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The Nuclear Magnetic Resonance Spectra of Olefinic Protons and the Substituent Effects. IV.*[1] Intramolecular Interactions between Substituents in *trans*-1, 2-Disubstituted Ethylenes*[2]

Jun NIWA

Chemical Laboratory, Department of General Education, Nagoya University, Chikusa-ku, Nagoya

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The olefinic proton chemical shifts (δ_{ji}), measured in parts per million from ethylene, in an extensive series of *trans*-1, 2-disubstituted ethylenes ($R_jCH_{ji}=CH_{ij}R_i$) show uniform deviations from the simple additivity of the substituent-shielding parameters. These deviations may be attributed to the interactions between the R_i and R_j substituents, so the chemical shift, δ_{ji} or δ_{ij}, may be expressed as $\delta_{ji}=d_C(R_i)+d_G(R_j)+I_{ji}$ or $\delta_{ij}=d_C(R_j)+d_G(R_i)+I_{ij}$. The abbreviations $d_C(R_i)$ and $d_G(R_j)$ represent the substituent-shielding parameters, while I_{ji} and I_{ij} represent the respective terms of the interactions. The chemical shifts, δ_{ji}, in each series of compounds bearing R_j as an invariable substituent are determined by the Hammett's σ-constants of R_i, and much more closely by $d_C(R_i)$. That is, $\delta_{ji}=d_G(R_j)+\rho_J\sigma_i$, and $\delta_{ji}=d_G(R_j)+\rho_J'd_C(R_i)$, where the susceptibility, ρ_J, is also related to ρ_J' by a linear function. By assuming that I_{ji} is approximately equal to I_{ij}, the following equations may be derived:

$$\rho_J' - \rho_0' = \kappa\sigma_j \text{ and } I_{ji} = \kappa\sigma_j d_C(R_i)$$

The applicabilities of these equations were tested graphically for the 70 shifts in series of *trans*-1, 2-disubstituted ethylenes. The results revealded that the chemical shift, δ_{ji} or δ_{ij}, was comprehensively expressed as:

$$\delta_{ji} = d_G(R_j) + (-0.59\,\sigma_j + 1.08)d_C(R_i)$$

or

$$\delta_{ij} = d_G(R_i) + (-0.59\,\sigma_i + 1.08)d_C(R_j)$$

with the exception of those compounds bearing halogen substituents. The values of standard deviation and the correlation coefficient were 0.08 and 0.994 respectively.

Recently, it has been demonstrated by Martin *et al.*¹⁾ that, in the chemical shifts of the ring protons next to substituents which are ortho to one another in a series of 1, 4-disubstituted benzenes, there are small uniform deviations from the additivity of the shifts, and that the chemical shifts of the 2 proton are expressed as:

$$\delta_2 = d_o(R_1) + \gamma(R_1)d_m(R_4) \tag{1}$$

The abbreviations $d_o(R_1)$, and $d_m(R_4)$, and $\gamma(R_1)$ represent the substituent-shielding parameters and the polarizability respectively.

Meanwhile, the present authors had noticed in a previous paper²⁾ that there was a linear correlation between the chemical shifts of the protons cis to substituents in 1-substituted *trans*-propenes/ and in ω-substituted *trans*-styrenes and those of the ring protons ortho to substituents in monosubstituted benzenes. This suggests that a similar relation to Eq. (1) holds for the chemical shifts of the protons cis to variable substituents (R_i) in a series of *trans*-1, 2-disubstituted ethylenes bearing a substituent (R_j) as an invariable substituent ($R_jCH_{ji}=CH_{ij}R_i$, R_j: invariable substituent, R_i: variable substituent).

The present author will represent the chemical shifts by the following abbreviations:

τ_{ji}: τ-value of the chemical shift of the H_{ji} proton in the 1, 2-disubstituted ethylene;

τ_{00}: τ-value of the chemical shift of the proton in ethylene;

$d_C(R_i)$; $d_G(R_j)$: the substituent-shielding parameter, *i. e.,* the chemical shift, measured in parts per million from the unsubstituted compound, of the proton cis to, and geminal to, the substituent in monosubstituted ethylene;

δ_{ji}: th relative shift, measured in parts per million from ethylene, of the H_{ji} proton in the 1, 2-disubstituted ethylene; therefore,

$$\delta_{ji} = \tau_{ji} - \tau_{00} \tag{2}$$

$\delta_{ji}{}^J$: the relative shift, measured in parts per

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*[1] Part III: J. Niwa and H. Kasiwagi, This Bulletin, **36**, 1414 (1963).

*[2] Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Hiyoshi, Yokohama, April, 1966.

1) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

2) H. Kasiwagi and J. Niwa, This Bulletin, **36**, 405 (1963).

million from the unsubstituted compound (R_jCH_{ji}=$CH_{ij}H$), of the H_{ji} proton in a series of *trans*-1, 2-disubstituted ethylenes bearing R_j as an invariable substituent (R_jCH_{ji}=$CH_{ij}R_i$); therefore,

$$\delta_{ji}{}^J = \tau_{ji} - \tau_{j0} = (\tau_{ji} - \tau_{00}) - (\tau_{j0} - \tau_{00}) = \delta_{ji} - d_G(R_j) \qquad (3)$$

If the chemical shifts of the protons on the 1, 2-disubstituted ethylenes are assumed to be simply additive, then each shift will be the algebraic sum of the substituent parameters appropriate to the various substituents and their positions. That is, the chemical shift of the H_{ji} proton in the 1, 2-disubstituted ethylene would be:

$$\tau_{ji} = \tau_{00} + d_C(R_i) + d_G(R_j) \qquad (4)$$

If any deviations occur, they may be interpreted as resulting from the interactions between the two substituents through the olefinic bond. Then, Eq. (4) may be corrected as:

$$\tau_{ji} = \tau_{00} + d_C(R_j) + d_G(R_j) + I_{ji} \qquad (5)$$

$$\text{or} \quad \delta_{ji} = \tau_{ji} - \tau_{00} = d_C(R_i) + d_G(R_j) + I_{ji} \qquad (6)$$

where the term of the interactions (I_{ji}) corresponds to the deviation from the simple sum of the substituent-shielding parameters appropriate to the two substituents.

This paper will investigate what factors determine the nature of the interactions of this type for the 70 shifts in series of *trans*-1, 2-disubstituted ethylenes.

Results and Discussion

Correlation of Chemical Shifts. The chemical shifts of the olefinic protons in an extensive series of *trans*-1, 2-disubstituted ethylenes, measured in a 10 mol per cent solution in carbon tetrachloride, have been reported in Parts I(2) and III(3). In these papers, it was indicated graphically that the Hammett relationship holds for the relative shifts of the H_{ji} protons ($\delta_{ji}{}^J$), except for the substituents, cyano and phenyl groups which exert considerably large magnetic anisotropies. Therefore,

$$\delta_{ji}{}^J = \rho_J \sigma_i \qquad (7)^{*3}$$

When the corrected values for the contributions for the anisotropies are used for these substituents.(4) the plots for them also fit the line predicted by Eq. (7) very closely on. Therefore, the following equation generally holds:

$$\delta_{ji}{}^J - a_i = \rho_J \sigma_i \qquad (8)$$

The a_i term represents the magnitude of the effect exerted on the H_{ji} proton by the magnetic anisotropy of the R_i substituent. The calculated values of ρ_J, S[*4] and the correlation coefficient are summarized in Table 1.

It is possible, however, to devise a linear function which fits much more closely. Its form is suggested by the linearity of the correlation graph,

Table 1. Values of ρ_J and ρ_J'

a) $\delta_{ji}{}^J = \rho_J \sigma_i$

R_j	ρ_J	S^a)	r^a)	n^a)
CH_3	−2.00	0.08	0.995	8
C_6H_5	−1.60	0.10	0.993	8
H	−1.48	0.10	0.991	8
CO_2CH_3	−1.30	0.12	0.948	7
$COCH_3$	−1.30	0.07	0.989	4
Br, Cl	−1.82	0.22	0.732	9
CN	−1.18	0.30	0.945	4
NO_2	−0.93	0.06	0.794	3

b) $\delta_{ji}{}^J = \rho_J' d_C(R_i)$

R_j	ρ_J'	S^a)	r^a)	n^a)
CH_3	1.36	0.10	0.989	8
C_6H_5	1.06	0.06	0.997	8
H	1.00	—	—	9
CO_2CH_3	0.85	0.04	0.987	7
CHO	0.83	—	—	2
$COCH_3$	0.77	0.04	0.992	4
COCl	0.78	0.19	0.999	3
Br, Cl	1.00	0.23	0.941	10
CN	0.57	0.03	0.995	3
NO_2	0.62	0.10	0.978	3

a) S: the standard deviation of experimental results from the regression line. r: the correlation coefficient. n: number of compounds.

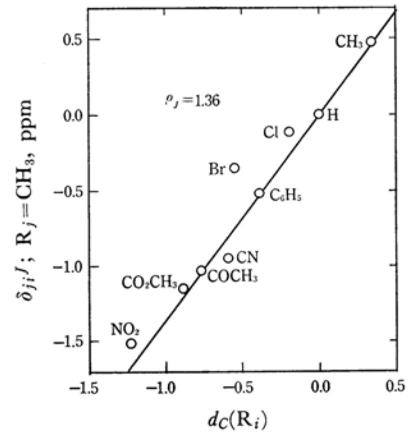

Fig. 1. The correlation between the substituent shielding parameters ($d_C(R_i)$) and the relative shifts cis to substituents in 1-substituted *trans*-propenes.

