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THE RELATIONSHIP BETWEEN ^{19}F CHEMICAL SHIFTS AND CALCULATED ELECTRON DENSITIES IN PERFLUORINATED ANNULENES

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Summary: Ab initio calculations for a series of perfluorinated annulenes suggest that there is a linear correlation between the total charge density at fluorine and the fluorine chemical shift. The STO-3G basis set overestimates the degree of pi-electron donation by fluorine.

It has long been recognized that there is a linear correlation between local pi-electron densities in aromatic hydrocarbons and the corresponding ^{13}C and ^{1}H nmr chemical shifts.[1] A similar correlation between pi-electron densities and ^{19}F chemical shifts in substituted aromatic hydrocarbons has been used as a probe for substituent effects.[2] We would like to report our results for a series of perfluorinated annulenes which suggest that the ^{19}F nmr chemical shifts in this series correlate with the total electron density at fluorine rather than the pi-electron density.

Ab initio calculations were carried out using the Gaussian 82 program[3] with the STO-3G and 3-21G basis sets and full geometry optimization. The results for the series perfluorocyclopropenium (1), perfluorotropylium (2), perfluorobenzene (3), and perfluorocyclopentadienyl (4) are shown in Table 1. All compounds maintained their expected D_{nh} (n=3,5,6,7) symmetries.

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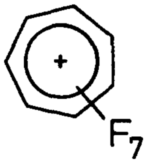

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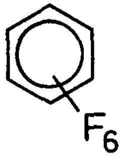

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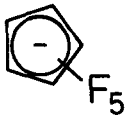

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Table 1. Geometrical Parameters[a], and Charge Densities for Perfluorinated Annulenes Derived from Ab Initio Calculations.

	Basis	r(C-C)	r(C-F)	$q^{pi}(F)$	$q^{t}(F)$
1	STO-3G	1.39	1.30	1.86	8.97
	3-21G	1.36	1.28	1.87	9.25
2	STO-3G	1.42	1.35	1.90	9.04
	3-21G	1.37	1.33	1.90	9.30
3	STO-3G	1.40	1.36	1.93	9.11
	3-21G	1.37	1.34	1.93	9.36
4	STO-3G	1.40	1.37	1.96	9.19
	3-21g	1.39	1.37	1.95	9.42

a. All distances are in angstroms.

It is known that fluorine can donate pi electron density to an electron deficient center when needed (Hammett $\sigma^+ = -0.07$).[4] This can be observed in the present case by the change in pi-electron density calculated at fluorine as one moves from 4 to 1. One can also see that the resonance form $C=F^+$ in which there is partial carbon-fluorine double bond character is also important by observing the dramatic change in C-F bond length (0.1 A°) in the same series. The results of both basis sets lead to the same conclusions.

The ^{19}F nmr chemical shifts have been reported for 1 (63.1 ppm)[5], 2 (99.5 ppm)[6], 3 (163.5 ppm) and 4 (209.0 ppm).[7] We wanted to determine if there was a relationship between the charge density calculated at fluorine and the ^{19}F chemical shift. There are theoretical reasons[2] for believing that the chemical shifts may depend on the pi-electron density at fluorine, the pi-electron densities of the bonded carbon, the change in the C-F bond order and the ionic character of the C-F sigma bond. In the present case, we have found that there is a very good correlation between the total electron density calculated at fluorine using the 3-21G basis set and the ^{19}F chemical shifts (Figure 1). The slope of the line fitted using a least-squares analysis is 850 ppm per electron with a standard deviation of 3.9 ppm.

