences lie in the range 0.10–0.15 ppm.

At present it is not possible to calculate anisotropy effects and electric field effects with any pretension of accuracy. It appears, however, from the work of Spiesscke and Schneider<sup>80</sup> on the NMR spectra of monosubstituted benzenes, that "extraneous" effects in the present context are small in methoxybenzenes (and presumably also in phenols) and these compounds should thus be comparatively favourable for a study of the connection between nuclear magnetic shielding data and theoretical  $\pi$ -electron densities.

Proton shielding data for phenol and di- and tri-substituted hydroxybenzenes have been measured by Shug and Deck.<sup>70</sup> As a consequence of the limited solubility of the phenols the shielding data had to be extracted from spectra in relatively polar solvents. The primary shielding data were subsequently corrected for the medium effects and extrapolated to shielding data valid for a medium with the dielectric constant  $\epsilon = 1$ . The corrections are based upon a theory<sup>81</sup> which is exactly valid only if no specific solvent-solute interactions occur. The possibility of hydrogen bonding between solvent and solute in the actual case casts some doubt on the reliability of the extrapolation procedure. Shug and Deck also made an attempt to calculate the influence of the electric dipole field of the OH-substituents on the ring proton shielding constants. Both the shielding data extrapolated to  $\epsilon = 1$  and the data "corrected" for the field effects are given in Table 3. Experimental proton shielding data of mono- and di-methoxybenzenes in non-polar solvents have been obtained by Zweig *et al.*<sup>71</sup> and these results are also given in Table 3.

In order to compare the theoretical  $\pi$ -electron densities and the proton shielding data we have performed a least-squares treatment of the coefficients  $K$  and  $K'$  in the equation

$$\Delta\sigma_i = K(q_i - 1) + K' \quad (30)$$

which is the same as eqn. (29) except for the term  $K'$  which allows for the fact that the correlation line will not necessarily pass through the point  $\Delta\sigma_i = 0$  when  $q_i = 1.000$ . The results of the least-squares treatment are summarized in Table 4. The outcome will be discussed below in connection with the discussion of the <sup>13</sup>C-data.

For <sup>13</sup>C nuclei the variations in shielding constants encountered in organic molecules are too large to be understandable solely as due to variations in diamagnetic shielding.

The diamagnetic shielding ( $\sigma_d$ ) can be approximately calculated from the following eqn.<sup>72,83</sup>

$$\sigma_d = (e^2/3 mc^2) \sum_i \langle 1/r_i \rangle \quad (31)$$

where  $\langle 1/r_i \rangle$  is the mean inverse distance of electron  $i$  from the carbon nucleus under consideration. For a Slater-type  $2p$ -orbital the value of  $\langle 1/r_i \rangle$  equals  $Z/2 a_0$  where  $Z$  is the effective nuclear charge and  $a_0$  is the Bohr radius. This

Table 3. Experimental Nuclear Magnetic Resonance data on phenols and methoxybenzenes. The chemical shifts  $\Delta\sigma_i$  (ppm) =  $(\sigma_i - \sigma_{\text{benzene}}) \times 10^6$ . The  $^1\text{H}$ -data for methoxybenzenes are due to Zweig *et al.*<sup>71</sup>, the  $^1\text{H}$ -data for hydroxybenzenes are due to Shug and Deck<sup>70</sup> and the  $^{13}\text{C}$ -data are due to Lauterbur.<sup>82</sup>

Compound	ring position	$\Delta\sigma_i$ for $^1\text{H}$ -nuclei	$\Delta\sigma_i$ for $^{13}\text{C}$ -nuclei
anisole	1	—	— 32.3
	2,6	0.54	+ 14.0
	3,5	0.08	— 2.0
	4	0.54	+ 7.0
1,2-dimethoxybenzene	1,2	—	— 12.6
	3,6	0.53	+ 15.5
	4,5	0.53	+ 6.9
1,3-dimethoxybenzene	1,3	—	— 33.3
	2	1.00	+ 37.0
	4,6	0.89	+ 21.7
	5	0.23	— 2.2
1,4-dimethoxybenzene	1,4	—	— 26.4
	2,3,5,6	0.59	+ 13.1
phenol	1	—	— 27.6
	2,6	0.648 <sup>a</sup>	0.796 <sup>b</sup>
	3,5	0.175 <sup>a</sup>	0.218 <sup>b</sup>
	4	0.458 <sup>a</sup>	0.483 <sup>b</sup>
1,2-dihydroxybenzene	1,2	—	—
	3,6	0.688 <sup>a</sup>	0.879 <sup>b</sup>
	4,5	0.618 <sup>a</sup>	0.686 <sup>b</sup>
1,3-dihydroxybenzene	1,3	—	—
	2	1.232 <sup>a</sup>	1.528 <sup>b</sup>
	4,6	1.151 <sup>a</sup>	1.324 <sup>b</sup>
	5	0.395 <sup>a</sup>	0.512 <sup>b</sup>
1,4-dihydroxybenzene	1,4	—	—
	2,3,5,6	0.716 <sup>a</sup>	0.907 <sup>b</sup>

<sup>b</sup> extrapolated to be valid in a solvent with the dielectric constant  $\epsilon = 1$ .

<sup>a</sup> corrected for electric-dipole effects.

implies that  $\sigma_d$  for a  $^{13}\text{C}$  nucleus will increase only *ca.* 15 ppm when an electron is introduced in a  $2p$ -orbital. Theoretical calculations as well as experimental data indicate that the value of the paramagnetic shielding term  $\sigma_p$  largely determines the total shielding for  $^{13}\text{C}$ -nuclei.

Table 4. Correlation of proton shielding constants ( $\sigma$ ) and theoretical  $\pi$ -electron densities ( $\rho$ ). Least-squares estimates of  $K$  and  $K'$  in the relation  $4\sigma_i = K(\rho_i - 1) + K'$ .

