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# Studies on the Nuclear Magnetic Resonance Spectra in Aromatic Systems. VII. Preliminary Discussions on the Coupling Constants in Substituted Aromatics

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The coupling constants in substituted benzenes have been discussed with respect to substituent constants $\sigma_i$ and $\sigma_\pi$, and $\Delta J$—excess $J$ value—has been devided into 2 contributions from $\sigma$- and $\pi$-electronic effects. The $J$ values of *vicinal* $^1$H and those of *meta* to one another are shown to be estimated from Eq. (1) and Eq. (2), respectively.

$$J \doteqdot (J^i+J^\pi)\text{ ref.} +\sum \Delta J^i \qquad (1)$$

$$J \doteqdot (J^i+J^\pi)\text{ ref.} +\sum (\Delta J^i+\Delta J^\pi) \qquad (2)$$

Above simple additive relations are not reliable in tetra-substituted benzenes, probably due to the mutal substituent interactions.

## Introduction

The magnitude of coupling constant—$J$ value—in aromatic system has been shown to be determined from both $\sigma$- and $\pi$-bond coupling mechanism. Accordingly, $J$ values among ring $^1$H nuclei–$J_{\mathrm{HH'}}$–may be written as below:

$$J_{\mathrm{HH'}} = J_{\mathrm{HH'}}(\sigma) + J_{\mathrm{HH'}}(\pi)$$

where $J_{\mathrm{HH'}}(\pi) = \pi$-electronic contribution

$J_{\mathrm{HH'}}(\sigma) = \sigma$-electronic contribution

Recently, several workers[2,3,4,5] have examined the characters of these constants, but relative contributions from two factors–$J_{\mathrm{HH'}}$ ($\sigma$) and $J_{\mathrm{HH'}}$ ($\pi$)–have not been settled.

In this work, above problems in several substituted aromatics have been settled with respect to substituent constants $\sigma_i$ and $\sigma_\pi$,[6] and empirical rules have been proposed for above systems in order to examine the substituent effects on $J$ values.

### Method of Analysis

The observed $J$ values in monosubstituted benzene derivatives[4] were correlated with modified substituent constants $\sigma_i - a\sigma_\pi'$ where $0<a<1$, and nearly linear relations were observed (*cf.* Fig. 1), and the relative contributions from $\sigma_i$- and $\pi$-electronic effects on $J$ values were estimated from the coefficient of $\sigma_i$ and $\sigma_\pi$ in $\sigma_i - a\sigma_\pi$.

## Results and Discussion

### Relative Contributions from Two Effects on *J* Values

As are shown in Fig. 1, correlations of $J$ values in monosubstituted benzenes with modified substituent constants are as follows:

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[1] Location: *Toneyama, Toyonaka, Osaka.*
[2] A.A. Bothner-By, "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, 1965, p. 195.
[3] B. Dischler, *Z. Natur Forsch.*, **20a**, 888 (1965).
[4] S. Castellano, R. Kostelnik and C. Sun, *Tetrahedron Letters*, **1967**, 5205, 5211.
[5] J.M. Read, Jr. and J.H. Goldstein, *Tetrahedron Letters*, **1968**, 1215.
[6] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan* (*Pure Chemistry Section*), **86**, 873 (1965).