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3) J. Niwa and H. Kasiwagi, This Bulletin, **36**, 1414 (1963).

[*3] The abbreviation σ_i represents the Hammett substituent constant (σ_p-value) of the R_i substituent.

4) C. E. Johnson, Jr., and E. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); G. S. Reddy, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

[*4] The standard deviation of experimental results from the regression line.

Fig. 1, in which the chemical shifts of the protons cis to variable substituents in a series of 1-substituted *trans*-propenes are plotted against those of the protons cis to the corresponding substituents in monosubstituted ethylenes ($d_C(\mathrm{R}_i)$). (The plot for the bromine substituent deviates considerably from the correlation line. The present author will discuss the anomalous behavior of halogen substituents later in the present paper.) If additivity were present, this straight line would be of a unit slope. As is shown in Fig. 1, however, the slope of the correlation line was 1.36. Moreover, similar linear correlations also exist for the chemical shifts in the remaining seven series, except for the case of a series of compounds bearing halogen as an invariable substituent. Using the slope, it is possible to construct an equation of the form:

$$\delta_{ji}{}^J = \rho_J{}' d_C(\mathrm{R}_i) \qquad (9)$$

The values of two substituent-shielding parameters, $d_C(\mathrm{R}_i)$ and $d_G(\mathrm{R}_j)$, are given in Table 2. In the table, the substituent-shielding parameters ($d_C(\mathrm{R}_i)$) of CHO and COCl were derived from the chemical shifts in the corresponding 1-substituted propenes and ω-substituted styrenes by using Eq. (8). Those of $d_G(\mathrm{R}_j)$ for CHO and COCl were obtained from the correlation line between the chemical shifts of the proton geminal to substituents in 1-substituted propenes/ and ω-substituted styrenes and those in monosubstituted ethylenes (Fig. 2). Meanwhile, Martin *et al.* have presented the substituent-shielding parameters, $d_0(\mathrm{R}_1)$, for the chemical shifts of the protons ortho to substituents on the benzene ring.[1] Figure 3 shows that there is a linear correlation between $d_C(\mathrm{R}_i)$ and $d_o(\mathrm{R}_1)$, except for the bromine substituent. In the figure the plots of $d_C(\mathrm{R}_i)$ for CHO and COCl derived by the present author also fall close to the line. For the sake of comparison, the values of $d_o(\mathrm{R}_1)$ are also listed in Table 2, where the values of $d_o(\mathrm{R}_1)$ for C_6H_5 and CO_2CH_3 were calculated by the method of least squares.

TABLE 2. SUBSTITUENT SHIELDING PARAMETERS (ppm)

Substituent	$d_G(\mathrm{R}_j)$	$d_C(\mathrm{R}_i)$	$d_0(\mathrm{R}_1)$[a]
CH_3	−0.40	0.37	0.183
H	0.00	0.00	0.000
C_6H_5	−1.36	−0.38	*−0.26*[b]
Cl	−0.97	−0.19	0.000
Br	−1.16	−0.55	−0.159
CO_2CH_3	−0.66	−0.89	*−0.67*[b]
$COCH_3$	−0.95	−0.76	−0.64
CN	−0.20	−0.58	−0.27
COCl	−1.04[c]	−1.08[d]	−0.83
NO_2	−1.79	−1.22	−0.955
CHO	−1.04[c]	−0.76[d]	−0.54

a) Cited from the paper by Matin *et al.*[1]
b) These values were derived from the correlation line between $d_C(\mathrm{R}_i)$ and $d_0(\mathrm{R}_1)$.
c) These values were obtained from the correlation line between the chemical shifts geminal to substituents in 1-substituted propenes/ and ω-substituted styrenes and those in monosubstituted ethylenes.
d) These values were derived from the chemical shifts in the corresponding 1-substituted propenes and ω-substituted styrenes using Eq. (8).

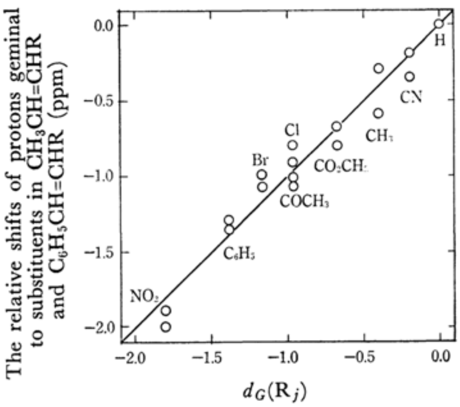

Fig. 2. The correlation between the substituent shielding parameters ($d_G(\mathrm{R}_j)$) and the relative shifts of the protons geminal to substituents in 1-substituted *trans*-propenes/ and ω-substituted *trans*-styrenes.

