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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFT OF THE SIDE-CHAIN C_β-ATOMS IN SUBSTITUTED PHENYLALKANES, PHENYLCYCLOPROPANES, AND α-METHYLSTYRENES. EFFECT OF HYBRIDIZATION AND CONTRIBUTION OF 1,3-THROUGH-SPACE INTERACTION

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The normal and inverse substituent effects on the C-13 chemical shifts of C_β-atoms in the titled compounds are explained by the π bond character of the C_α-C_β bond. The transmission mode in m- and p-series has been discussed in terms of 1,3-through-space interaction. Therefore, both series should be treated separately.

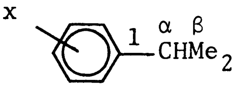
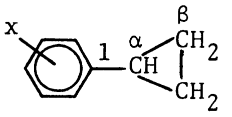
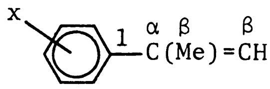
Reynolds et al.$^{1)}$ reported that the "inverse" substituent effect (positive Hammett ρ) on the C-13 chemical shifts of C_β-atoms (C_β-SCS) in p-substituted phenylalkanes and 1-phenyl-2,2-dichlorocyclopropanes (1) is explained by change of the conformation of alkyl group.

We wish to report that the substituent effect on C_β-SCS is generally dominated by π bond character of the C_α-C_β bond.

We determined the C-13 chemical shifts of the side chain C_α- and C_β-atoms and C_1-atom (C_α-, C_β-, and C_1-SCS) in substituted 2-phenylpropanes (2), phenylcyclopropanes (3), and α-methylstyrenes (4). The data are given in Table. The C_β-SCS were treated with Hammett σ, where a negative sign was used for a downfield shift.

Hybridization Effect. It has been reported that the α-methyl group in α-methylstyrenes (4) adopts a conformation with the C_α-Me bond at 30° to the plane of the phenyl ring.$^{2)}$ Therefore, normal substituent effect (negative Hammett ρ) would be expected, because the bond is near the plane of the phenyl ring.$^{1)}$

Table. Data on C-13 Chemical Shifts (δ_C)[a] for 2-Arylpropanes (2), Arylcyclopropanes (3) and α-Methylstyrenes (4)

X	 (2)			 (3)			 (4)			
	δC_1	δC_α	δC_β	δC_1	δC_α	δC_β	δC_1	δC_α	$\delta C_\beta(=CH_2)$	$\delta C_\beta(Me)$
H	148.75[a]	34.15	24.02	143.90	15.42	9.09	141.22	143.30	112.33	21.75
p-MeO	-7.77[b]	-0.87	0.11	-8.13	-0.75	-0.65	-7.51	-0.82	-1.75	0.12
p-Me	-2.95	-0.39	0.07	-3.13	-0.42	-0.32	-2.85	-0.26	-0.85	0.07
p-Cl	-1.49	-0.52	-0.06	-1.51	-0.49	0.13	-1.56	-1.17	0.58	-0.06
p-Br	-1.10	-0.52	-0.19	-0.99	-0.42	0.13	-1.17	-1.17	0.58	-0.13
p-NO_2	7.80	0.13	-0.45	8.69	0.42	1.88	6.43	-1.69	3.96	-0.19
m-MeO	1.76	0.07	-0.13	1.74	0.03	0.00	1.63	-0.13	0.26	0.13
m-Me	—	—	—	-0.08	-0.16	-0.13	0.00	0.07	-0.20	0.07
m-Cl	2.08	-0.13	-0.19	2.26	-0.16	0.19	1.89	-1.23	1.23	-0.13
m-Br	2.34	-0.19	-0.26	2.45	-0.23	0.26	2.15	-1.36	1.23	-0.13
m-NO_2	2.02	-0.13	-0.32	2.45	-0.10	0.78	1.62	-2.08	2.66	-0.19

[a] C-13 chemical shifts measured at 15.1 MHz using 1.0 M solutions in $CDCl_3$ on a JEOL FX-60 FT NMR spectrometer. Accuracies of δ_C (ppm downfield from internal tetramethylsilane) are about ±0.1 ppm.

