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Substituent Effect Study on ^{15}N-NMR Chemical Shifts of Aromatic Amides and Anilines

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The ^{15}N chemical shifts (δ^{15}N) of various m- and p-substituted anilides and relevant compounds were correlated with the σ or σ^- constants. The plotted points for the m- and the p-substituted derivatives tend to lie on the two separate lines. This anomalous substituent effect is interpreted.

We previously reported that the ^{1}H and ^{13}C chemical shifts of substituted benzanilides $XC_6H_4CONHC_6H_4Y$ [X-BzAN, Y-BzAN] could be correlated well with $\sigma(\sigma^-)$.1) In contrast to the good δ^1H and δ^{13}C vs. σ correlations, the δ^{15}N vs. $\sigma(\sigma^-)$ plots2) didn't give good correlations. We used some other substituent constants in order to improve the correlations, but the trials were not successful.

In search for the reason for the inapplicability of the Hammett rule, we examined the substituent effects on δ^{15}N of benz-, acet-, and trifluoroacetanilides and relevant compounds. The results are given in Table 1. In these cases, the correlations as a whole assembly including m- and p-substituted derivatives are again only fair. As easily suspected from Fig.1(a) and (b), the plots for m- and p-substituted anilides seemed to lie on separate straight lines. Thus, the Hammett plots for m-derivatives and for p-derivatives were carried out separately. The unsubstituted derivative (Y=H) was included in the plots of both m- and p-derivatives. The best-fit lines for these Hammett plots are also shown in Fig.1(a) and (b). The results show that the separate δ^{15}N vs. σ_m and δ^{15}N vs. $\sigma_p(\sigma^-)$ plots considerably improve the correlations in any of the anilides examined. This suggests that the electronic behavior of the amide nitrogen atom is somewhat different between m- and p-derivatives.

We infer that this phenomenon is caused by the difference in the conjugational or migrating ability of the lone pair electrons of the amide nitrogen. In order to examine the generality of this phenomenon, δ^{15}N of

Table 1. The ^{15}N-NMR chemical shifts[a] ($\delta^{15}N$) in several series of $RNHC_6H_4Y$ type compounds and the results of Hammett plots of $\delta^{15}N$

Y	$\sigma(\sigma^-)$	$\delta^{15}N$ of $RNHC_6H_4Y$ (ppm) / Solvent				
		$R=C_6H_5CO$ [Y-BzAN][b] $DMSO-d_6$	$R=CH_3CO$ [AcAN] $DMSO-d_6$	$R=CF_3CO$ [TFAcAN] $DMSO-d_6$	R=H [AN] $DMSO-d_6$	R=ClH-H [AN-HCl] D_2O
$p-NMe_2$	-0.83	127.0	137.7	132.3	(58.7)	(51.3)
p-OH	-0.37	129.3	137.8	132.3	58.4	49.5
p-OMe	-0.27	132.1	137.9	132.2	59.6	49.6
p-Me	-0.17	133.4	139.3	133.0	62.8	50.1
m-Me	-0.07	134.1	139.8	133.4	64.9	52.0
H	0	133.9	140.0	133.4	64.3	52.1
m-OMe	0.12	134.6	140.2	133.7	65.7	(51.4)
p-Cl	0.23	133.2	139.1	132.5	67.3	51.1
m-Cl	0.37	133.7	139.5	132.9	67.8	52.2
m-CN	0.56	133.6	139.4	132.5	69.1	52.2
p-CN	(0.88)	136.2	142.1	134.3	78.1	54.1
$m-NO_2$	0.71	133.5	139.6	132.8	70.4	52.3
$p-NO_2$	(1.24)	136.8	142.9	134.5	85.3	53.7

Hammett plots

m-,p-	intercept	132.47	139.22	132.90	63.86	51.06
	ρ	3.850	2.288	0.888	14.656	2.516
	s[c]	0.755	0.431	0.303	1.278	0.463
	r[d]	0.838	0.848	0.662	0.964	0.875
m-	intercept	134.16	139.94	133.46	64.84	52.09
	ρ	-0.916	-0.692	-1.205	7.755	0.281
	s	0.449	0.345	0.391	0.563	0.064
	r	0.714	0.708	0.839	0.990	0.930
p-	intercept	132.34	139.35	132.96	64.34	50.83
	ρ	4.423	2.765	1.208	16.286	2.892
	s	0.802	0.372	0.252	0.521	0.537
	r	0.914	0.950	0.891	0.997	0.924

a) Downfield chemical shifts from NH_3 (external).
b) Abbreviated series name is given in brackets.
c) s ; standard deviation of ρ. d) r ; correlation coefficient.