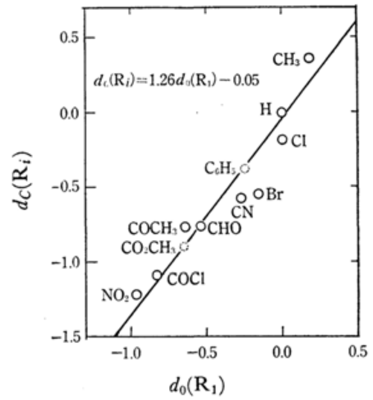

Fig. 3. The correlation between $d_C(\mathrm{R}_i)$ and Martin's substituent shielding parameters, $d_0(\mathrm{R}_1)$.

The chemical shifts of monosubstituted ethylenes are regarded as belonging to 1, 2-disubstituted *trans*-ethylenes bearing, as an invariable substituent, hydrogen with $\rho_J{}'=1.00$; The susceptibilities, $\rho_J{}'$, given in Table 1 are thus established. The parameter, $\rho_J{}'$, is a measure of the susceptibility of the proton geminal to the invariable substituent (R_j) to purturbation by variable substituents (R_i).

Interpretation of the Interaction Term. The term of the interaction (I_{ji}) that is defined by Eq. (6) presumably represents a measure of the effect which the interactions between R_j and R_i through the olefinic bond produce on the H_{ji} proton. The I_{ij} term also corresponds to the effect on the H_{ij} proton. From Eqs. (3) and (6), the I_{ji} term is rearranged to:

$$I_{ji} = (\delta_{ji} - d_G(R_j)) - d_C(R_i)^{*5}$$
$$= \delta_{ji}{}^J - \delta_{0i}{}^0 \qquad (10)$$

Using Eq. (8), Eq. (10) is expressed as:

$$I_{ji} = (\rho_J\sigma_i + a_i) - (\rho_0\sigma_i + a_i)$$
$$= (\rho_J - \rho_0)\sigma_i \qquad (11)$$

Since the H_{ij} proton is regarded as the proton cis to the variable substituents (R_j) in a series of compounds bearing R_i as an invariable substituent, the I_{ij} term is defined as:

$$I_{ij} = (\rho_I - \rho_0)\sigma_j \qquad (12)$$

When the value of I_{ji} is compared with that of I_{ij} for each pair of substituents, R_i and R_j, there may be seen a roughly linear relation between them extending over about 1 ppm, as is shown in Fig. 4. Accordingly, even if the value of I_{ji} is not strictly equal to that of I_{ij}, it may be assumed that I_{ji} is approximately equal to I_{ij} for each pair of R_i and R_j substituents in the 1, 2-disubstituted ethylenes. Then, Eqs. (11) and (12) may be combined to give:

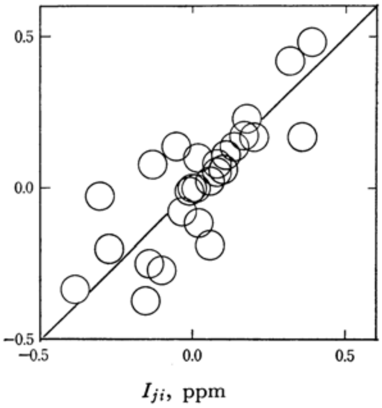

Fig. 4. The correlation between I_{ji} and I_{ij} for each pair of substituents R_j and R_i.

$$(\rho_J - \rho_o)\sigma_i = (\rho_I - \rho_o)\sigma_j$$
$$\frac{\rho_J - \rho_o}{\sigma_j} = \frac{\rho_I - \rho_o}{\sigma_i} = \gamma$$
$$\rho_J - \rho_o = \gamma\sigma_j \qquad (13)$$

When Eq. (13) is tested graphically in Fig. 5, it is shown that the relation between ρ_J and σ_j is approximately expressed as:

$$\rho_J = 0.86\sigma_j - 1.68 \qquad (14)$$

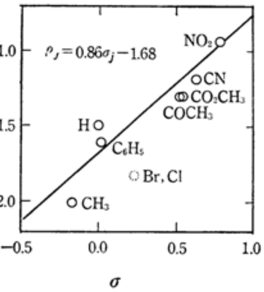

Fig. 5. The correlation between ρ_J-values and the substituent constants (σ) of the invariable substituents, R_j.