$J_{23} \propto \sigma_i - 0.4\sigma_\pi$

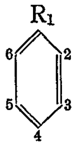
$J_{34} \propto \sigma_i - \sigma_\pi$

$J_{26} \propto \sigma_i - 0.5\sigma_\pi$

$J_{35} \propto \sigma_i - \sigma_\pi$

$J_{24} \propto \sigma_i - 0.7\sigma_\pi$

$J_{25} \propto \sigma_i - \sigma_\pi$



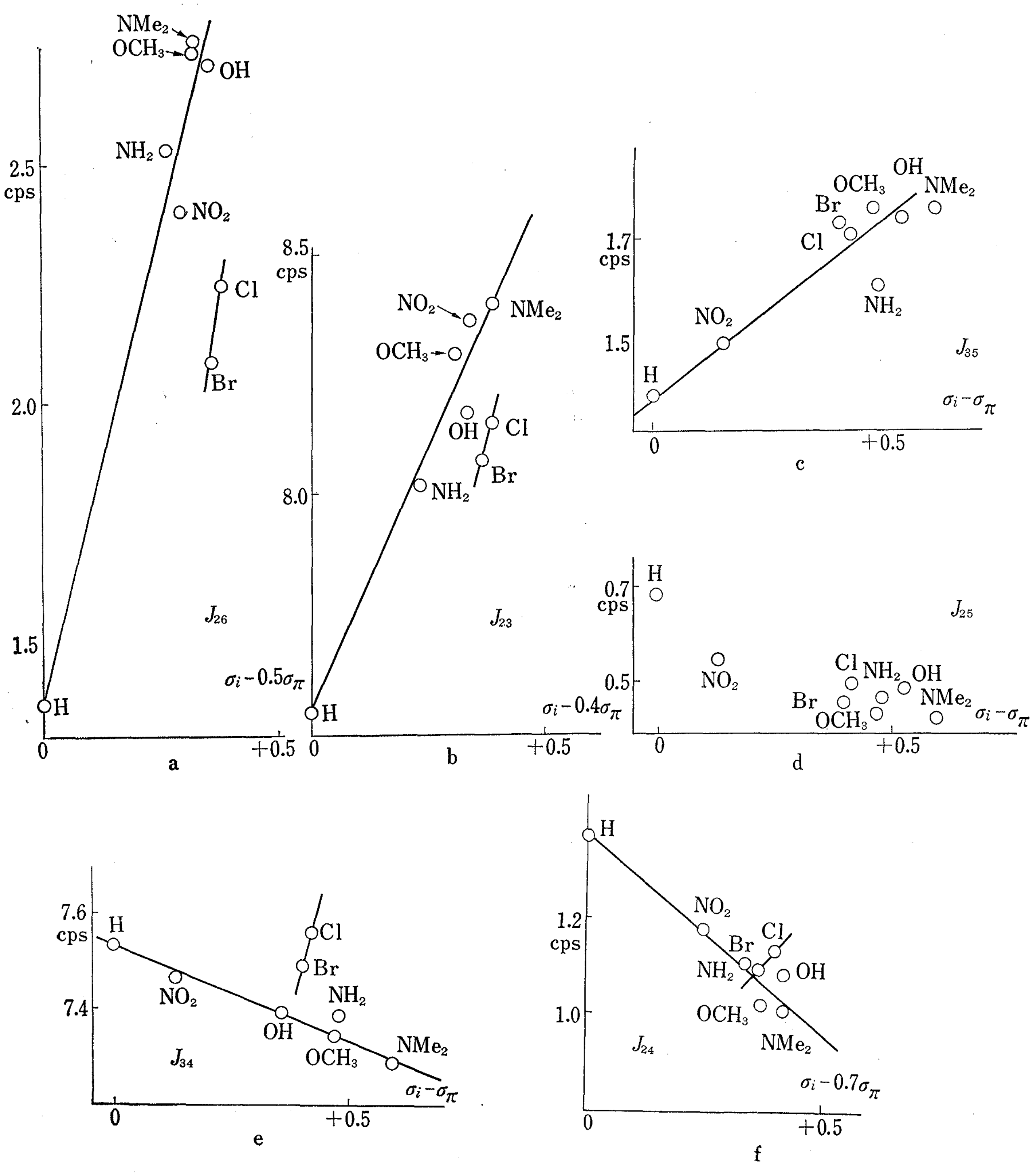


Fig. 1

Consequently, following results are deduced.

| | | |
|---|---|---|
| $J_{23}$ | $J^i_{23}\sim 72\%$ | $J^\pi_{23}\sim 28\%$ |
| $J_{34}$ | $J^i_{34}\sim 50\%$ | $J^\pi_{34}\sim 50\%$ |
| $J_{26}$ | $J^i_{26}\sim 67\%$ | $J^\pi_{26}\sim 33\%$ |
| $J_{35}$ | $J^i_{35}\sim 50\%$ | $J^\pi_{35}\sim 50\%$ |
| $J_{24}$ | $J^i_{24}\sim 59\%$ | $J^\pi_{24}\sim 41\%$ |
| $J_{25}$ | $J^i_{25}\sim 50\%$ | $J^\pi_{25}\sim 50\%$ |

On the basis of above results, attempts were made to divide experimentally the observed $\Delta J$ values[7] into 2 parts—namely, the contributions from $\sigma$- and $\pi$-electronic effect—and results are summarized in Table I.

