The Linearity of the Substituent-induced Carbon-13 Chemical Shifts of *α*-Carbons with Charge Densities in Aromatic Side Chains. Semi-empirical Calculations for 4-Substituted Derivatives of Styrenes, *α*-Methylstyrenes, and Biphenyls

Jun Niwa
College of General Education, Nagoya University, Chikusa, Nagoya 464

(Received October 31, 1977)

The contributions to ^{13}C shifts from the diamagnetic term of the neighboring carbon atom and from the "ring-current" have been estimated by means of the equations given in a previous paper (J. Niwa, *Bull. Chem. Soc. Jpn.*, **48**, 118 (1975)). A semi-empirical expression has been derived for the substituent-induced ^{13}C chemical shift in an aromatic side chain by considering such contributions in addition to the local diamagnetic and paramagnetic terms of the carbon atom in question. The applicability of the expression has been examined for α-carbons of 4-substituted derivatives of styrenes and α-methylstyrenes, and for 1′-carbons of 4-substituted biphenyls.

The linearity of ^{13}C nuclear shielding with electron density is widely accepted on the basis of the Karplus and Pople LCAO-MO theory of diamagnetism.[1] The attempt to interpret the ^{13}C chemical shift induced by substituents (SCS) along the lines of their approach has been successfully performed for the *para*-carbon of the benzene ring.[2] The SCS of the terminal carbon of a conjugated aromatic side chain can also be treated in the same way, whereas that of α-carbon is not always directly correlated with the electron density; for example, in the ^{13}C shielding of α- and *β*-carbons for the series of substituted styrenes, α-carbon absorbs over a relatively narrow range, about 2 ppm, while *β*-carbon differs by 10 ppm. The trend of the latter is clear; an electron-withdrawing substituent decreases the *β*-carbon shielding, while an electron-releasing substituent increases it. This trend has been nicely correlated with the electron density. In contrast to the *β*-carbon, the electron-withdrawing substituent tends to increase the α-carbon shielding. The effect, however, is small and is not linearly correlated with the electron density, as is shown in Fig. 1. Its interpretation awaits a more refined theory of ^{13}C nuclear shielding.

The dominant factor governing the ^{13}C shielding must be the local paramagnetic term, σ^{AA}_{para}, but the magnetic contributions from the rest of the molecule may also not be ignored for the SCS, the range of which is relatively narrow; in the case of styrenes, the failure of the linearity of the SCS of the α-carbon with the electron density may be attributed to ignoring the contributions from the neighboring carbon atoms and the long-range shielding effect of the "ring-current."

The premises of the present approach are: (i) it is based on the Saika-Slichter expression for the nuclear magnetic shielding;[3] (ii) it continues the use of Pople's average excitation energy approximation for the paramagnetic term;[1] (iii) it considers the magnetic contribution from the neighboring carbon atom which is situated at the site near to the substituent, and (iv) it takes the long-range shielding effect of the "ring-current" into account. In our preceding paper,[4] we derived the equations for estimating the contributions from the diamagnetic term of the neighboring carbon atom and from the "ring-current." We can derive a semi-empirical expression for obtaining the ^{13}C SCS in an aromatic side chain by considering such contributions in addition to the local diamagnetic and the local paramagnetic terms of the relevant carbon atom.

The aim of the present paper is to demonstrate the validity of the predictions by an expression for a variety of substituents in the series of 4-substituted derivatives of styrenes, α-methylstyrenes, and biphenyls and, in particular, to examine the propriety of the expression for understanding and predicting the SCS of α-carbons of the styrenes and the α-methylstyrenes, and those of 1′-carbons of the biphenyls.

