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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XIV.[1] On the *meta* ^{1}H and ^{13}C Chemical Shift of Monosubstituted Benzene and Pyridine Series

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Meta ^{1}H and ^{13}C chemical shifts of monosubstituted benzene and pyridine derivatives have been correlated with respect to the substituent constants σ_i and σ_π, and following results are presented.

a) The π-electronic contributions observed among both ^{1}H and ^{13}C shifts are positive.

b) Above conclusions are also reliable in substituted pyridines.

Introduction

Recently, the difference between π-electron charge density from the corrected aromatic ring ^{1}H chemical shift and that from Hueckel molecular orbital calculation has been observed in an excess charge density of substituent's *meta* position, namely, that of the former is positive, whereas the latter negative, and this problem was settled by refining the mathematical treatment.[3] Nevertheless, on the origin of discrepancy observed in *meta* position, some doubts are remain unsettled. Formerly, several groups of workers[4-6] have discussed on the origin of *meta* ^{1}H shift, and concluded that they were controled mainly from the linear combination of inductive and resonance contribution, etc.

Table I. Calculated and Observed *meta* ^{1}H Chemical Shifts (ppm) of Monosubstituted Benzenes

Substituent	Effective shielding constant	D_i	ΔE	d_m rev.	$\Delta E+d_m$ rev.	d_m
NR_2	−1.57	−1.26	−0.05	+0.15	+0.10	+0.13[a]
OH	−2.56	−2.05	−0.08	+0.09	+0.01	+0.12[a]
OR	−2.36	−1.89	−0.07	+0.08	+0.01	+0.06[a]
Me	−0.47	−0.38	−0.01	+0.03	+0.02	+0.10[b]
Ac	−1.70	−1.36	−0.05	−0.08	−0.13	−0.09[b]
CO_2R	−1.55	−1.24	−0.05	−0.06	−0.11	−0.10[c]

d_m = *meta* shielding parameter
d_m rev. = revised *meta* shielding parameter
a) S. Castellano, C. Sun and R. Kostelnik, *Tetrahedron Letters*, **1967**, 5205
b) J. S. Martin and B.P. Daily, *J. Chem. Phys.*, **39**, 1722 (1963)
c) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961)

1) Part XIII: Y. Sasaki, M. Hatanaka and M. Suzuki, *Yakugaku Zasshi*, **89**, 64 (1969).
2) Location: *Toneyama 6-5, Toyonaka, Osaka.*
3) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1090 (1969).
4) R.R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).
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6) R.W. Taft and H.D. Evans, *J. Chem. Phys.*, **27**, 1427 (1957).

In this work, both ^1H and ^{13}C chemical shifts of monosubstituted benzene and pyridine series have been analysed with respect to the substituent constants σ_i and σ_π,[7] and semiquantitative contribution from π as well as sigma electronic effect—in other word, field effect[8]—have been examined.

Results and Discussion

1. *meta* ^1H Chemical Shift

In this section, the details among revised[9] and observed *meta* ^1H chemical shifts are summarised in Table I, and which showed comparable agreement with $\Delta E+d_m$ rev. and d_m. Where, ΔE is a field effect component estimated from Branch & Calvin's approximation[10] and σ_i fraction of substituted alkyl derivatives,[11] instead of Buckingham's electric field model.[12]

Table II. Separation of Sigma and π Electronic Fraction of *meta* ^{13}C Chemical Shifts of Monosubstituted Benzenes (ppm)

Substituent	δ_c *meta*	$D_{p_i\text{-}meta}$	$D_{i\text{-}meta}$
Me	−0.3	+0.12	−0.18
OMe	−0.9	+0.36	−0.54
NH_2	−1.3	+0.52	−0.78
NMe_2	−0.9	+0.36	−0.54
Ac	−0.2	−0.08	−0.12
OH	−1.7	+0.68	−1.02
NO_2	−0.8	−0.32	−0.48
C_6H_5	−0.4	+0.16	−0.24

Namely, sigma electronic contribution of a substituent ΔE in aliphatic system is expressed as below:

$$\Delta E=\varepsilon^n \times D_i \qquad (1)$$

where D_i = effect of substituent on an adjacent atom

n = number of bonds between substituent and functional group

ε = empirical number 1/3

Moreover, as is shown in the previous study,[11] the effective shielding constants[13] have been shown in terms of $\sigma_i-0.25\,\sigma_\pi$, then we are able to estimate tentatively σ_i fraction D_i and ΔE values of *meta* ^1H shifts.