TABLE I.[a] Separation of $\Delta J$ Values (cps) in Monosubstituted Benzene Derivatives

| R | $\Delta J_{26}$ | $\Delta J_{26}$ | | $\Delta J_{23}$ | $\Delta J_{23}$ | | $\Delta J_{34}$ | $\Delta J_{34}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | $i$ | $\pi$ | | $i$ | $\pi$ | | $i$ | $\pi$ |
| $NMe_2$ | 1.39 | 0.93 | 0.46 | 0.86 | 0.60 | 0.26 | −0.26 | −0.13 | −0.13 |
| $NH_2$ | 1.16 | 0.77 | 0.39 | 0.48 | 0.34 | 0.14 | −0.16 | −0.08 | −0.08 |
| OH | 1.34 | 0·89 | 0.45 | 0.63 | 0.44 | 0.19 | −0.14 | −0.07 | −0.07 |
| $OCH_3$ | 1.37 | 0.91 | 0.46 | 0.76 | 0.53 | 0.23 | −0.18 | −0.09 | −0.09 |
| Cl | 0.87 | 0.58 | 0.29 | 0.61 | 0.43 | 0.18 | 0.04 | 0.02 | 0.02 |
| Br | 0.71 | 0.47 | 0.24 | 0.50 | 0.35 | 0.15 | −0.08 | −0.04 | −0.04 |
| $NO_2$ | 1.03 | 0.69 | 0.34 | 0.82 | 0.59 | 0.23 | −0.08 | −0.04 | −0.04 |

| R | $\Delta J_{24}$ | $\Delta J_{24}$ | | $\Delta J_{25}$ | $\Delta J_{25}$ | | $\Delta J_{35}$ | $\Delta J_{35}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | $i$ | $\pi$ | | $i$ | $\pi$ | | $i$ | $\pi$ |
| $NMe_2$ | −0.36 | −0.22 | −0.14 | −0.26 | −0.13 | −0.13 | 0.38 | 0.19 | 0.19 |
| $NH_2$ | −0.27 | −0.16 | −0.11 | −0.22 | −0.11 | −0.11 | 0.22 | 0.11 | 0.11 |
| OH | −0.28 | −0.17 | −0.11 | −0.2 | −0.1 | −0.1 | 0.38 | 0.19 | 0.19 |
| $OCH_3$ | −0.35 | −0.21 | −0.14 | −0.26 | −0.13 | −0.13 | 0.4 | 0.2 | 0.2 |
| Cl | −0.23 | −0.14 | −0.09 | −0.2 | −0.1 | −0.1 | 0.34 | 0.17 | 0.17 |
| Br | −0.27 | −0.16 | −0.11 | −0.24 | −0.12 | −0.12 | 0.36 | 0.18 | 0.18 |
| $NO_2$ | −0.19 | −0.11 | −0.08 | −0.14 | −0.07 | −0.07 | 0.12 | 0.06 | 0.06 |

*a*) $J$ values (cps) in $C_6H_6$ are as follows[4]:
$J_{23}=7.54$, $J_{35}=1.37$, $J_{25}=0.69$ $\Delta J_{XY}=J_{obs.\,XY}-J_{C_6H_6\cdot XY}$, X,Y=$^1$H position number

## Additive Rule of *J* Values in Substituted Aromatics

The substituent effects on $J$ values have already been suggested to be nearly additive between *meta* positions in *para*-disubstituted benzenes.[3] In this work, however, $J$ values among vicinal protons have been shown empirically as below. This equation (1) suggests

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

that only $\sigma$-electronic effects are additive for $J$ value. On the other hand, among $^1$H *meta* to one another, $J$ values are expressed in terms of simple additive relation as follows.

