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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFT OF THE SIDE-CHAIN C_α-ATOM IN SUBSTITUTED BENZENES. THROUGH-SPACE INTERACTION IN META-SERIES AND HYBRIDIZATION EFFECT

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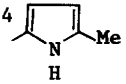
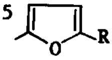
We reported in previous papers that the ^{13}C chemical shifts of *ipso*- and *meta*-carbon atoms (C_i- and C_m-SCS) in substituted benzenes are correlated with the electronegativity (χ_x) of the substituents (X)[1] and showed periodical character[2] whereas C_p-SCS is controlled by the Hammett σ_p. We now report on the basis of investigations of twenty-seven aromatic series that the ^{13}C chemical shifts of α-carbon atoms (C_α-SCS) in p-substituted benzenes are dominated by χ_x and to a small extent by resonance effect, and that in the m-series, through-space interaction between the C_α-atom and both C_o- and C_p-atoms plays an important role in the transmission of substituent effects.

Since the C_α-SCS can be expected to be correlated with χ_x analogously to C_i- and C_m-SCS,[1,2] the C_α-SCS values in p-substituted styrenes[3] were plotted against χ_x. As shown in FIG. 1, the plots formed two separate lines of X substituents having lone-pair electrons ($\ddot{A}$) such as NH_2, OCH_3, and F,[4] and those having no lone-pair electron (A) such as NO_2, CF_3, and COMe. The degree of separation between the two lines depended on the series of aromatics, suggesting a difference in the degree of contribution of extra resonance from the $\ddot{A}$ groups.

Therefore, the C_α-SCS of the following p- and m-series was examined with various substituent constants, using reported and newly determined data.[5]

p-Series (p-XC_6H_4Y)

sp^3: Y = Me (1),[1] Et (2),[5] CMe_3 (3),[6] $(CH_2)_2R$ (R = Br, $\overset{+}{S}Me_2$) (4),[7] CH_2F (5);[8]

sp^2: Y = CHO (6),[5] COMe (7),[5] CO_2H (8),[9] $CO_2(CH_2)_2\overset{+}{N}HEt_2\overset{-}{C}l$ (9),[10] $CH{=}CH_2$ (10),[3]
$CR{=}CH_2$ (R = Me, CMe_3) (11),[11] CH=NPh (12),[12] $CH{=}C(CN)_2$ (13),[13]
C_6H_5 (14),[14]  (15),[15]  (R = H, Me) (16);[15]

sp: Y = C≡CH (17),[16] CN (18)[1,17]

m-Series (m-XC_6H_4Y)

sp^3: Y = Me (19);[1] sp^2: Y = CHO (20),[5] COMe (21),[5] CO_2H (22),[9] $CH{=}CH_2$ (23);[18]

sp : Y = CN (24)[5,17]

p-Series.

Reports state that the C_α-SCS of 1,[1] 4,[7] 6,[19] 7,[20] and 10[18] were not correlated with Hammett σ_p. We examined the correlation of C_α-SCS with Hammett σ_m, trying to understand better the mechanism of transmission involved, and obtained two lines due to Ä and A groups analogous to those in C_m-SCS of substituted benzenes and biphenyls.[14]

C_α-sp^3. In the cases of 1-3, the slopes (ρ) of the two lines were both negative and had the same sign as that in the C_p-SCS (FIG. 2). The Ä-line was situated at higher fields, which indicates the contribution of extra resonance from the Ä groups. However, in the cases of 4 and 5, which possess an electronegative atom in the side chain, the line for the A groups had a positive slope and that for the Ä groups was at higher fields (FIG. 3), suggesting a lesser contribution of Ä group resonance.

C_α-sp^2 and -sp. In the cases of 9-12 and 14-16, the C_α-SCS was correlated well with σ_m. In the cases of 6-8, 13, 17, and 18, the A-lines also had a positive slope, but the Ä-lines differed with the series: (i) a negative slope and higher fields (6 and 13); (ii) a positive slope and higher fields (7); (iii) a positive slope and lower fields (8, 17, and 18) (see FIG. 4). Case (iii) indicates contribution of extra resonance. In fact, series 8, 17, and 18 were correlated fairly with σ_p, $\sigma_p°$, and σ_p of Ä groups, respectively. In case (i), the C_α-SCS was correlated well with χ_x only (FIG. 5).

