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Studies on the Proton Magnetic Resonance Spectra in Aromatic Systems. XI. Heteroaromatic Series. III. Discussions on the Coupling Constants of Substituted Pyridines[1]

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The coupling constants of substituted pyridines have been discussed with respect to substituent constant σ_i and σ_π. And, for the estimations of coupling constants, empirical equations:

$$J \fallingdotseq (J^i + J^\pi)_{\text{ref.}} + \sum \Delta J^i \quad (1)$$

and

$$J \fallingdotseq (J^i + J^\pi)_{\text{ref.}} + \sum \Delta J \quad (2)$$

showed reliabilities in numerous substituted pyridines.

Introduction

Recently, accurate spectral parameters of substituted pyridines have been reported from several groups of workers.[3—6] In the previous paper of this series, it is concluded that coupling constant—J value—in substituted aromatics has been estimated empirically from following equations (1) and (2).
Namely, for *vicinal* ^{1}H coupling constant

$$J \fallingdotseq (J^i + J^\pi)_{\text{ref.}} + \sum \Delta J^i \quad (1)$$

And, for *meta* ^{1}H coupling constant intervening the substituent

$$J \fallingdotseq (J^i + J^\pi)_{\text{ref.}} + \sum \Delta J \quad (2)$$

where

$(J^i + J^\pi)_{\text{ref.}}$ = reference J value
ΔJ^i = σ-electronic contribution in excess J value
ΔJ = excess J value

In this work, J values of mono-substituted pyridines have been treated in a same manner as in the previous work,[7] and the reliabilities of above equations (1) and (2) have been discussed for several polysubstituted pyridines.

Methods of Analyses

The J values of 2-, 3- and 4-pyridines[5,6] are correlated with substituent constant σ_i and σ_π[8] (*cf.* Fig. 1—3), and following correlations are acknowledged.

1) Part X: Y. Sasaki, K. Iwasaki, M. Suzuki and K. Nishimoto, *Yakugaku Zasshi*, **89**, 25(1969).
2) *Location*: *Toneyama 6-5, Toyonaka, Osaka.*
3) S. Castellano, C. Sun and R. Kostelnik, *J. Chem. Phys.*, **46**, 327 (1967).
4) T.K. Wu, *J. Phys. Chem.*, **71**, 3089(1967).
5) V.T. Kowalewski and D.G.de Kowalewski, *J. Chem. Phys.*, **36**, 266(1962); *ibid.*, **37**, 2603(1962).
6) W. Brügel, *Z. Elektrochem.*, **66**, 159 (1962).
7) Y. Sasaki, M. Suzuki and S. Ozaki, *Chem. Pharm. Bull.* (Tokyo), **16**, 2145 (1968).
8) Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan* (*Pure Chemistry Section*), **86**, 873(1965).