It is possible, however, to improve the linear relation between the susceptibility and the substituent constant. From Eqs. (9) and (10), I_{ji} is also expressed as:

$$I_{ji} = \delta_{ji}{}^J - \delta_{0i}{}^0$$
$$= (\rho_J{}' - \rho_0{}')d_C(R_i) \qquad (15)$$

where $\rho_0{}' = 1.00$. As has been stated above, since the following equation holds except for cyano and phenyl groups:

$$d_C(R_i) = \delta_{0i}{}^0 = \rho_0\sigma_i$$

Eq. (15) turns to:

$$I_{ji} = (\rho_J{}' - \rho_0{}')\rho_0\sigma_i \qquad (16)$$

This means that the susceptibility in a series of the 1, 2-disubstituted ethylenes bearing an invariable substituent is substantially determined by the susceptibility of the correlation line on which the plots for cyano and phenyl groups are excluded. Therefore, in order to examine merely the relation between the ρ_J-values and the $\rho_J{}'$-values, it may be enough to compare the slopes of the correlation lines with each other, these lines being determined by a set of substituents from which cyano and phenyl groups are excluded. Then, Eqs. (11) and (16) may be combined to give:

$$(\rho_J - \rho_0) = (\rho_J{}' - \rho_0{}')\rho_0 \qquad (17)$$

As Fig. 6 shows, Eq. (17) holds for all the other

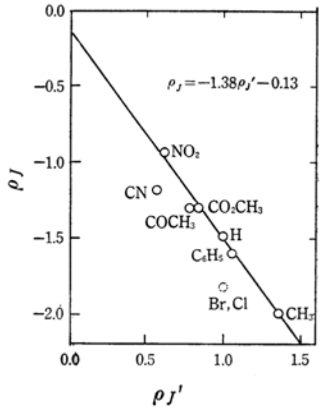

Fig. 6. ρ-Values correlation: ρ_J *vs.* $\rho_J{}'$

[*5] $d_C(R_i)$ is the relative shift itself of the proton cis to the substituent in monosubstituted ethylene, so $d_C(R_i) = \delta_{0i}{}^0 = \rho_0\sigma_i + a_i$.

series except for a series of the compounds bearing halogen as an invariable substituent; the relation is expressed as:

$$\rho_J = -1.38\rho_J' - 0.13$$

The magnitudes of the slope and the intercept were comparable with those of ρ_0 and the intercept predicted by Eq. (17) ($\rho_0 = -1.48$; the intercept: $\rho_0(1-\rho_0') = 0.00$).

From Eqs. (13) and (17), the following equation is derived:

$$(\rho_J' - \rho_0')\rho_0 = \gamma\sigma_j$$

$$(\rho_J' - \rho_0') = \kappa\sigma_j \quad \left(\kappa = \frac{\gamma}{\rho_0}\right) \qquad (18)$$

The applicability of Eq. (18) is tested graphically in Fig. 7. The figure reveals that ρ_J' is related to the σ-constant of the invariable substituent by a linear function of the form:

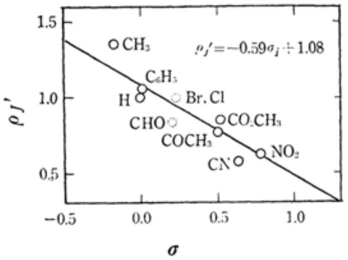

Fig. 7. The correlation between ρ_J'-values and the substituent constants (σ) of the invariable substituents, R_j.

$$\rho_J' - 1.08 = -0.59\sigma_j \qquad (19)$$

The values of the slope and the intercept were about equal to those of κ and ρ_0' respectively ($\rho_0' = 1.00$, $\kappa = -0.58$). The calculated values of S*4 and the correlation coefficient were 0.28 and 0.985 respectively. This interlocking of ρ with substituent constants means that the difference between ρ-values of the two series of compounds will be proportional to the difference between the σ-constants of the invariable substituents.

Analogous studies of reactivity have been presented by several workers.5,6) For example, Ritchie *et al.*6) derived the relation

$$\Delta\rho = q\Delta\sigma'$$

to illustrate the multiple dependency $\log k = f(\sigma, \sigma')$, in which $\log k$ is separately linear in σ and σ', where $\sigma' = \sigma^*$, σ^+, σ^-, *etc.*

Using Eqs. (11) and (13), the interaction term, I_{ji}, is expressed as:

$$I_{ji} = \gamma\sigma_j\sigma_i \quad (\gamma = 0.86) \qquad (20)$$

In a like manner,

$$I_{ij} = \gamma\sigma_i\sigma_j \qquad (21)$$

Figure 8 shows the trend of such a linear relation as predicted by Eqs. (20) and (21). Using Eqs. (15) and (18), however, such relations may be much improved. That is, I_{ji} is represented by the form:

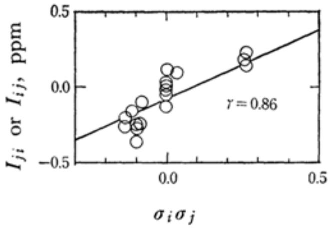

Fig. 8. The correlation between I_{ji} (and I_{ij}) and $\sigma_i\sigma_j$. The value of slope ($\gamma = 0.86$) is the value predicted by Eq. (20). The plots for halogen substituents are excluded from the figure.

$$I_{ji} = \kappa\sigma_j d_C(\mathrm{R}_i) \qquad (\kappa = -0.58) \qquad (22)$$

or

$$I_{ij} = \kappa\sigma_i d_C(\mathrm{R}_j) \qquad (23)$$

A linear relation, as predicted by Eqs. (22) and (23), is shown in Fig. 9. This relation means that the interaction terms are determined uniformly by the σ-constant of an invariable substituent in each series.

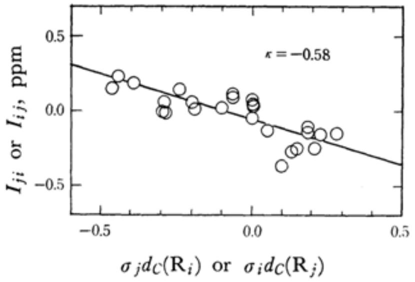

Fig. 9. The correlation between I_{ji} (and I_{ij}) and $\sigma_j d_C(\mathrm{R}_i)$ (and $\sigma_i d_C(\mathrm{R}_j)$). The value of slope ($\kappa = -0.58$) is the value predicted by Eq. (22). The plots for halogen substituents are excluded from the figure.

Comprehensive Expression of the Chemical Shifts. From Eqs. (3), (9) and (19), the chemical shift, δ_{ji}, may be comprehensively expressed as:

$$\delta_{ji} = d_G(\mathrm{R}_j) + (-0.59\sigma_j + 1.08)d_C(\mathrm{R}_i) \qquad (24)$$

In a like manner,

$$\delta_{ij} = d_G(\mathrm{R}_i) + (-0.59\sigma_i + 1.08)d_C(\mathrm{R}_j) \qquad (25)$$

The values of δ_{ji} and δ_{ij} predicted by Eqs. (24) and (25) are compared with those of the observed

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5) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959); S. I. Miller, *ibid.*, **81**, 101 (1959); R. A. M. O'Ferral and S. I. Miller, *ibid.*, **85**, 2440 (1963); G. S. Krishnamurthy and S. I. Miller, *ibid.*, **83**, 3961 (1961).

6) C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961); C. D. Ritchie, W. F. Sager and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 2349 (1962); C. D. Ritchie, J. D. Saltiel and E. S. Lewis, *ibid.*, **83**, 4601 (1961).

Table 3. Values of the chemical shifts of protons and the terms of interactions in *trans*-1, 2-disubstitutfd ethylenes (R_jCH_{ji}=$CH_{ij}R_i$), and comparison of the observed and the calculated chemical shifts

