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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFT OF SIDE-CHAIN CARBON ATOM IN SUBSTITUTED BENZENES. EFFECT OF HETERO-ATOM ON TRANSMISSION MECHANISM

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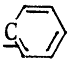
Side chain C-SCS of seventeen benzene derivatives having carbonyl group and hetero-atom in the transmission route were treated with our dual parameter equation $[\underline{a}(\iota + \underline{b}\sigma_R)]$, and the sign of the $\underline{a}$ values was explained in terms of conjugative and 1,3-through-space interactions and electronegativity combined with hyperconjugation of methyl group.

We reported previously that substituent effect on the C-13 chemical shifts of the side-chain C_α-atom (C_α-SCS) in m-substituted benzene derivatives is transmitted by 1,3-through-space (homoconjugative for sp^2- and sp-C_α-SCS) interaction between C_α- and C_p-atoms$^{1)}$ and that "inverse" substituent effect (i.e., higher field shift by electron-withdrawing group) on C_β-SCS in p-substituted arylalkanes is also explained in terms of a similar interaction between C_p- and C_β-atoms.$^{2)}$

We also reported that C-SCS in substituted benzene derivatives are formulated as $\underline{a}(\iota + \underline{b}\sigma_R)$ [1],$^{3)}$ where ι and σ_R represent inductive substituent parameter and resonance substituent constant of the second period substituent having lone pair electrons and C-C multiple bond, respectively.

This communication reports that the sign of the $\underline{a}$ values in the above dual parameter equation[1]$^{3)}$ is dependent on kinds of hetero-atom in the side-chain transmission route and explained mainly by conjugative and homoconjugative interactions combined with hyperconjugation. The C-SCS data of the following aromatic series were treated with the equation [1]. The results are summarized in Table.

$X\text{-}C_6H_4\text{-}Y$:
Y= m-$^{5,6)}$ and p-CO$\underline{Me}$ ($\underline{1}$),$^{6)}$ p-CO$\underline{C}$H=AsPh$_3$ ($\underline{2}$),$^{7)}$ m-$^{5)}$ and p-CO$\underline{C}$H=PPh$_3$ ($\underline{3}$),$^{8)}$
p-CO-$\underline{C}$ ($\underline{4}$),$^{9)}$ p-O-$\underline{C}$H=CH$_2$ ($\underline{5}$),$^{10,11)}$ p-S-$\underline{C}$H=CH$_2$ ($\underline{6}$)$^{10,11)}$ p-Se-$\underline{C}$H=
CH$_2$ ($\underline{7}$),$^{11)}$ m-$^{6)}$ and p-O$\underline{Me}$ ($\underline{8}$),$^{6,12)}$ m- and p-N$\underline{Me}_2$ ($\underline{9}$),$^{6)}$ p-S$\underline{Me}$ ($\underline{10}$),$^{4)}$
p-Si$\underline{Me}_3$ ($\underline{11}$),$^{13)}$ $\overset{+}{N}$-$\underline{C}$H$_3$Br$^-$ ($\underline{12}$), $^{14)}$ $\overset{+}{N}$-$\underline{C}$H$_2\underline{C}$OPh Br$^-$ ($\underline{13}$)$^{15)}$

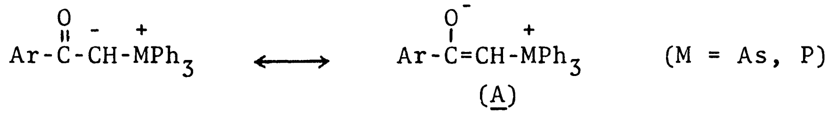
In the presence of α-carbonyl group (systems $\underline{1}$-$\underline{4}$), the $\underline{a}$ values is negative, except for that in $\underline{4}$. Since the Hammett ρ values for the sp^3- and sp^2- C_β-SCS in m- and p-substituted α-methylstyrenes analogous to $\underline{1}$ show positive and negative signs,$^{2)}$ respectively, and the signs of $\underline{a}$ and ρ values are same (from comparison of the results in refs. 1 and 2 with those of ref. 3), the negative $\underline{a}$ values in $\underline{1}$ are

