The Linearity of the Substituent-induced Carbon-13 Chemical Shifts of α-Carbons with Charge Densities in Aromatic Side Chains. II. 4-Substituted Phenylacetylenes

Jun NIWA

College of General Education, Nagoya University, Chikusa-ku, Nagoya 464

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Synopsis. The propriety of considering the magnetic contributions to the ^{13}C chemical shift from the neighboring carbon atoms and from the 'ring-current' has been examined for the SCS of α-carbons of 4-substituted phenylacetylenes. The SCS values corrected for the above contributions are well correlated with the 2p electron densities.

In our previous papers,[1,2] we derived expressions for estimating the contribution from the magnetic term of the neighboring carbon atom, B, which is bonded to the A atom in question (σ^{AB}_{dia}) and the long-range shielding effect of the 'ring-current' ($\sigma^{A,ring}$). It was shown that the corrected SCS values of α-carbons ($\Delta\delta^{\alpha}_{corr}$) come to be linearly correlated with the electron densities on the relevant carbon atoms, A, when the observed SCS are corrected for the above two contributions in the cases of sp^2-hybridized α-carbons of 4-substituted derivatives of styrenes, α-methylstyrenes, and biphenyls.[1]

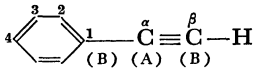
The aim of the present paper is to examine the propriety of considering the σ^{AB}_{dia} and the $\sigma^{A,ring}$ terms in interpreting the SCS of sp-hybridized α-carbons. For this purpose, we have chosen 4-substituted phenylacetylenes as a model system.

As has been shown in our previous paper,[2] the diamagnetic contribution, σ^{AB}_{dia}, from the sp-hybridized carbon atom can be expressed in the same form as the expression derived for the case of sp^2-hybridized carbon:

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

where r^{-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. In the present approach, we have considered the magnetic contributions from the two neighboring carbon atoms which are directly bonded to the α-carbon of the phenylacetylene. The paramagnetic contribution, σ^{AB}_{para}, from the B atom remains almost constant so long as we assume the same average excitation-energy approximation.[3]

The carbons of the phenylacetylenes were labeled as shown below:



All the bond angles and the bond lengths of the phenylacetylenes are taken from the standard compilations.[4] When the bond lengths of the C_1–C_α and the C_α–C_β are taken to be 1.46 Å and 1.204 Å respectively:

$$\sum_B \Delta\sigma^{AB}_{dia} = 6.43\Delta q_1 + 7.80\Delta q_\beta. \quad (2)$$

The expression of the 'ring-current' effect on the SCS is the same as that in the previous papers:[1,2]

$$\Delta\sigma^{A,ring} = -0.4 f(\rho, z) |\sigma_\pi|. \quad (3)$$

The value of the $f(\rho, z)$ in the case of the α-carbon of phenylacetylene has been graphically estimated to be −1.08 ppm by utilizing the table of the Johnson-Bovey ring-current shift.[5] In evaluating the σ^{AB}_{dia} term, we have used the CNDO/2 formalism. The calculated values of the $\Delta\sigma^{AB}_{dia}$ and the $\Delta\sigma^{A,ring}$ terms are listed in Table 1.

It is expected that the $\Delta\delta^{\alpha}_{corr}$ values are linearly correlated with the electron densities on the α-carbon atoms, because $\Delta\delta^{\alpha}_{corr}$ reflects only the local magnetic term of the α-carbon atom. In Figs. 1 and 2, plots

Table 1. Observed and corrected chemical shifts of α-carbons in 4-substituted phenylacetylenes[a]

	Substituent	$\Delta\sigma^{AB}_{dia}$		$\Delta\sigma^{A,ring}$	$\Delta\delta^{\alpha}_{obsd}$[c]	$\Delta\delta^{\alpha}_{corr}$[b]
		$6.43\Delta q_1$	$7.80\Delta q_\beta$	$-0.4 f(\rho, z) \|\sigma_\pi\|$		
1	NO_2	−0.145	−0.142	0.147	1.93	2.07
2	CN	−0.036	−0.048	0.108	1.69	1.67
3	CF_3	−0.131	−0.114	0.121	1.44	1.56
4	Cl	0.042	−0.023	0.030	1.16	1.11
5	F	0.123	0.004	0.051	1.09	0.91
6	C≡CH	0.013	−0.008	0.002	0.60	0.59
7	SCH_3	0.056	0.004	0.035	0.24	0.15
8	$CH=CH_2$	0.016	0.002	0.022	0.09	0.05
9	OCH_3	0.162	0.044	0.121	0.00	−0.33
10	CH_3	0.061	0.025	0.034	−0.10	−0.22
11	NH_2	0.243	0.094	0.180	−0.68	−1.20
12	$N(CH_3)_2$	0.213	0.082	0.233	−1.00	−1.53

