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Substituent Effects on the ^{13}C and ^{15}N NMR Spectra of *p*-Substituted Phenylacetonitriles

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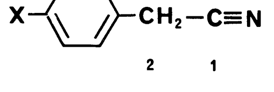
Synopsis. ^{13}C and ^{15}N NMR spectra have been measured for fifteen *p*-substituted phenylacetonitriles. The substituent-induced chemical shift changes (SCS) of C-1 had an inverse trend, while SCS (^{15}N) showed a normal trend. These SCS values were correlated by the normal substituent constant, σ^0. The observations are consistent with a pi-polarization mechanism in which the C≡N bond is polarized by the *p*-substituted phenyl moiety.

Substituent-induced chemical shift changes (SCS)[1,2] of side-chain carbons in *p*-disubstituted benzenes are considerably smaller than those of the benzene ring carbons, and the directions of SCS vary with the character of the side chain and the substituents. Though a wide range of normal, zero, and inversed substituent effects for side-chain atoms have emerged,[1,2] SCS for C_α of *p*-substituted styrenes[3] or *p*-substituted phenylethynes,[4] which takes a sp^2 or sp hybridization, shows an inverse trend (i.e. electron-attracting groups such as NO_2 lead a high field shift), while SCS (C_β) has a normal trend. Similar results have been reported for *p*-substituted benzonitriles: SCS (C_α) has an inverse trend and SCS (^{15}N) has a normal trend.[1,5,6] The most important interaction causing such SCS trends is a partial pi-polarization of the C≡N bond.[2,7,8] The direct resonance perturbation through *p*-phenylene is insignificant because of the unstable cumulene character of the polarized canonical form.[8]

In order to obtain further information concerning the substituent effect in *p*-disubstitued benzenes, the ^{13}C and ^{15}N chemical shifts of *p*-substituted phenylacetonitriles were measured and compared with SCS (C_α) and SCS (^{15}N) of *p*-substituted benzonitriles, and with the Hammett substituent constants. In *p*-substituted phenylacetonitriles, the cyano group is insulated from substituted phenyl by the methylene group, and no direct resonance exaltation contributes to SCS (C-1 and ^{15}N).[9]



To avoid solute-solute interactions, the concentrations of the samples for NMR measurements were under 0.5 mol dm^{-3}, considering infinitive dilution (Table 1). Because of the low natural abundance of ^{15}N and the insensitivity of ^{15}N in the C≡N group to NMR detection, ^{15}N NMR was measured with ^{15}N-labelled *p*-substituted phenylacetonitrile. All of the ^{13}C spectra were obtained at natural abundance for ca a 0.5 mol dm^{-3} solution of *p*-substituted phenylacetonitriles. The spectra were obtained in both chloroform-*d* and more polar acetone-d_6. ^{13}C and ^{15}N NMR chemical-shift data for *p*-substituted phenylacetonitriles are given in Table 2.

The values of SCS measured in chloroform-*d* were parallel to those of SCS measured in acetone-d_6, while the ranges of SCS (in acetone-d_6) were smaller than those of SCS (in chloroform-*d*). Hence, only SCS (in chloroform-*d*) is discussed in the following discussion. The SCS (C-1) values cover a range of 2 ppm, while the ^{15}N shifts are more sensitive to the substituents and range over 6 ppm. It is noticeable that the directions of the substituent effects are different at these two atomic sites: SCS (C-1) shows an "inverse" substituent effect similar to SCS (C_α) of *p*-substituted benzonitriles,[1] whereas SCS (^{15}N) has a normal trend, as does the SCS (^{15}N) of *p*-substituted benzonitriles.[6] There exsists an excellent linear relationship between SCS (C-1) and SCS (^{15}N) with a negative slope. This correlation indicates the significant polarization of the C≡N bond induced by *p*-substituted phenyl moiety.

$$\text{SCS (C-1)} = -0.38\ \text{SCS } (^{15}\text{N}) - 0.10,\ r = 0.994,^{10)}\ s = 0.080^{11)}$$

SCS (C-1) does not have a good linear correlation with SCS (C-2).[12] As expected, there is a good correspondence between SCS (C-1) or SCS (^{15}N) and the normal substituent constant, σ^0 values,[9] rather than original Hammett σ_p values.