a. 2-Pyridines

$$J_{34}=\sigma_i-\sigma_\pi$$

$$J_{35}=\sigma_i-1.5\sigma_\pi$$

$$J_{45}=\sigma_i-1.5\sigma_\pi$$

$$J_{46}=\sigma_i$$

$$J_{56}=\sigma_i-1.5\sigma_\pi$$

b. 3-Pyridines

$$J_{24}=\sigma_i-\sigma_\pi$$

$$J_{45}=\sigma_i$$

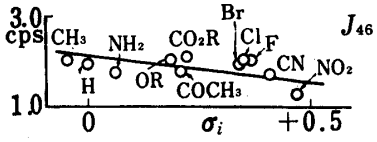
$$J_{46}=\sigma_i$$

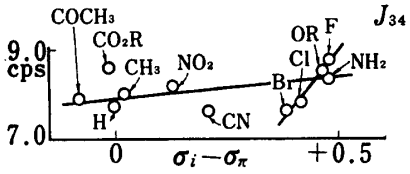
$$J_{56}=\sigma_i$$

c. 4-Pyridines

$$J_{23}=\sigma_i-0.5\sigma_\pi$$

$$J_{35}=\sigma_i-0.7\sigma_\pi$$





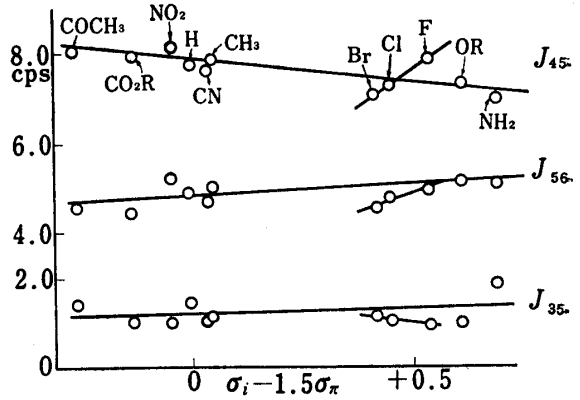
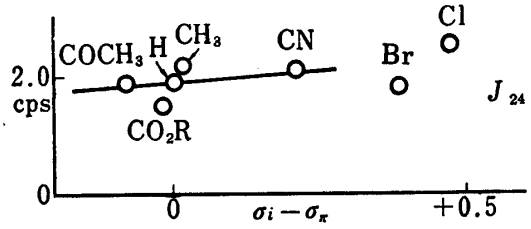


Fig. 1[a)]

a) The ^{1}H position numbers are as follows: 



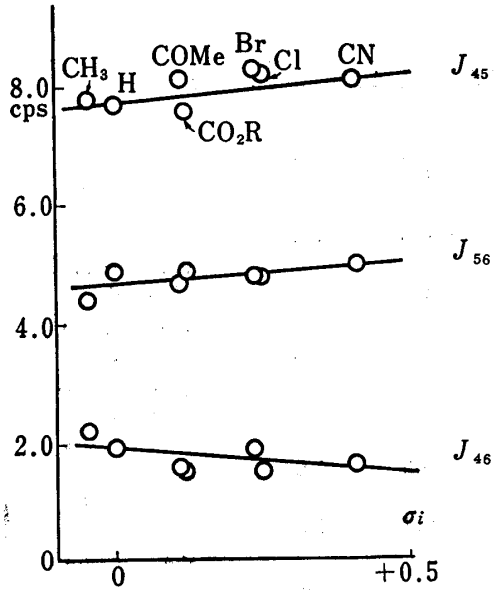
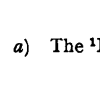
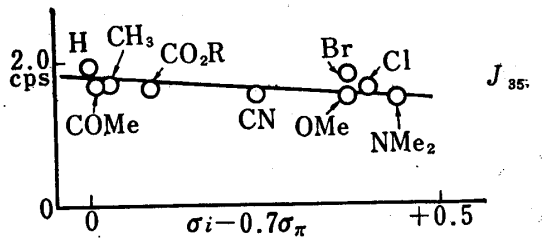


Fig. 2[a)]

a) The ^{1}H position numbers are as follows: 



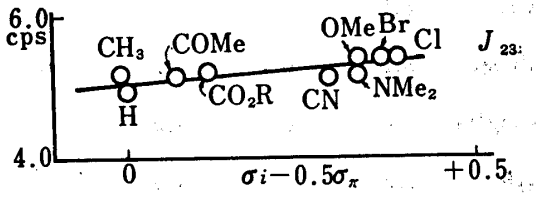
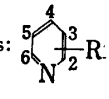


Fig. 3[a)]

a) The ^{1}H position numbers are as follows: 

Results and Discussion

From the observed J values and foregoing relations a, b and c, ΔJ values—excess J values obtained from subtracting the Castellano's[3] data—are divided into two parts, ΔJ^i and ΔJ^π (*cf.* Table I, II, III).

