A Semi-empirical Calculation of the Substituent Effects on ^{1}H Chemical Shifts in Aromatic Side-chains

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(Received June 14, 1974)

The diamagnetic contribution of the hydrogen atom in the C–H bond and that from its bonded carbon have been semi-empirically expressed. By considering the "ring-current" effect in addition to such contributions, a semi-empirical expression has been obtained for ^{1}H chemical shifts relative to the unsubstituted compound in substituted aromatic side-chains. The applicability of the expression has been examined for *m*- and *p*-substituted phenylacetylenes, styrenes, toluenes, and benzaldehydes.

The well-known expression for obtaining a simple relationship for the magnetic shielding constant of the hydrogen atom, σ^{A}, in an aromatic side-chain can be described as a sum of the following contributions:[1)]

$$\sigma^{A} = \sigma_{dia}^{AA} + \sum_{B \neq A}(\sigma_{dia}^{AB} + \sigma_{para}^{AB}) + \sigma^{A,ring} \tag{1}$$

where σ_{dia}^{AA} is the local diamagnetic term of the hydrogen atom, A; where σ^{AB} is the contribution from currents on the B atom to the shielding of A, and where $\sigma^{A,ring}$ is the contribution to the shielding of A from the "ring current".

Recently, Kajimoto and Fueno[2)] have presented an improved LCAO MO expression for the shielding of a hydrogen atom, A (σ^{A}), in aliphatic compounds; their expression is derived on the basis of Ramsey's equation,[3)] containing two of Pople's three assumptions,[4)] (1) a zero-differential atomic integral and (2) an average excitation energy approximation, but without invoking (3) the magnetic dipole approximation. They have concluded that the diamagnetic shielding from the neighboring carbon (σ_{dia}^{AB}) constitutes an important contribution, together with the σ_{dia}^{AA} term to the chemical shifts, whereas the paramagnetic term (σ_{para}^{AB}) remains almost constant for various substituted olefinic compounds.

It is well established that the contribution from the "ring current" should be taken into consideration for the ^{1}H chemical shifts in aromatic side-chains.[5)] Figeys and Flammang have indicated that the introduction of a substituent into a benzene ring decreases the effect of the "ring current" and that this effect can be interpreted as arising from the fact that an additional contribution due to the "quinonoid" structure in the resonance hybrid leads to some degree of decrease in the ring current.[6)] Yamada, Yukawa, and Tsuno have shown that the extent of the contribution of the "quinonoid" structure depends on the resonance ability of the substituent introduced,[7)] and they have presented an equation ($\varDelta\sigma^{A,ring}$) to describe the contribution relative to the unsubstituted compound to the ^{1}H chemical shifts in *m*-substituted aromatic side-chains, utilizing Johnson and Bovey ring-current shifts:[5b)]

$$\varDelta\sigma^{A,ring} = -0.4f(\rho, z)|\sigma_{\pi}| \tag{2}$$

where $f(\rho, z)$ is the Johnson and Bovey ring-current shift in ppm, which is expressed as a function of the geometric factors for the proton located at the cylindrical co-ordinates, ρ and z, and where σ_{π} is Yukawa-Tsuno's parameter for measuring the resonance ability of the substituent.[8)]

In the present paper, we will first attempt to evaluate the diamagnetic term, σ_{dia}^{AB}, semi-empirically. Second, we will reveal that Eq. (2) can also be applied to the case of *p*-substituted compounds. By taking the "ring-current" effect into account in addition to the diamagnetic terms, σ_{dia}^{AA} and σ_{dia}^{AB}, we have obtained a semi-empirical expression for the ^{1}H chemical shifts relative to the unsubstituted compound in substituted aromatic side-chains. We will report to what degree of accuracy the expression reproduces the chemical shifts observed for protons in side-chain of *m*- and *p*-substituted phenylacetylenes, styrenes, toluenes, and benzaldehydes.

Results and Discussion

Kajimoto *et al.*[2)] have shown that the local diamagnetic term of the hydrogen atom, A (σ_{dia}^{AA}), is given by Eq. (3), using Slater's effective nuclear charge modified to $z_{eff}=1.2-0.3(q_{H}-1)$ for the 1s orbital of hydrogen:

$$\begin{aligned}\sigma_{dia}^{AA} &= (e^2/3mc^2)p_{1s,1s}^{A}\langle\phi_{1s}^{A}|1/r_{A}|\phi_{1s}^{A}\rangle \\ &= 17.75\times10^{-6}(-0.3q_{H}^{2}+1.5q_{H}) \end{aligned}\tag{3}$$

where q is the electron density on the 1s orbital of hydrogen. The value of σ_{dia}^{AA} relative to the unsubstituted compound is linearly correlated with the increment in the electron density on the hydrogen atom:

$$\varDelta\sigma_{dia}^{AA} = a \times 10^{-6}\varDelta q^{A} \tag{4}$$

where the value of a has been obtained as 16.0 by Kajimoto *et al.*[2)] for the case of substituted olefinic compounds.