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[7] $\Delta J$=excess $J$ value from reference

$$J \doteqdot (J^{i}+J^{\pi})\,\text{ref.}+\sum\Delta J \qquad (2)$$

where $\Delta J=\Delta J^{i}+\Delta J^{\pi}$

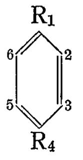
i) Disubstituted Benzenes3,8)

(1) *para*-Disubstituted benzenes

(2) Symmetrically *mata*-disubstituted benzenes

(3) *ortho*-Disubstituted benzenes

The $^1$H positions are as follows:



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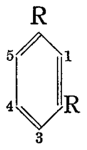

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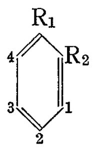

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The results cited in Table II, III and IV confirm the additive relations mentioned in preceding section. Namely, in *para*–disubstituted benzenes all of $J_{23}$ are more profitable in terms of Eq. (1) than Eq. (2), whereas observed $J_{26}$ and $J_{35}$ show satisfactory agreements with $J$ values estimated from Eq. (2). Also, in *meta*–disubstituted benzenes, the observed $J_{34}$ and $J_{13}$ can be shown by Eq. (1) and Eq. (2), respectively. The $J$ values in *ortho*–disubstituted series show similar results as above two series.

Table II.9) Observed and Calculated Coupling Constants (cps) of *para*-Disubstituted Benzene Derivatives

| Substituent | | $J_{23}$ | | | $J_{26}$ | | | $J_{35}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | $R_4$ | Observed8) | Calcd. | | Observed8) | Calcd. | | Observed8) | Calcd. | |
| | | | (1) | (2) | | (1) | (2) | | (1) | () |
| $NH_2$ | $OCH_3$ | 8.5 | 8.4 | 10.1 | 2.8 | 2.3 | 2.9 | 2.8 | 2.4 | 3.0 |
| $NH_2$ | Cl | 8.6 | 8.3 | 9.6 | 2.8 | 2.3 | 2.9 | 2.5 | 2.1 | 2.5 |
| $NH_2$ | Br | 8.5 | 8.2 | 9.4 | 2.9 | 2.3 | 2.9 | 2.3 | 2.0 | 2.3 |
| $NH_2$ | $NO_2$ | 9.0 | 8.5 | 9.6 | 2.6 | 2.2 | 2.7 | 2.3 | 2.2 | 2.6 |
| $OCH_3$ | Cl | 8.8 | 8.5 | 9.8 | 3.1 | 2.5 | 3.1 | 2.5 | 2.2 | 2.6 |
| $OCH_3$ | Br | 8.7 | 8.4 | 9.6 | 3.1 | 2.5 | 3.1 | 2.5 | 2.0 | 2.5 |
| $OCH_3$ | $NO_2$ | 9.0 | 8.7 | 9.9 | 2.7 | 2.3 | 2.9 | 2.7 | 2.3 | 2.8 |
| Br | $NO_2$ | 8.9 | 8.5 | 9.3 | 2.6 | 1.9 | 2.2 | 2.2 | 2.2 | 2.8 |
| Cl | $NO_2$ | 8.7 | 8.6 | 9.4 | 2.8 | 2.0 | 2.4 | 2.2 | 2.2 | 2.7 |

Table III.9) Observed and Calculated Coupling Constants (cps) of Symmetrically *meta*-Disubstituted Benzene Derivatives

| Substituent R | $J_{34}$ | | | $J_{13}$ | | |
|---|---|---|---|---|---|---|
| | Observed8) | Calcd. | | Observed8) | Calcd. | |
| | | (1) | (2) | | (1) | (2) |
| Br | 8.1 | 7.9 | 7.8 | 1.8 | 1.7 | 1.8 |
| $NO_2$ | 8.3 | 8.1 | 8.3 | 2.2 | 2.0 | 2.2 |

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8) J. Martin and B.P. Dailey, *J. Chem. Phys.*, 37, 2594 (1962).

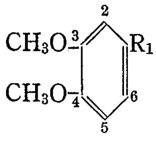
9) (1),(2) = $J$ values estimated from Eq. (1) and (2).

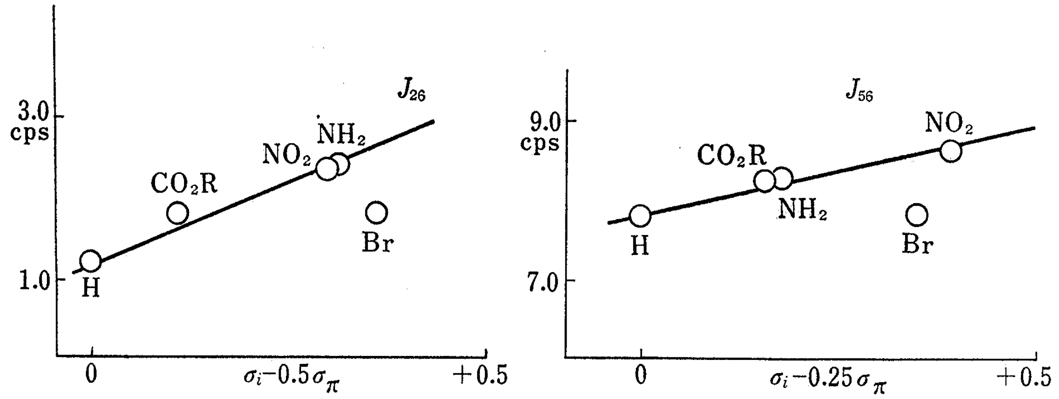
Table IV.[9] Observed and Calculated Coupling Constants (cps) of *ortho*-Disubstituted Benzene Derivatives