$W\sigma'$ (eV)	$\beta_{C-\dot{O}}$ (eV)	Proton shielding in phenols. Experimental data according to Shug and Deck <sup>70</sup> cf. Table 3.				Proton shielding in methoxy-benzenes. Experimental data according to Zweig <i>et al.</i> <sup>71</sup> cf. Table 3.			
		$K$	$K'$	$K$	$K'$	$K$	$K'$	$K$	$K'$
-10.50	-1.30	16.8 ± 2.3	0.43 ± 0.05	20.2 ± 3.0	0.52 ± 0.07	14.2 ± 1.8	0.34 ± 0.04	14.2 ± 1.8	0.34 ± 0.04
	-1.50	12.7 ± 2.0	0.42 ± 0.06	15.3 ± 2.6	0.51 ± 0.08	11.0 ± 1.4	0.33 ± 0.04	11.0 ± 1.4	0.33 ± 0.04
	-1.70	10.3 ± 1.4	0.43 ± 0.05	12.5 ± 1.8	0.52 ± 0.07	8.7 ± 1.1	0.34 ± 0.04	8.7 ± 1.1	0.34 ± 0.04
	-1.90	8.5 ± 1.2	0.43 ± 0.05	10.3 ± 1.5	0.52 ± 0.07	7.2 ± 0.9	0.34 ± 0.04	7.2 ± 0.9	0.34 ± 0.04
-11.50	-1.30	19.0 ± 3.1	0.42 ± 0.06	22.8 ± 4.0	0.52 ± 0.08	16.4 ± 2.1	0.33 ± 0.04	16.4 ± 2.1	0.33 ± 0.04
	-1.50	14.5 ± 2.4	0.43 ± 0.06	17.5 ± 3.0	0.52 ± 0.08	12.5 ± 1.6	0.33 ± 0.04	12.5 ± 1.6	0.33 ± 0.04
	-1.70	11.5 ± 1.9	0.43 ± 0.06	13.9 ± 2.4	0.52 ± 0.08	10.0 ± 1.3	0.33 ± 0.04	10.0 ± 1.3	0.33 ± 0.04
	-1.90	9.4 ± 1.5	0.43 ± 0.06	11.4 ± 2.0	0.52 ± 0.08	8.1 ± 1.1	0.33 ± 0.04	8.1 ± 1.1	0.33 ± 0.04
-12.50	-1.30	19.8 ± 4.2	0.43 ± 0.08	23.7 ± 5.4	0.53 ± 0.10	17.6 ± 2.8	0.33 ± 0.05	17.6 ± 2.8	0.33 ± 0.05
	-1.50	15.1 ± 3.2	0.43 ± 0.08	18.2 ± 4.1	0.52 ± 0.10	13.4 ± 2.1	0.33 ± 0.05	13.4 ± 2.1	0.33 ± 0.05
	-1.70	12.0 ± 2.5	0.43 ± 0.08	14.4 ± 3.2	0.52 ± 0.10	10.7 ± 1.7	0.33 ± 0.05	10.7 ± 1.7	0.33 ± 0.05
	-1.90	9.9 ± 1.8	0.43 ± 0.08	11.8 ± 2.6	0.52 ± 0.10	8.7 ± 1.4	0.33 ± 0.05	8.7 ± 1.4	0.33 ± 0.05

Measurements of  $^{13}\text{C}$  shielding constants in the iso- $\pi$ -electronic series of compounds cyclopentadienyl anion ( $\text{C}_5\text{H}_5^-$ ), benzene ( $\text{C}_6\text{H}_6$ ), tropylium cation ( $\text{C}_7\text{H}_7^+$ ) and cyclooctatrienyl dianion ( $\text{C}_8\text{H}_8^{2-}$ ) indicate that the  $^{13}\text{C}$ -shielding constants are roughly linearly dependent on the  $\pi$ -electron densities.<sup>67</sup> The constant of proportionality between  $^{13}\text{C}$ -shift and  $\pi$ -electron density is of the order of 200 ppm/electron.<sup>67,82,84</sup>

Now an equation such as (29) cannot account for the variations in  $^{13}\text{C}$ -shielding observed in alternant hydrocarbons<sup>85</sup> where the  $\pi$ -electron density is unity to a good approximation. An approximate theoretical expression relating the  $^{13}\text{C}$ -shielding constant ( $\sigma_i$ ) with the  $\pi$ -electron density ( $\rho_i$ ) and the free valence index ( $F_i$ ) has been derived by Karplus and Pople.<sup>83</sup> The relation is

$$(\sigma_i - \sigma_{\text{benzene}}) \times 10^6 = (86.7 + 46.0 \lambda_x) (\rho_i - 1) + 46.0 (F_i - 0.3987) \quad (32)$$

where the  $^{13}\text{C}$ -shieldings have been referred to the shielding value for benzene and  $\lambda_x$  is a polarity parameter which takes into account some ionic character in the  $\text{C}_i-\text{X}$  bond. For  $\text{X} = \text{H}$  the value of  $\lambda$  is probably small.

The relation due to Karplus and Pople does not seem to provide a possibility for calculating accurate  $^{13}\text{C}$  shielding data in aromatic compounds;<sup>72</sup> in particular, eqn. (32) predicts a dependence of the  $^{13}\text{C}$  shielding constants on the  $\pi$ -electron densities which is about half that found from the measurements on the positive and negative aromatic ions. The variations in the  $^{13}\text{C}$ -shieldings in alternant hydrocarbons can, however, be semiquantitatively accounted for by the variations in the free valency index  $F_i$ .<sup>83</sup>

Accurate experimental  $^{13}\text{C}$ -shielding data on phenol, anisole and the three possible dimethoxybenzenes have been obtained by Lauterbur.<sup>82</sup> His results are summarized in Table 3. (Note that the numbering of the ring positions differs in Tables 1 and 3). In the comparison of the experimental shielding constants and the results of the theoretical calculations we have limited ourselves to the methoxybenzenes in order to have an internally consistent set of data; the  $^{13}\text{C}$ -shieldings in phenol and anisole are, however, very similar. Furthermore, we have treated the shielding data for hydrogen substituted and oxygen substituted carbons separately.