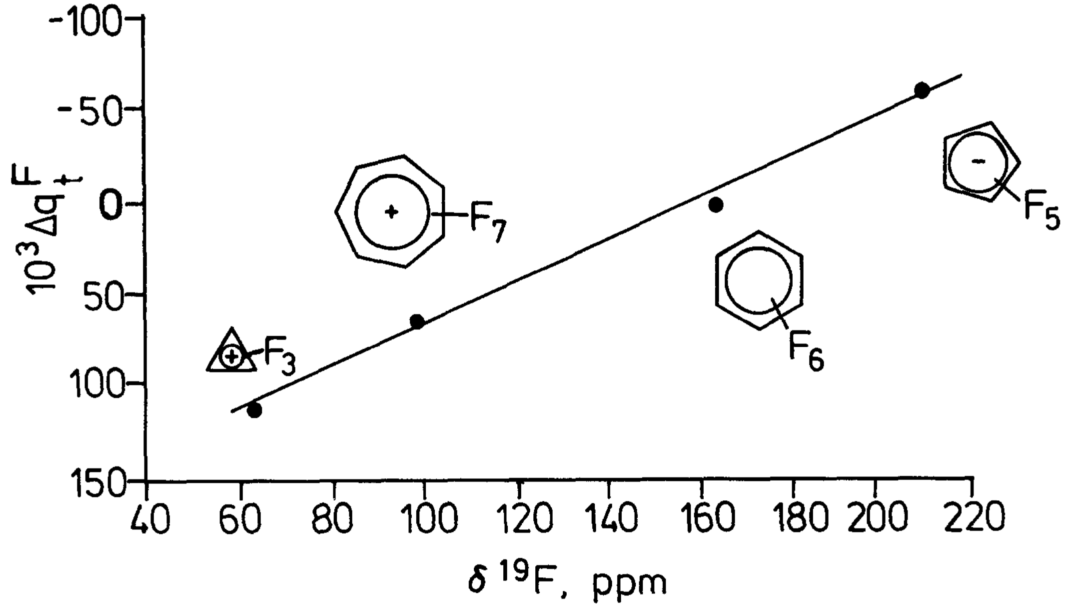

Figure 1. Total Charge Density at Fluorine Calculated Using a 3-21G Basis versus Fluorine Chemical Shift.

A poorer correlation is found if one considers the STO-3G results or the pi-electron densities calculated using the 3-21G basis set. Previous workers have used the STO-3G basis and have found a linear relationship between the pi-electron density at fluorine and the ^{19}F chemical shifts.[2] However it is known that the STO-3G basis set overestimates the degree of fluorine-carbon backbonding and charge alternation.[8] For example, we have calculated the geometry of the cyclopropenium ion and the fluorocyclopropenium ion at both the STO-3G and 3-21G levels. The results are shown in Table 2.

Table 2. Geometrical Parameters for Cyclopropenium Ion (5) and Fluorocyclopropenium Ion (6) Derived from Ab Initio Calculations.

	Basis	r(C-H)	r(C-F)	r(C_1-C_2)	r(C_2-C_3)
5	STO-3G	1.09		1.37(7)	
	3-21G	1.06		1.36(1)	
6	STO-3G	1.09	1.30	1.38(4)	1.37(9)
	3-21G	1.06	1.28	1.35(3)	1.37(2)

At the STO-3G level, the carbon-carbon bond opposite the fluorine is slightly shorter (0.005 A) than the carbon-carbon bonds adjacent. This suggest a contribution from the resonance structure which places a positive charge on fluorine.

However at the 3-21G level, this trend is reversed and one now finds that it is the carbon-carbon bond adjacent to the fluorine which is shortened and the bond opposite which is lengthened. This agrees with the experimental results of Craig and coworkers who found that fluorine substitution of the cyclopropenium system results in a strengthening of the bonds adjacent and a weakening of the bond opposite the substituent relative to the parent.[9] This overestimation of the pi-donating effect of fluorine predicted by the STO-3G basis set may well be a reason why previous workers found such a good correlation between pi-electron density calculated at fluorine and the fluorine chemical shift. We hope our results will lead to a renewed interest in developing a theoretical model for predicting fluorine chemical shifts.

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