They have also derived an LCAO MO expression for the σ_{dia}^{AB} term in the case of olefinic compounds:

$$\sigma_{dia}^{AB} = (e^2/3mc^2)\sum_{i}p_{ii}^{B}\langle\phi_{i}^{B}|1/r_{AB}|\phi_{i}^{B}\rangle \tag{5}$$

$$= 10^{-6}\{8.362q_{2s}^{B}+10.073q_{2pz}^{B}+7.564(q_{2px}^{B}+q_{2py}^{B})\} \tag{6}$$

where q's are the electron densities on specified atomic orbitals and where the C–H bond length is taken to be 1.08 Å.[2)] The value of σ_{dia}^{AB} relative to the unsubstituted compound can be correlated with the increment in the total (2s and 2p) electron density on the B atom:

$$\varDelta\sigma_{dia}^{AB} = 8.39\times10^{-6}\varDelta q^{B} \tag{7}$$

In order to empirically evaluate the σ_{dia}^{AB} term we will replace the quantum mechanical average of r^{-1} from each atomic orbital on the B atom with the inverse

Table 1. Comparison of values (in ppm) of σ^{AB}_{dia} calculated by Eq. (7) with those calculated by Eq. (10) in monosubstituted ethylenes

$\underset{(B)(A)}{XCH{=}CH_2}$

Substituent	q^B	$8.70\Delta q^B$	$8.39\Delta q^B$
H[a)]	3.9945	0.00	0.00
H[b)]	4.0312	0.00	0.00
OCH_3[a)]	4.1058	0.97	0.93
CN[a)]	3.9748	−0.17	−0.17
NO_2[a)]	3.9483	−0.40	−0.39
CH_3[a)]	4.0253	0.27	0.26
Cl[b)]	4.0667	0.31	0.30

a) All electron densities were calculated by the INDO method. b) The electron density was calculated by the CNDO/2 method. The values of the third and fourth columns for chloroderivatives are relative to the unsubstituted compound, the electron density of which was calculated by the CNDO/2 method.

distance of A from the point charge on B. Then Eq. (5) becomes:

$$\sigma^{AB}_{dia} = (e^2/3mc^2)r_{AB}^{-1}q^B \qquad (8)$$

$$= b \times 10^{-6}\, q^B \qquad (9)$$

The expression of Eq. (9), relative to the unsubstituted compound, is given as:

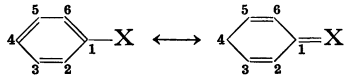
$$\Delta\sigma^{AB}_{dia} = b \times 10^{-6}\Delta q^B \qquad (10)$$

When Eq. (8) is applied to substituted ethylenes, where the C–H bond length is taken to be 1.08 Å, the value of b is 8.70. Table 1 shows that the respective values of $\Delta\sigma^{AB}_{dia}$, as calculated by Eqs. (7) and (10) for substituted ethylenes, agree within errors of only a few percent. Moreover, when the C–H bond length is taken to be 1.064 Å in the ethynyl bond, $\sigma^{AB}_{dia}=8.83\times 10^{-6}\, q^B$ using Eq. (8). In acetylene, the value of σ^{AB}_{dia} is 35.82 ppm, while the strict MO calculation by Katô has given 35.71 ppm for it, taking the 2s and 2p orbitals on carbon into account.[9)] These results mean that Eq. (8) is applicable to the calculation of the substituent effect on the σ^{AB}_{dia} term in the cases of olefinic and ethynyl protons.

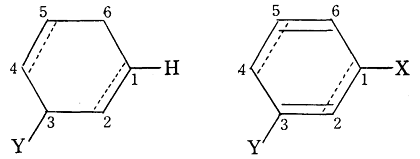
The paramagnetic term, σ^{AB}_{para}, calculated according to Pople's expression[4)] remains almost constant for the series of compounds examined, so long as we assume the same average excitation energy and the same value of the integral $\langle r_{AB}{}^{-3}\rangle$ for the same series of compounds.