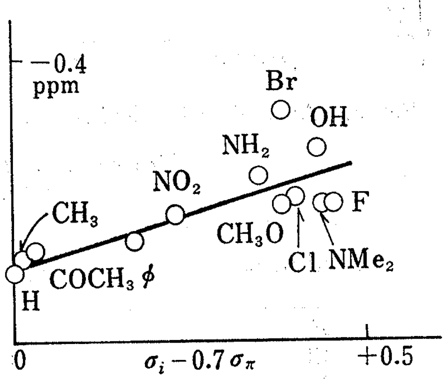

Fig. 1. *meta* ^{13}C Chemical Shifts of Monosubstituted Benzenes

7) Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan.* (Pure Chemistry Section), **86**, 873 (1965).
8) M.J.S. Dewar and P.J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539 (1962); **84**, 3548 (1962).
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13) B.P. Daily and J.N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

Table III. Alkyl ^{13}C Chemical Shift and Sigma Electronic Fraction (ppm)

Substituent	Observed	ΔCH_4	D_i	$1/27 \times D_i$
CH_4	130.8	0		
MeF	53.3	−77.5		
MeCl	103.8	−27.0		
MeBr	119.3	−11.5		
Me_2O	69.3	−61.5	−43.7	−1.62
Me_3N	81.2	−49.6	−35.2	−1.30
$MeNO_2$	71.4	−59.4	−42.2	−1.56
Acetone	104.0	−26.8	−19.0	−0.70
Me_2SO	85.2	−45.6	−32.4	

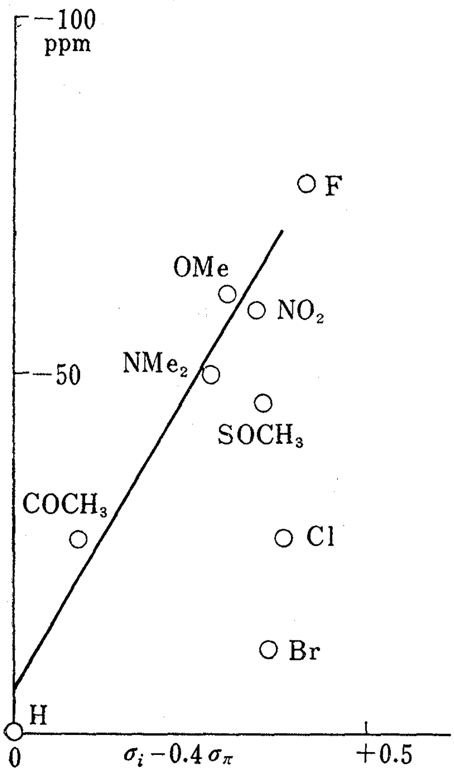

Fig. 2. Alkyl ^{13}C Chemical Shifts

2. *meta* ^{13}C Chemical Shift

In this section, observed *meta* ^{13}C chemical shifts of monosubstituted benzenes[14] have been treated similarly as in section 1, and proved linear with $\sigma_i - 0.7\,\sigma_\pi$ (*cf.* Fig. 1 and Table II).

Consequently, it is concluded that in *meta* ^{13}C chemical shifts of monosubstituted benzenes the *pi*-electronic—in other words, resonance—effect contribution is positive.

3. Alkyl ^{13}C Chemical Shift

In this section, alkyl ^{13}C chemical shifts[15] have been correlated with substituent constants, and proved linear with $\sigma_i - 0.4\,\sigma_\pi$ (*cf.* Fig. 2).

From above relation, substituent's sigma electronic or field effect contributions D_i and those on *meta* positions $1/27 \times D_i$ are estimated (*cf.* Table III), and, fortunately, D_{i-meta} in Table II shows comparable correspondence with $1/27 \times D_i$ in Table III.

Table IV. *meta* ^{13}C Chemical Shifts of Monosubstituted Pyridines from Pyridine Reference (ppm)

Substituent	2-Pyridine C-4	2-Pyridine C-6	3-Pyridine C-5	4-Pyridine C-2
F	−5.4	−2.3		
Cl	−3.0	0	−0.9	
Br	−3.3	−0.4	−1.0	−1.2
NH_2	−1.7	1.6		1.0
OMe	−1.8	2.6		
Et	0.1	0.8	0.4	0.8
Me	−0.8	0.8	0.4	0.5
CN	−0.8	0.8	0.4	0.5
CHO	−1.3	0.1	−0.5	−0.9
Ac	−1,0	2.1	0.2	−0.8

14) G.E. Maciel and J.J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).
15) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

4. *meta* ^{13}C Chemical Shifts of 2-, 3- and 4-Substituted Pyridines

Recently, ^{13}C chemical shifts of 2-, 3- and 4-substituted pyridines have been presented by Retcofsky and Friedel[16] (*cf.* Table IV).
In the previous papers of this series,[17,18] the corrected ring ^{1}H chemical shifts of *meta* position in 3- and 4-substituted series have been treated with substituent constants σ_π, and positive correlations are acknowledged. But, in the present step, contrary to ^{1}H resonance, the correction terms from ring current, nitrogen magnetic anisotropy and electric field effects are not known in ^{13}C resonance.