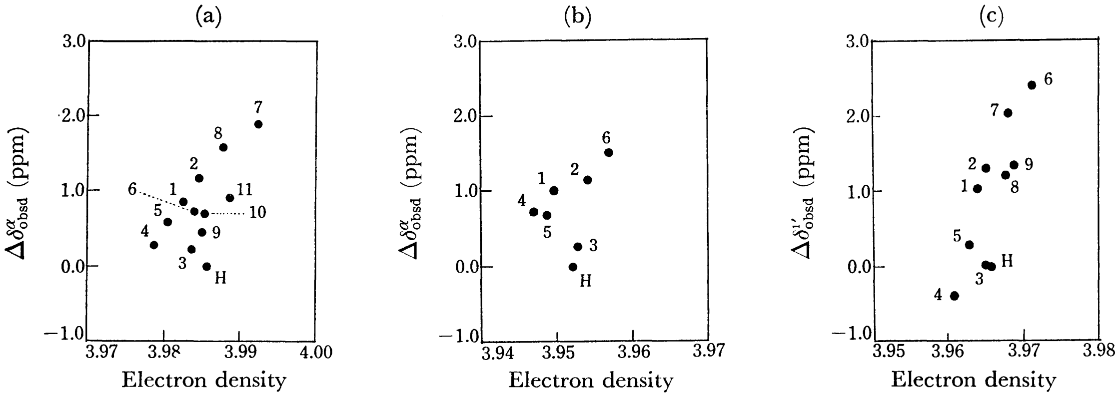


Fig. 1. Plots of $\Delta\delta_{obsd}$ against the electron density on α-carbon atom; (a) 4-substituted styrenes (b) 4-substituted α-methylstyrenes (c) 4-substituted biphenyls. Numbered points correspond to entries in Table 1.

Calculation, Results, and Discussion

The Saika-Slichter expression for obtaining a simple relationship for the nuclear magnetic shielding, σ^A, is given as[3]

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

where σ^{AA} is the local diamagnetic and the local paramagnetic terms of the A atom in question; σ^{AB} is the contribution from currents on the B atom to the shielding of A, and $\sigma^{A,ring}$ is the contribution to the shielding of A from the "ring-current."

The local diamagnetic term, σ_{dia}^{AB}, is given by

$$\sigma_{dia}^{AA} = e^2/3mc^2\sum_i\langle r_i^{-1}\rangle, \tag{2}$$

where $<r_i^{-1}>$ is the mean inverse distance of the i-th electron from a nucleus and where the summation is taken over all the electrons being considered; the diamagnetic shielding constant, σ_d', per 2s or 2p electron has been given by Yonezawa, Morishima, and Kato as[5]

$$\sigma_d'(\text{2s or 2p}) = 4.45z^*,$$

where z^* is the "effective nuclear charge" estimated according to Slater's rules. The σ_{dia}^{AA} term has been defined in terms of the four valence electrons of a carbon atom:

$$\sigma_{dia}^{AA} = 4.45z^*q^A. \tag{3}$$

According to Pople's theory,[1] the zz-component of the local paramagnetic term, σ_{para}^{AA}, is given by

$$(\sigma_{para}^{AA})_{zz} = (-e^2\hbar^2/2m^2c^2\Delta E)\langle r^{-3}\rangle_{2p}\{(Q_{AA})_{zz} + \sum_{B\neq A}(Q_{AB})_{zz}\}, \tag{4}$$

where

$$(Q_{AA})_{zz} = 2-2(P_{xAxA}-1)(P_{yAyA}-1) + 2P_{xAyA}{}^2, \tag{5}$$

and

$$(Q_{AB})_{zz} = -2P_{xAxB}P_{yAyB} + 2P_{xAyB}P_{yAxB} \tag{6}$$

with corresponding expressions for other components. $\sum_{B\neq A}$ is a summation over all the atoms other than A, $<r^{-3}>_{2p}$ is the mean inverse cube radius for carbon 2p orbitals, ΔE is the average electronic excitation energy, and $P_{\mu\nu}$ are elements of the charge density and the bond-order matrix in the MO theory of the unperturbed molecule. The suffixes xA, xB, yA, yB,··· correspond to the various 2p atomic orbitals of the A and B atoms. The $<r^{-3}>$ factor is given as[1,5]

$$\langle r^{-3}\rangle_{2p} = 1/24a_0{}^3\{3.25-0.35(P_{2p}-3)\}^3, \tag{7}$$

where a_0 is a Bohr radius and where $(P_{2p}-3)$ is the excess charge density of the 2p electron. The local paramagnetic term, σ_{para}^{AA}, becomes

$$\sigma_{para}^{AA} = -10.06/\Delta E\{3.25-0.35(P_{2p}-3)\}^3Q_{AB} \tag{8}$$

with $Q_{AB}=\sum_B\{(Q_{AA})_{\mu\mu}+\sum_{B\neq A}(Q_{AB})_{\mu\mu}\}$. The ΔE value has been assumed to be 8 eV to fit the chemical shifts observed for the α- and β-carbons of styrene and α-methylstyrene according to Pople's treatment.[1] In the same way, we have obtained 8.5 eV as the ΔE value for the 1′-carbon of biphenyl.

