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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFTS OF SUBSTITUTED BENZENES. A NEW PROPOSITION OF ELECTRONEGATIVITY CORRELATION OF META-CARBON CHEMICAL SHIFTS

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We found that ^{13}C chemical shifts of meta-ring carbons in a series of substituted benzenes are correlated with substituent electronegativities. While many attempts have been made to correlate ^{13}C chemical shifts with physical properties of molecules, the Hammett σ parameters are generally accepted as being more useful for understanding substituent effects on ^{13}C chemical shifts. In fact, earlier,[1] relative para-substituent chemical shifts (C_p-SCS) were found to be correlated satisfactorily with the Hammett σ parameters.[2] On the other hand, the data on C_m-SCS showed an irregular trend against the Hammett σ.[1,2a,3] Thus, only limited discussion on C_p-SCS developed,[4] and an attempt was made to correlate C_p- and C_m-SCS, separately.[5] Re-investigating ^{13}C-SCS of 3- and 4-substituted toluenes[5] and benzonitriles[6] in $CDCl_3$, we confirmed that their C_p-SCS can be correlated well with the Hammett σ, as listed in the TABLE. However, we also failed to obtain good Hammett relationships for C_m-SCS even with separate plottings. Side-chain α-carbon SCS (C_α-SCS) can be correlated fairly well with the Hammett σ in the case of this present study; this problem will be investigated in a separate paper.

If the paramagnetic shielding due to atoms or substituents mainly controls ^{13}C-SCS, then correlations with electronegativity are to be expected. Relative SCS values for aryl carbons directly bonded to a substituent (C_s-SCS) were reported to be approximately related to substituent electronegativity in monosubstituted benzenes.[1] Since a contribution arising from substituent electronegativity can be expected to extend as far as the meta-carbons, we thought it worthy to explore an empirical correlation between

TABLE. Data on ^{13}C Chemical Shifts (δ_C)[a] and ρ and $a(\chi_X)$ Values[b] for Toluenes and Benzonitriles