$$\text{SCS } (^{15}\text{N}) = 4.76\,\sigma^0 - 0.19,\ r = 0.990,\ s = 0.269$$

$$\text{SCS } (^{15}\text{N}) = 3.74\,\sigma_p + 0.32,\ r = 0.983,\ s = 0.337$$

$$\text{SCS (C-1)} = -\,1.80\,\sigma^0 - 0.03,\ r = 0.984,\ s = 0.124$$

Table 1. Effect of the Concentration on the ^{15}N Chemical Shift of [^{15}N]Phenylacetonitrile in $CDCl_3$

Concentration mol dm^{-3}	Chemical shift[a] ppm	Concentration mol dm^{-3}	Chemical shift[a] ppm
3	228.05	0.25	227.61
1.5	227.78	0.125	227.61
1.0	227.70	0.063	227.60
0.5	227.63	0.031	227.60

a) ppm from external [^{15}N]NH_4NO_3.

Table 2. ^{13}C and ^{15}N Substituent-induced Chemical Shifts ($\delta_X - \delta_H$, ppm) of *p*-Substituted Phenylacetonitrile (Positive Values Represent Down Field Shifts)

Nuclei	^{15}N		C-1		C-2		C-ipso	
Solvent	$CDCl_3$	CD_3COCD_3	$CDCl_3$	CD_3COCD_3	$CDCl_3$	CD_3COCD_3	$CDCl_3$	CD_3COCD_3
Subst.								
$N(Me)_2$	−2.21	−1.64	0.65	0.63	−0.84	−0.98	−12.93	−13.14
NH_2	−1.82	−1.61	0.64	0.34	−0.72	−0.87	−10.77	−11.43
MeO	−1.06	−0.73	0.31	0.37	−0.74	−0.84	−8.18	−8.33
EtO	−0.94	−0.70	0.25	0.32	−0.65	−0.82	−8.39	−8.36
Me	−0.62$^{a)}$ (1.53)$^{b)}$	−0.42	0.25	0.14	−0.46	−0.42	−2.00	−3.45
t-Bu	−0.51$^{a)}$ (1.60)$^{b)}$	−0.06	0.04	0.14	−0.38	−0.50	−3.15	−3.05
F	0.49$^{a)}$ (1.61)$^{b)}$	0.12	−0.32	0.00	−0.78	−0.68	−4.37	−3.78
H	0.00 227.60$^{c)}$	0.00 228.20$^{c)}$	0.00 117.97$^{d)}$	0.00 119.55$^{d,e)}$	0.00 23.46$^{d)}$	0.00 23.87$^{d,e)}$	0.00 130.08$^{d)}$	0.00 132.68$^{d,e)}$
Cl	1.04$^{a)}$ (1.60)$^{b)}$	0.90	−0.47	−0.31	−0.43	−0.53	−1.54	−1.04
Br	1.31$^{a)}$ (1.60)$^{b)}$	1.02	−0.69	−0.39	−0.29	−0.44	−1.12	−0.47
MeOCO	1.83$^{a)}$ (1.53)$^{b)}$	1.22$^{a)}$ (1.68)$^{b)}$	−0.85	−0.44	0.21	0.08	4.82	5.37
EtOCO	1.80$^{a)}$ (1.60)$^{b)}$	1.27	−0.83	−0.49	0.20	0.06	4.73	5.16
CF_3	2.20$^{a)}$ (1.52)$^{b)}$	1.30$^{a)}$ (1.53)$^{b)}$	−0.95	−0.40	0.10	0.16	3.94	5.03
CN	3.36$^{a)}$ (1.60)$^{b)}$	1.84	−1.44	−0.77	0.37	0.23	5.09	5.68
NO_2	3.65$^{a)}$ (1.52)$^{b)}$	2.16	−1.32	−0.81	0.11	0.06	7.21	7.68

a) A center of triplet. b) $^3J_{NH}$ (Hz). c)Chemical shift from external [^{15}N]NH_4NO_3. d) Chemical shift from TMS. e) Chemical shifts were measured with respect to a center of acetone-d_6 and converted to TMS reference by additing 30.10 ppm.