TABLE 1. CALCULATED AND OBSERVED CHEMICAL SHIFTS OF α- AND β-CARBONS IN 4-SUBSTITUTED STYRENES AND 4-SUBSTITUTED α-METHYLSTYRENES, AND 1′-CARBONS IN 4-SUBSTITUTED BIPHENYLS[a]

	Substituent	$\Delta\sigma_{dia}^{AA}$ [b]	$\Delta\sigma_{para}^{AA}$ [b]	$\Delta\sigma_{dia}^{AB}$	$\Delta\sigma^{A,ring}$	$\Delta\delta_{calcd}$	$\Delta\delta_{obsd}$ [c,g]
(i) 4-Substituted styrenes[c]							
			a) α-Carbons[d]				
1	F	−0.025	−0.233	0.124	0.106	−0.03	0.85
2	Cl	−0.004	0.009	0.043	0.031	0.08	1.27
3	CH_3	−0.016	−0.257	0.060	0.034	−0.18	0.23
4	$N(CH_3)_2$	−0.056	−0.808	0.210	0.238	−0.42	0.29
5	OCH_3	−0.039	−0.504	0.168	0.124	−0.25	0.67
6	SCH_3	−0.012	−0.140	0.056	0.035[f]	−0.06	0.75
7	NO_2	0.056	0.863	−0.144	0.150	0.93	1.93
8	CN	0.016	0.236	−0.036	0.110	0.33	1.57
9	$CH{=}CH_2$	−0.003	−0.120	0.015	0.022[f]	−0.09	0.47
10	C≡CH	−0.001	−0.044	0.012	0.002[f]	−0.03	0.74
11	$COCH_3$	0.026	0.277	−0.080	0.128	0.35	0.89
			b) β-Carbons[e]				
1	F	0.024	0.377	−0.012	0.022	0.41	−0.23
2	Cl	−0.011	−0.149	−0.004	0.013	−0.15	−0.77
3	CH_3	0.027	0.401	−0.013	0.014	0.43	1.00
4	$N(CH_3)_2$	0.093	1.346	−0.047	0.099	1.49	4.27
5	OCH_3	0.057	0.837	−0.033	0.052	0.91	2.22
6	SCH_3	0.009	0.119	−0.010	0.015	0.13	0.56
7	NO_2	−0.123	−1.640	0.048	0.063	−1.66	−4.70
8	CN	−0.039	−0.481	0.014	0.046	−0.46	−3.85
9	$CH{=}CH_2$	0.003	0.086	−0.002	0.009[f]	0.10	0.00
10	C≡CH	−0.003	−0.006	−0.001	0.001[f]	−0.01	−1.24
11	$COCH_3$	−0.050	−0.826	0.022	0.053	−0.80	−2.71

TABLE 1. (Continued)

Substituent	$\Delta\sigma^{AA}_{dia}$ b)	$\Delta\sigma^{AA}_{para}$ b)	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	$\Delta\delta_{calcd}$	$\Delta\delta_{obsd}$ c,g)
(ii) 4-Substituted α-Methylstyrenes c)						
			a) α-Carbons d)			
1. F	−0.023	−0.192	0.124	0.106	0.02	0.98
2. Cl	−0.004	0.078	0.042	0.031	0.15	1.08
3. CH_3	−0.013	−0.180	0.059	0.034	−0.10	0.23
4. $N(CH_3)_2$	−0.044	−0.555	0.208	0.238	−0.15	0.69
5. OCH_3	−0.032	−0.361	0.161	0.124	−0.11	0.67
6. NO_2	0.037	0.499	−0.140	0.150	0.55	1.47
			b) β-Carbons e)			
1. F	0.018	0.261	−0.019	0.023	0.28	0.04
2. Cl	−0.010	−0.150	−0.004	0.014	−0.15	−0.60
3. CH_3	0.020	0.279	−0.010	0.015	0.30	0.85
4. $N(CH_3)_2$	0.069	0.951	−0.036	0.106	1.09	3.48
5. OCH_3	0.043	0.592	−0.027	0.055	0.66	1.76
6. NO_2	−0.092	−1.182	0.031	0.067	−1.18	−3.69
(iii) 4-Substituted Biphenyls g)						
			1′-Carbons d)			
1. F	−0.017	−0.093	0.123	0.049	0.06	1.04
2. Cl	−0.005	0.083	0.041	0.029	0.15	1.32
3. CH_3	−0.011	−0.157	0.057	0.032	−0.08	0.04
4. NH_2	−0.045	−0.547	0.235	0.175	−0.18	−0.41
5. OCH_3	−0.027	−0.278	0.158	0.117	−0.03	0.29
6. NO_2	0.039	0.503	−0.138	0.141	0.55	2.40
7. CN	0.012	0.172	−0.035	0.104	0.25	2.05
8. $COCH_3$	0.017	0.206	−0.081	0.121	0.26	1.20
9. CO_2CH_3	0.021	0.271	−0.100	0.116 f)	0.31	1.28