With regard to the "ring-current" effect on the ^{1}H chemical shifts in aromatic side-chains, Eq. (2) can not axiomatically hold in the case of the proton at the position *para* to substituent, where a conjugative interaction through the benzene ring between the substituent and the side-chain group might result in the difference in the "ring-current" effect compared with the case of *m*-substituted compounds.

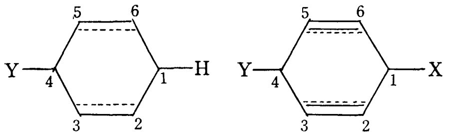
The "ring-current" effect on the ^{1}H chemical shift in monosubstituted benzene may consist of two factors: the ring-current intensity due to the total π-electron density on the benzene ring and the decrease in the ring current arising from the contribution of the "quinonoid" structure due to an introduced substituent. The degree of the contribution of the "quinonoid" structure to the benzene ring due to an introduced substituent may be reflected in changes in the absolute values of the π-electron densities on carbon atoms at the C_1 and C_4 positions.



If it is assumed that the contributions of the "quinonoid" structure arising from the introduction of the X and Y substituents (Y: the side-chain group) are put one upon another in either *m*- or *p*-substituted compounds, as is shown in Fig. 1, the relative contribution of the "quinonoid" structure between the substituted and the unsubstituted compounds can be determined only by the contribution of the X substituent, because the contributions of the side-chain group, Y, cancel each other out in the same series of compounds. Accordingly, if the total π-electron density (q^{π}_{ring}) of the aromatic ring of the *m*-substituted compound is equal to that of the *p*-substituted one, bearing the same substituent, and if the absolute values of the relative π-electron densities on C_1 (and C_4) between the substituted and the unsubstituted compounds ($|\Delta q_\pi(C_1)|$ and $|\Delta q_\pi(C_4)|$) are equal in the two compounds, the contributions by the X substituent may be regarded as equal in the two compounds. The results summarized in Table 2 show that the q^{π}_{ring} value of the *m*-substituted compound scarcely differs from that of the *p*-sbustituted one, and that the values of $|\Delta q_\pi(C\_)|$ (and $|\Delta q_\pi(C_4)|$) are almost equal in *m*- and *p*-substituted compounds. Therefore, it may be concluded that the relative contributions of the "ring current" to the unsubstituted compound are equal in *m*- and *p*-substituted compounds.



(I) *m*-Substituted compounds



(II) *p*-Substituted compounds

Y: $-C{\equiv}CH$, $-CH{=}CH_2$, $-CH_3$, $-CHO$

Fig. 1. Offset of quinonoid structure due to the side-chain group Y in *m*- and *p*-substituted aromatic compounds.

By combining Eqs. (2), (4), and (10), we obtain the following equation for the ^{1}H chemical shifts, $\delta(\equiv\Delta\sigma^A)$, in ppm, relative to the unsubstituted compound in *m*- and *p*-substituted aromatic side-chains:

$$\delta_{calc} = a\Delta q^A + b\Delta q^B - 0.4f(\rho, z)|\sigma_\pi| \qquad (11)$$

Since the electron density on an aromatic side-chain can be altered by the substituent polar effect (the mesomeric and inductive (through bond) effects), its contribution to the ^{1}H chemical shift in the side-chain may be included in the first and second terms of Eq.

TABLE 2. π-ELECTRON DENSITIES ON AROMATIC RINGS

(i) *m*- and *p*-Substituted phenylacetylenes.[a]

Substituent	q^{π}_{ring}[b]	$\lvert\Delta q^{\pi}(C_1)\rvert$[c]	$\lvert\Delta q^{\pi}(C_4)\rvert$[c]
H	5.996	0.000	0.000
H[d]	6.007	0.000	0.000
m-CH_3	6.007	0.018	0.009
p-CH_3	6.004	0.019	0.009
m-CH_3O	6.074	0.042	0.037
p-CH_3O	6.066	0.043	0.036
m-NO_2	5.981	0.065	0.030
p-NO_2	5.983	0.069	0.025
m-Cl[d]	6.029	0.012	0.006
p-Cl[d]	6.026	0.009	0.005

(ii) *m*- and *p*-Substituted styrenes.[d]

Substituent	q^{π}_{ring}[b]	$\lvert\Delta q^{\pi}(C_1)\rvert$[c]	$\lvert\Delta q^{\pi}(C_4)\rvert$[c]
H	5.988	0.000	0.000
m-CH_3	6.012	0.028	0.015
p-CH_3	6.008	0.029	0.015
m-Cl	6.031	0.005	0.012
p-Cl	6.027	0.004	0.009
m-NO_2	5.984	0.064	0.030
p-NO_2	5.987	0.070	0.038
m-CN	5.984	0.000	0.006
p-CN	5.983	0.001	0.009
m-NH_2[e]	6.096	0.072	0.059
p-NH_2[e]	6.083	0.077	0.060