Table I.[a] Coupling Constants (cps) in 2-Substituted Pyridine Series

R/J	J_{34}	ΔJ_{34} i	ΔJ_{34} π	J_{45}	ΔJ_{45} i	ΔJ_{45} π	J_{56}	ΔJ_{56} i	ΔJ_{56} π	J_{35}	ΔJ_{35} i	ΔJ_{35} π	J_{46}	ΔJ_{46} i
NH_2	8.3	+0.6	+0.3 +0.3	6.9	−0.8	−0.32 −0.48	5.0	+0.1	+0.04 +0.06	1.8	+0.4	+0.16 +0.24	1.7	−0.2
OR	8.5	+0.8	+0.4 +0.4	7.3	−0.4	−0.16 −0.24	5.1	+0.2	+0.08 +0.12	0.9	−0.5	−0.2 −0.3	2.0	+0.1
CH_3	8.0	+0.3	+0.15 +0.15	7.8	+0.1	+0.04 +0.06	5.0	+0.1	+0.04 +0.06	1.1	−0.3	−0.12 −0.18	2.0	+0.1
F	8.7	+1.0	+0.5 +0.5	7.8	+0.1	+0.04 +0.06	4.9	0	0 0	0.9	−0.5	−0.2 −0.3	2.0	+0.1
Cl	7.8	+0.1	+0.05 +0.05	7.2	−0.5	−0.2 −0.3	4.7	−0.2	−0.08 −0.12	0.96	−0.4	−0.16 −0.24	2.0	+0.1
Br	7.6	−0.1	−0.05 −0.05	7.0	−0.7	−0.28 −0.42	4.5	−0.4	−0.16 −0.24	1.1	−0.3	−0.12 −0.18	1.9	0
CN	7.6	−0.1	−0.05 −0.05	7.6	−0.1	−0.04 −0.06	4.6	−0.3	−0.12 −0.18	1.2	−0.2	−0.08 −0.12	1.7	−0.2
$COCH_3$	7.9	+0.2	+0.1 +0.1	8.0	+0.3	+0.12 +0.18	4.5	−0.4	−0.16 −0.24	1.4	0	0 0	1.8	−0.1
CO_2R	8.6	+0.9	+0.45 +0.45	7.9	+0.2	+0.08 +0.12	4.4	−0.5	−0.20 −0.30	1.0	−0.4	−0.16 −0.24	2.1	+0.2
NO_2	8.2	+0.5	+0.25 +0.25	8.1	+0.4	+0.16 +0.24	5.2	+0.3	+0.12 +0.18	1.0	−0.4	−0.16 −0.24	1.2	−0.7
H[3]	7.7			7.7			4.9			1.4			1.9	

a) The ^1H position numbers are as follows:

Table II.[a] Coupling Constants (cps) in 3-Substituted Pyridine Series

R/J	J_{45}	ΔJ_{45} i	J_{56}	ΔJ_{56} i	J_{46}	ΔJ_{46} i	J_{24}	ΔJ_{24} i	ΔJ_{24} π
CH_3	7.8	+0.1	4.4	−0.5	2.2	+0.3	2.2	+0.3	+0.15 +0.15
Cl	8.2	+0.5	4.8	−0.1	1.5	−0.4	2.5	+0.6	+0.3 +0.3
Br	8.3	+0.6	4.8	−0.1	1.9	0	1.8	−0.1	−0.05 −0.05
CN	8.1	+0.4	5.0	+0.1	1.6	−0.3	2.1	+0.2	+0.1 +0.1
COMe	8.1	+0.4	4.7	−0.2	1.6	−0.3	1.9	0	0 0
CO_2CH_3	7.6	−0.1	4.9	0	1.5	−0.4	1.5	−0.4	−0.2 −0.2
H[3]	7.7		4.9		1.9		1.9		

a) The ^1H position numbers are as follows:

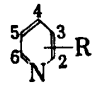


TABLE III.[a] Coupling Constants (cps) in 4-Substituted Pyridine Series

R/J	J_{23}	ΔJ_{23} i	ΔJ_{23} π	J_{35}	ΔJ_{35} i	ΔJ_{35} π
NMe_2	5.2	+0.3		1.5	−0.4	
		+0.2	+0.1		−0.24	−0.16
OCH_3	5.4	+0.5		1.5	−0.4	
		+0.33	+0.17		−0.24	−0.16
CH_3	5.2	+0.3		1.7	−0.2	
		+0.2	+0.1		−0.12	−0.08
Cl	5.4	+0.5		1.6	−0.3	
		+0.33	+0.17		−0.18	−0.12
Br	5.4	+0.5		1.8	−0.1	
		+0.33	+0.17		−0.06	−0.04
CN	5.1	+0.2		1.5	−0.4	
		+0.13	+0.07		−0.24	−0.16
CH_3CO	5.1	+0.2		1.7	−0.2	
		+0.13	+0.07		−0.12	−0.08
CO_2R	5.2	+0.3		1.6	−0.3	
		+0.20	+0.10		−0.18	−0.12
H[3]	4.9			1.9		

a) The ^1H position numbers are as follows:

In the next place, the observed J values[4,6] have been compared with those from equations (1) and (2) in several polysubstituted pyridines, and passable agreements have been acknowledged (*cf.* Table IV, V).