a) All the values listed are relative to the unsubstituted compound, from the chemical shift of which upfield shifts are represented in ppm by positive values. b) For the α-carbon of styrene, σ^{AA}_{dia}: 57.733, σ^{AA}_{para}: −323.099 and for the β-carbon, σ^{AA}_{dia}: 58.262, σ^{AA}_{para}: −300.629. For the α-carbon of α-methylstyrene, σ^{AA}_{dia}: 57.459, σ^{AA}_{para}: −323.427 and for the β-carbon, σ^{AA}_{dia}: 58.453, σ^{AA}_{para}: −299.007. For the 1′-carbon of biphenyl, σ^{AA}_{dia}: 57.570, σ^{AA}_{para}: −325.839. c) Cited from Ref. 10, in which all the chemical shifts were measured in CCl_4 with 8% C_6D_{12}. d) The symbol A refers to the α-carbon (and the 1′-carbon), and the symbol B, to the C_1-carbon. e) The symbol A refers to the β-carbon, and the symbol B, to the α-carbon. f) The σ-values necessary to calculate the $\Delta\sigma^{A,ring}$, which had not been established from the reactivity data, were obtained from the correlation between the π-electron densities on *para*-carbons in monosubstituted benzenes and the known σ_π-values of the other substituents: σ_π(−CH=CH$_2$), −0.05; σ_π(−C≡CH), −0.005; σ_π(SCH$_3$), −0.08; σ_π(CO$_2$CH$_3$), 0.28. g) Cited from Ref. 12, in which all the chemical shifts were measured in acetone with 10% benzene.

The calculated values of the local diamagnetic (σ^{AA}_{dia}) and the local paramagnetic terms (σ^{AA}_{para}), relative to the unsubstituted compound, are summarized in Table 1. They are linearly correlated with the increments in the electron density on the carbon atom A:

$$\Delta\sigma^{AA}_{dia} + \Delta\sigma^{AA}_{para} = a\Delta q^{A}. \tag{9}$$

As has been shown in our preceding paper,[4] the diamagnetic contribution, σ^{AB}_{dia}, from the sp^2 hybridized carbon atom B to the A atom, to which the B atom is bonded, can be expressed as

$$\begin{aligned}\sigma^{AB}_{dia} &= e^2/3mc^2\sum_{i}\langle r_{AB}^{-1}\rangle \\ &= e^2/3mc^2 r_{AB}^{-1}q^{B},\end{aligned} \tag{10}$$

where r_{AB}^{-1} is the inverse distance of the A atom from the point charge on the B atom and where q is the total (2s and 2p) electron density on the B atom. The expression of Eq. 10, relative to the unsubstituted compound, is given as

$$\Delta\sigma^{AB}_{dia} = b\Delta q^{B}. \tag{11}$$

The paramagnetic contribution, σ^{AB}_{para}, from the B atom has been calculated according to Pople's expression.[1] It remains almost constant for a series of compounds, 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. Accordingly, the contribution of the paramagnetic term to the SCS can be ignored.

The "ring-current" effect on the SCS in an aromatic side chain can be expressed as[4,6]

$$\Delta\sigma^{A,ring} = -0.4f(\rho, z)|\sigma_\pi|, \tag{12}$$

where $f(\rho,z)$ is the Johnson-Bovey ring-current shift, which is expressed as a function of the geometric factor for the atom located at the cylindrical co-ordinates, ρ and z, and where σ_π is the Yukawa-Tsuno parameter for measuring the resonance ability of the substituent.