The experimental and theoretical data have been treated in different ways: First we have tried to correlate the experimental shielding constant ( $\sigma_i$ ) with the  $\pi$ -electron densities ( $\rho_i$ ) by means of an equation analogous to that employed for the  $^1\text{H}$ -shielding data

$$\Delta\sigma_i = C(\rho_i - 1) + C' \quad (33)$$

The constants  $C$  and  $C'$  have been obtained by a least-squares treatment. The resulting values of  $C$  and  $C'$  are given in Table 5.

Secondly, we have assumed that the  $^{13}\text{C}$ -shielding depends on the  $\pi$ -electron densities and the free valency index ( $F_i$ ) according to a modified relation of the Karplus-Pople type

$$\Delta\sigma_i = D(\rho_i - 1) + 46 (F_i - 0.3987) + D' \quad (34)$$

Table 5. Correlation of  $^{13}\text{C}$ -shielding constants ( $\sigma$ ) and theoretical  $\pi$ -electron densities ( $\rho$ ). Least-squares estimates of  $C$  and  $C'$  in the relation  $\Delta\sigma_i = C(\rho_i - 1) + C'$  and  $D$  and  $D'$  in the relation  $\Delta\sigma_i = D(\rho_i - 1) + 46 (F_i - 0.3987) + D'$  (cf. section 4.1). Experimental shielding data according to Lauterbur<sup>32</sup> cf. Table 3.

$A$	$W\sigma'$ (eV)	$\beta_{\text{C}-\delta}$ (eV)	Hydrogen-substituted $^{13}\text{C}$ -nuclei in methoxybenzenes				Methoxy-substituted $^{13}\text{C}$ -nuclei in methoxy benzenes			
			$C$	$C'$	$D$	$D'$	$C$	$C'$	$D$	$D'$
-10.50		-1.30	511 ± 36	+ 3.8 ± 0.8	494 ± 36	+ 3.7 ± 0.8	383 ± 21	-27.6 ± 0.2	381 ± 57	-20.5 ± 0.7
		-1.50	392 ± 35	3.5 ± 1.0	375 ± 33	3.4 ± 1.0	299 ± 17	-27.5 ± 0.2	299 ± 55	-19.7 ± 0.8
		-1.70	316 ± 22	3.7 ± 0.8	297 ± 21	3.6 ± 0.8	244 ± 13	-27.3 ± 0.2	235 ± 39	-18.8 ± 0.7
		-1.90	260 ± 18	3.7 ± 0.8	242 ± 17	3.6 ± 0.9	203 ± 11	-27.2 ± 0.3	218 ± 18	-18.2 ± 0.4
-11.50		-1.30	590 ± 44	3.5 ± 0.9	544 ± 43	3.4 ± 0.9	456 ± 46	-26.6 ± 0.5	433 ± 45	-20.0 ± 0.5
		-1.50	452 ± 34	3.5 ± 0.9	438 ± 33	3.4 ± 0.9	353 ± 35	-26.5 ± 0.5	329 ± 34	-19.1 ± 0.5
		-1.70	359 ± 27	3.5 ± 0.9	344 ± 26	3.3 ± 0.8	283 ± 28	-26.4 ± 0.5	259 ± 27	-18.3 ± 0.5
		-1.90	294 ± 22	3.5 ± 0.9	279 ± 21	3.3 ± 0.9	235 ± 23	-26.3 ± 0.5	210 ± 22	-17.6 ± 0.5
-12.50		-1.30	633 ± 75	3.5 ± 1.4	617 ± 74	3.4 ± 1.4	531 ± 87	-25.8 ± 0.8	490 ± 31	-19.5 ± 0.3
		-1.50	484 ± 56	3.5 ± 1.4	468 ± 56	3.4 ± 1.4	408 ± 66	-25.7 ± 0.8	368 ± 20	-18.8 ± 0.2
		-1.70	384 ± 44	3.5 ± 1.4	368 ± 44	3.4 ± 1.3	326 ± 52	-25.6 ± 0.8	289 ± 14	-18.0 ± 0.2
		-1.90	317 ± 30	4.0 ± 1.2	302 ± 30	3.9 ± 1.2	268 ± 42	-25.5 ± 0.8	235 ± 10	-17.3 ± 0.2

where  $D$  and  $D'$  have been treated as constants and been determined by a least-squares treatment.

If the free-valency dependent term in eqn. (34) has any relevance one would expect this equation to give a better fit to the experimental data than eqn. (33). The results of the least-squares treatment of eqn. (34) are given in the last columns of Table 5.

The present SCF MO calculations reaffirm the existence of a nearly linear relationship between  $\pi$ -electron densities and  $^1\text{H}$  and  $^{13}\text{C}$ -shielding constants in aromatic systems. With the sets of parameters  $W_{\delta'}$  and  $\beta_{\text{C}-\delta}$  that gave theoretical values of other ground state properties close to values inferred from experiments, the constant of proportionality between shielding constants and  $\pi$ -electron densities is about 7–10 ppm/electron for  $^1\text{H}$ -nuclei, and 200–250 ppm/electron for  $^{13}\text{C}$ -nuclei. As was mentioned earlier these values are close to those deduced from experimental studies of aromatic cations and anions, which is very gratifying. The  $^{13}\text{C}$ -shielding constants are seen to be more closely linearly correlated with  $\pi$ -electron densities than are the  $^1\text{H}$ -shielding data. The average deviation obtained with the set of parameters which in this work has gradually come to appear to be the "best", *i.e.*  $W_{\delta'} = -10.50$  eV and  $\beta_{\text{C}-\delta} = -1.70$  to  $-1.90$  eV, is about  $\pm 7\%$  in the case of hydrogen substituted  $^{13}\text{C}$ -nuclei and about  $\pm 12\%$  in the case of  $^1\text{H}$ -nuclei.