Summarizing our observations, we found with Ä groups, that an electron-donating extra resonance contributes to the transmission in series 1-3, 8, 17, and 18, but scarcely in series 4, 6, 7, and 13. Of the A groups, the slopes were always positive except for series with alkyl side-chains (1-3), where the C_α-atoms are purely sp^3-hybridized. In pure sp^3-C_α atoms, the ρ value of C_α-SCS should be negative owing to dominating transmission through the σ-bond from the p-carbon, which possesses a negative ρ value. On the other hand, substitution of a hydrogen atom in the alkyl groups by an electronegative atom (4 and 5) increases the s-character as indicated by J_{C-H} values.[21] When the s-character of the C_α-atom becomes larger than 1/4, the transmission mode is controlled by the π-inductive effect as those of the π-electron system ('Effect-4' of Katritzky and Topsom[22]), which is transmitted alternatively;[23] then the ρ value becomes positive.

Therefore, the C_α-SCS in the p-series are governed largely by χ_x and to a small extent by resonance effect (σ_R),[24] depending on the electronegativity of the side chain (Y). Examples of these dual parameter equations are:

For 1, $C_\alpha\text{-SCS} = -0.32\ (\chi_x + 5.04\sigma_R) + 0.82$ (r = 0.907, n = 12)

For 8, $C_\alpha\text{-SCS} = +1.05\ (\chi_x + 1.16\sigma_R^+) - 2.45$ (r = 0.957, n = 7)

For 18, $C_\alpha\text{-SCS} = +1.67\ (\chi_x + 1.18\sigma_R^+) - 3.94$ (r = 0.957, n = 11)

m-Series.

In all cases (19-24), the C_α-SCS was correlated well with σ_p, but not with σ_m (FIG. 6). The $\rho_{C\alpha}$ values were always positive and opposite to those of the C_p atom (see the TABLE); this sign alternation can not be expected from the results with the p-series. The considerably large magnitude of the $\rho_{C\alpha}$ values can hardly be explained merely by the transmission of the substituent effect from C_1 to C_α which must be weakened at C_m. Thus, we infer from the good correlation with Hammett σ_p that a through-space interaction between the C_α-atom and both

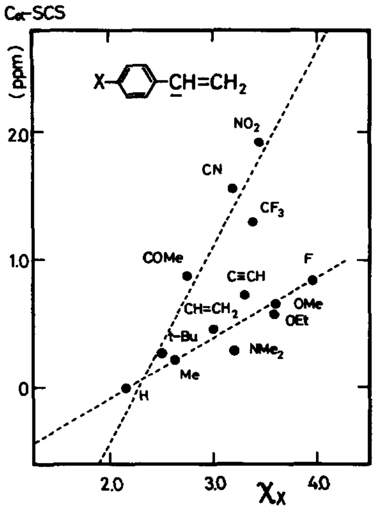


FIG. 1. C_α-SCS vs. χ_X for p-substituted styrenes.

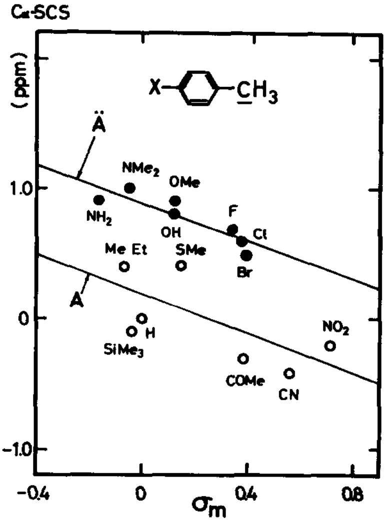


FIG. 2. C_α-SCS vs. σ_m for p-substituted toluenes.