$$\text{SCS (C-1)} = -1.41\,\sigma_p + 0.32,\ r = 0.974,\ s = 0.162$$

Therefore, SCS (C-1) and SCS (^{15}N) can be rationalized to be perturbed in a through-space manner by the polar *p*-substituted phenyl moiety.[7,8] As shown in Figs. 1 and 2, SCS (C-1) and SCS (^{15}N) showed a linear relation with SCS (C_α) and SCS (^{15}N) for *p*-substituted benzonitrile, respectively, while the amino and dimethylamino groups deviated measurably from the regression line (Fig. 1). Thus, the C≡N bonds of *p*-aminobenzonitrile and *p*-dimethylaminobenzonitrile were strongly perturbed by a so-called secondary resonance effect, as substantiated for SCS (^{15}N, ^{17}O) in *p*-substituted nitrobenzenes.[7]

SCS (C-2) showed a normal trend, while the effects of the electron-attractive groups were very small. The application of the LSFE (linear substituend free energy) equation[13] to SCS (C-2) afforded a correlation: SCS (C-2) $= -0.39\ \sigma_i + 1.21\ \sigma_\pi^+ + 2.31\ \sigma_\pi^- - 0.23$ (r=0.925, s=0.18). The absolute values of 3.1 and 5.9 for ρ_π^+/ρ_i and ρ_π^-/ρ_i, respectively, reveal that SCS (C-2) is mainly controlled by a resonance effect.

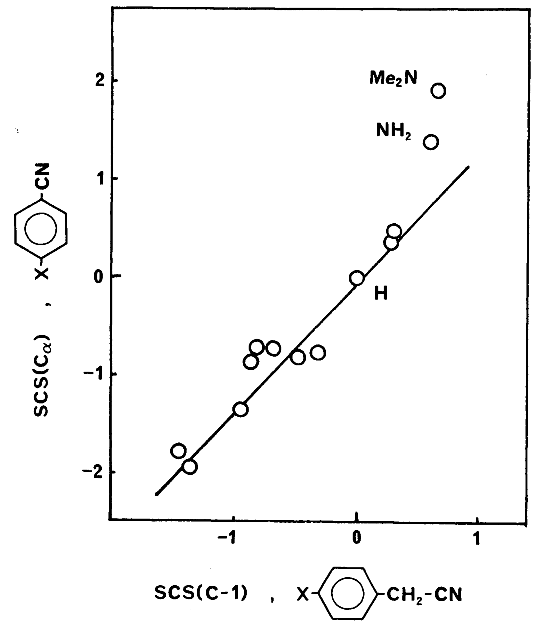


Fig. 1. Plot of SCS(C_α) of *p*-substituted benzonitriles versus SCS(C-1) of *p*-substituted phenylacetonitriles measured in chloroform-*d*.

Experimental

Most of the ^{15}N-labelled *p*-substituted phenylacetonitriles were prepared by a reaction of the corresponding substituted benzyl chlorides with potassium [^{15}N]cyanide. *p*-Nitrophenyl-acetonitrile was obtained by the nitration of [^{15}N] phenylacetonitrile. The *p*-dimethylamino derivative was

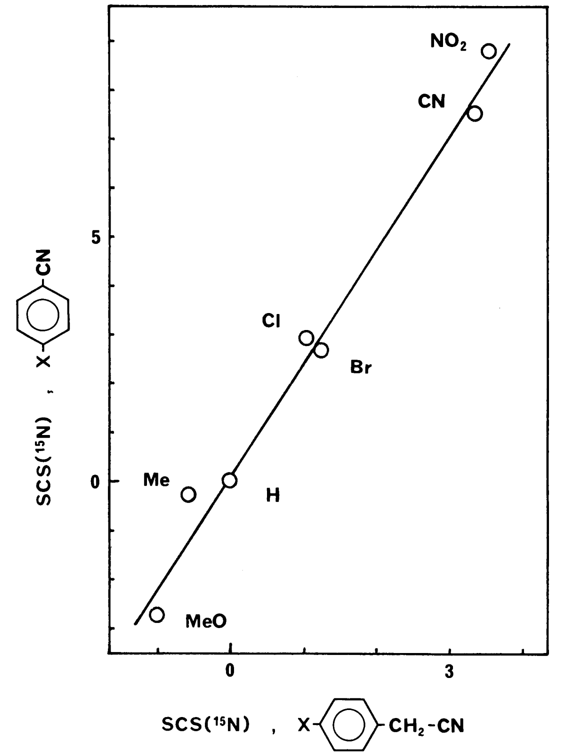


Fig. 2. SCS(^{15}N) values in ppm for 4-substituted benzonitriles versus SCS(^{15}N) for 4-substituted phenylacetonitriles.