[b] Chemical shift relative to unsubstituted derivative. Positive chemical shifts are downfield. In the Hammett treatment, reverse sign was used.

However, "inverse" substituent effect (ρ=0.30) for C_β(Me)-SCS in p-substituted 4 was observed.

Furthermore, in phenylcyclopropane, bisected form is the most stable conformation, indicating dihedral angle of ca. 30° for the C_α-CH_2 bond relative to the plane of the phenyl ring, but normal substituent effect (ρ=-2.56) was observed for C_β-SCS in p-substituted 3. The result is analogous to that for C_β(=CH_2)-SCS in p-substituted 4 (ρ=-4.46). Moreover, "inverse" substituent effect (ρ=0.54) was observed for C_β-SCS in p-substituted 2. On the other hand, C_β(=CH_2)-SCS in p-substituted α-t-butylstyrenes showed normal substituent effect, though the dihedral angle is ca. 65° for the C_α=CH_2 bond.2)

The reported sp^3-C_β-SCS indicate "inverse" substituent effect for ethylbenzenes,1) t-butylbenzenes,3,4) and phenethyl systems.5) On the contrary, sp^2- and sp-C_β-SCS indicate normal substituent effect for styrenes,6) β-methylstyrenes,[7] benzylidenemalononitriles,[8] biphenyls,[9] 1-aryl-1,3-butadienes,[10] aryl-acetylenes,[11] and 1-aryl-2-methylacetylenes.[7]

The facts suggest that the π bond character of the C_α-C_β bond mainly dominates the substituent effect of C_β-SCS.

This consideration can very well explain the result in 3, because the cyclopropyl group is analogous to a double bond in spectroscopic and chemical respects.[12] In the case of p-substituted 1,[1] $C_\beta(CCl_2)$- and $C_\beta(CH_2)$-SCS are positive (0.81) and negative ρ values (-0.49), respectively, suggesting an increase of π bond character in the C_α-$C_\beta(CH_2)$ bond.

Transmission Mode in m- and p-Series. Generally the Hammett plot of C_β-SCS gave two lines due to m- and p-substituents (for example: ρ(p)=0.54, ρ(m)=0.43 for 2; ρ(p)=0.45, ρ(m)=0.57 for t-butylbenzenes;[4] ρ(p)=-2.56, ρ(m)=-1.07 for 3; ρ(p)=0.30, ρ(m)=0.37 for C_β(Me) in 4; ρ(p)=-5.66,[6a] ρ(m)=-5.11[6b] for styrenes; ρ(p)=-4.46, ρ(m)=-2.58 for $C_\beta(CH_2)$ in 4). The observation suggests a difference of transmission mode in m- and p-series.

In the systems containing C_α-C_β unsaturated bond, the sign of the ρ value for C_β-SCS is opposite to that for C_α-SCS.[13] The sign alternation in p-series can be explained in terms of alternative transmission mode by π-inductive effect,[14] and for those of the m-series, the substituent (X) can conjugate with the C_α-C_β unsaturated bond through 1,3-through-space interaction (homoconjugation) between the C_o- and C_p-atoms and C_α-atom as proposed in the explanation of C_α-SCS of the m-series[13] (Fig. 1). Thus, the ρ values in m-series become much smaller than those in p-series because of the 1,3-through-space interaction.

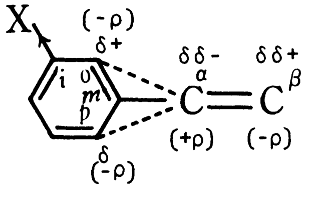
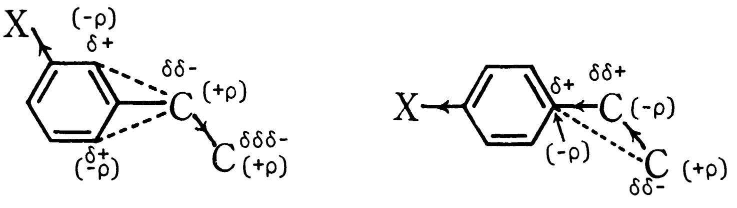


