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PHOTOELECTRON SPECTRA OF FLUORINATED BENZENES

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Recent work here[1] has led to the development of an SCF MO treatment of conjugated molecules that allows their ground state properties to be predicted with surprising accuracy. We have been trying to extend this treatment to aromatic fluoro compounds in the hope of interpreting their nmr spectra, but this work has been hampered by lack of experimental data that could be used to determine the necessary parameters. We were therefore interested in a recent paper by Clark and Frost[2] reporting photoelectron spectra for various fluorinated benzenes; we hoped that comparison of the observed ionization potentials with calculated orbital energies might provide the basis we needed.

However it soon became apparent that the reported assignments of the ionizations were incorrect. Clark and Frost[2] assumed that the π-ionization potentials all lie below the σ-ionization potentials, following an argument by El-Sayed and Kasha[3] that the second ionization potential of benzene (11.489 ev[3], 11.49 ev[4]) corresponds to a π-ionization. Previously it had been suggested[5] that this is in fact a σ-ionization, and the arguments for this seem well balanced.

Recent work here[6] has led to the development of a semiempirical SCF MO treatment of organic molecules in which all the valence electrons are included, and which gives surprisingly good results for the ground states of organic molecules. In particular the photoelectron ionization potentials of Al-Joboury and Turner[4] are reproduced with satisfying accuracy up to an energy of 20 ev, assuming that ionization potentials can be equated to orbital energies. In the case of benzene, the calculations (Table I) lead to a clear prediction that the ionization potential at 11.49 ev corresponds to σ-ionization, in agreement with the views of Price and Wood[5].

TABLE I

Ionization Potentials (ev) of Benzene.

Measured		Calculated		
Ref. 2	Ref. 3	σ-approximation	assignment	π-approximation[a]
9.25	9.25	10.15	π	10.69
11.51	11.49	11.54	σ	
-	12.49[b]	12.72	σ	
13.88	13.67	12.86	π	13.44
14.87[b]	14.44[b]	13.45	σ	
15.54[b]	-	15.67	σ	
16.84	16.73	16.07	σ	
18.22	18.75	18.98	σ	

(a) Calculated with W_C = 11.16 ev.
(b) Values reported as dubious.

Further work[7] has shown that there is a close parallel between the π-MO energies calculated for a variety of aromatic compounds by the treatment[6] in which σ-electrons are included, and by the earlier[1] π-approximation; this is illustrated by the values for benzene listed in Table I. It seems reasonable on this basis to assume that the same will hold generally for conjugated molecules of other types. We have therefore carried out π-calculations for the compounds studied by Clark and Frost[2], for a wide range of values of β_{CF} (the one-electron resonance integral). The results are summarized in Figure 1.

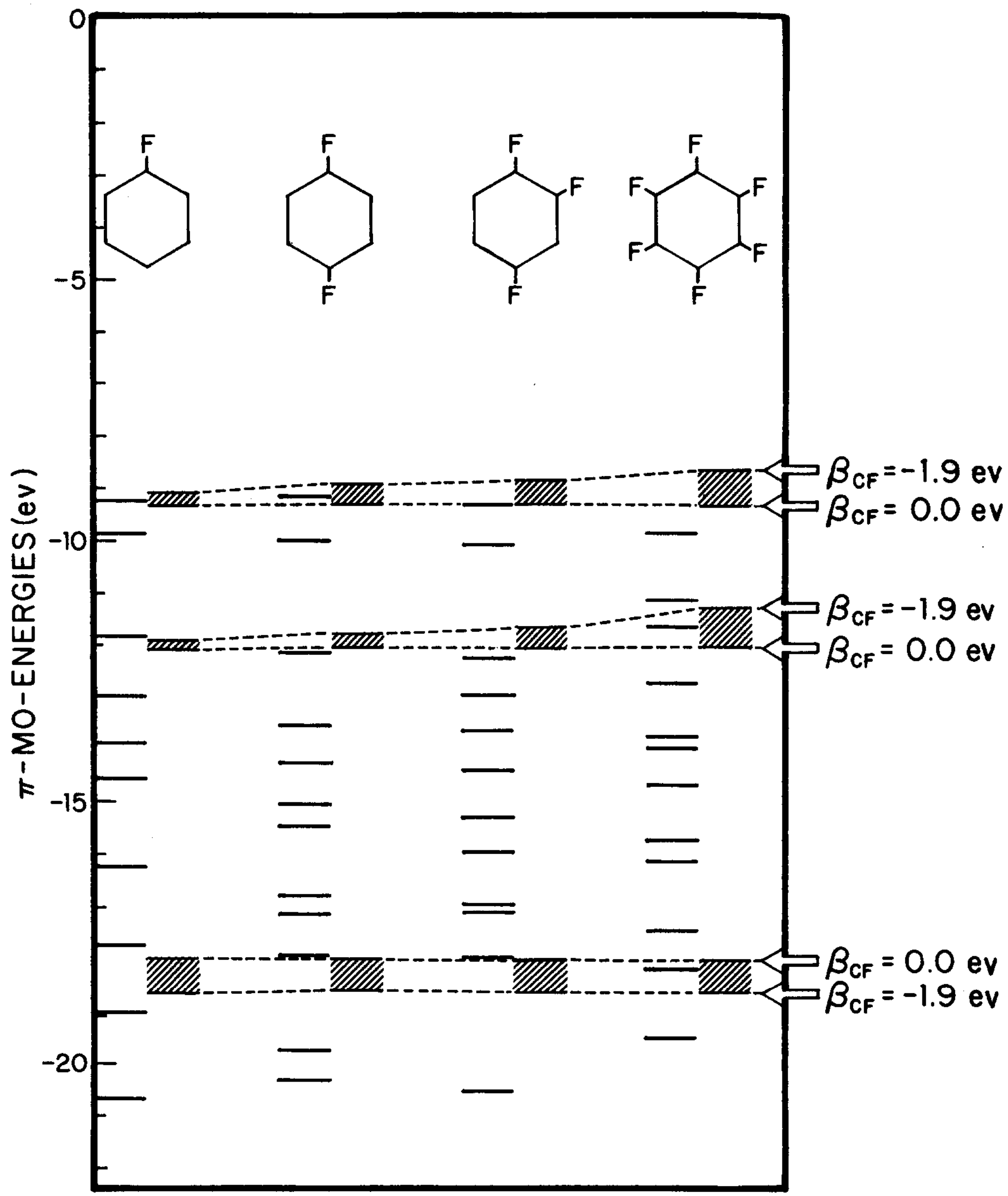

Figure 1. Comparison of observed[2] ionization potentials (ev)(——) for fluorinated benzenes with values calculated ▨ by the π-approximation for a range of β_{CF} from zero to -1.9 ev, and with $W_c = 9.77$ ev.

Three conclusions seem to follow very clearly from this work. Firstly, the comparisons lead to an assignment of the π-ionization potentials which is very different from that previously suggested[2]; since the results are almost insensitive to choice of β_{CF}, this assignment seems strongly indicated. Secondly, the second ionization potential in each case is predicted to correspond to σ-ionization, in agreement with the corresponding assignment for benzene. Thirdly, the surprising insensitivity of the results to β_{CF} show that this procedure cannot be used to determine the best value of this parameter.

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