THE ORIGIN OF FLUORINE-19 AND CARBON-13 SUBSTITUENT

CHEMICAL SHIFTS IN SUBSTITUTED BENZYL FLUORIDES

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Fluorine-19 substituent chemical shifts (SCS) in aromatic systems have been rationalised in terms of substituent induced modifications of electron densities around the fluorine nucleus.[1,2] In a number of aliphatic fluoride systems the direction of the F-19 SCS is reversed compared with normal expectations.[3,4] For example in the substituted benzylfluoride series the SCS for acceptor substituents is upfield indicating that the fluorine nucleus has become more shielded relative to the hydrogen substituent. When these shifts are related to Hammett substituent parameters the resulting slope is opposite in sign to that obtained from a corresponding series of fluorobenzenes. The F-19 chemical shift anomalies observed in this[3] and other systems[6] have not been rationalised in terms of electron density populations and thus a number of mechanisms, including substituent induced structural distortions[6], have been proposed.

The factors that control C-13 and F-19 substituent chemical shifts are thought to be similar[7], and thus we have measured the C-13 SCS and remeasured the F-19 SCS of a series of para-substituted benzylfluorides in an attempt to obtain a better understanding of the mechanisms involved. Table 1 shows the F-19 and C-13 SCS's of the fluorine atom, the carbon of the $-CH_2$ group and the ipso ring carbon in the p-substituted benzylfluorides.

Table 1   F-19 and C-13 SCS in p-substituted benzylfluorides in p.p.m.[a]

Subst.	F-19[b]	ΔqF[d]	C-13(CH_2)[c]	ΔqC[d]	C-13(ipso)[c]	ΔqC[d]
NO_2	-8.86	-58.3	-1.79	-6.7	+7.79	-190
CN	-8.41	-41.5	-1.55	-5.5	+5.17	-130
H	0.0	0	0.0	0	0.0	0
Me	+3.03	9.7	0.0	-0.3	-3.06	- 74
Cl	-0.74	-	-0.84	-	-2.44	-
F	+2.74	0.5	-0.68	-5.3	-4.18	84
OMe	+7.46	16.4	-0.07	-4.7	-8.59	150
NH_2	-	24.4	-	-3.1	-	143

(a) Positive chemical shifts are downfield in all cases. (b) Shifts were measured at 94.07 MHz as 0.3% w/v solutions in $CDCl_3$. The shift corresponding to the -H substituent is 93.50 p.p.m. upfield from tetrachlorotetrafluorocyclobutane. (c) Shifts were measured at 25.15 MHz as 6% w/v solutions in $CDCl_3$. The shift for the CH_2 group corresponding to the -H substituent is 7.57 p.p.m. downfield from the centre peak of $CDCl_3$. The shift for the c (ipso) carbon corresponding to the -H substituent is 59.17 p.p.m. downfield from the centre peak of $CDCl_3$. (d) Substituent electron densities $\times 10^4$ calculated by STO-3G method.[10]

The relationships between these data and Hammett substituent constants using the Dual Substituent Parameter analysis[8] all show good correlations. These equations are shown below and several important observations can be made from them.

$$F\text{-}19 \begin{cases} p\text{-}x \\ \text{-}H \end{cases} = -10.2\sigma_I - 17\sigma_R{}^{BA} \quad SD = 0.37$$

$$C\text{-}13 \ (CH_2) \ \delta = - 2.5\sigma_I - 1.1\sigma_R{}^{BA} \quad SD = 0.09$$

$$C\text{-}13 \ (ipso) \ \delta = + 4.6\sigma_I + 17.6\sigma_R{}^{BA} \quad SD = 0.80$$

Firstly both the $-CH_2$ carbon SCS and the F-19 SCS have the same sign of dependence on inductive and resonance parameters, although as expected in different proportions. Secondly this dependence is opposite to that found for the ipso carbon which has a similar electronically induced C-13 SCS to that in mono-substituted benzenes.[9]

These correlations, together with the calculated electron densities[10] shown in Table 1 have enabled us to exclude a number of the suggested mechanisms

for the reverse fluorine and carbon SCS's.

The close relationship between the carbon (CH_2) and the fluorine SCS's indicate that structural distortion must be rejected as a special mechanism contributing to F-19 shifts. Also structural distortion is unable to explain the reversed carbon shift in this series and a number of others.[11] Further evidence against this mechanism is seen from the carbon (ipso) correlation which is normal and similar to the equivalent position in substituent toluenes.[12] In the latter case both the methyl and _ipso_ carbon SCS are in the normal direction.

It has been suggested[13] that the carbon SCS direction would be a function of the total charge on the atom concerned. The $-CF_3$ group in benzotrifluor-*ides has a very much lower carbon electron density than that of the carbon in* the $-CH_2F$ group, yet both their SCS's are similar and anomalous which we *believe refutes this argument in these cases.*

It is also thought that substituent interactions with the excited state orbital could result in unusual chemical shift effects through variation in ΔE (the mean excitation energy approximation).[14] From the molecular orbital calculations we have examined the substituent effect on the first excited state and find the trends similar to those in monosubstituted benzenes. In general transition energies do not correlate well with substituent effects and since these shifts are related to substituent effects we must exclude this possibility.

The calculated electron densities as shown in Table 1 indicate that while the trends for the C(ipso) atom are as expected the electron densities on the $-CH_2$ carbon are unusual. The way in which substituents modify this electron density can be investigated by correlating the electron density changes with the Hammett substituent parameters using the DSP method as shown below.

$$\Delta q \ (CH_2) = -9\sigma_I + 6\sigma_R \text{ in units of } 10^4 \text{ electrons.}$$

This equation indicates that while inductive withdrawing substituents reduce the electron density, resonance withdrawing substituents in contrast increase the density at this site. Thus the direction of the chemical shift on this carbon is consistent with the charge resulting from resonance inter-

action of substituents. Similar logic cannot be applied to the fluorine

electron densities which are similar to those on the ipso carbon.

It is concluded from this study that there are components of the electron

density on the $-CH_2$ carbon that are consistent with the direction of the C-13

SCS. In this case, and for the fluorine SCS it will be necessary to evaluate

many more of the electronic contributions to the paramagnetic screening term

than has been the case for carbons in benzene rings.

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