Fluorine Nuclear Coupling Constants in Fluorobenzenes: the Influence of the Orbital Term on J^{FF}_{meta}

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Summary Calculations by the perturbed self-consistent molecular orbital INDO method on hexafluorobenzene, pentafluoroaniline, and pentafluoronitrobenzene give almost constant values for the *ortho* and *para* fluorine–fluorine coupling constants, in agreement with experiment, and show that the large variation in some of the *meta* coupling constants is due to the orbital term.

In a study of the relative signs of *meta* fluorine–fluorine coupling constants J^{FF} in amino- and nitro-fluorobenzenes Peake and Thomas[1] found that the sign as well as the magnitude varies with the substituent. Thus J^{FF}_{26} si $+6$ Hz in pentafluoroaniline and -10 Hz in pentafluoronitrobenzene, whereas J^{FF}_{24} is $-8{\cdot}2$ Hz in the former and $+6$ Hz in the latter. This remarkable variation is in contrast to the values for J^{FF}_{35}, which are -3 Hz in pentafluoroaniline and 0 in pentafluoronitrobenzene, and to the constancy of the *ortho* and *para* couplings. In a series of mono-substituted derivatives of hexafluorobenzene[2] J^{FF}_{23} is -21 ± 1 Hz and J^{FF}_{25} is 6 ± 2 Hz. It was suggested that a π-mechanism might be responsible.[3,4] Abraham *et al.*[4] made some calculations based on McConnell's formula for the effect of hyperfine interaction, which involves Fermi and dipolar terms. This formula, however, yields positive contributions only; so it cannot provide a complete explanation of the changes in sign.

It has often been suggested that orbital and dipolar contributions, as well as the Fermi term, are important in F–F coupling.[5]

TABLE. J^{FF}_{meta} *in fluorobenzenes (Hz)*

Molecule	Term	Positions 2,4	 2,6	 3,5
$C_6F_5NH_2$	Fermi	−2·4	−2·6	−2·9
	Orbital	−1·0	6·3	3·6
	Dipolar	0·6	1·7	1·6
	Total	−2·8	5·4	2·3
	Expt.[1]	−8·2	6	−3
$C_6F_5NO_2$	Fermi	−3·1	−3·1	−3·8
	Orbital	9·0	−3·2	2·7
	Dipolar	2·4	0·7	3·5
	Total	8·3	−5·6	2·4
	Expt.[1]	6	−10	0
C_6F_6	Fermi	—	—	−3·5
	Orbital	—	—	2·3
	Dipolar	—	—	1·3
	Total	—	—	0·1
	Expt.[9]	—	—	−4

The object of this communication is to report the results of some calculations on hexafluorobenzene, pentafluoroaniline, and pentafluoronitrobenzene which show that the change in the signs of J^{FF}_{24} and J^{FF}_{26} in the last two compounds is due to the effect of the orbital term. The equations have been given by Blizzard and Santry.[5,6]

The computations were carried out on the KDF9 computer and runs of 1—2 h were necessary to obtain convergence for the orbital and dipolar terms. The original INDO parameters[7] were used, with bond angles of 120°, bond lengths C–C 1·40, C–F 1·33, C–N 1·40, N–O 1·24 and N–H 1·036 Å, and the corrected Hartree–Fock values[8] $< r^{-3} >$ 7·546 a.u., $|\psi(O)|^2$ 11·3966 a.u.

In the three molecules, J^{FF}_{ortho} and J^{FF}_{para} were found to be almost constant, with values of -22 ± 2 Hz and 11 ± 1 Hz respectively, in good agreement with the experimental pattern. Values for J^{FF}_{meta} are shown in the Table. It can be seen that the Fermi term is always negative and the dipolar term always positive. The orbital term changes sign in the same way as the experimental values for J^{FF}_{26} and J^{FF}_{24}. Thus the effect of the substituents on the *ortho* and *para* positions shows itself through the orbital term. For J^{FF}_{35} the orbital and dipolar terms are positive and the Fermi term is negative. The small magnitude is due to the approximately equal magnitudes of the positive and negative terms. The calculations give somewhat too positive values, but the order is the same as for the experimental values.

These results for J^{FF}_{24} and J^{FF}_{26} provide the first clear-cut example of a dominant contribution from the orbital term in nuclear coupling.

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