prepared by the methylation of the *p*-amino derivative, which was obtained by the reduction of the ^{15}N-labelled *p*-nitrophenylacetonoitrile using tin and hydrochloric acid. The boiling and melting points of these ^{15}N-labelled phenylacetonitriles were as follows: substituent, bp(°C/mmHg)[14] or mp(°C); (Me)$_2$NH, 52; NH$_2$, 45; MeO, 110/3; EtO, 110/2.5; Me, 117/12; *t*-Bu, 116—119/3.5; F, 109/12; H, 81—82/4; Cl, 102—108/4; Br, 109—113/3; COOMe, 51.5; COOEt, 144—145/2.5; CF$_3$, 105/9, 40; CN, 99.5; NO$_2$, 116—117.

The ^{13}C and ^{15}N spectra were recorded on a JEOL EX90 spectrometer at 22.4 MHz for ^{13}C and at 9.0 MHz for ^{15}N, respectively. For ^{15}N NMR measurements, 10 mm sample tubes were used; the peaks were referenced to aqueous [^{15}N]NH$_4$NO$_3$ in the inserted 5 mm tube. The typical experimental conditions were a 14.5 μs pulse width (45 flip angle), an acquisition time of 6.55 s, a spectral width of 5000 Hz, and 65 K data points. The digital resolution was 0.017 ppm (0.15 Hz), and the reproducibility was +0.05 ppm. The conditions for ^{13}C NMR measurements were as good as those reported in a previous study.[15]

References

1) J. Bromilow, R. T. C. Brownlee, and D. J. Craik, *Aust. J. Chem.,* **30**, 351 (1977).

2) D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.,* **14**, 1 (1983).

3) G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Can. J. Chem.,* **51**, 897 (1973); J. Bromilow and R. T. C. Brownlee, *Tetrahedron Lett.,* **1975**, 2113.

4) D. A. Dawson and W. F. Reynolds, *Can. J. Chem.,* **53**, 373 (1975).

5) F. W. Wehrli, J. W. D. Haan, A. I. M. Keulemans, O. Exner, and W. Simon, *Helv. Chim. Acta,* **52**, 103 (1969).

6) P. S. Pregosin, E. W. Randall, and A. I. White, *J. Chem. Soc., Perkin Trans. 2,* **1972**, 513.

7) D. J. Craik, G. C. Levy, and T. C. Brownlee, *J. Org. Chem.,* **48**, 1601 (1983).

8) C. DellErba, F. Sancassan, M. Novi, G. Petrillo, A. Mugnoli, D. Spinelli, G. Consiglio, and P. Gatti, *J. Org. Chem.,* **53**, 3564 (1988).

9) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.,* **39**, 2274 (1966).

10) Correlation coefficient.

11) Standard deviation.

12) Correlation coefficient: 0.842, standard deviation: 0.38.

13) $\mathrm{SCS} = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^-$: a) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi,* **86**, 837 (1965); b) Y. Tsuno, M. Fujio, and Y. Yukawa, *Bull. Chem. Soc. Jpn.,* **48**, 3324 (1975); c) M. Sawada, Y. Takai, S. Yamano, S. Misumi, T. Hanafusa, and Y. Tsuno, *J. Org. Chem.,* **53**, 191 (1988); d) M. Sawada, Y. Takai, T. Tanaka, T. Hanafusa, M. Okubo, and Y. Tsuno, *Bull. Chem. Soc. Jpn.,* **63**, 702 (1990).

14) 1 mmHg = 133.322 Pa.

15) Y. Kusuyama, T. Kagosaku, and T. Hasegawa, *Bull. Chem. Soc. Jpn.,* **63**, 2836 (1990).