A peculiarity common to both the  $^{13}\text{C}$ -data (for  $^{13}\text{C}$ -atoms with contiguous hydrogen atoms) and  $^1\text{H}$ -data — although less pronounced in the former case — is that the correlation lines do not pass through the shift value found in benzene when  $\rho_i = 1.000$ . This feature was noted earlier in correlations between  $^1\text{H}$ -shieldings and  $\pi$ -electron densities calculated by the Hückel MO theory.<sup>70,71,73</sup> The corrections for the electric dipole field-effects applied by Shug and Deck on their  $^1\text{H}$ -shielding data on phenols (Table 4) tend to increase the value of  $K'$  in eqn. (30). Although the field-effect corrections involve some arbitrariness it does not appear likely from the above result that a phenomenon of the dipole-field type is responsible for the fact that the correlation lines do not pass through the point  $\Delta\sigma_i = 0$  for  $\rho_i = 1.000$ .

One might ask whether the relatively large values of  $K'$  are indications that the calculated  $\pi$ -electron densities are in general too small. Since the value of  $K'$  is of the order of 0.4 ppm and a reasonable value of  $K$  is *ca.* 8 ppm/electron this would mean that the theoretical  $\rho$ -values are too low by *ca.* 0.050 electron. An underestimate of the  $\pi$ -electron densities of this magnitude does not seem very likely. The value of  $C'$  is *ca.* 3.5 ppm which with a value of  $C$  equal to 200 ppm/electron leads to a somewhat lower error of 0.018 electron. The cause of the non-zero values of  $K'$  and  $C'$  in Tables 4 and 5 remains an open question.

The  $^{13}\text{C}$ -data for the oxygen-substituted ring carbons are as well correlated with the theoretical  $\pi$ -electron densities as are the hydrogen-substituted carbon atoms but they fall on different correlation lines. For the oxygen-substituted ring carbons the correlation lines are far removed from the shielding value in benzene when  $\rho_i = 1.000$ . The  $F_i$  dependent term in the modified Karplus-Pople equation reduces the difference somewhat but it appears that the Karplus-Pople theory needs to be modified to take the polarization of the  $\sigma$ -core into account.

It is obvious from Table 5 that for hydrogen substituted  $^{13}\text{C}$ -nuclei eqn. (34) leads to a hardly significantly better fit of experimental and theoretical data than does eqn. (33) and the theoretically predicted  $F_i$ -dependence of the  $^{13}\text{C}$ -shielding seems barely evident. For methoxy substituted  $^{13}\text{C}$ -nuclei a better fit with eqn. (34) is obtained only for  $W_{\text{O}'} - 11.50$  and  $-12.50$  eV.

#### 4.2. Properties involving excited states

Theoretical calculations of electronic absorption spectra of aromatic hydrocarbon and heteroaromatic molecules with the Pariser, Parr, and Pople SCF MO theory have shown that the experimental electronic spectra are better reproduced when excited states are described by a superposition of several configurations  $V_{ij}$  (a singly excited singlet state formed when an electron in the MO  $\varphi_i$  is raised to  $\varphi_j$  will be denoted  $V_{ij}$  and the corresponding triplet state will be denoted  $T_{ij}$ ).

In the present SCF calculations we have included all possible singly excited states in the configuration interaction treatment.

The molecular  $\pi$ -electron skeleton of phenol (anisole) and the 1,2- and 1,3-disubstituted hydroxy-(methoxy-)benzenes all belong to the point group  $C_{2v}$ , whereas the 1,4-disubstituted derivatives belong to the point group  $D_{2h}$ . In the molecules of  $C_{2v}$  symmetry the molecular orbitals belong to the irreducible representations  $A_2$  and  $B_2$  — the possible singly excited states belong to the representations  $A_1$  and  $B_1$ . The coordinate system has been chosen as in the figures found at the heads of Tables 6a-d. The  $z$ - and  $x$ -axes belong to the representations  $A_1$  and  $B_1$  respectively, which implies that transitions from the totally symmetric ground state ( $^1A_1$ ) to excited  $^1A_1$  states are allowed in the  $z$ -direction and transitions from  $^1A_1$  to  $^1B_1$  states are allowed in the  $x$ -direction.

In the molecules of  $D_{2h}$  symmetry the molecular orbitals belong to the representations  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$ . The fifteen singly excited configurations belong to one of the irreducible representations  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2u}$  and  $B_{3u}$ . The  $x$ - and  $y$ -axes (*cf.* Figure in Table 6d) belong to the representations  $B_{3u}$  and  $B_{2u}$ , respectively, which in this case means that transitions from the ground state ( $^1A_{1g}$ ) to  $^1B_{3u}$  states are allowed in the  $x$ -direction and transitions to  $^1B_{2u}$  states are allowed in the  $y$ -direction. All other transitions from the ground state are electronically symmetry forbidden.

In Tables 6a-d we have grouped the singly excited states included in the configuration interaction calculations according to their symmetry properties. We also give the frequencies and the concomitant oscillator strengths of the four lowest singlet transitions and the frequencies of the lowest "forbidden" triplet transitions. It is evident from Tables 6a-d that the calculated transition frequencies for a given molecule are fairly insensitive to the value of  $W_{\text{O}'}$  and  $\beta_{\text{co}}$ .

Experimental electronic absorption spectra of phenols and methoxybenzenes have been measured by several workers and the results are condensed in Table 7. The absorption band in the 35 000—38 000  $\text{cm}^{-1}$  region displays vibrational fine structure, and the frequencies and extinction coefficients of

Table 6a. Transition frequencies and oscillator strengths in phenol (anisol) after configuration interaction calculations including all singly excited states.