Substituent (X)	Electronegativity (χ_X)	3-X-toluenes 1(m)	2(o)	3(s)	4(o)	5(m)	6(p)	Me(α)	4-X-toluenes 1(p)	2(m)	3(o)	4(s)	Me(α)	4-X-benzonitriles 1(p)	2(m)	3(o)	4(s)	CN(α)
H	2.17	137.6	129.0	128.3	125.3	128.3	129.0	21.3	137.6	129.0	128.3	125.3	21.3	112.5	132.0	129.3	132.8	118.8
Me	2.63	137.7	130.0	137.7	126.2	128.3	126.2	21.3	134.6	129.1	129.1	134.6	20.9	109.6	132.0	130.0	143.7	119.0
Et	2.57	--	--	--	--	--	--	--	135.0	129.1	127.8	141.3	20.9	--	--	--	--	--
CHO	2.79	138.9	129.9	136.8	127.1	128.8	135.1	21.1	145.5	129.8	129.8	134.4	21.8	117.7	133.0	129.8	138.9	117.7
COMe	2.75	138.3	128.8	137.2	125.6	128.4	133.8	21.3	143.8	129.1	128.4	134.8	21.6	116.4	132.5	128.7	140.0	117.9
C≡N	3.17	139.3	132.2	112.3	129.1	129.1	133.6	20.9	143.7	130.0	132.0	109.6	21.7	116.9	132.8	132.8	116.9	117.1
$SiMe_3$	1.68	--	--	--	--	--	--	--	138.5	128.6	133.4	136.8	21.4	--	--	--	--	--
NH_2	3.40	139.1	116.0	146.5	112.3	129.2	119.5	21.4	127.7	129.6	115.1	143.8	20.4	99.4	133.7	114.4	151.0	120.5
NMe_2	3.21	138.6	113.5	150.8	110.0	128.9	117.7	21.9	125.6	129.6	113.2	148.9	20.3	97.0	133.1	111.4	152.4	120.5
NO_2	3.45	139.9	123.7	148.3	120.6	129.1	135.3	21.1	146.2	130.0	123.5	146.2	21.5	118.4	133.6	124.3	150.2	116.8
OH	3.89	139.9	116.2	155.2	112.4	129.5	121.8	21.3	130.2	130.2	115.4	153.2	20.5	--	--	--	--	--
OMe	3.60	139.4	115.0	159.9	111.0	129.3	121.6	21.5	129.6	129.8	113.9	157.8	20.4	103.9	134.0	114.9	163.1	119.2
SMe	2.58	138.2	127.3	138.5	123.7	128.7	125.9	21.3	134.8	129.6	127.4	135.0	20.9	--	--	--	--	--
F	3.94	140.5	116.0	163.0	112.3	129.6	124.8	21.3	133.4	130.3	115.0	161.2	20.6	--	--	--	--	--
Cl	3.00	139.7	129.1	134.0	125.5	129.3	127.1	21.0	136.1	130.4	128.4	131.2	20.7	111.0	133.4	129.7	139.4	117.8
Br	2.68	140.1	132.1	122.3	128.5	129.7	127.7	21.1	136.5	130.6	131.2	119.0	20.8	--	--	--	--	--
ρ_σ[b,c]		-1.7_7	--	--	--	-0.5_0	-11.5_9	$+0.3_6$	-13.1_8	-1.2_4	--	--	-0.9_1	-13.7_0	$+0.1_7$	--	--	$+2.3_3$
r[d]		0.51_7				0.28_4	0.95_1	0.70_6	0.93_8	0.57_3			0.80_5	0.96_8	0.13_9			0.98_7
ρ_{σ^+}[b,c,]		-1.7_6	--	--	--	-0.5_0	-7.6_0	$+0.2_3$	-8.7_4	-1.2_7	--	--	-0.6_3	-0.91_6	-0.2_8	--	--	$+1.4_6$
r[d]		0.51_1				0.28_1	0.96_9	0.67_9	0.96_0	0.58_0			0.86_4	0.99_1	0.12_3			0.94_9
$a(\chi_X)$[b,e]		-1.6_1	$+11.6_4$	-18.7_7	$+10.6_0$	-0.8_9	$+6.3_9$	$+0.0_6$	$+5.6_8$	-0.7_7	$+11.6_5$	-16.8_2	$+0.5_6$	$+9.8_9$	-1.6_9	$+16.1_3$	-18.9_6	-0.8_3
r[d]		0.89_5	0.80_9	0.92_9	0.53_3	0.95_7	0.45_2	0.12_9	0.38_8	0.85_7	0.83_3	0.89_1	0.52_1	0.43_1	0.91_9	0.77_4	0.87_8	0.23_0

[a] The natural-abundance ^1H-noise-decoupled ^{13}C FT NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz and 30°C using about 1 mmol/cm^3 $CDCl_3$ solutions in 8-mm spinning tubes. Accuracies of δ_C (ppm downfield from internal TMS) are about ±0.1. Signals were assigned by known chemical shift rules[2c,e] and single-frequency off-resonance decoupling techniques. [b] In accordance with the procedure of other related studies, we use here a negative sign for a downfield signal shift. [c] Hammett ρ values.[11] [d] Correlation coefficients. [e] Electronegativity correlations for the 2nd-period substituents (see text).

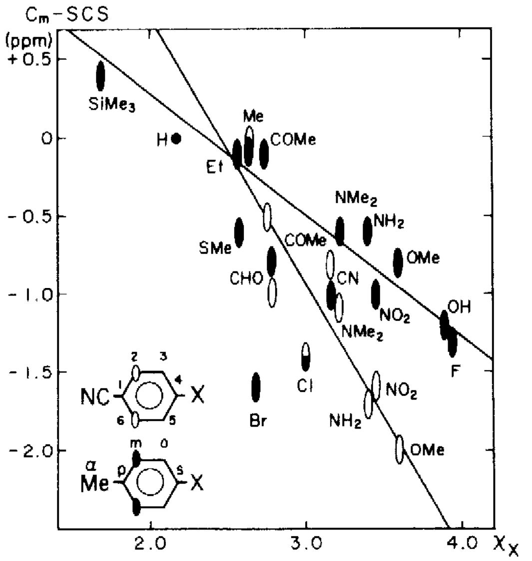

FIG. 1. Plots of C_m-SCS ($\Delta\delta_{C-2(6)}$) vs. substituent electronegativity (χ_X) for 4-substituted toluenes and benzonitriles.

