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SUBSTITUENT EFFECTS ON ^{13}C-SCS OF SUBSTITUTED ETHENES AND PROPENES

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Abstract: C_α-SCS in $XCH{=}CH_2$ exhibited three linear relationships with the ι(iota) value depending upon the hybridization due to the substituent, and C_β-SCS showed an approximate correlation with σ_R°. Other ^{13}C-SCS in alkanes could be expressed by the ι-σ_R° DSP equation.

^{13}C-SCS of the C_1 atom (C_1-SCS) in monosubstituted ethenes (A) show no correlation with C_2-SCS,[1] but a correlation exists between C_1- and C_2-SCS in 3-substituted 1-propenes (B)[2] and 4-substituted 1-butene (C)[3] which have more remote substituent. C_2-SCS of A[4] and C_1- and C_2-SCS of B[5] and C[3] can be correlated with Taft's DSP equation.[6] C_2- and C_3-SCS of 3-substituted 5,5-dimethyl-2-cyclohexenones (D)[7] do not show clear correlations for several parameters. However, Bedford and Taylor[8] suggested that C_3- and C_2-SCS of D can be correlated with substituent electronegativities (χ_X) and Taft's σ_R° values, respectively.

We previously proposed a new inductive substituent parameter (ι, iota)[9] and showed that ^{13}C-SCS are generally represented by Eq. (1).[10] C_α-SCS of monosubstituted alkanes are especially correlated only with ι values.[9a,c]

$$^{13}\text{C-SCS} = a\Delta\iota + b\sigma_R^\circ + c \qquad (1)$$

where $\Delta\iota = \iota - \iota_H = \iota - 2.000$.

Reexamination of ^{13}C-SCS in series A and B using various other substituents showed that C_1- and C_2-SCS in A are approximately correlated with ι and σ_R° values, respectively.

Table 1 shows the new and reported data for series A and B. Good correlations were observed among the corresponding ^{13}C-SCS in A, D, and 2-substituted indenes (E).[11] The results of statistical treatment with Eq. (1) and Taft's DSP equation are shown in Table 2, where the excluded substituents indicated a considerable deviation from a linear relationship between the corresponding ^{13}C-SCS in each system.

Table 1. ^{13}C-SCS data[a] in $X\overset{1}{C}H=\overset{2}{C}H_2$ (A) and $X\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$ (B)

X	A	C_1-SCS	C_2-SCS	X	B	C_3-SCS	C_2-SCS	C_1-SCS
H		(122.8)[b]	(122.8)[b]	H		(18.7)[b]	(136.2)[c]	(115.9)[c]
Me[d]		-10.8	6.8	Me[d]		-8.7	-4.3	2.4
Et[d]		-17.7	9.3	Et[e]		-17.5	-2.8	1.4
n-Pr[e]		-16.2	8.3	n-Pr[d]		-15.2	-2.6	1.7
n-Bu[d]		-16.0	8.6	$CH=CH_2$[f]		-19.0	-0.5	0.3
t-Bu[c]		-26.9	13.0	Ph		-21.6	-1.2	0.2
Ph		-14.1	9.0	CN		-2.8	10.2	-3.8
CN		15.0	-14.5	COOH		-20.2	6.5	-3.2
CHO		-15.8	-14.8	$SiMe_3$		-6.0	1.0	3.3
COMe		-14.7	-6.1	NH_2		-26.2	-3.8	2.4
$CONH_2$		-7.5	-4.7	NMe_2		-44.3	0.2	-1.4
COOH		-5.5	-10.0	NEt_2		-37.7	0.1	-1.0
COOMe		-5.5	-7.8	$NHCSNH_2$		-28.4	3.7	-1.9
COOEt		-6.0	-7.6	NCS		-29.0	5.7	-1.8
COCl		-10.3	-13.7	OH		-44.8	-1.3	0.8
CCl_3[g]		-17.5	7.7	OMe[f]		-54.2	0.5	0.2
$SiMeCl_2$		-10.5	-14.0	OEt[f]		---	0.4	1.2
NH_2[h]		-16.3	38.5	OPh		-50.0	2.8	-1.6
NO_2[c]		-22.8	0.4	OAc		-46.5	3.9	-2.3
OMe		-30.1	37.3	SH		-8.9	-1.2	0.5
OAc		-18.5	25.2	Cl		-26.5	2.2	-2.6
SMe[i]		-10.6	15.1	Br		-14.0	1.9	-3.1
SEt		-9.5	12.3	I		13.3	0.5	-1.8
F[c]		-29.3	30.8					
Cl[j]		-3.3	5.4					
Br		8.8	1.0					
I[c]		37.4	-7.7					