$W\dot{\sigma}'$ (eV)	$\beta_{C-\dot{O}}$ (eV)	${}^1B_1$ ( $x$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1A_1$ ( $z$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1A_1$ ( $z$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1B_1$ ( $x$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^3A_1$ $\nu$ (cm $^{-1}$ )	${}^3B_1$ $\nu$ (cm $^{-1}$ )	${}^3A_1$ $\nu$ (cm $^{-1}$ )
-10.50	-1.30	38.339	0.001	42.706	0.003	57.865	1.26	58.103	1.21	24.291	33.870	33.972
	-1.50	38.248	0.002	42.601	0.004	57.736	1.27	57.980	1.19	24.847	33.693	33.887
	-1.70	38.150	0.004	42.499	0.006	57.622	1.29	57.860	1.18	24.770	33.476	33.797
	-1.90	38.045	0.005	42.401	0.008	57.521	1.29	57.747	1.16	24.692	33.222	33.705
-11.50	-1.30	38.217	0.002	42.483	0.006	57.010	1.13	57.799	1.16	24.805	33.704	33.839
	-1.50	38.097	0.004	42.350	0.008	56.955	1.18	57.636	1.14	24.703	33.467	33.726
	-1.70	37.970	0.005	42.228	0.011	56.914	1.22	57.488	1.13	24.597	33.187	33.609
	-1.90	37.838	0.008	42.119	0.014	56.885	1.25	57.358	1.11	24.492	32.868	33.495
-12.50	-1.30	38.013	0.003	42.041	0.014	54.445	0.66	57.100	1.03	24.601	33.426	33.601
	-1.50	37.852	0.005	41.895	0.019	55.006	0.85	56.924	1.02	24.450	33.106	33.449
	-1.70	37.689	0.008	41.775	0.023	55.418	1.00	56.786	1.01	24.301	32.745	33.303
	-1.90	37.525	0.011	41.681	0.028	55.715	1.11	56.682	1.00	24.157	32.350	33.166

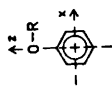


Table 7a.  
Symmetry of  
singly excited  
states

( $V$  = singlets;  
( $T$  = triplets)

$V_{15}, T_{15} = B_1$   
 $V_{16}, T_{16} = A_1$   
 $V_{17}, T_{17} = A_1$   
 $V_{23}, T_{23} = B_1$   
 $V_{28}, T_{28} = A_1$   
 $V_{27}, T_{27} = A_1$   
 $V_{35}, T_{35} = A_1$   
 $V_{38}, T_{38} = B_1$   
 $V_{37}, T_{37} = B_1$   
 $V_{45}, T_{45} = B_1$   
 $V_{46}, T_{46} = A_1$   
 $V_{47}, T_{47} = A_1$



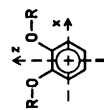


Table 6b. Transition frequencies and oscillator strengths in 1,2-dihydroxy (dimethoxy) benzene after configuration interaction calculations including all singly excited states.

$W_0'$ (eV)	$\beta_{C-O}$ (eV)	${}^1B_1$ ( $x$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1A_1$ ( $z$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1A_1$ ( $z$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1B_1$ ( $x$ -pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^3A_1$ $\nu$ (cm $^{-1}$ )	${}^3B_1$ $\nu$ (cm $^{-1}$ )	${}^3A_1$ $\nu$ (cm $^{-1}$ )
-10.50	-1.30	37.442	0.004	41.061	0.012	54.558	0.69	53.399	0.81	24.039	32.573	33.221
	-1.50	37.150	0.007	40.759	0.016	54.600	0.81	53.709	0.95	23.743	32.029	32.988
	-1.70	36.856	0.011	40.490	0.020	54.512	0.88	53.923	1.05	23.439	31.431	32.765
	-1.90	36.564	0.015	40.250	0.025	54.374	0.92	54.078	1.11	23.134	30.789	32.558
-11.50	-1.30	37.817	0.003	41.844	0.005	56.567	1.06	56.136	1.14	24.420	33.160	33.543
	-1.50	37.593	0.004	41.573	0.008	56.272	1.06	55.942	1.17	24.205	32.758	33.356
	-1.70	37.357	0.007	41.313	0.011	55.989	1.06	55.778	1.20	23.978	32.295	33.168
	-1.90	37.115	0.010	41.068	0.014	55.721	1.06	55.644	1.22	23.743	31.777	32.984
-12.50	-1.30	38.048	0.002	42.269	0.003	57.424	1.18	57.296	1.25	24.644	33.498	33.745
	-1.50	37.875	0.003	42.051	0.004	57.147	1.17	57.050	1.26	24.848	33.198	33.597
	-1.70	37.688	0.005	41.833	0.006	56.871	1.16	56.826	1.26	24.313	32.843	33.444
	-1.90	37.492	0.007	41.617	0.008	56.602	1.14	56.625	1.27	24.132	32.433	33.288

Table 7b.  
Symmetry of  
singly excited  
states  
( $V$  = singlets;  
 $T$  = triplets)

- $V_{16}, T_{16} = A_1$
- $V_{17}, T_{17} = B_1$
- $V_{18}, T_{18} = B_1$
- $V_{26}, T_{26} = B_1$
- $V_{27}, T_{27} = A_1$
- $V_{28}, T_{28} = A_1$
- $V_{36}, T_{36} = A_1$
- $V_{37}, T_{37} = B_1$
- $V_{38}, T_{38} = B_1$
- $V_{46}, T_{46} = B_1$
- $V_{47}, T_{47} = A_1$
- $V_{48}, T_{48} = A_1$
- $V_{56}, T_{56} = B_1$
- $V_{58}, T_{58} = B_1$

Table 6c. Transition frequencies and oscillator strengths in 1,3-dihydroxy (dimethoxy) benzene after configuration interaction calculations including all singly excited states.