(iii) *m*- and *p*-Substituted toluenes.[d]

Substituent	q^{π}_{ring}[b]	$\lvert\Delta q^{\pi}(C_1)\rvert$[c]	$\lvert\Delta q^{\pi}(C_4)\rvert$[c]
H	6.013	0.000	0.000
m-CH_3	6.027	0.027	0.015
p-CH_3	6.023	0.028	0.015
m-CH_3O	6.083	0.049	0.041
p-CH_3O	6.075	0.048	0.039
m-F	6.069	0.036	0.031
p-F	6.063	0.037	0.029
m-CN	5.998	0.000	0.007
p-CN	5.994	0.001	0.009
m-NO_2	5.996	0.065	0.032
p-NO_2	5.997	0.068	0.038

(iv) *m*- and *p*-Substituted benzaldehydes.[a]

Substituent	q^{π}_{ring}[b]	$\lvert\Delta q^{\pi}(C_1)\rvert$[c]	$\lvert\Delta q^{\pi}(C_4)\rvert$[c]
H	5.952	0.000	0.000
H[d]	5.957	0.000	0.000
m-CH_3	5.959	0.019	0.010
p-CH_3	5.961	0.020	0.010
m-CH_3O	6.030	0.043	0.037
p-CH_3O	6.025	0.042	0.037
m-NO_2	5.938	0.064	0.029
p-NO_2	5.944	0.069	0.033
m-Cl[d]	5.990	0.006	0.007
p-Cl[d]	5.988	0.005	0.010

a) Electron densities were calculated by the INDO method. Values of bond lengths and bond angles of compounds examined were chosen from Ref. 10. b) The total π-electron density on the aromatic ring. c) Absolute values of relative π-electron densities on C_1 and C_4 between the substituted and the unsubstituted compounds. Numbering of atoms C_1 and C_4 correspond to that in Fig. 1. d) Electron densities were calculated by the CNDO/2 method. e) A planar model was used for amino groups.

TABLE 3. VALUES OF *a*, *b*, AND $f(\rho, z)$ IN Eq. (9) in ppm

Side-chain system		*a*	*r*[a]	*s*[a]	*b*	$f(\rho, z)$
$XC_6H_4C{\equiv}CH$		16.7	0.9998	0.0009	8.83	−0.21[b]
$XC_6H_4\diagdown\quad\diagup H_\beta$	α	16.1	0.9999	0.0070	8.70	−0.25[c]
$C{=}C$	β	16.2	0.9999	0.0006	8.70	−0.54[c]
$H_\gamma\diagup\quad\diagdown H_\alpha$	γ	16.1	1.0000	0.0004	8.70	−0.58[c]
$XC_6H_4CH_3$		16.0	0.9999	0.0008	8.52	−0.57[b]
XC_6H_4CHO		15.2	0.9999	0.0010	8.43	−0.61[b]

a) *r*: correlation coefficient, *s*: standard deviation. b) Cited from Ref. 7. c) Calculated from the table of the Johnson and Bovey's ring current shifts (Ref. 11). The basis of this calculation consists in that the total π-electron density on aromatic ring scarcely differs from that of benzene (see Table 2) and that the contribution due to the "quinonoid" structure of the side-chain group cancels each other out in the same seires of compounds.

(11) to a first approximation. In order to examine the applicability of Eq. (11), we have chosen ethynyl, olefinic, saturated aliphatic, and formyl groups as model

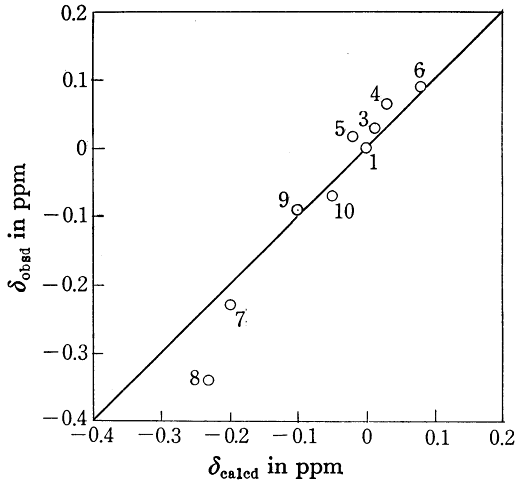


Fig. 2. Plots of δ_{calcd} against δ_{obsd} in *m*- and *p*-substituted phenylacetylenes. Numbered points correspond to entries in Table 4-(i).