| Substituent | | $J_{12}$ | | | | $J_{23}$ | | | | $J_{34}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Observed | | Calcd. | | Observed | | Calcd. | | Observed | | Calcd. | |
| $R_1$ | $R_2$ | | | (1) | (2) | | | (1) | (2) | | | (1) | (2) |
| Cl | Cl | 7.9[8] | 8.0[2] | 8.0 | 7.9 | 7.5[8] | 7.4[2] | 7.6 | 7.6 | | | | |
| Cl | Br | 8.3 | 8.0 | 7.9 | 8.1 | 7.5 | 7.4 | 7.5 | 7.5 | 8.3 | 8.1 | 7.9 | 8.1 |
| Cl | $NO_2$ | | 8.1 | 7.9 | 8.1 | | 7.4 | 7.5 | 7.5 | | 8.2 | 8.2 | 8.4 |
| Br | Br | 8.1 | 8.0 | 7.9 | 8.0 | 7.3 | 7.5 | 7.5 | 7.4 | | | | |
| $NO_2$ | $NO_2$ | | 8.1 | 8.1 | 8.3 | | 7.7 | 7.5 | 7.4 | | | | |
| OH | $NO_2$ | | 8.5 | 7.9 | 8.1 | | 7.2 | 7.4 | 7.3 | | 8.5 | 8.1 | 8.2 |

ii) Tri-and Tetra-Substituted Benzenes

1-Substituted 3,4-dimethoxybenzenes[10] have been examined as an example of tri-substituted benzenes. The correlations of $J$ values with modified substituent constants have been shown in Fig. 2, and following results can be deduced.





a b

Fig. 2

$$J_{26} \propto \sigma_i - 0.5\sigma_\pi$$

$$J_{56} \propto \sigma_i - 0.25\sigma_\pi$$

Accordingly, relative contributions from $\sigma$- and $\pi$-electronic effects are as follows:

$J^i_{26}$~66% $J^\pi_{26}$~33%

$J^i_{56}$~80% $J^\pi_{56}$~20%

The $\Delta J$ values separated into $\Delta J^i$ and $\Delta J^\pi$ have been summarized in Table V, and it has been recognized that $J_{26}$ showed satisfactory agreements with $J$ values estimated from Eq. (2), whereas $J_{56}$ with those from Eq. (1) (*cf.* Table VI).

In the next step, observed and calculated $J$ values for another tri-and tetra-substituted benzenes have been summarized in Table VII. It is probable that there is significant difference among observed and calculated $J$ values from Eq. (1) even in the case of $J_{12}$ or $J_{23}$, whereas those calculated from Eq. (2) show somewhat better agreements with observed ones. The

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10) Y. Sasaki, M. Suzuki, T. Hibino and K. Karai, *Chem. Pharm. Bull.* (Tokyo), **15**, 599 (1967).

Table V.[7] Separation of $\Delta J$ Values (cps) in 1-Substituted-3,4-dimethoxy Benzene Derivatives

| R | $\Delta J_{26}$ | $\Delta J_{26}$ |  | $\Delta J_{56}$ | $\Delta J_{56}$ |  |
|---|---|---|---|---|---|---|
|  |  | $i$ | $\pi$ |  | $i$ | $\pi$ |
| $NO_2$ | 1.0 | 0.66 | 0.34 | 1.2 | 0.96 | 0.24 |
| H | −0.17 | −0.11 | −0.06 | 0.3 | 0.24 | 0.06 |
| $NH_2$ | 1.0 | 0.66 | 0.34 | 0.7 | 0.56 | 0.14 |
| Br | 0.43 | 0.27 | 0.16 | 0.26 | 0.21 | 0.05 |