$W_{0'}$ (eV)	$\beta_{c-0}$ (eV)	${}^1B_1$ ( <i>x</i> -pol.) $\nu$ (cm <sup>-1</sup> )	$f$	${}^1A_1$ ( <i>z</i> -pol.) $\nu$ (cm <sup>-1</sup> )	$f$	${}^1A_1$ ( <i>z</i> -pol.) $\nu$ (cm <sup>-1</sup> )	$f$	${}^1B_1$ ( <i>x</i> -pol.) $\nu$ (cm <sup>-1</sup> )	$f$	${}^3A_1$ $\nu$ (cm <sup>-1</sup> )	${}^3B_1$ $\nu$ (cm <sup>-1</sup> )	${}^3A_1$ $\nu$ (cm <sup>-1</sup> )
-10.50	-1.30	37,538	0.003	41,290	0.009	55,619	0.98	52,440	0.67	24,164	32,743	33,352
	-1.50	37,294	0.005	41,087	0.012	55,504	1.02	52,812	0.82	23,938	32,313	33,179
	-1.70	37,061	0.007	40,936	0.014	55,285	1.01	53,124	0.96	23,732	31,868	33,081
	-1.90	36,844	0.010	40,833	0.017	55,049	0.99	53,381	1.07	23,556	31,417	32,913
-11.50	-1.30	37,882	0.002	41,968	0.004	56,966	1.16	55,860	1.08	24,611	33,267	33,634
	-1.50	37,688	0.003	41,760	0.006	56,702	1.15	55,674	1.14	24,346	32,936	33,492
	-1.70	37,494	0.005	41,583	0.008	56,439	1.13	55,525	1.19	24,190	32,574	33,363
	-1.90	37,306	0.007	41,440	0.010	56,181	1.11	55,408	1.23	24,051	32,192	33,252
-12.50	-1.30	38,097	0.001	42,346	0.002	57,589	1.21	57,264	1.25	24,715	33,572	33,813
	-1.50	37,945	0.002	42,171	0.003	57,356	1.20	57,013	1.27	24,592	33,318	33,699
	-1.70	37,787	0.003	42,010	0.004	57,122	1.19	56,783	1.28	24,473	33,030	33,590
	-1.90	37,629	0.005	41,867	0.006	57,889	1.17	56,580	1.30	24,364	32,714	33,484



Table 7c  
Symmetry of  
singly excited  
states  
(*V* = singlets;  
*T* = triplets)

$V_{16}, T_{16} = A_1$   
 $V_{17}, T_{17} = B_1$   
 $V_{18}, T_{18} = A_1$   
 $V_{19}, T_{19} = B_1$   
 $V_{20}, T_{20} = B_1$   
 $V_{21}, T_{21} = A_1$   
 $V_{22}, T_{22} = B_1$   
 $V_{23}, T_{23} = A_1$   
 $V_{24}, T_{24} = B_1$   
 $V_{25}, T_{25} = A_1$   
 $V_{26}, T_{26} = B_1$   
 $V_{27}, T_{27} = A_1$   
 $V_{28}, T_{28} = B_1$   
 $V_{29}, T_{29} = A_1$   
 $V_{30}, T_{30} = B_1$   
 $V_{31}, T_{31} = A_1$   
 $V_{32}, T_{32} = B_1$   
 $V_{33}, T_{33} = A_1$   
 $V_{34}, T_{34} = B_1$   
 $V_{35}, T_{35} = A_1$   
 $V_{36}, T_{36} = B_1$   
 $V_{37}, T_{37} = A_1$   
 $V_{38}, T_{38} = B_1$   
 $V_{39}, T_{39} = A_1$   
 $V_{40}, T_{40} = B_1$   
 $V_{41}, T_{41} = A_1$   
 $V_{42}, T_{42} = B_1$   
 $V_{43}, T_{43} = A_1$   
 $V_{44}, T_{44} = B_1$   
 $V_{45}, T_{45} = A_1$   
 $V_{46}, T_{46} = B_1$   
 $V_{47}, T_{47} = A_1$   
 $V_{48}, T_{48} = B_1$   
 $V_{49}, T_{49} = A_1$   
 $V_{50}, T_{50} = B_1$   
 $V_{51}, T_{51} = A_1$   
 $V_{52}, T_{52} = B_1$   
 $V_{53}, T_{53} = A_1$   
 $V_{54}, T_{54} = B_1$   
 $V_{55}, T_{55} = A_1$   
 $V_{56}, T_{56} = B_1$   
 $V_{57}, T_{57} = A_1$   
 $V_{58}, T_{58} = B_1$

Table 6d. Transition frequencies and oscillator strengths in 1,4-dihydroxy (dimethoxy) benzene after configuration interaction calculations including all singly excited states.

$W_0'$ (eV)	$\beta_{C-\ddot{O}}$ (eV)	${}^1B_{2u}$ (x-pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1B_{2u}$ (y-pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1B_{2u}$ (y-pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^1B_{2u}$ (x-pol.) $\nu$ (cm $^{-1}$ )	$f$	${}^3B_{3u}$ $\nu$ (cm $^{-1}$ )	${}^3B_{3u}$ $\nu$ (cm $^{-1}$ )	${}^3B_{2u}$ $\nu$ (cm $^{-1}$ )
-10.50	-1.30	37.377	0.012	41.117	0.044	54.631	0.99	56.526	1.02	24.025	32.214	33.200
	-1.50	37.036	0.019	40.842	0.056	55.033	1.15	56.385	1.01	23.719	31.475	33.006
	-1.70	36.680	0.028	40.607	0.068	55.312	1.26	56.314	1.00	23.409	30.678	32.833
	-1.90	36.313	0.038	40.409	0.080	55.507	1.34	56.306	0.99	23.105	29.841	32.681
-11.50	-1.30	37.783	0.008	41.880	0.020	56.586	1.25	57.340	1.13	24.424	32.827	33.536
	-1.50	37.525	0.013	41.625	0.028	56.519	1.30	57.160	1.11	24.205	32.234	33.370
	-1.70	37.244	0.020	41.388	0.037	56.469	1.34	57.029	1.10	23.975	31.564	33.210
	-1.90	36.945	0.028	41.173	0.046	56.431	1.37	56.947	1.08	23.742	30.886	33.062
-12.50	-1.30	38.032	0.006	42.296	0.010	57.476	1.31	57.767	1.18	24.656	33.223	33.747
	-1.50	37.834	0.009	42.090	0.015	57.314	1.33	57.610	1.17	24.494	32.750	33.610
	-1.70	37.614	0.014	41.887	0.020	57.176	1.35	57.478	1.15	24.323	32.196	33.475
	-1.90	37.374	0.020	41.692	0.027	57.058	1.37	57.381	1.14	24.144	31.573	33.343