a) All the values listed are relative to the unsubstituted compound, from the chemical shift of which the upfield shifts are represented in ppm by positive values. b) $\Delta\delta^{\alpha}_{corr} = \Delta\delta^{\alpha}_{obsd} - \sum\Delta\sigma^{AB}_{dia} - \Delta\sigma^{A,ring}$. c) Cited from Ref. 7.

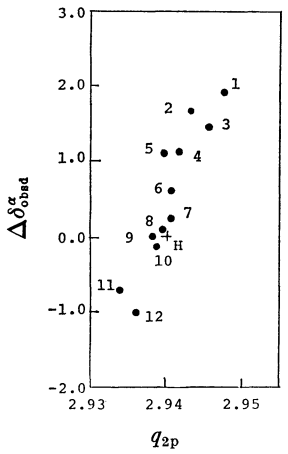


Fig. 1. Plots of $\Delta\delta^{\alpha}_{obsd}$ against the 2p electron densities on the α-carbon atoms.
Numbered points correspond to entries in Table 1.

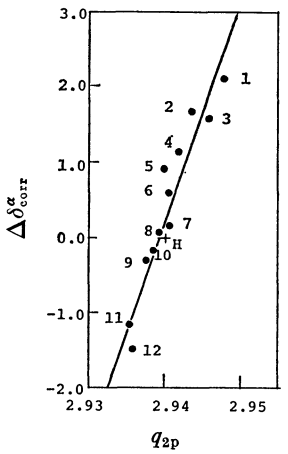


Fig. 2. Plots of $\Delta\delta^{\alpha}_{corr}$ against the 2p electron densities on the α-carbon atoms.
Numbered points correspond to entries in Table 1.

of the observed and the corrected SCS values are shown against the 2p electron densities (q_{2p})*. It may be reasonable to correlate the local magnetic terms with the 2p electron densities,[6] because the contribution of the local diamagnetic term to the SCS is very small compared with that of the local paramagnetic term. The respective correlations are expressed by least-squares fitting as:

$$\Delta\delta^{\alpha}_{obsd} = 235\Delta q_{2p} + 0.40 \quad (r=0.897,\ s=0.41) \tag{4}$$

and:

$$\Delta\delta^{\alpha}_{corr} = 295\Delta q_{2p} + 0.23 \quad (r=0.928,\ s=0.42), \tag{5}$$

where r is the correlation coefficient and s is the standard deviation. The values of both the intercept and the correlation coefficient in the latter case are much improved compared with those in the former case, although the values of the standard deviations are almost equal in the two cases.

This result provides further proof that it is appropriate to consider the σ^{AB}_{dia} and the $\sigma^{A,ring}$ terms in interpreting the aspect of the SCS of α-carbons in the side chains of conjugated aromatic hydrocarbons by relating the SCS to the electron densities.

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

* The correlations between the corrected (and the observed) SCS and the total electron densities are: $\Delta\delta^{\alpha}_{corr}=508\Delta q_{total}+0.66$ ($r=0.868$, $s=0.5$); $\Delta\delta^{\alpha}_{obsd}=400\Delta q_{total}+0.72$ ($r=0.817$, $s=0.55$). In the case of the styrenes,[1] too, when the $\Delta\delta^{\alpha}_{corr}$ values are correlated with the 2p electron densities, the correlation is improved: $\Delta\delta^{\alpha}_{corr}=135\Delta q_{total}+0.77$ ($r=0.782$, $s=0.40$); $\Delta\delta^{\alpha}_{corr}=122\Delta q_{2p}+0.69$ ($r=0.844$, $s=0.34$).

References

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