Then, in the analogous way, *meta* ^{13}C shifts of above three series have been analysed directly with respect to substituent constants (*cf.* Fig. 3a—c), and following results are obtained.

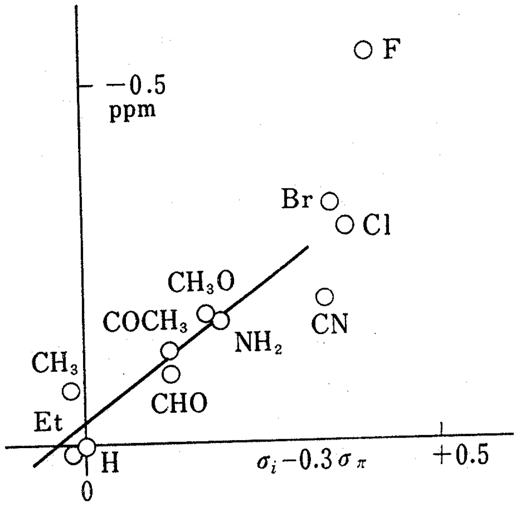

Fig. 3a. C_4 Chemical Shifts of 2-Pyridines

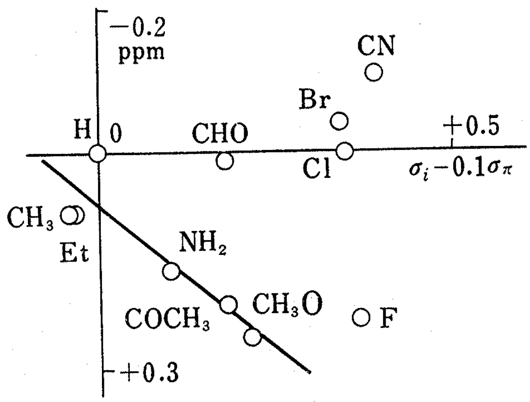

Fig. 3b. C_6 Chemical Shifts of 2- Pyridines

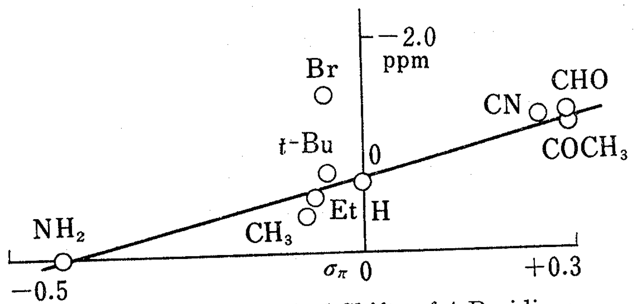

Fig. 3c. $C_{2.6}$ Chemical Shifts of 4-Pyridines

2-pyridines	$C_4 \propto \sigma_i - 0.4\sigma_\pi$
	$C_6 \propto \sigma_i - 0.1\sigma_\pi$
3-pyridines	$C_5 \propto$?
4-pyridines	$C_{2,6} \propto \sigma_\pi$

Consequently, it is concluded that positive π-electronic effect is operative in *meta* position.

And, an anomalous behaviour observed in C-6 shift of 2-pyridines suggests that negative sigma electronic effect plays an important role. This is because the contribution from $C_6 \rightarrow N$ sigma bond polarisation is reduced as that of $C_2 \rightarrow$substituent sigma bond, which is opposed to $C_2 \rightarrow N$ sigma bond polarisation, increases.

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16) H.L. Retcofsky and R.A. Friedel, *J. Phys. Chem.*, **71**, 3592 (1967); **72**, 2619 (1968).
17) Y. Sasaki, M. Hatanaka, I. Shiraishi, M. Suzuki and K. Nishimoto, *Yakugaku Zasshi*, **89**, 21 (1969).
18) Y. Sasaki, M. Suzuki and M. Hattori, *Chem. Pharm. Bull.* (Tokyo), **17**, 1515 (1969).