TABLE IV.[a] Observed and Calculated Coupling Constants (cps) in Symmetrically 3,5- and 2,6-Disubstituted Pyridine Derivatives

R	$J_{obs.}$[4]	$J_{calcd.}$	
3.5-CN	2.0	1.8	
3.5-Br	2.0	1.8	
3.5-Cl	2.2	2.1	J_{24}
3.5-CH_3	2.7	2.5	
2.6-NH_2	7.5	7.7	
2.6-OCH_3	7.7	7.9	
2.6-CH_3	7.8	7.9	J_{34}
2.6-Cl	7.6	7.6	
2.6-$COCH_3$	7.8	7.9	

a) The ^1H position numbers are as follows:

Conclusion

The empirical equation

$$J \fallingdotseq (J^i + J^\pi)_{ref.} + \sum \Delta J^i \quad (1)$$

and

$$J \fallingdotseq (J^i + J^\pi)_{ref.} + \sum \Delta J \quad (2)$$

TABLE V.[a] Observed and Calculated Coupling Constants (cps) of Di- andTri-Substituted Pyridine Derivatives

R	$J_{obs.}$[b]	$J_{calcd.}$
2.6 di-CN	$J_{34}=\sim 8$	$J_{34}=7.6$
2-CN, 6-CH_3	$J_{34}=7.8$	$J_{34}=7.7$
	$J_{35}=1.2$	$J_{35}=1.2$
	$J_{45}=8.0$	$J_{45}=7.8$
2-COMe, 6-CH_3	$J_{34}=7.4$	$J_{34}=7.8$
	$J_{35}=1.3$	$J_{35}=1.3$
	$J_{45}=7.5$	$J_{45}=7.9$
2-CO_2R, 6-CH_3	$J_{34}\simeq 8$	$J_{34}=8.2$
	$J_{35}\simeq 1$	$J_{35}=1.1$
	$J_{45}\simeq 8$	$J_{45}=7.9$
2-CH_3, 3-CO_2R	$J_{45}=7.9$	$J_{45}=7.6$
	$J_{46}=1.8$	$J_{46}=1.6$
	$J_{56}=4.9$	$J_{56}=4.9$
2-CH_3, 3-$COCH_3$	$J_{45}=7.9$	$J_{45}=8.1$
	$J_{46}=1.7$	$J_{46}=1.7$
	$J_{56}=4.8$	$J_{56}=4.7$
2-CH_3, 3-CN	$J_{45}=8.2$	$J_{45}=8.1$
	$J_{46}=1.5$	$J_{46}=1.7$
	$J_{56}=4.9$	$J_{56}=5.0$
2.3 di-Cl	$J_{45}=7.3$	$J_{45}=8.0$
	$J_{46}=1.7$	$J_{46}=1.6$
	$J_{56}=4.8$	$J_{56}=4.7$
2-CH_3, 5-alkyl	$J_{34}=8.1$	$J_{34}=8.0$
	$J_{46}=2.4$	$J_{46}=2.3$
2.5 di-Br	$J_{34}=8.3$	$J_{34}=8.3$
	$J_{46}=2.5$	$J_{46}=1.8$
2.5 di-Cl	$J_{34}=9.0$	$J_{34}=8.3$
	$J_{46}=3.0$	$J_{46}=2.6$
3.5 di-Cl	$J_{24}=1.7$	$J_{24}=2.1$
2.6 di-CH_3, 3-$COCH_3$	$J_{45}=8.4$	$J_{45}=8.3$
2.6 di-CH_3, 3-CO_2H	$J_{45}=8.1$	$J_{45}=7.8$
2.4 di-CH_3, 6-CO_2H	$J_{35}<0.5$	$J_{35}=1.0$

a) The ^1H position numbers are as follows: 

,which are accepted in substituted aromatics, are also reliable for J value estimation in substituted pyridines.