Y-substituted anilines (AN) and Y-substituted anilinium hydrochlorides (AN-HCl) were measured. The $\delta^{15}N$ of p-substituted anilines have already been reported by Yokoyama et al.[3] However, only a few $\delta^{15}N$ data of m-substituted anilines have been reported. These two series of compounds were chosen from the view point of the migrating ability of the nitrogen lone pair electrons. The lone pair electrons of the anilines occupy a relatively high energy HOMO and can migrate to the ring easily, while the anilinium ions have no such lone pair electrons.

All observed ρ_p values are positive and their magnitudes vary in the following order:

AN >> BzAN > AcAN > AN-HCl > TFAcAN

As expected, p-substituted anilines have a positive ρ value, considerably larger than those for the anilides (Table 1). This can be attributed to a strong electron donating interaction of amino nitrogen through direct resonance with Y-substituent on the aromatic ring. In contrast, AN-HCl has a very small ρ value due to the lack of the resonance effect (Table 1). Even in the case of anilinium salts, m- and p-substituted derivatives behave differently (Fig.1(c)), probably because of the inductive effects caused by the change in electron density on ipso carbon.

In BzAN, AcAN, and TFAcAN systems, local polarization in the amide group prevents the extensive conjugative interaction with the aromatic ring, and results in relatively low ρ values for the p-substituted derivatives of anilides. Thus, the magnitude of the substituent effect on the $\delta^{15}N$ of anilides and relevant compounds is dependent on the migrating ability of lone pair electrons on nitrogen atom in the series of p-substituted derivatives.

The $\delta^{15}N$ values of substituted anilines could be correlated roughly ($r=0.908$) with the electronic transition energies calculated from the wavelengths at the maxima of their ultraviolet absorption bands.4) This fact suggests the contribution of the electronic excited states to the downfield shift. Therefore, the contribution of the paramagnetic term must be significant with the $\delta^{15}N$. In fact, the ^{15}N nuclei of the anilinium salts resonate at the highest field in spite of the lowest electron density. This showed the $\delta^{15}N$ values are not governed merely by the electron density. On the other hand, the downfield shift by a strongly electron-withdrawing p-substituent should be ascribed to the electron-density effect. Thus the ^{15}N chemical shift should be interpreted by the two cooperating effects.

Electron-withdrawing inductive effect by the m-substituent can be expected to decrease the core electron density on the nitrogen, stabilizing the ground state energy. In particular, the stabilization of the nitrogen lone pair electrons should be significant, raises, in turn, the $n-\pi^*$ transition energy and reduces the contribution of the paramagnetic term of the chemical shift. As the conjugation effect by the ring substituent Y is not transmitted effectively to the nitrogen, this inductive effect predominates over the conjugation effect causing the slight negative ρ_m value. At present, we have no clear evidence for this interpretation, though the correlation with the ultraviolet spectral data and the unusually high chemical shift of anilinium ions may support it.

