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REVERSE SUBSTITUENT CHEMICAL SHIFT EFFECTS IN THE C-13 NMR SHIFTS OF SUBSTITUTED BENZONITRILES

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There are many literature examples correlating C-13 n.m.r. substituent chemical shifts in substituted benzenes with Hammett substituent constants.[1] The direction of these substituent chemical shifts has been logically explained in terms of substituent electronic properties; the electron donors resulting in upfield shifts, and the acceptors downfield. In this letter we report an example of a 'reverse' substituent chemical shift.

The Table shows the relevant substituent chemical shifts in a series of *meta*- and *para*- substituted benzonitriles having a basis set[2] of substituents. It is apparent from this data that the direction of the substituent chemical shift of the cyanide carbon and the adjacent ring carbon is reversed. This observation is confirmed using the Dual Substituent Parameter Hammett analysis[2] which gives the following correlations.

Meta Series:

$\delta_{CN} = 3.4\sigma_I + 1.2\sigma_R$ SD = 0.15

$\delta_{C\alpha} = -3.0\sigma_I + 0.2\sigma_R$ SD = 0.20

Para Series:

$\delta_{CN} = 2.7\sigma_I + 1.1\sigma_R^+$ SD = 0.07

$\delta_{C\alpha} = -5.4\sigma_I - 8.9\sigma_R^+$. SD = 0.93

These correlations show quantitatively the reversal of both the inductive and resonance effects in the *para*-position between the cyanide and adjacent carbon. Of interest is the good correlation between the *meta*-carbon chemical shift and substituent parameters. Here resonance effects are almost absent; a result remarkably similar to the F-19 substituent chemical shifts in *meta*- substituted fluorobenzenes,[3] a correlation that has been said to be abnormal.[4] It appears that the large charge separation in the cyanide substituent is responsible for this reversal in the direction of substituent effects. The precise correlation of the *para*-cyanide carbon with σ_R^+ is expected in this case as a result of the large electron demand placed on the substituent by the strong electron withdrawing cyanide group, and could be used to estimate new σ_R^+ values.

The chemical shifts and correlations reported here contrast those reported for these compounds[5] demonstrating the need to measure compounds in an inert solvent and at reasonably low concentration.

In view of this 'reverse' correlation considerable care is necessary in interpreting chemical shifts in terms of substituent electronic effects.

Chemical shifts of the cyanide carbon and the α carbon in the benzene ring in meta- and para-substituted benzonitriles as 0.4M solutions in $CDCl_3$.

	para substituents		meta substituents	
Subst.	CN	Cα	CN	Cα
NMe_2	-1.91[a]	15.11[b]	-0.97[a]	-0.31[b]
NH_2	-1.40	12.55	-0.47	-0.27
OMe	-0.43	8.47	0.04	-0.73
F	0.77	3.89	1.28	-1.53
Cl	0.81	1.60	1.39	-1.55
Br	0.73	1.13	1.51	-1.82
CH_3	-0.35	3.15	-0.27	0.16
CF_3	1.32	- 3.72	1.43	-1.12
CN	1.78	- 4.31	2.17	-1.78
NO_2	1.94	- 6.31	2.25	-1.74

[a] Chemical shifts in ppm are relative to the -H substituent, negative chemical shifts are downfield. The chemical shift of the -H subst. is -41.70 ppm. from the middle peak of the deuterochloroform solvent. [b] The -H subst. is -35.34 ppm from $CDCl_3$.

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