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Self Consistent Field Molecular Orbital Calculations for Mono and Disubstituted Benzenes*

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The semi-empirical modifications introduced into the self-consistent field molecular orbital method (SCFMO) by Pople [*13*] and Pariser and Parr [*10*] make it quite feasible to compute the excited state energies of monosubstituted benzenes using self-consistent field orbitals. The only published work on this topic has been on aniline [*12, 11*]. In one of these studies [*12*] the energy levels were not reported and in the other [*11*] the agreement between experiment (Tab. 1) and theory (Tab. 1) was not very good for the second transition. Since data on the effect of polar substituents on the properties of benzene form a large part of the experimental results available for testing theories of molecular structure, it is important that the theoretical calculation of such properties be carried out with as much detail as is possible.

As part of a more general programme on the calculation of molecular properties of disubstituted benzenes we have applied the SCFMO method to phenol, to aniline and to benzaldehyde where the substituents are a weakly interacting electron donating one, a strongly interacting electron donating one and a strongly interacting electron attracting one, respectively.

The calculation of the SCF ground state orbitals was made by the semi-empirical MO method [*13*] using empirical values of the resonance integrals from the literature.

i.e. β_{C-C} ($r = 1.39$ Å) $= -2.39$ ev, β_{C-C} ($r = 1.48$ Å) $= -1.68$ ev,
$\beta_{C-O} = -2.12$ ev [*9*], $\beta_{C-N} = -2.74$ ev [*12*], and $\beta_{C=O} = -2.70$ ev [*1*].

The core integrals with the exception of that of nitrogen, were those also used by previous workers,

i.e. $W_{C^+} = -11.28$ ev [*10*], $W_{O^+} = -18.29$ ev [*1*], and $W_{O^{2+}} = -34.95$ ev [*9*].

For nitrogen $W_{N^{2+}} = -24.56$ is less than that usually used, i.e. $W_{N^{2+}} = 27.114$ ev [*2*] but similar to that used by McEwen for nitroamide ($W_{N^{2+}} = -24.83$ ev [*5*]). The effect of varying the value of the core integral will be discussed elsewhere. The molecular repulsion integrals were calculated using the approximation suggested by Mataga [*4*], rather than the more usual Pariser and Parr

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approximation [*10*]. The results are compared with experimental transition energies (E) and oscillator strengths (f) in Tab. 1. The agreement with experiment is quite satisfactory. Self consistent orbitals, obtained as described above, may be used as a basis for the calculation of energy states of conjugated molecules *R*—*S* by treating the bond between the two fragments *R* and *S* as a perturbation on excited configurations built up from SCF wave functions of *R*—*H* and *S*—*H* [*8*, *7*]. The configurations are of two kinds, locally excited (LE) ones involving the orbitals of *R* or of *S* only, and electron transfer (ET) configurations, involving electron transfer between *R* and *S*.

Table 1. *SCF Calculations on Monosubstituted Benzenes*

	E (ev)	f*	E (ev)	f	E (ev)	f
$C_6H_5NH_2$. Exp.	4.30	.03	5.27	.17	6.4	—
Prev. Calc. [*11*]	4.30	—	4.30	—	6.1	—
New Calc.	4.24	.09	5.29	.44	6.57	—
					6.61	—
C_6H_5OH. Exp.	4.60	.02	5.83	.10	6.54	1.00
Calc.	4.80	.01	5.96	.06	6.82	1.20
					6.83	1.09
C_6H_5CHO. Exp.	4.50	.01	5.16—5.30	.25	6.36	—
Calc.	4.69	.03	5.39	.39	6.48	.83
					6.88	.99

* As defined in ref. [*6*].

Preliminary results using this method for benzaldehyde and the three hydroxybenzaldehyde isomers are given in Tab. 2. The experimental data recorded are those for the methoxybenzaldehydes, since this eliminates the necessity of taking into consideration the effect of intramolecular hydrogen bonding. The purely electronic effect of replacing hydroxyl by methoxyl is known to be small [*3*]. The SCF orbitals of *R* and *S* were taken as those of phenol and of formaldehyde, while the energies of the LE states were taken from the observed spectra of these molecules. Further details together with further calculations on substituted nitro compounds and anilines will be reported elsewhere.

Table 2. *Intramolecular Charge Transfer Calculations*

	E (ev)	f	E (ev)	f
C_6H_5CHO. Exp.	4.50	.01	5.20	.25
Calc.	4.80	.01	5.30	.15
para-$OMeC_6H_4CHO$. Exp.	4.4	.01	4.50	.42
Calc.	4.5	.00	4.83	.20
meta-$OMeC_6H_4CHO$. Exp.	4.30	.05	5.00	.14
Calc.	4.47	.07	5.30	.16
ortho-$OMeC_6H_4CHO$. Exp.	4.00	.06	5.00	.22
Calc.	4.38	.08	5.28	.16

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