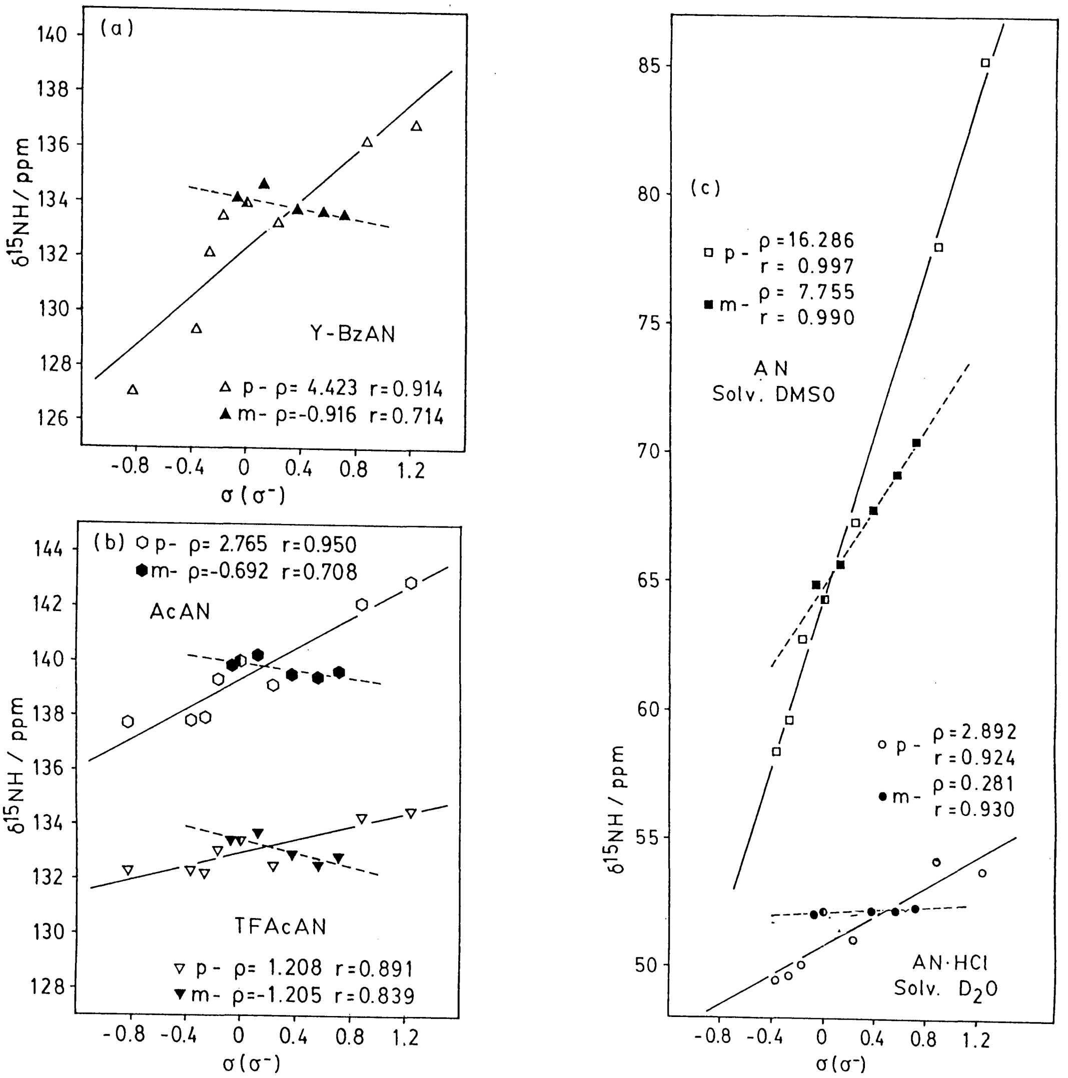

Fig.1. The δ^{15}N vs. $\sigma(\sigma^-)$ plots (a)for Y-BzAN, (b)for AcAN and TFAcAN, and (c)for AN and AN-HCl.

References

1) H.Suezawa, T.Yuzuri, M.Hirota, Y.Ito, and Y.Hamada, *Bull.Chem.Soc.Jpn.*, **63**, 328 (1990).

2) As the nitrogen lone pair can conjugate directly with the p-substituent Y in the anilino derivatives bearing p-electron-withdrawing substituent, σ^- values, in place of σ, were employed for such p-substituents.

3) T.Yokoyama, I.Hanazome, M.Mishima, M.J.Kamlet, and R.W.Taft, *J.Org. Chem.*, **52**, 163 (1987).

4) UV data from "DMS UV Atlas of Organic Compounds," Butterworths, London (1966). BzlnAN 262 nm (ε:17000), AcAN 239 nm (ε:10400), AN 230 nm (ε:8200), AN-HCl 203 nm (ε:7600)

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