TABLE. Treatment of C-SCS with dual parameter equation [1][a]

System		a	b	n[b]	r[c]	System		a	b	n[b]	r[c]
m-1	β	-0.23	0.78	8	0.850	m-8	β	-0.88	1.04	9	0.963
p-1	β	-0.59	1.50	11	0.948	p-8	β	-0.70	—	12	0.861
p-2	β	-3.92	1.48	9	0.920	m-9	β	0.64	1.05	6	0.911
m-3	β	-2.64	1.15	8	0.978	p-9	β	0.45	4.81	12	0.921
p-3	β	-4.42	1.42	8	0.924	p-10	β	1.53	3.11	7	0.979
p-4	β	1.84	1.66	9	0.984	p-11	β	0.13	4.15	8	0.923
	γ	-0.26	1.94	9	0.717	m-12	α	-0.68	1.24	10	0.727
p-5	β	2.69	1.78	8	0.958	p-12	α	-1.22	4.67	10	0.928
	γ	-5.01	1.51	8	0.948	m-13	α	-1.16	0.91	6	0.837
p-6	β	4.86	1.57	9	0.954		β	2.55	1.36	6	0.912
	γ	-7.47	1.59	9	0.948	p-13	α	-1.95	2.41	9	0.959
p-7	β	4.00	1.52	9	0.957		β	2.27	1.69	9	0.981
	γ	-6.44	1.52	9	0.944						

a) In this treatment, higher field shifts were taken as positive.
b) Numbers of data points. c) Correlation coefficient.

probably attributed to a contribution of partial double bond character in the CO-Me bond because of a similar trend to the ylides (2 and 3) where there is a large contribution of a canonical form (A).[5,7,8]



$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}\overset{-}{C}H{-}\overset{+}{M}Ph_3} \longleftrightarrow \underset{(A)}{\mathrm{Ar{-}\overset{\overset{O^-}{|}}{C}{=}CH{-}\overset{+}{M}Ph_3}} \quad (M = As,\ P)$$

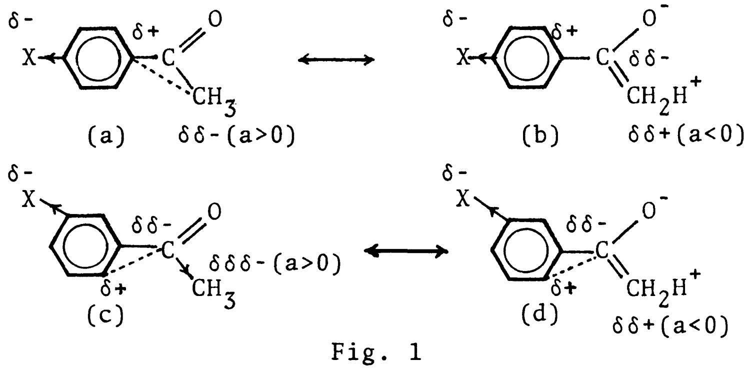


Fig. 1

Thus, in p-series of 1, a conjugation between the substituent (X) and the C_β-atom, by which the a value is expected to be negative similarly to the case of p-substituted styrenes[2] (Fig. 1(b)), overcomes 1,3-through-space interaction between C_p- and C_β-atoms, by which the a value becomes positive similarly to the cases of arylalkanes[2] (Fig. 1(a)). In the m-series of 1, similarly a homoconjugation (Fig. 1(d)) overcomes 1,3-through-space interaction followed by through-bond transmission (Fig. 1(c)).