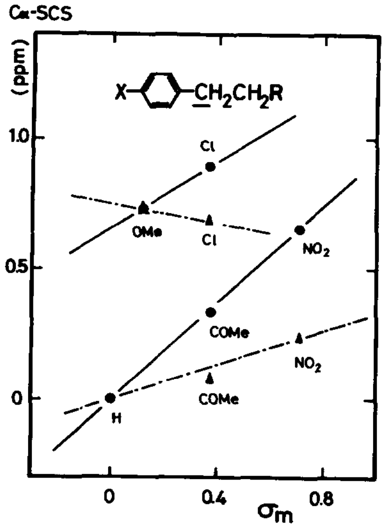


FIG. 3. C_α-SCS vs. σ_m. ●, R = Br; ▲, R = $\overset{+}{S}Me_2$

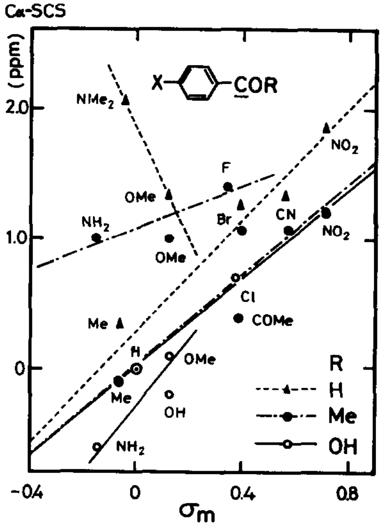


FIG. 4. C_α-SCS vs. σ_m for p-substituted benzaldehydes, acetophenones, and benzoic acids.

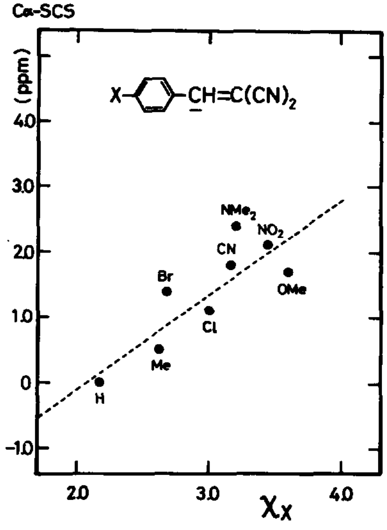


FIG. 5. C_α-SCS vs. χ_X for p-substituted benzylidenemalononitriles.

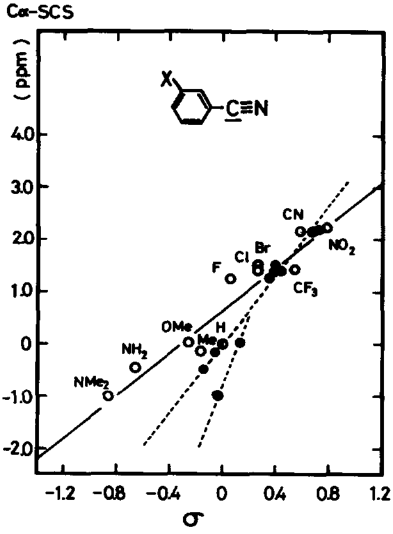


FIG. 6. C_α-SCS vs. σ_p and σ_m for m-substituted benzonitriles. ○, σ_p; ●, σ_m

TABLE. ρ Values for C_m-, C_p-, and C_α-SCS of the meta-Series

Compound	m-$XC_6H_4CH_3$ (19)[1]			m-XC_6H_4CHO (20)[5]			m-XC_6H_4COMe (21)[5]			m-XC_6H_4CN (24)[5,7]		
Carbon	C_m(1)	C_p(6)	C_α	C_m(1)	C_p(6)	C_α	C_m(1)	C_p(6)	C_α	C_m(1)	C_p(6)	C_α
ρ[a]	-1.77	-11.59	0.42	-1.32	-9.14	2.70	-0.81	-10.40	2.24	-2.51	-10.35	2.03
r[b]	0.517	0.951	0.808	0.567	0.908	0.926	0.530	0.945	0.977	0.970	0.941	0.945

[a] Against Hammett σ_m for C_m-, and σ_p for C_p- and C_α-SCS. [b] Correlation coefficients.

C_o- and C_p-atoms is important. If this interaction is assumed to be π-inductive-like, the sign of the ρ_{C_α} values becomes opposite to that of C_o- and C_p-SCS (FIG. 7). This kind of interaction is also seen in the through-space J_{F-F}[25] and homo-hyperconjugation in ESR spectroscopy.[26]

Recently, C_α-SCS has also been treated with the σ_I-σ_R method for **3**,[6] **5**,[8] **9**,[10] **18**,[17] and **24**,[17] the FR method for **10**[3] and **11**,[11] the Yukawa-Tsuno equation for **8** and **22**,[9a] and the modified Dewar equation for **14**.[14] The C_α-SCS of o-substituted toluenes and benzaldehydes were also formulated by a combination of σ_I, $\sigma_R{}^\circ$, and the polarizability of a substituent.[27] Thus, we believe our analysis of C_α-SCS is a new idea.

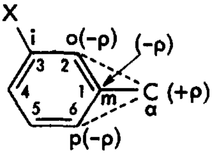


FIG. 7

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