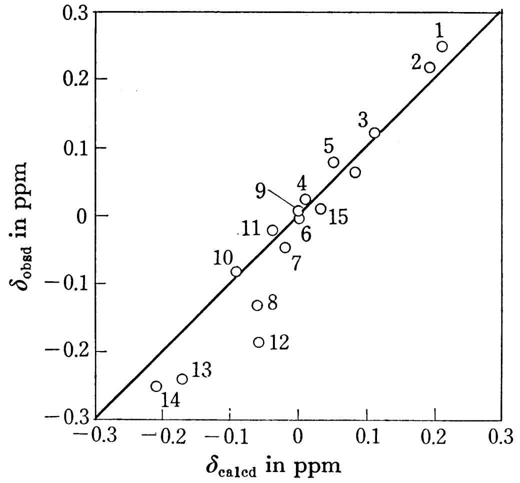


Fig. 3(a). Plots of δ_{calcd} against δ_{obsd} for protons, Hα, in *m*- and *p*-substituted styrenes. Numbered points correspond to entries in Table 4-(ii), (a).

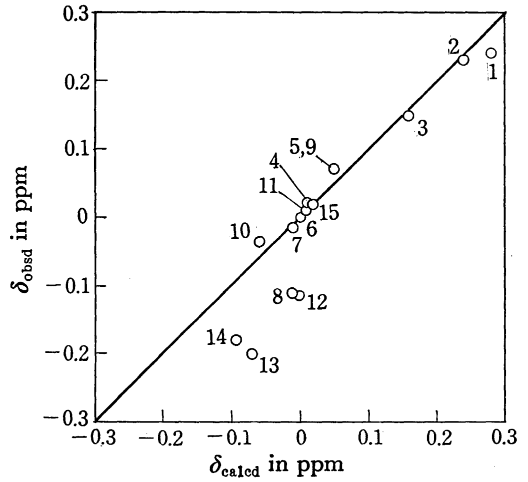


Fig. 3(b). Plots of δ_{calcd} against δ_{obsd} for protons, Hβ, in *m*- and *p*-substituted styrenes. Numbered points correspond to entries in Table 4-(ii), (b).

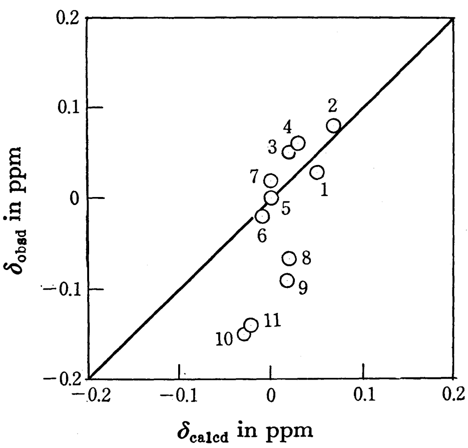


Fig. 4. Plots of δ_{calcd} against δ_{obsd} in *m*- and *p*-substituted toluenes. Numbered points correspond to entries in Table 4-(iii).

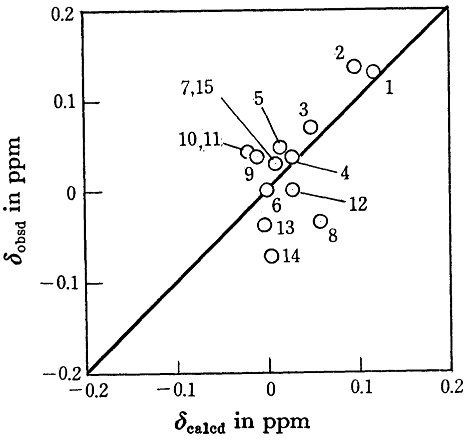


Fig. 3(c). Plots of δ_{calcd} against δ_{obsd} for protons, Hγ, in *m*- and *p*-substituted styrenes. Numbered points correspond to entries in Table 4-(ii), (c).