	R_j	R_i	τ_{ji} ppm	I_{ji} ppm	τ_{ij} ppm	I_{ij} ppm	δ_{ji}^{obsd} ppm	δ_{ji}^{calcd} ppm	δ_{ij}^{obsd} ppm	δ_{ij}^{calcd} ppm
1	H	CH_3[a]	5.04	0.00	4.27	0.00	0.37	0.37	−0.40	−0.40
2	H	H[b]	4.67	0.00	4.67	0.00	0.00	0.00	0.00	0.00
3	H	C_6H_5[b]	4.29	0.00	3.35	0.00	−0.38	−0.38	−1.36	−1.36
4	H	Br[b]	4.12	0.00	3.51	0.00	−0.55	−0.55	−1.16	−1.16
5	H	Cl[b]	4.48	0.00	3.70	0.00	−0.19	−0.19	−0.97	−0.97
6	H	CO_2CH_3	3.78	0.00	4.01	0.00	−0.89	−0.89	−0.66	−0.66
7	H	$COCH_3$	3.91	0.00	3.72	0.00	−0.76	−0.76	−0.95	−0.95
8	H	CN[b]	4.09	0.00	4.47	0.00	−0.58	−0.58	−0.20	−0.20
9	H	NO_2[c]	3.45	0.00	2.88	0.00	−1.22	−1.22	−1.79	−1.79
10	CO_2CH_3	CH_3	4.24	−0.14	3.13	−0.25	−0.43	−0.38	−1.54	−1.45
11	CO_2CH_3	Cl	3.84	0.02	2.69	−0.12	−0.83	−0.81	−1.98	−1.70
12	CO_2CH_3	Br	3.52	0.06	2.43	−0.19	−1.15	−1.08	−2.24	−1.89
13	CO_2CH_3	CO_2CH_3	3.26	0.14	3.26	0.14	−1.41	−1.35	−1.41	−1.35
14	CO_2CH_3	$COCH_3$	3.43	0.18	3.06	0.23	−1.24	−1.25	−1.61	−1.64
15	CO_2CH_3	COCl	3.04	0.10	3.04	0.06	−1.63	−1.49	−1.63	—[d]
16	CO_2CH_3	C_6H_5	3.69	0.06	2.43	0.02	−0.98	−0.95	−2.23	−2.31
17	$COCH_3$	CH_3	3.99	−0.10	3.24	−0.27	−0.68	−0.67	−1.43	−1.30
18	$COCH_3$	C_6H_5	3.35	0.01	2.55	0.00	−1.32	−1.24	−2.12	−2.17
19	CH_3	CH_3[a]	4.75	0.11	4.75	0.11	0.08	0.04	0.08	0.04
20	CH_3	Cl	4.16	0.08	4.12	0.05	−0.51	−0.62	−0.55	−0.67
21	CH_3	Br	3.92	0.20	4.05	0.17	−0.75	−1.05	−0.62	−0.86
22	CH_3	C_6H_5	3.76	−0.13	3.76	0.08	−0.91	−0.85	−0.91	−0.96
23	CH_3	CN[a]	3.32	−0.37	4.69	−0.15	−1.35	−1.08	0.02	0.02
24	CH_3	CHO	3.21	−0.30	3.97	−0.03	−1.46	−1.30	−0.70	−0.69
25	CH_3	COCl	2.81	−0.38	3.91	−0.33	−1.86	−1.67	−0.76	—[d]
26	CH_3	NO_2	2.78	−0.27	3.05	−0.20	−1.89	−1.84	−1.62	−1.56
27	C_6H_5	Cl	3.46	0.34	3.80	0.48	−1.21	−1.56	−0.87	−1.28
28	C_6H_5	Br	3.12	0.36	3.30	0.17	−1.55	−1.95	−1.37	−1.47
29	C_6H_5	C_6H_5	3.01	0.08	3.01	0.08	−1.66	−1.77	−1.66	−1.77
30	C_6H_5	CN	2.68	−0.05	4.23	0.14	−1.99	−1.98	−0.44	−0.44
31	C_6H_5	CHO	2.57	0.02	3.35	0.10	−2.10	−2.17	−1.32	−1.40
32	C_6H_5	COCl	2.20	−0.03	3.41	−0.08	−2.47	−2.52	−1.26	—[d]
33	C_6H_5	NO_2	2.08	−0.01	2.49	−0.01	−2.59	−2.67	−2.18	−2.03
34	Br	Br[e]	3.38	0.42	3.38	0.42	−1.29	−1.68	−1.29	−1.68
35	Cl	Cl[e]	3.68	0.17	3.68	0.17	−0.99	−1.15	−0.99	−1.15

a) Adopted from the data measured in the same condition of the present measurements by Bothner-By *et al.*, and by Reddy *et al.* A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); G. S. Reddy, J. H. Goldstein and L. Mandel, *ibid.*, **83**, 1300 (1961).

b) Cited from the data measured in the same condition by Banwell *et al.* C. N. Banwell and N. Sheppard, *J. Mol. Phys.*, **3**, 351 (1960).

c) Cited from the data measured by Fraser. R. A. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).

d) The calculated shifts could not been obtained, because the reliable value of the σ-constant for COCl has not been established.

e) These data were added in the present investigation. Measurements were performed under the same conditions reported in Part I.[2]

shifts in Table 3. The aspect of the correlation is shown in Fig. 10. Equations (24) and (25) hold for the 47 shifts in a series of *trans*-1, 2-disubstitued ethylenes, except for the 20 shifts in the series of compounds bearing halogen as substituents and the 3 shifts in the compounds bearing COCl as an invariable substituent. The chemical shifts in the latter compounds could not be calculated, because the appropriate σ-constant has not been established. The values of the standard deviation of the observed shifts from the regression line and the correlation coefficient were 0.08 and 0.994 respectively.