Fig. 1



(A) (B)

Fig. 2

On the other hand, in the m-substituted phenylalkanes, the effect of the substituent (X) is transmitted to the C_α-atom by 1,3-through-space interaction[13] and then to the C_β-atom by through-bond fashion (see Fig. 2(A)). Therefore, the ρ value for C_β-SCS is the same sign as those for C_1- and C_α-SCS. However, in the p-series, the sign is opposite. The fact may be explained considering 1,3-through-space interaction between C_p- and C_β-atoms in analogous alternative fashion (see Fig. 2(B)).

Very recently, C_β-SCS of N-phenacylpyridinium salts have been reported[16] and the result can be explained by the present interpretation, though the C_β-atom is carbonyl carbon atom. The detail will be discussed in a forthcoming paper.

C_α-SCS in 3. The C_α-SCS of 1 are governed mainly by substituent electronegativity, and show rather sp^2-C_α type trend similar to those of benzylidenemalononitriles,[13] being in accordance with the relatively larger bond order of the C_α-$C_\beta(CH_2)$ bond. On the other hand, the C_α-SCS of p-substituted 3 show a similar trend to those of 2, indicating sp^3-C_α type trend.[13] In this case, it is considered that the p-character on C_α-atom may be smaller than that of 1, and thus sp^3 character overcomes sp^2.

In conclusion, the sp^3-C_β-SCS are mainly dominated by 1,3-through-space interaction, though a conformational requirement is necessary to the interaction.

REFERENCES

1) W. F. Reynolds, R. H. Kohler, and G. K. Hamer, Tetrahedron Lett., 1976, 4671.
2) G. K. Hamer, I. R. Peat, and W. F. Reynolds, Can. J. Chem., 51, 915 (1973).
3) C. D. Schaeffer, Jr., J. J. Zuckerman, and C. H. Yoder, J. Organometal. Chem., 80, 29 (1974).
4) S. Berger, Tetrahedron, 32, 2451 (1976).
5) L. F. Blackwell, P. D. Buchley, and K. W. Jolley, Tetrahedron Lett., 1975, 4271; Aust. J. Chem., 29, 2423 (1976).
6) a) G. K. Hamer, I. R. Peat, and W. F. Reynolds, Can. J. Chem., 51, 897 (1973); b) K. S. Dhami and J. B. Stothers, ibid., 43, 510 (1965).
7) K. Izawa, T. Okuyama, and T. Fueno, Bull. Chem. Soc. Jpn., 46, 2881 (1973).
8) T. B. Posner and C. D. Hall, J. C. S. Perkin II, 1976, 729.
9) E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, J. Org. Chem., 39, 2686 (1974).
10) T. Okuyama, K. Izawa, and T. Fueno, Bull. Chem. Soc. Jpn., 47, 410 (1974).
11) D. A. Dawson and W. F. Reynolds, Can. J. Chem., 53, 373 (1975).
12) a) G. L. Closs and H. B. Klinger, J. Am. Chem. Soc., 87, 3265 (1965); b) K. Oyama and T. T. Tidwell, J. Am. Chem. Soc., 98, 947 (1976) and the papers cited therein.
13) N. Inamoto, S. Masuda, K. Tori, and Y. Yoshimura, Tetrahedron Lett., 1977, 737.
14) a) A. R. Katritzky and R. D. Topsom, J. Chem. Educ., 48, 427 (1971); b) W. F. Reynolds and G. K. Hamer, J. Am. Chem. Soc., 98, 7296 (1976); c) R. T. C. Brownlee, G. Butt, M. P. Chan, and R. D. Topsom, J. C. S. Perkin II, 1976, 1486.

The evidence was obtained by Kajimoto and Fueno.[15]
15) O. Kajimoto and T. Fueno, Tetrahedron Lett., 1972, 3329.
16) A. D. Harsch, S. Johnson, and D. W. Boykin, J. C. S. Chem. Commun., 1977, 119.

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