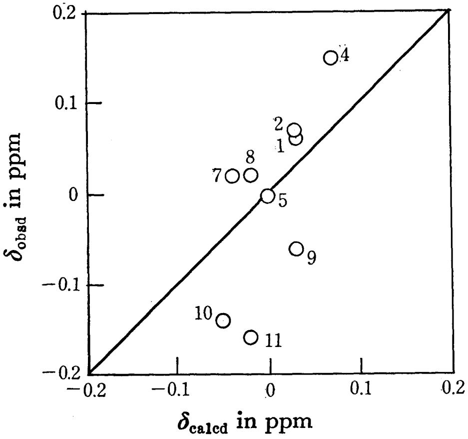


Fig. 5. Plots of δ_{calcd} against δ_{obsd} in *m*- and *p*-substituted benzaldehydes. Numbered points correspond to entries in Table 4-(iv).

systems of aromatic side-chains. Above all, the advantage of styrenes in examining the success of Eq. (11) is that they have three hydrogen atoms situated in different magnetic environments in the side-chain.

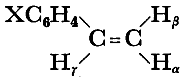
The values of *a*, *b*, and *f*(ρ, *z*) obtained for the compounds examined are listed in Table 3. In Table 4, the chemical shifts calculated by Eq. (11) are compared with those observed for *m*- and *p*-substituted phenylacetylenes, styrenes, toluenes, and benzaldehydes. Even though it is a rather optional expansion to apply Eq. (8) to calculation of the σ^{AB}_{dia} term in the cases of toluenes and benzaldehydes, the results of the calcula-

Table 4. Chemical shifts of protons in side-chains of *m*- and *p*-substituted aromatic compounds[a)]

(i) *m*- and *p*-Substituted phenylacetylenes.[b)]

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[c)]
1	H	0.9484	4.0991	0.000	0.000	0.000	0.00	0.000
2	H[d)]	0.9378	4.1110	0.000	0.000	0.000	0.00	0.000
3	*m*-CH_3	0.9487	4.0992	0.005	0.001	0.007	0.01	0.030
4	*p*-CH_3	0.9488	4.1012	0.007	0.019	0.007	0.03	0.065
5	*m*-CH_3O	0.9479	4.0949	−0.008	−0.037	0.024	−0.02	0.020
6	*p*-CH_3O	0.9488	4.1050	0.007	0.052	0.024	0.08	0.090
7	*m*-NO_2	0.9430	4.0833	−0.090	−0.140	0.029	−0.20	−0.233
8	*p*-NO_2	0.9430	4.0801	−0.090	−0.168	0.029	−0.23	−0.340
9	*m*-Cl[d)]	0.9353	4.1034	−0.042	−0.067	0.006	−0.10	−0.085
10	*p*-Cl[d)]	0.9361	4.1077	−0.028	−0.029	0.006	−0.05	−0.068

(ii) m- and p-Substituted styrenes.[d]



$$\begin{array}{ccc} XC_6H_4 & & H_\beta \\ & C=C & \\ H_\gamma & & H_\alpha \end{array}$$

(a) H$_\alpha$

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[e]	δ_{obsd}[h]
1	p-N(CH$_3$)$_2$[f]	0.9966	4.0569	0.050	0.109	0.054	0.21	0.250	—
2	p-NH$_2$	0.9967	4.0558	0.052	0.099	0.042	0.19	0.223	—
3	p-CH$_3$O[f]	0.9946	4.0520	0.018	0.066	0.028	0.11	0.127	0.124
4	m-CH$_3$	0.9939	4.0436	0.006	−0.007	0.008	0.01	—	0.026
5	p-CH$_3$	0.9944	4.0473	0.014	0.025	0.008	0.05	0.078	0.063
6	H	0.9935	4.0444	0.000	0.000	0.000	0.00	0.000	0.000
7	p-C≡CH[f,g]	0.9928	4.0438	−0.011	−0.005	0.001	−0.02	−0.047	—
8	p-COCH$_3$[f]	0.9912	4.0383	−0.037	−0.053	0.029	−0.06	−0.129	—
9	p-F[f]	0.9918	4.0462	−0.027	0.016	0.012	0.00	0.012	—
10	m-Cl	0.9904	4.0392	−0.050	−0.045	0.007	−0.09	—	−0.078
11	p-Cl	0.9913	4.0433	−0.035	−0.009	0.007	−0.04	−0.021	−0.036
12	p-CN	0.9907	4.0402	−0.045	−0.036	0.025	−0.06	−0.186	—
13	m-NO$_2$	0.9858	4.0356	−0.124	−0.076	0.034	−0.17	—	−0.240
14	p-NO$_2$	0.9858	4.0313	−0.124	−0.114	0.034	−0.21	−0.249	—
15	p-CH=CH$_2$[f]	0.9937	4.0455	0.003	0.010	0.011	0.03	0.012	—