a) ^{13}C NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz at ordinary probe temperature (30°C) using about 1 mmol/ml $CDCl_3$ solution. Accuracies of δ_C (ppm downfield from internal TMS) are about ±0.1. Positive sign shows high ^{13}C field shift. Values in parentheses are δ values. b) J.B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972). c) Ref. 1. d) J.W. de Haan, L.J.M. van de Ven, A.R.N. Wilson, A.E. van der Hoult-Lodder, C. Altona, and D.H. Faber, Org. Magn. Reson., 8, 477 (1976). e) "Selected ^{13}C-NMR Spectral Data," Texas A & M Univ. (API Research Project No. 44), Vol. 1 (1975). f) Ref. 2. g) F.K. Velichko, V.I. Dostovalova, N.A. Kuzmina, E.I. Fedin, and R.Kh. Freidlina, Org. Magn. Reson., 7, 46 (1975). h) J.L. Ripoll, H. Lebrum, and A. Thuillier, Tetrahedron, 36, 2497 (1980). i) G.A. Kalabin, B.A. Trofimov, V.M. Bzhezovskii, D.F. Kushnarev, S.V. Amosova, N.K. Gusarova, and M.L. Al'pert, Izv. Akad. Nauk SSSR, Ser. Khim., 576 (1975). j) J. Paasivirta, R. Versterinen, L. Virkki, and P. Pyykkö, Org. Magn. Reson., 10, 265 (1977).

Table 2. Statistical Analysis of ^{13}C-SCS in A and B[a)]

	C-SCS	Analysis	a or ρ_I	b or ρ_R	c	r	n	
A	$\Delta\delta(C_1)$	Eq. (1)	-17.05	11.57	-6.98	0.785	21	(excluding t-Bu, Cl, Br, I, CN, and $SiMeCl_2$)
		Taft's DSP	-18.08	22.46	-8.51	0.676	21	
	$\Delta\delta(C_2)$	Eq. (1)	8.11	-71.97	-0.60	0.977	24	(excluding Cl, Br, and I)
		Taft's DSP	8.58	-77.85	-0.02	0.973	24	
		σ_R°	-	-75.30	2.12	0.967	24	
B	$\Delta\delta(C_3)$	Eq. (1)	-50.84	17.13	-2.04	0.960	18	(excluding I, CN, NCS, and $SiMe_3$)
		Taft's DSP	-32.93	53.05	-8.76	0.777	18	
	$\Delta\delta(C_2)$	Eq. (1)	11.77	13.61	-1.70	0.812	19	(excluding Cl, Br, I, and $SiMe_3$)
		Taft's DSP	18.22	5.17	-1.67	0.906	19	
	$\Delta\delta(C_1)$	Eq. (1)	-4.66	-5.35	0.70	0.663	19	
		Taft's DSP	-7.71	-1.99	0.80	0.785	19	

a) The σ_I and σ_R° values were taken from the following literatures: S. Ehrenson, R.T.C. Brownlee, and R.W. Taft, Progr. Phys. Org. Chem., 10, 13 (1973); O. Exner, "Advances in Linear Free Energy Relationships," ed. N.B. Chapman and J. Shorter, Chapt. 1, Plenum Press, London (1972); O. Exner, "Correlation Analysis in Chemistry. Recent Advances," ed. N.B. Chapman and J. Shorter, Chapt. 10, Plenum Press, London (1978).