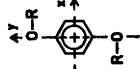


Table 7d  
Symmetry of  
singly excited  
states

( $V$  = singlets;  
 $T$  = triplets)

- $V_{16}, T_{16} = B_{1g}$
- $V_{17}, T_{17} = A_{1g}$
- $V_{18}, T_{18} = B_{2u}$
- $V_{19}, T_{19} = B_{3u}$
- $V_{20}, T_{20} = B_{3u}$
- $V_{21}, T_{21} = B_{3u}$
- $V_{22}, T_{22} = A_{1g}$
- $V_{23}, T_{23} = B_{1g}$
- $V_{24}, T_{24} = B_{1g}$
- $V_{25}, T_{25} = A_{1g}$
- $V_{26}, T_{26} = B_{2u}$
- $V_{27}, T_{27} = B_{2u}$
- $V_{28}, T_{28} = B_{2u}$
- $V_{29}, T_{29} = B_{3u}$
- $V_{30}, T_{30} = B_{1g}$
- $V_{31}, T_{31} = B_{1g}$
- $V_{32}, T_{32} = B_{3u}$
- $V_{33}, T_{33} = B_{3u}$
- $V_{34}, T_{34} = A_{1g}$

the most intense of these peaks are given in papers by Dearden and Forbes.<sup>86,87</sup> It is generally accepted that the 38 000  $\text{cm}^{-1}$  band in benzene is due to an electronically forbidden transition from the totally symmetrical ground state to a  ${}^1B_{2u}$  state. In benzene this transition is vibrationally induced by a single excitation of a ring vibration of  $e_{2g}$  symmetry, and the observed fine structure in the 38 000  $\text{cm}^{-1}$  band arises from multiple excitations of a (*ca.* 920  $\text{cm}^{-1}$ )  $a_{1g}$  vibration. In the mono- and di-substituted benzenes excitation of the  $e_{2g}$  distortion vibration is no longer a necessary condition for "allowness", and the vibrational fine structure arises from multiple excitations of the 920  $\text{cm}^{-1}$   $a_{1g}$  vibration beginning with the O—O transition. As discussed by Petruska,<sup>90</sup> in addition to the above substituent-induced fine structure in the 38 000  $\text{cm}^{-1}$  band there are also vibrationally-induced absorption peaks. From a detailed analysis of the absorption pattern in the 38 000  $\text{cm}^{-1}$  band of several substituted benzenes, Petruska has tried to separate the substituent-induced and the vibration-induced components and has given estimated oscillator strengths ( $f_p$  and  $f_v$ ) of the respective components. The quantities of interest in this work are the substituent-induced oscillator strengths, and these are given in Table 7. The wave-number of the O—O transition in the 38 000  $\text{cm}^{-1}$  band given by Petruska generally agrees well with the first intense transition at lower frequencies observed by Dearden and Forbes.

The polarization relative to the molecular symmetry axis of the absorption bands at *ca.* 35 000  $\text{cm}^{-1}$  and *ca.* 43 000  $\text{cm}^{-1}$  in 1,4-dimethoxybenzene has been measured on a thin single crystal by Albrect and Simpson.<sup>89</sup> They found that the 35 000  $\text{cm}^{-1}$  band is polarized in the molecular plane at right angles to the long-axis (*i.e.* along the  $x$ -axis in Table 6d) and that the 43 000  $\text{cm}^{-1}$  is polarized in the molecular plane along the long-axis (*i.e.* along the  $y$ -axis in Table 6d). The theoretically calculated polarization directions for the first two singlet transitions are in agreement with the experiments (Table 6d). The investigations mentioned indicate that the 35 000  $\text{cm}^{-1}$  and the 43 000  $\text{cm}^{-1}$  bands in other mono- and disubstituted benzenes included in the present work may be assigned to transitions from the symmetrical ground state to  ${}^1A_1$  and  ${}^1B_1$  states, respectively.

If we return to the theoretical transition frequencies in Table 6 we see that the SCF calculations place the four lowest absorption maxima in three regions: *ca.* 37 000  $\text{cm}^{-1}$ , *ca.* 42 000  $\text{cm}^{-1}$ , and at *ca.* 55 000  $\text{cm}^{-1}$ .

For the two low frequency bands the agreement between theory and experiment is reasonably good. It should perhaps be mentioned again that the parameter scheme adopted in the present work was not primarily aimed at producing an excellent fit to electronic spectral transitions — as are many other proposed parameter evaluation schemes — but rather to give a satisfactory description of *both* ground state properties and excitation processes.<sup>8</sup>

Due to lack of experimental UV data below 200  $m\mu$  reported in the literature the calculated transition frequencies for the 55 000  $\text{cm}^{-1}$  band can be compared with experiment only for phenol and 1,4-dihydroxybenzene. The calculations indicate that in phenol two highly allowed transitions to  ${}^1A_1$  and  ${}^1B_1$  states should appear close together near 57 000  $\text{cm}^{-1}$  — in phenol and intense absorption band ( $\log \epsilon = 4.75$ ) is observed near 53 000  $\text{cm}^{-1}$  but the polarization of this band is unknown. In the case of 1,4-dihydroxy-

benzene two transitions to  ${}^1B_{2u}$  and  ${}^1B_{3u}$  states are calculated to fall near  $56\,000\text{ cm}^{-1}$ : for this compound an experimental absorption band is observed at *ca.*  $52\,000\text{ cm}^{-1}$  ( $\log \epsilon = 4.40$ ).

