

Notes

Self-Consistent Methods in Hückel & Extended Hückel Theories: Part IV—Substitution Effect in Benzene

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A self-consistent extended Hückel theory, developed earlier [*Int J quantum Chem*, **19** (1981) 515] has been used for the calculation of ground state properties of some fluorobenzenes. The results show an overall improvement over those obtained by the simple extended Hückel method.

Rai and coworkers¹ calculated properties of some fluorobenzenes using the extended Hückel method and compared the results with those obtained by more sophisticated methods. We felt it worthwhile to see whether these results could be improved by the introduction of self-consistency in the simple extended Hückel theory (EHT) according to a procedure developed by us earlier². The choice of fluorobenzenes for the purpose was largely dictated by the fact that large separation of charges is expected in these compounds and self-consistent EHT optimising charges on the centres should give overall improvement in the results as compared to those obtained by the simple EHT.

The method of calculation has been given in detail in an earlier paper².

The basis consists of non-orthogonal Slater orbitals where the required exponents are decided by Slater's rules. For hydrogen, however, a value of 1.2 has been used, because this value has been used by most of the previous workers with considerable success. The constant *K* required for the construction of off-diagonal matrix elements has been assigned a value of 1.75 originally used by Hoffmann³, and justified later

by Lowe⁴. The values of diagonal elements of the hamiltonian have been taken from Anderson *et al.*⁵ without further refinement. The only optimizable parameter is, therefore, ω , the values found being -2.5, -0.31 and -0.7 respectively for H, C and F. Planarity is assumed for all the molecules with bond lengths 1.39, 1.35 and 1.09 Å respectively for C-C, C-F and C-H bonds. The bond angles are assumed to be 120°.

Unless the overlap is very small and the closed and open shell hamiltonians are almost equal no simple formula for the ionization potential (*I*), as given by us in an earlier paper⁶, is available. The calculation can however be done⁷ using the relation

$$I = E_{\text{cation}} - E_{\text{molecule}} \\ = 2 \operatorname{tr} (R_1 + \frac{1}{2} R_2) H' - 2 \operatorname{tr} R H$$

where *H* and *H'* are the hamiltonian matrices for the molecule and its cation respectively; *R* is the density matrix of the molecule; and *R*₁ and *R*₂ respectively are the density matrices of the closed and open shells of the cation.

Instead of documenting all the results we record only those which basically differ from those of EHT calculation and need special consideration. In Table I the ionization potentials of some fluorobenzenes calculated by the present method have been compared with those obtained by EHT, CNDO, INDO, VEPPP methods and also with the experimental values wherever they are available. It is really gratifying to note that the results obtained by the present method, which uses a truly self-consistent procedure, are better than those obtained by EHT, CNDO and INDO methods and comparable with the VEPPP values claimed to be the best by Rai and coworkers¹. For the disubstituted fluorobenzenes the order of ionisation potential values obtained by the present method is *ortho* ~ *meta* > *para* as against the order *meta* > *ortho*

Table I—Ionisation Potentials of Fluorobenzenes [Values in eV]

Molecule	CNDO ^a	INDO ^a	VEPPP ^a	EHT ^a	Present method	Experimental ^a
C ₆ H ₅ F	13.37	12.75	10.00	11.60	9.53	9.26
<i>o</i> -C ₆ H ₄ F ₂	13.33	12.68	9.76	11.83	9.59	9.31
<i>m</i> -C ₆ H ₄ F ₂	13.48	12.87	9.78	12.05	9.59	9.37
<i>p</i> -C ₆ H ₄ F ₂	13.02	12.38	9.67	11.48	9.57	9.15
1,2,3-C ₆ H ₃ F ₃	13.72	13.09	9.64	12.27	9.65	
1,2,4-C ₆ H ₃ F ₃	13.18	12.55	9.48	11.93	9.62	
1,3,5-C ₆ H ₃ F ₃	13.98	13.37	9.67	12.37	9.66	

^a From ref. 1.

Table 2—Dipole Moments of Fluorobenzenes [Values in Debye]

Molecule	CNDO ^a	INDO ^a	EHT	Present method	Experimental ^a
C ₆ H ₅ -F	1.76	1.85	10.86	4.53	1.57
<i>o</i> -C ₆ H ₄ -F ₂	3.0	3.12	18.96	7.89	2.38
<i>m</i> -C ₆ H ₄ -F ₂	1.74	1.81	10.78	4.55	—
1,2,3-C ₆ H ₃ -F ₃	3.53	3.71	21.93	9.23	—
1,2,4-C ₆ H ₃ -F ₃	1.77	1.87	10.94	4.51	—

^a From ref. 1.

Table 3—Net Charges on Fluorine Atoms

Molecule	CNDO ^a	INDO ^a	VEPPP ^a	EHT ^a	Present method
C ₆ H ₅ F	-0.209	-0.251	+0.04	-0.67	-0.63
<i>o</i> -C ₆ H ₄ F ₂	-0.192	-0.232	+0.038	-0.67	-0.61
<i>m</i> -C ₆ H ₄ F ₂	-0.209	-0.251	—	-0.67	-0.63
<i>p</i> -C ₆ H ₄ F ₂	-0.205	-0.210	+0.039	-0.67	-0.62
1,2,3-C ₆ H ₃ F ₃					
Position-1	-0.174	-0.212	+0.038	-0.67	-0.61
Position-2	-0.209	-0.251	+0.037	-0.68	-0.63
1:2:4-C ₆ H ₃ F ₃					
Position-1	-0.240	-0.251	+0.038	-0.67	-0.63
Position-2	-0.188	-0.228	+0.039	-0.67	-0.61
1,3,5-C ₆ H ₃ F ₃	-0.197	-0.238	+0.039	-0.66	-0.62

^a From ref. 1.

> *para* obtained by all other methods. This may be attributed to the close proximity of the experimental as well as the VEPPP ionization potential values for the compounds and the slight difference is not easily discernible within the limits of accuracy of an EHT method. The trisubstituted fluorobenzene however maintain the expected order 1,3,5 > 1,2,3 > 1,2,4.

The poor charge density generally obtained by the traditional EHT method demands that the charge density obtained by the present method is also to be closely scrutinised. One can calculate the dipole moments for the purpose as a measure for charge density distributions. The dipole moment values for the compounds show that the EHT values are very poor and deviate much from those calculated by more sophisticated methods like CNDO, INDO etc. (see Table 2). The values obtained by the present method are decidedly better than the EHT values.

The charges on the fluorine atoms in the EHT, though quite large are nearly the same in all the cases while these are small and largely different in the CNDO and INDO results, indicating the mutual interaction between the substituents. The reason, as rightly pointed out by Rai and coworkers¹, is that the electronic hamiltonian in EHT does not explicitly contain the effect of electronic interaction. In the present case we find that the net charges are quite large, the charge differences are not as prominent as in the

CNDO and INDO results (see Table 3) yet quite perceptible even within the accuracy of the EHT. This is because the present method attempts to calculate the electronic charges on the centres, and hence the effect of repulsions, in a more logical and self-consistent way. This observation reveals that it might be possible to study the steric properties of large organic molecules with the help of the self-consistent EHT. It may be concluded that when the size of a compound demands that only a method using one electron hamiltonian is to be used, it is always better to use self-consistent EHT instead of a simple EHT for results to have some practical value.

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