(b) H$_\beta$

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[e]	δ_{obsd}[h]
1	p-N(CH$_3$)$_2$[f]	0.9868	4.0569	0.049	0.109	0.117	0.28	0.237	—
2	p-NH$_2$	0.9868	4.0558	0.049	0.099	0.091	0.24	0.227	—
3	p-CH$_3$O[f]	0.9857	4.0520	0.031	0.066	0.061	0.16	0.148	0.149
4	m-CH$_3$	0.9839	4.0436	0.002	−0.007	0.017	0.01	—	0.021
5	p-CH$_3$	0.9845	4.0472	0.011	0.025	0.017	0.05	0.073	0.060
6	H	0.9838	4.0444	0.000	0.000	0.000	0.00	0.000	0.000
7	p-C≡CH[f,g]	0.9837	4.0438	−0.002	−0.005	0.001	−0.01	−0.013	—
8	p-COCH$_3$[f]	0.9824	4.0383	−0.023	−0.053	0.063	−0.01	−0.109	—
9	p-F[f]	0.9845	4.0462	0.011	0.016	0.025	0.05	0.078	—
10	m-Cl	0.9821	4.0392	−0.028	−0.045	0.016	−0.06	—	−0.036
11	p-Cl	0.9837	4.0433	−0.002	−0.009	0.016	0.01	0.018	0.011
12	p-CN	0.9829	4.0400	−0.015	−0.036	0.054	0.00	−0.114	—
13	m-NO$_2$	0.9799	4.0356	−0.063	−0.076	0.073	−0.07	—	−0.200
14	p-NO$_2$	0.9808	4.0313	−0.049	−0.114	0.073	−0.09	−0.177	—
15	p-CH=CH$_2$[f,g]	0.9841	4.0455	0.005	0.010	0.005	0.02	0.020	—

(c) H$_\gamma$

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[e]	δ_{obsd}[h]
1	p-N(CH$_3$)$_2$[f]	1.0010	3.9907	0.060	−0.063	0.125	0.12	0.126	—
2	p-NH$_2$	1.0011	3.9912	0.061	−0.059	0.097	0.10	0.135	—
3	p-CH$_3$O[f]	0.9991	3.9930	0.029	−0.043	0.065	0.05	0.068	0.072
4	m-CH$_3$	0.9976	3.9986	0.005	0.006	0.017	0.03	—	0.042
5	p-CH$_3$	0.9983	3.9963	0.016	−0.014	0.017	0.02	0.055	0.048
6	H	0.9973	3.9979	0.000	0.000	0.000	0.00	0.000	0.000
7	p-C≡CH[f,g]	0.9974	3.9981	0.002	0.002	0.001	0.01	0.032	—
8	p-COCH$_3$[f]	0.9950	4.0001	−0.037	0.027	0.067	0.06	−0.035	—
9	p-F[f]	0.9964	3.9956	−0.014	−0.020	0.027	−0.01	0.039	—
10	m-Cl	0.9941	3.9997	−0.052	0.016	0.015	−0.02	—	0.045
11	p-Cl	0.9957	3.9970	−0.026	−0.008	0.015	−0.02	0.047	0.043
12	p-CN	0.9948	3.9993	−0.040	0.012	0.058	0.03	−0.001	—
13	m-NO$_2$	0.9910	4.0003	−0.101	0.021	0.079	0.00	—	−0.034
14	p-NO$_2$	0.9902	4.0029	−0.114	0.043	0.079	0.01	−0.073	—
15	p-CH=CH$_2$[f,g]	0.9976	3.9972	0.005	−0.006	0.012	0.01	0.029	—

(iii) *m*- and *p*-Substituted toluenes.[d]

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[c]
1	*m*-CH_3O	0.9933	4.0206	−0.034	0.017	0.064	0.05	0.030
2	*p*-CH_3O	0.9978	4.0146	0.038	−0.034	0.064	0.07	0.078
3	*m*-CH_3	0.9954	4.0191	0.001	0.005	0.018	0.02	0.053
4	*p*-CH_3	0.9967	4.0169	0.021	−0.014	0.018	0.03	0.057
5	H	0.9954	4.0185	0.000	0.000	0.000	0.00	0.000
6	*m*-F	0.9916	4.0209	−0.061	0.020	0.027	−0.01	−0.022
7	*p*-F	0.9955	4.0156	0.002	−0.025	0.027	0.00	0.022
8	*m*-CN	0.9926	4.0193	−0.045	0.006	0.057	0.02	−0.067
9	*p*-CN	0.9924	4.0199	−0.048	0.011	0.057	0.02	−0.090
10	*m*-NO_2	0.9881	4.0201	−0.117	0.013	0.077	−0.03	−0.150
11	*p*-NO_2	0.9868	4.0233	−0.138	0.040	0.077	−0.02	−0.140