Table VI.[9] Observed and Calculated $J$ Values (cps) in 1-Substituted-3,4-dimethoxy Benzene Derivatives

| Substituent R | $J_{26}$ |  |  | $J_{56}$ |  |  |
|---|---|---|---|---|---|---|
|  | Observed[10] | Calcd. |  | Observed[10] | Calcd. |  |
|  |  | (1) | (2) |  | (1) | (2) |
| $NO_2$ | 2.4 | 2.1 | 2.4 | 8.6 | 8.6 | 8.9 |
| H | 1.2 | 1.4 | 1.3 | 7.8 | 8.0 | 7.1 |
| $NH_2$ | 2.4 | 2.1 | 2.4 | 8.2 | 8.3 | 8.9 |
| Br | 1.8 | 1.8 | 2.1 | 8.3 | 8.3 | 8.6 |

Table VII.[9] Tri- and Tetra-Substituted Benzene Derivatives

| Substituents |  |  |  |  |  | $J$ cps |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |  | Observed | Calcd. |  |  | Observed | Calcd. |  |
|  |  |  |  |  |  |  |  | (1) | (2) |  |  | (1) | (2) |
|  |  |  | $OCH_3$ | OH | $OCH_3$[a] | $J_{12}$ | 8.8 | 7.9 | 8.0 |  |  |  |  |
| Cl |  |  | $NO_2$ |  | $NO_2$[b] | $J_{23}$ | 8.7 | 8.5 | 8.9 | $J_{35}$ | 2.7 | 2.1 | 2.6 |
| OH |  |  | $NO_2$ |  | $NO_2$[b] | $J_{23}$ | 9.2 | 8.5 | 8.9 | $J_{35}$ | 2.9 | 2.1 | 2.6 |
| OH |  |  | Cl |  | $NO_2$[a] | $J_{23}$ | 9.0 | 8.4 | 8.7 | $J_{35}$ | 2.5 | 1.8 | 2.4 |
|  | Cl |  | Cl |  | Cl[c] | $J_{13}$ | 2.2 | 1.7 | 1.8 |  |  |  |  |
|  | Br |  | Br |  | Br[c] | $J_{13}$ | 1.7 | 1.5 | 1.6 |  |  |  |  |
|  | $NO_2$ |  | $NO_2$ |  | $NO_2$[c] | $J_{13}$ | 1.9 | 1.8 | 2.0 |  |  |  |  |
| OH | Br |  | Br |  | Br[c] | $J_{35}$ | 2.3 | 1.7 | 2.0 |  |  |  |  |
| OH | Cl |  | Cl |  | Cl[c] | $J_{35}$ | 2.5 | 1.9 | 2.1 |  |  |  |  |
| OH | $NO_2$ |  | $NO_2$ |  | $NO_2$[c] | $J_{35}$ | 2.8 | 2.0 | 2.4 |  |  |  |  |
| OH | $NO_2$ |  | Cl |  | $NO_2$[c] | $J_{35}$ | 2.8 | 1.9 | 2.2 |  |  |  |  |
| OH | Br |  | $NO_2$ |  | Br[c] | $J_{35}$ | 3.3 | 1.9 | 2.2 |  |  |  |  |

a) E.A. Allan and L.W. Reeves, *J. Phys. Chem.*, **67**, 591 (1963)
b) S.S. Dharmatti, G. Govil, C.L. Khetrapal, C.R. Kanekar and Y.P. Virmani, *Proc. Indian Acad. Sci. Sect.*, A **54**, 331 (1961)
c) H.M. Hutten, W.F. Reynolds and T. Schaefer, *Can. J. Chem.*, **40**, 1758 (1962)

fact that observed *values* are generally larger than those of calculated from both equation (1) and (2) suggests the presence of additional interactions among substituents as the number of substituent increases. The theoretical approach is now in progress.

## Conclusion

The $J$ values of vicinal $^1H$ can be estimated as a sum of $\sigma$-electronic contribution of substituent. On the other hand, for $^1H$ *meta* to one another both $\sigma$- and $\pi$-electronic contributions are shown to be additive. On the other hand, in the compounds with more than three substituents, the calculated values are generally small than those of observed ones.