The results in Table 2 show that in substituted ethene systems (A, D, and E) C_α-SCS are better represented by Eq. (1) and C_β-SCS can be expressed equally well by both Eq. (1) and Taft's DSP equation and show an approximate correlation with the σ_R° value as suggested previously.[8] In series B, C_3-SCS are expressed well by Eq. (1), but C_2- and C_1-SCS by Taft's DSP equation. A similar trend was observed for the corresponding ^{13}C-SCS in D and E.

However, C_1-SCS in A showed a poor correlation with the ι values (Fig. 1). The plot gave three lines: 1) through H and alkyl groups, 2) through CCl_3- and COÄ-type groups, and 3) through other types of groups. Each line was treated separately with ι and the correlation coefficients were calculated as a total of the three lines. Similar treatment was applied to C_3-SCS in D and C_2-SCS in E. The results are as follows:

$$\text{A } \delta(C_1) = \left\{ \begin{array}{ll} -107.24\Delta\iota + 0.23 & 1) \\ 80.28\Delta\iota - 34.27 & 2) \\ -20.77\Delta\iota - 7.12 & 3) \end{array} \right\} (r = 0.971,\ n = 22)$$

(excluding t-Bu, Cl, Br, I, and $SiMeCl_2$)

$$\text{D } \delta(C_3) = \left\{ \begin{array}{ll} -85.51\Delta\iota & 1) \\ 73.24\Delta\iota - 25.24 & 2) \\ -18.78\Delta\iota - 7.47 & 3) \end{array} \right\} (r = 0.975,\ n = 9)$$

(excluding Cl and Br)

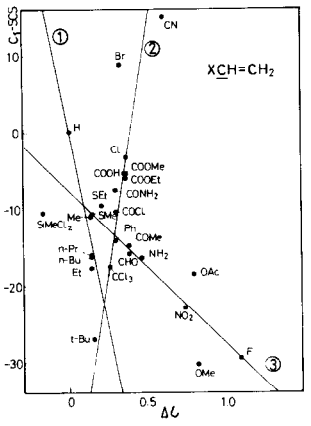

Fig. 1. Plot of C_1-SCS in $XCH=CH_2$ against $\Delta\iota$.

$$\underline{E}\ \delta(C_2) = \begin{cases} -87.68\Delta\iota & 1) \\ 80.32\Delta\iota - 36.46 & 2) \\ -36.30\Delta\iota - 0.87 & 3) \end{cases} \begin{matrix} (r = 0.941, \\ n = 11) \end{matrix}$$

(excluding i-Pr, t-Bu, Cl, and Br)

This treatment greatly improved the correlation for sp^2-C_{ipso}-SCS, that is, ^{13}C-SCS of the sp^2 carbon atom directly bonded by the substituent. The trend of the silyl group is similar to that of C_{ipso}-SCS in monosubstituted benzenes (F).[9a] Since C_1-SCS in A were correlated with the C_{ipso}-SCS in F (C_{ipso}-SCS = 0.95·C_1-SCS + 0.05, r = 0.972, n = 19) including Cl, Br, I, and CN groups, the ruling factor is the same in both cases. The main factor is the difference in hybridization due to the three types of substituents, which depends on the $\Delta\iota$ value. Fig. 2 shows that C_1-SCS can be correlated with ∠XCH (= θ),[12] except for Cl, Br, and CN groups. C_{ipso}-SCS show a rough correlation with the ι values.[9a] The difference may be attributed to the rigidity in F.

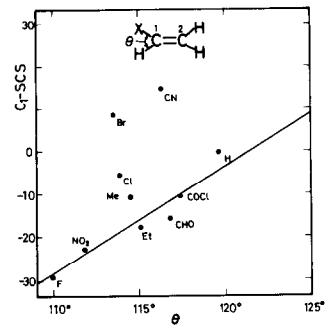

Fig. 2. Plot of C_1-SCS against θ.

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