(iv) *m*- and *p*-Substituted benzaldehydes.[b]

	Substituent	q^A	q^B	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[i]
1	*m*-CH_3	1.0869	3.6735	0.005	0.006	0.019	0.03	0.06
2	*p*-CH_3	1.0879	3.6719	0.020	−0.008	0.019	0.03	0.07
3	*m*-CH_3O	1.0853	3.6756	−0.020	0.023	0.069	0.02	—
4	*p*-CH_3O	1.0893	3.6683	0.041	−0.038	0.069	0.07	0.15
5	H	1.0866	3.6729	0.000	0.000	0.000	0.00	0.00
6	H[d]	1.0495	3.7660	0.000	0.000	0.000	0.00	0.00
7	*m*-Cl[d]	1.0455	3.7668	−0.061	0.007	0.017	−0.04	0.02
8	*p*-Cl[d]	1.0479	3.7467	−0.024	−0.011	0.017	−0.02	0.02
9	*p*-CN[d]	1.0836	3.6744	−0.046	0.014	0.061	0.03	−0.06
10	*m*-NO_2	1.0775	3.6735	−0.138	0.006	0.083	−0.05	−0.14
11	*p*-NO_2	1.0777	3.6771	−0.135	0.036	0.083	−0.02	−0.16

a) All values are relative to the unsubstituted compound. b) All electron densities in substituted phenylacetylenes and benzaldehydes were calculated by the INDO method except for chloroderivatives, for which was used the CNDO/2 method. c) The chemical shifts were measured in carbon tetrachloride. Cited from Ref. 7. d) All electron densities were calculated by the CNDO/2 method. e) The chemical shifts were measured in cyclohexane. Cited from Ref. 12. f) The electron densities in these compounds were cited from the data, calculated by the CNDO/2 method in Ref. 12. g) The σ_π-values necessary to calculate the $\Delta\sigma^{A,ring}$, which have not been established, were obtained from the correlation between π-electron densities on the carbon at *para*-position to substituent in monosubstituted benzenes and the known σ_π-values of the other substituents: σ_π (*p*-C≡CH), −0.005 and σ_π (*p*-CH=CH_2), −0.05. h) The chemical shifts were measured in CCl_4. Cited from Ref. 13. i) The chemical shifts were measured in carbon tetrachloride except for nitro- and cyano-derivatives, those of which are relative to the unsubstituted compound measured in $CDCl_3$. (Ref. 14)

tion show that the application of Eq. (11) is not unreasonable.* In Figs. 2—5, plots of the calculated chemical shifts are shown against the observed shifts. As may clearly be seen in Figs. 2, 3(a), and 3(b), the calculated chemical shifts correctly reproduce the observed shifts in the case of terminal protons, which are three bond lengths removed from the ring carbon, to which the side-chain group is bonded. On the other hand, in protons directly bonded to the carbon atom adjoining the aromatic ring (Figs. 3(c), 4 and 5), the correlation between the calculated and the observed shifts collapses to some degree. This result may be mainly attributed to the inadequacy introduced by ignoring magnetic contributions from atoms other than the bonded carbon. Even in this case, the accuracy of the chemical shifts calculated by Eq. (11) is not inferior to those which have been calculated strictly theoretically.[2,4] Therefore, Eq. (11) provides us with a brief method for predicting the substituent effect on ^1H chemical shifts in *m*- and *p*-substituted aromatic side-chains.

The INDO and CNDO/2 calculations were carried out on FACOM-230 computers at the Computation Centers of Kyoto University and Nagoya University. We wish to express our gratitude to Professor Hiroshi Kato of our college and to Dr. Naoya Nakagawa of the University of Electro-Communications for their helpful instructions and encouragements.

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* When Eq. (8) is applied to calculation of the relative chemical shifts (in ppm) for methyl protons in ethyl derivatives CH_3CH_2X, the chemical shifts calculated and observed give respectively the values of 0.01 and −0.28 for X=OCH_3, −0.16 and −0.05 for X=CH_3, −0.29 and −0.70 for X=NO_2. The accuracy of the chemical shifts calculated for ethyl derivatives is not inferior to that of the chemical shifts calculated for monosubstituted ethylenes by Kajimoto *et al.*[2] This result implies the propriety of the application of Eq. (8).

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