The positive a value in the C_β-SCS of p-series of 4 is explained by a homoconjugation between both benzene rings. The series 5-7 are homoconjugation systems and thus the a values for C_β- and C_γ-SCS become positive and negative, respectively, analogously to C_α- and C_β-SCS of styrenes.2)

The systems containing α-hetero-atom (9-10) showed positive a values for C_β-SCS, but the a value in 8 was negative exceptionally. In these cases, an electron-withdrawing substituent can conjugate directly (in p-series) or through 1,3-through-space interaction (in m-series) with a hetero-atom (Y) having lone pair electrons. As the result, the attached methyl group can conjugate with the positively charged hetero-atom by hyperconjugation and the C_β-SCS shifts to higher field, indicating positive a value (Fig. 2(a)). Since oxygen atom is strongly electronegative, the C_β-atom becomes positive corresponding to negative a value (Fig. 2 (b)). Therefore, in the cases of 8 (Y=O), the latter effect is predominant. In the cases of 9(Y=NMe) and 10 (Y=S), the hetero-atom (Y) are less electronegative. Thus the former effect is predominant and the a values become positive. In these p-series, 1,3-through-space interaction between C_p- and C_β-atoms is considered to be not so important.

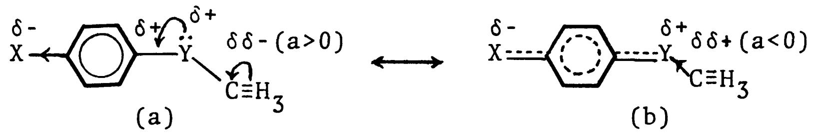


Fig. 2

The p-series of 11 are analogous to arylalkanes2) because of no lone pair electrons on the electropositive silicon atom, indicating an importance of 1,3-through-space interaction between C_p- and C_β- atoms.

In the N-pyridinium salts (12 and 13), the a values for C_β-SCS are expected to be positive as shown in Fig. 3 and these are the case. However, for C_α-SCS, the actual a values in m-series are negative and the trend is opposite to that in m-substituted toluenes.1,3)

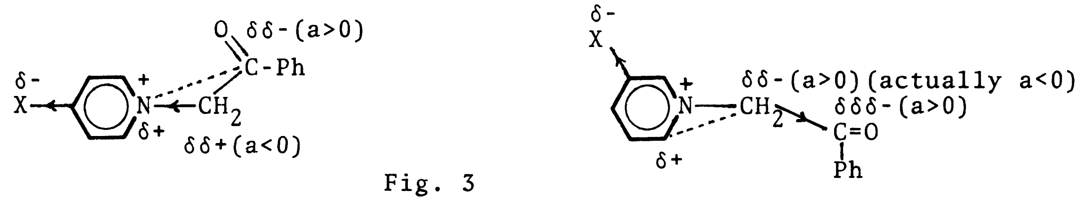
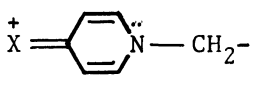
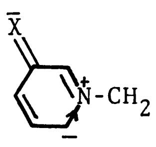


Fig. 3

In the case of 12, it has been found that C_α-SCS shift to higher field because of ion pair effect as the concentration becomes higher. When X is electron-donating group, C_α-SCS are considered to shift to higher field by a large contribution of the following canonical structures (B and C) because of partial neutralization of positive charge on the nitrogen atom.



(B)



(C)

As the result, the $\underline{a}$ values become more negative than those in neutral molecules. Thus, in the m-series, the $\underline{a}$ values of C_α-SCS become negative.

In conclusion, our interpretation is simple and very useful for prediction of substituent effect on C-13 chemical shifts of side-chain carbon atoms in aromatic derivatives, including the previous results.[1,2,16]

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16) Reverse sign of the $\underline{a}$ values in the C_α-SCS of $Ar\underline{C}H_2CH_2B\ddot{r}$, $Ar\underline{C}H_2CH_2\overset{+}{\underset{..}{S}}Me_2$, $Ar\underline{C}H_2\ddot{F}$, $ArC\ddot{F}_3$,[1] and p-substituted 1-aryl-2,2-dichlorocyclopropanes (C_α and $\underline{C}Cl_2$)[2] may be interpreted by donation of lone pair electrons through 1,3-through-space interaction and conjugation-like interaction. The detail will be discussed in full paper.

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