One might raise an objection that Eq. 12 should contain the magnetic contribution from the ring-carbon C_1, because the Johnson-Bovey ring-current shift, $f(\rho,z)$, was originally estimated by measuring the difference in the ^1H chemical shift between benzene and ethylene; if so, according to the Saika-Slichter expression for the nuclear shielding, the $f(\rho,z)$ value for the ring proton might also contain the local diamagnetic term of the hydrogen atom, $\sigma_{\mathrm{dia}}^{\mathrm{AA}}$, and the magnetic contributions from the bonded carbon atom, $\sigma_{\mathrm{dia}}^{\mathrm{AB}}$ and $\sigma_{\mathrm{para}}^{\mathrm{AB}}$, in addition to the effect of the "net" ring-current, $\sigma_{\mathrm{net.}}^{\mathrm{A.ring}}$,

$$\Delta\sigma = f(\rho, z) = \Delta\sigma_{\mathrm{dia}}^{\mathrm{AA}} + \Delta\sigma_{\mathrm{dia}}^{\mathrm{AB}} + \Delta\sigma_{\mathrm{para}}^{\mathrm{AB}} + \sigma_{\mathrm{net}}^{\mathrm{A.ring}}, \quad (13)$$

where $\Delta\sigma = \sigma(C_6H_6) - \sigma(C_2H_4)$. However, when the $\sigma_{\mathrm{dia}}^{\mathrm{AA}}$ and $\sigma_{\mathrm{net}}^{\mathrm{AB}}$ terms are calculated by means of the Eqs. 3 and 8 given in Ref. 4 and by using the CNDO/2 formalism:

$$\Delta\sigma_{\mathrm{dia}}^{\mathrm{AA}} = \sigma_{\mathrm{dia}}^{\mathrm{AA}}(C_6H_6) - \sigma_{\mathrm{dia}}^{\mathrm{AA}}(C_2H_4) = 0.355, \quad (14)$$

$$\Delta\sigma_{\mathrm{dia}}^{\mathrm{AB}} = \sigma_{\mathrm{dia}}^{\mathrm{AB}}(C_6H_6) - \sigma_{\mathrm{dia}}^{\mathrm{AB}}(C_2H_4) = -0.329. \quad (15)$$

The diamagnetic terms of benzene and ethylene almost cancel each other out; then Eq. 13 becomes

$$f(\rho, z) = \sigma_{\mathrm{para}}^{\mathrm{AB}}(C_6H_6) - \sigma_{\mathrm{para}}^{\mathrm{AB}}(C_2H_4) + \sigma_{\mathrm{net}}^{\mathrm{A.ring}}(C_6H_6). \quad (16)$$

Equation 16 shows that the $f(\rho,z)$ term does not depend on the nature of the resonating nucleus, A. The $f(\rho,z)$ term of monosubstituted benzene ($f(\rho, z)_X$) is given as

$$f(\rho, z)_X = \sigma_{\mathrm{para}}^{\mathrm{AB}}(C_6H_5X) - \sigma_{\mathrm{para}}^{\mathrm{AB}}(C_2H_4) + \sigma_{\mathrm{net}}^{\mathrm{A.ring}}(C_6H_5X). \quad (17)$$

On the other hand, the following relationship holds so long as we assume the same average excitation energy and the same value of the integral $\langle r_{\mathrm{AB}}^{-3} \rangle$ for the same series of compounds:

$$\sigma_{\mathrm{para}}^{\mathrm{AB}}(C_6H_6) \rightleftharpoons \sigma_{\mathrm{para}}^{\mathrm{AB}}(C_6H_5X). \quad (18)$$

Therefore, the difference in the $f(\rho,z)$ term between benzene and monosubstituted benzene is expressed as

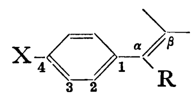
$$f(\rho, z)_X - f(\rho, z) = \sigma_{\mathrm{net}}^{\mathrm{A.ring}}(C_6H_5X) - \sigma_{\mathrm{net}}^{\mathrm{A.ring}}(C_6H_6) = \Delta\sigma_{\mathrm{net}}^{\mathrm{A.ring}}(C_6H_5X). \quad (19)$$

The $(f(\rho,z)_X - f(\rho,z))$ term was empirically expressed by Eq. 12 on the basis of the correlation between the ^1H SCS of *m*-substituted aromatic side chains and the Hammett σ_m values reported by Yamada *et al.*[6] We showed in our preceding paper[4] that Eq. 12 can reasonably be applied to the calculation of the ^1H SCS in aromatic side chain. Therefore, Eq. 12 can be applied, just as it is, to the calculation of the ^{13}C SCS in aromatic side chains.*

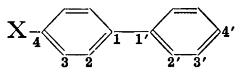
The values of $f(\rho,z)$ for the α- and β-carbons of the styrenes and the α-methylstyrenes and for the 1′-carbons of the biphenyls have been graphically estimated by utilizing the table of the Johnson-Bovey ring-current shift.[7]

To estimate elements of the charge density and the bond-order matrix, the CNDO/2 formalism has been used.