When the corrected values for the substituents,

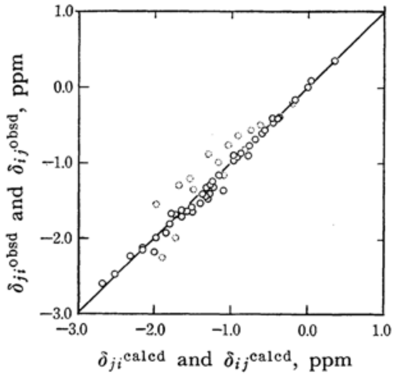

Fig. 10. The correlation between the values of observed shifts and those calculated by Eqs. (24) and (25) in *trans*-forms of 1, 2-disubstituted ethylenes. The plots for halogen substituents are described by dotted circles.

cyano and phenyl groups which exert quite large magnetic anisotropies and the usual Hammett equations are applied to the shifts, δ_{ji} and δ_{ij} are expressed as:

$$\delta_{ji} = d_G(\mathrm{R}_j) + (0.86\sigma_j - 1.68)\sigma_i \qquad (26)$$

$$\delta_{ij} = d_G(\mathrm{R}_i) + (0.86\sigma_i - 1.68)\sigma_j \qquad (27)$$

In this case, there is an approximately linear correlation between the observed shifts and those predicted by Eqs. (26) and (27), as Fig. 11 shows.

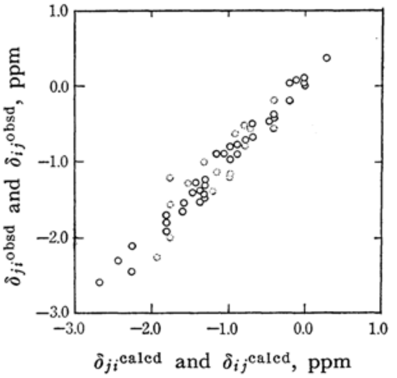

Fig. 11. The correlation between the values of observed shifts and those calculated by Eqs. (26) and (27). The plots for halogen substituents are described by dotted circles.

Deviations of Halogen Substituents from the Correlation Line. It may be worth mentioning the anomalous behaviors of halogen substituents, which have been so far excluded from the present paper. As has been briefly stated above, the plots for halogen substituents deviate considerably from the correlation line between $\delta_{ji}{}^J$ and $d_C(\mathrm{R}_i)$ in the series of compounds bearing methyl and phenyl groups respectively as the invariable substituents. These deviations can not be attributed to the contributions of the magnetic anisotropies of halogens, because the substituent-shielding parameters, $d_C(\mathrm{R}_i)$, are the relative shifts themselves in monosubstituted ethylenes and contain the contributions of the anisotropies. Rather, these deviations must be attributed to the difference between the modes of the conjugation of halogen with a methyl or phenyl group through the olefinic bond and those of halogen with the substituents other than methyl and phenyl groups.

This viewpoint is suggested by the correlation between $\delta_{ji}{}^J$ and $d_C(\mathrm{R}_i)$ in the series of the compounds bearing halogen as an invariable substituent shown in Fig. 12, where the correlation line seems to be divided in two lines. That is, one line consists of the plots for halogen, methyl and phenyl groups, while the other consists of those for hydrogen and the methoxycarbonyl group. Such aspects are revealed much more clearly in Figs. 10 and 13.

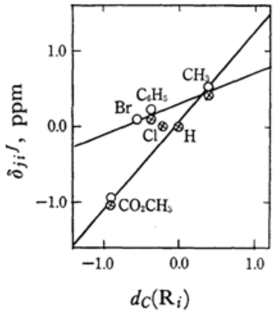

Fig. 12. The relation between the relative shifts and $d_C(\mathrm{R}_i)$ in series of compounds bearing halogen as an invariable substituent; ○: R_j=Br, ⊗: R_j=Cl.

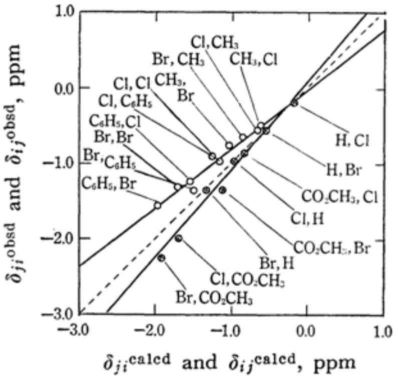

Fig. 13. The aspects of proton chemical shifts for halogen substituents.

The plots for halogen which are described by a dotted circle in Fig. 10 deviate considerably from the correlation line. Their deviations, however, seem to be systematic along the line. Figure 13 reveals that the plots for halogen may be classified into two groups. One group consists of pairs of substituents, halogen, and hydrogen or a methoxycarbonyl group which has a +M effect. The other consists of pairs of substituents, halogen, and a methyl or phenyl group which has a −M effect. Accordingly, the difference between these aspects may be attributed to the difference between the modes of the conjugation of halogen with the other substituents through the olefinic bond. The halogen substituent which has quite a large −M effect in comparison with the other substituents examined in the present paper may conjugate with a methyl or phenyl group to increase the electron density on the proton more than is predicted by Eq. (24). Moreover, and inversely the halogen substituent may conjugate with a methoxycarbonyl group to decrease the electron density on the proton.