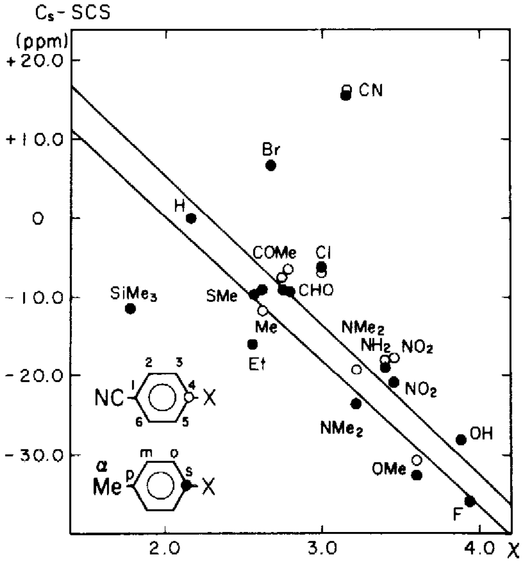

FIG. 2. Plots of C_s-SCS ($\Delta\delta_{C-4}$) vs. substituent electronegativity (χ_X) for 4-substituted toluenes and benzonitriles.

substituent electronegativity and C_m-SCS.

The observed C_m-SCS values [$\Delta\delta_{C-2(6)}$] were plotted against substituent electronegativity (χ_X) for the 4-substituted toluenes and benzonitriles as shown in FIG. 1. Although the substituent electronegativity was assumed to be that of the atom directly bonded to a ring carbon in the earlier study,[1] we use here modified values[7] derived by regarding substituents as pseudo-atoms for a more conventional approach (see the TABLE). The C_m-SCS values for substituents of elements of the second period lie close to a line encompassing Me and F (or OMe) [slopes $\alpha(\chi_X) = -0.7_7$ and -1.6_9, correlation coefficients $r = 0.85_7$ and 0.91_9 for the toluenes and benzonitriles, respectively]. Apparently, the plots for H, SMe, Cl, and Br deviate from this line. This anomaly will be discussed in the following paper.[8] Similar results were obtained for the C_m-SCS values ($\Delta\delta_{C-1}$ and $\Delta\delta_{C-5}$) for 3-substituted toluenes (see the TABLE).

To test the generality of the present substituent electronegativity correlation of C_m-SCS, literature was further examined for several series of compounds having second-period central atoms as substituents: 4-substituted <u>tert</u>-butylbenzenes[9] [$\alpha(\chi_X)_{C-2(6)} = -1.1_5$, $r = 0.96_8$, $n = 5$], styrenes[4a] [$\alpha(\chi_X)_{C-2(6)} = -1.0_9$, $r = 0.80_2$, $n = 9$], and phenylacetylenes[4b] [$\alpha(\chi_X)_{C-2(6)} = -1.4_3$, $r = 0.92_9$, $n = 8$]. The correlations obtained were reasonably good in all the cases examined.

Similar behavior is seen for the electronegativity correlations of C_s-SCS. The results obtained here for the substituted toluenes and benzonitriles substantiate the substituent electronegativity effect for the second-period element groups[8] with the marked exception of CN as shown in FIG. 2 (see also the TABLE) *Apparently, other factors such as magnetic anisotropy[10] contribute substantially to the* C_s-SCS in the case of the CN group.[8]

In conclusion, we propose that in a series of substituted benzenes, ^{13}C-SCS of both aryl carbons directly bonded to a substituent and meta-carbons are controlled by the substituent electronegativity whereas Hammett relationships hold for those of para-carbons.

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