The standard geometry of the styrenes is assumed to be planar in the present calculation.[8] The C_1–C_α bond length and the C_1–C_α–C_β valence angle are taken to be, respectively, 1.46 Å and 128°, and the phenyl-vinyl dihedral angle, θ, is taken to equal 0° on the basis of the MO calculations performed by Hehre, Radom, and Pople.[9] The geometry of α-methylstyrene may not be planar because of the steric repulsion between the phenyl ring and the methyl group of the side chain. For α-methylstyrene with an experimental dihedral angle $\theta = 30°$, the C_1–C_α bond length is taken to be 1.46 Å and the C_1–C_α–C_β valence angle, to be 120°;[10] we have not attempted more rigorous energy optimizations. The respective values of the phenyl-phenyl dihedral angle and the C_1–$C_{1'}$, bond length of biphenyl are taken to be 45° and 1.48 Å.[11] The other bond angles and bond lengths for all the compounds are taken from the standard complications.[11] The carbons of the compounds examined were labeled as shown below:



R: H or CH_3
4-Subustituted styrenes and α-methylstyrenes



4-Substituted biphenyls

By combining Eqs. 3, 8, 10, and 12, we can calculate the ^{13}C SCS in an aromatic side chain. In Table 1, the calculated SCS values are compared with the observed SCS. In calculating the SCS of the α-carbon (and the 1′-carbon), the magnetic contribution from

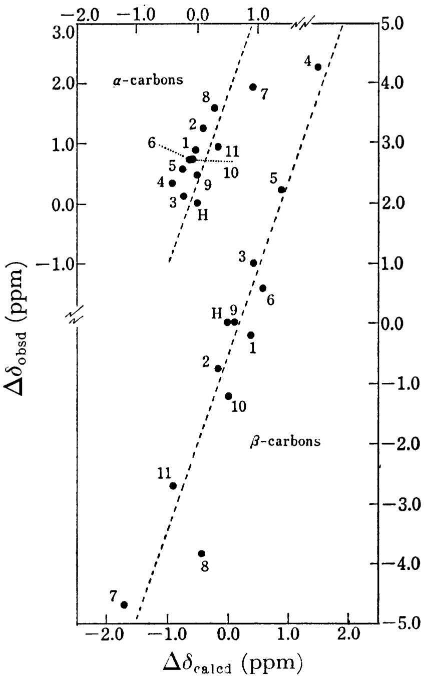


Fig. 2. Plots of $\Delta\delta_{\mathrm{obsd}}$ against $\Delta\delta_{\mathrm{calcd}}$ for α- and β-carbons of 4-substituted styrenes. Numbered points correspond to entries in Table 1.

---

* One of the referees expressed doubt about using the factor, −0.4 in Eq. 12 for the ^{13}C SCS because the factor was empirically estimated for the ^1H SCS; he advised determining the value of the factor, *c*, of the third term in the following equation by statistical treatment so as to make the slope of the correlation line between the observed and the calculated shift unity,

$$\Delta\delta_{\mathrm{calcd}} = a\Delta q^{\mathrm{A}} + b\Delta q^{\mathrm{B}} + cf(\rho, z)|\sigma_\pi|,$$

where the values of *a* and *b* are taken from Table 2. However, this statistical treatment may result in overestimating the contribution of the 'ring-current' effect.

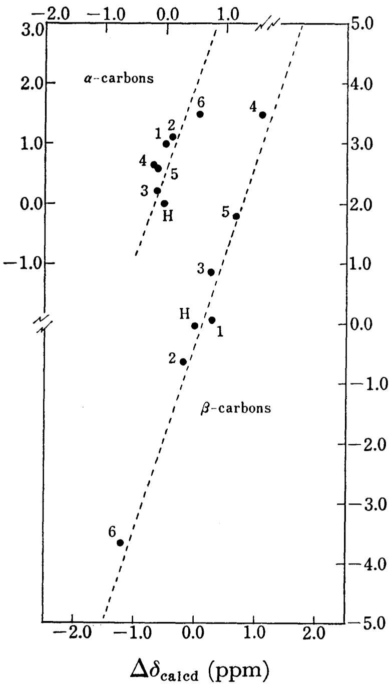


Fig. 3. Plots of $\Delta\delta_{\text{obsd}}$against $\Delta\delta_{\text{calcd}}$ for α- and β-carbons of 4-substituted α-methylstyrenes. Numbered points correspond to entries in Table 1.