The theoretical oscillator strengths for the  $35\,000\text{ cm}^{-1}$  transitions calculated with the parameters  $W_{\delta'} = -10.50$  and  $\beta_{C-O} = -1.70$  to  $-1.90\text{ eV}$  agree comparatively well with the  $f_q$  values given by Petruska (*cf.* Table 7).

Transition energies for triplet-singlet transitions are available for phenol and anisole. The maximum frequency of the transition from metastable triplet states to the singlet ground state has been measured by Nauman (cited by McClure<sup>91</sup>). The transition frequencies are  $28\,600\text{ cm}^{-1}$  for phenol and  $28\,200\text{ cm}^{-1}$  for anisole. The lowest theoretical singlet-triplet transition in phenol (anisole) is predicted at *ca.*  $25\,000\text{ cm}^{-1}$ .

## 5. CONCLUDING REMARKS

The results obtained show that it is possible to give a reasonably satisfactory description of a number of ground state properties and electronic transition energies in hydroxy and methoxy substituted benzenes within the theoretical framework of the Pariser, Parr, and Pople SCF method. The best overall account of the molecular properties considered in the present work is acquired with the heteroatom parameters  $W_{\delta'}$  *ca.*  $-10.5\text{ eV}$  and  $\beta_{C-O}$  in the range  $-1.70$  to  $-1.90\text{ eV}$ . The above value of  $W_{\delta'}$  is in accordance with the negative of the ionization potential of  $C_2H_5OH$  which is very gratifying (*cf.* discussion on p. 2032).







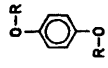
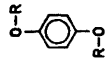
It has been suggested by Sidman<sup>93</sup> that the C=O bond in ethylene ( $R = 1.337\text{ \AA}$ ) and the C=O bond in carbonyl groups ( $R \approx 1.22\text{ \AA}$ ) could be considered as prototypes of the "normal" carbon-carbon and carbon-oxygen double bonds. Sidman also demonstrated that a satisfactory description of the  $\pi$ -electron ionization potential and electronic transition energies in formaldehyde was obtained by a Pariser, Parr, Pople-type calculation when a value of  $\beta_{C-O}$  close to the value of  $\beta_{C=C}$  in ethylene was used. Similar results have been obtained in other studies on formaldehyde.<sup>25</sup>

If we may look at carbon-oxygen bonds in the manner suggested by Sidman it is perhaps not unreasonable to assume that the  $\beta$ -values for carbon-carbon and carbon-oxygen bonds in a limited range of bond distances will depend on the interatomic distance in a congruous way (*i.e.*  $\beta_{CC}(1.337 + \Delta R) \approx \beta_{CO}(1.22 + \Delta R)$ ).

Now, if we use the relation between  $\beta_{CC}$  and the interatomic carbon-carbon distance employed by Skancke<sup>23,24</sup> (this relation has been obtained using  $\beta = -2.85\text{ eV}$  at  $R = 1.337\text{ \AA}$  (ethylene) and  $\beta = -2.39\text{ eV}$  at  $R = 1.397\text{ \AA}$  (benzene)) a value of  $\beta_{CO} = -1.87\text{ eV}$  is derived for a carbon-oxygen bond length of  $1.36\text{ \AA}$ . This value compares favourably with the  $\beta$ -values which have emerged as the "best" in the present investigation.

An important question in the Pariser-Parr-Pople SCF method is the transferability of the parameters between different types of molecules.<sup>94</sup> Preliminary SCF calculations on vinyl ethers and furanes with the use of the "best" parameters found in the present work have, however, indicated that the above parameters lead to satisfactory results also in these latter molecules.

Table 7. Experimental electronic transition data on hydroxy- and methoxy-benzenes.

Compound	Transition frequencies (cm <sup>-1</sup> ), logarithms of the molar extinction coefficients or oscillator strengths ( <i>f</i> ); ( <i>S</i> <sub>h</sub> = shoulder).
	R = H 53 020 (4.75) [86]; 47 620 (3.78); 38 020 (3.15); 37 170 (3.34); 36 230 (3.32) [86] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 36 050 ( <i>f</i> <sub>g</sub> = 0.015) [90]
	R = CH <sub>3</sub> 45 450 (3.88); 44 840 (3.78); 38 020 (3.15); 37 170 (3.32); 36 360 (3.32) [87] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 36 000 ( <i>f</i> <sub>g</sub> = 0.018) [90]
	R = H 46 730 (3.83); 37 040 (3.34); 36 500 (3.40); 35 710 (3.35) [86] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 33 150 ( <i>f</i> <sub>g</sub> = 0.024) [90]
	R = CH <sub>3</sub> 44 440 (3.85); 36 900 (3.39); 36 360 (3.41); 35 710 (3.28) [87] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 35 450 ( <i>f</i> <sub>g</sub> = 0.026) [90]
	R = H 46 080 (3.83); 37 310 <i>S</i> <sub>h</sub> (3.32); 36 560 (3.33); 35 780 (3.26) [86] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 35 250 ( <i>f</i> <sub>g</sub> = 0.020) [90]
	R = CH <sub>3</sub> 45 450 (3.86); 37 450 <i>S</i> <sub>h</sub> (3.23); 36 830 (3.34); 36 040 (3.23) [87] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 35 350 ( <i>f</i> <sub>g</sub> = 0.022) [90]
	R = H 52 080 (4.40) [88]; 44 840 (3.64); 35 090 <i>S</i> <sub>h</sub> (3.40); 34 600 (3.46); 33 440 (3.34) [86] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 32 450 ( <i>f</i> <sub>g</sub> = 0.030) [90]
	R = CH <sub>3</sub> 47 390 (3.76); 44 250 (3.99); 35 710 <i>S</i> <sub>h</sub> (3.40); 34 900 (3.51); 34 480 (3.51); 33 670 (3.41) [87] "O-O", trans. ( <sup>1</sup> <i>L</i> <sub>b</sub> ): 33 350 ( <i>f</i> <sub>g</sub> = 0.030) [90] ca. 43 600 ( <i>y</i> -polarized); ca. 34 500 ( <i>x</i> -polarized) [89]

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