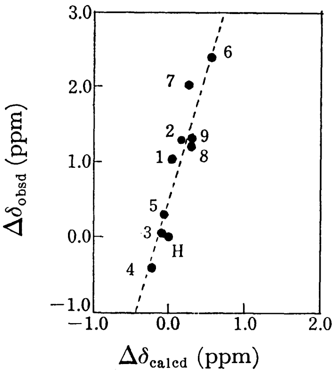


Fig. 4. Plots of $\Delta\delta_{\text{obsd}}$ against $\Delta\delta_{\text{calcd}}$ for 1′-carbons of 4-Substituted biphenyls. Numbered points correspond to entries in Table 1.

the β-carbon (and the 2′-carbon) has not been taken into account, because it may be small compared with that from the C_1-carbon. In Figs. 2—4, plots of the observed SCS are shown against the calculated SCS. As may clearly be seen in Table 1, the contributions from the diamagnetic term of the neighboring carbon atom, $B(\Delta\sigma^{AB}_{\text{dia}})$, and from the long-range shielding of the "ring-current" ($\Delta\sigma^{A,\text{ring}}$) can not be ignored in the case of the SCS of the α-carbons (and the 1′-carbon), while the local diamagnetic term ($\Delta\sigma^{AA}_{\text{dia}}$) can be ignored compared with the local paramagnetic term. The contributions of the $\Delta\sigma^{AB}_{\text{dia}}$ and the $\Delta\sigma^{A,\text{ring}}$ terms tend to almost cancel each other out in the case of the electron-withdrawing substituent, whereas both the $\Delta\sigma^{AB}_{\text{dia}}$ and the $\Delta\sigma^{A,\text{ring}}$ terms operate to cause a high-field shift in the case of the electron-releasing substituent.

We can express the SCS of the α-carbons of 4-substituted styrenes and α-methylstyrenes, and that of the 1′-carbons of 4-substituted biphenyls, by Eq. 20 in the same form as the expression derived for the ^{1}H SCS in an aromatic side chain, because the $\Delta\sigma^{AA}_{\text{dia}}$ and the $\Delta\sigma^{AA}_{\text{para}}$ terms are defined in terms of the electron density using Eq. 9:

$$\Delta\delta^{\alpha}_{\text{calcd}}(\text{or } \Delta\delta^{1'}_{\text{calcd}}) = a\Delta q^{A}+b\Delta q^{B}-0.4f(\rho, z)|\sigma_{\pi}|. \quad (20)$$

The a, b, and $f(\rho,z)$ obtained are listed in Table 2.

TABLE 2. VALUES OF a, b AND $f(\rho, z)$ IN Eqs. 9, 11, AND 12 IN ppm

Compound		a	b	$f(\rho, z)$
Styrenes	α	124	6.43	−1.10
	β	121	7.01	−0.46
α-Methylstyrene	α	115	6.43	−1.10
	β	115	7.01	−0.49
Biphenyls	1′	108	6.35	−1.04

The results summarized in Table 1 show that the $\Delta\sigma^{AA}_{\text{dia}}$, the $\Delta\sigma^{AB}_{\text{dia}}$ and the $\Delta\sigma^{A,\text{ring}}$ terms do not make important contributions to the SCS of the β-carbons of the styrenes and the α-methylstyrenes. Therefore, the SCS of the β-carbon can be correlated only with the increments in the electron density on the β-carbon atom:

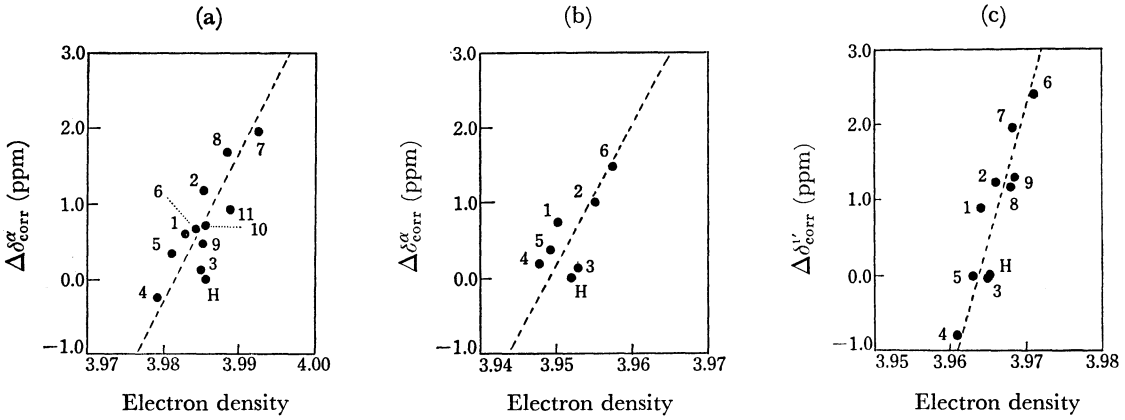


Fig. 5. Plots of $\Delta\delta_{\text{corr}}$ against the electron density on α-carbon (1′-carbon) atom; (a) 4-substituted styrenes (b) 4-substituted α-methylstyrenes (c) 4-substituted biphenyls. Numbered points correspond to entries in Table 1.

$$\Delta\delta^{\beta}_{\text{calcd}} = a\Delta q^{\text{A}}. \qquad (21)$$

The calculated SCS values can reasonably reproduce all the observed SCS for the α- and β-carbons of the styrenes and the α-methylstyrenes, and for the 1′-carbons of the biphenyls, as is shown in Figs. 2—4. However, Figs. 2—4 also show that Eqs. 20 and 21 can not sufficiently reproduce the observed shifts. The shortcomings of Eqs. 20 and 21 may be attributed to adopting the same average excitation energy for all the derivatives in a series of compounds, as has been indicated by Bloor *et al.*,[2] who have calculated the SCS of ring-carbons of monosubstituted benzenes by the Karplus-Pople theory using $\delta^{13}\text{C(A)} = \sigma^{\text{AA}}_{\text{dia}} + \sigma^{\text{AA}}_{\text{para}}$**.

When the observed SCS of the α- and the 1′-carbons are corrected for the $\Delta\sigma^{\text{AB}}_{\text{dia}}$ and the $\Delta\sigma^{\text{A,ring}}$ terms, the corrected SCS values, $\Delta\delta^{\alpha}_{\text{corr}}$ (and $\Delta\delta^{1'}_{\text{corr}}$), come to be fairly well correlated with the electron densities on the α-carbons (and the 1′-carbons), as is shown in Fig. 5. This result implies that it may be appropriate to take the contributions of the $\Delta\sigma^{\text{AB}}_{\text{dia}}$ and the $\Delta\sigma^{\text{A,ring}}$ terms into consideration, so long as we interpret the SCS of α-carbon (and 1′-carbon) on the basis of the Saika-Slichter expression and Pople's average excitation energy approximation.

The CNDO/2 calculations were carried out on a FACOM-230 75 computer at the Nagoya University Computation Center.

References

1) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962); M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).

2) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

3) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

4) J. Niwa, *Bull. Chem. Soc. Jpn.*, **48**, 118, 1737 (1975); J. Niwa, *ibid.*, **50**, 979 (1977).

5) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Jpn.*, **39**, 1398 (1965).

6) H. Yamada, Y. Tsuno, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **43** 1459 (1970).

7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford (1965), Vol. 1, p. 595; G. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

8) P. L. Britton, C. L. Cheng, R. J. W. LeFevre, L. Radom, and G. L. Ritchie, *J. Chem. Soc.*, *B*, 2100 (1971); M. Barfield, C. J. MacDonald, I. R. Peat, and W. F. Reynolds, *J. Am. Chem. Soc.*, **93**, 4195 (1971).

9) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).

10) G. K. Hamer, J. R. Peat, and W. F. Reynolds, *Can. J. Chem.*, **51**, 897, 915 (1973).

11) "Tables of Interactomic Distance and Configuration in Molecules and Ions," Chem. Soc., London, Spec. Publ., No. 11 (1958).

12) E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, **39**, 2686 (1974).

** For example, if it is permitted to assume empirically the appropriate ΔE value for each derivative within the range from 7.99 eV (for *p*-NMe_2) to 8.02 eV (for *p*-NO_2) for the α-carbons of the styrenes, the calculated shifts can reproduce the observed shifts fairly well. However, the MO Calculations (*e.g.*, the CNDO/2 and the INDO formalisms with the CI method) have not succeeded in reproducing the excitation energies to a degree of accuracy sufficient to examine the above assumption.