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CORRELATION OF ^{13}C-H AND ^{13}C-C-H COUPLING CONSTANTS OF THE FORMYL GROUP IN SUBSTITUTED BENZALDEHYDES WITH HAMMETT σ CONSTANTS[1)]

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The values of ^{13}C-H and ^{13}C-C-H coupling constants of the formyl group in substituted benzaldehydes followed the Hammett equation. The $\rho(J_{C-H})$ value was found to be considerably larger than that for substituted toluenes. Values for $\rho_o(J_{C-H})$ and $\rho_o(J_{C-C-H})$ are also discussed.

We have found considerably larger Hammett ρ_o, ρ_m, and ρ_p values for $J_{^{13}C-H}$ of the formyl group in a series of benzaldehydes than those reported for substituted toluenes[2)] and other series of substituted benzene derivatives (see Table 1), and have also observed that $J_{^{13}C-C-H}$ involving the formyl proton follows the Hammett equation with an abnormal trend in ρ_o values.

The $J_{^{13}C-H}$ and the $J_{^{13}C-C-H}$ values obtained in carbon tetrachloride, chloroform-$\underline{d}$, and acetone-$\underline{d}_6$ are shown in Table 2. The J values measured in neat liquid were in good accordance with the reported data.[3-5)] The magnitudes of $J_{^{13}C-H}$ for the meta and para derivatives correlated very well with the Hammett σ_m and σ_p constants,[6)] respectively. The slopes (ρ) for each series are listed in Table 3 together with the correlation coefficients (r). These remarkably large $\rho(J_{C-H})$ values for the benzaldehydes are approximately four times those reported for the systems containing sp^3 hybridized carbon atoms, as can be seen from Table 1. In the case of ^{1}H chemical shifts, however, the ρ values reported for substituted toluenes[7)] and substituted benzaldehydes[8)] are close to each other (see Table 1). Obvious solvent effects observed on the ρ values will be discussed in our full paper.

The magnitude of $J_{^{13}C-H}$ is generally accepted to be related to the hybridization and the polarity of the relevant C-H bond.[9)] The remarkable differences between the $\rho(J_{C-H})$ values of substituted toluenes and those of benzaldehydes can mainly be ascribed to the difference in the hybridization of the carbon atom in their methyl and formyl groups. The result is the first example of an amplified effect of an sp^2 carbon on the substituent effects on NMR parameters.

In the ortho-substituted benzaldehydes, a poor correlation (r = 0.840 in carbon tetrachloride) was observed when the σ_p constants were applied, but linearity was improved by using the σ_m constants. The fairly large $\rho_o(J_{C-H})$ value compared to the $\rho_p(J_{C-H})$ value may be explained in terms of the strong inductive effect at this position.

Table 1. The ρ values and correlation coefficients (r) for the $J_{^{13}C-H}$-σ and chemical shift δ_H-σ relationships in various series of meta and para substituted benzene derivatives

Systems	$J_{^{13}C-H}$-σ		δ_H-σ	
	ρ (Hz)[a]	r	ρ (Hz)[a]	r
$X\text{-}C_6H_4C\underline{H}_3$	1.72 [b]	0.925	12.8 [c]	0.884
$X\text{-}C_6H_4C(C\underline{H}_3)_3$	1.03 [b]	0.928	4.56 [b]	0.946
$X\text{-}C_6H_4N(C\underline{H}_3)_2$	1.74 [b]	0.945	9.59 [b]	0.964
$X\text{-}C_6H_4OC\underline{H}_3$	1.77 [d] 1.83 [b]	0.950 0.915	16.2 [e]	0.891
$X\text{-}C_6H_4SC\underline{H}_3$	1.15 [d] 1.29 [f]	0.945 0.934	6.88 [c]	0.937
$X\text{-}C_6H_4COC\underline{H}_3$	0.850 [d]	0.994	8.34 [c]	0.975
$X\text{-}C_6H_4CO_2C\underline{H}_3$	0.912 [g]	0.930	9.21 [g]	0.950
$X\text{-}C_6H_4C\underline{H}O$	7.21 [h]	0.987	14.4 [i]	0.847

[a] In CCl_4 solution. [b] Taken from ref 2. [c] Taken from ref 7. [d] N. Inamoto, S. Masuda, K. Tori, and M. Nishikida, the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1970, Abstracts p. 1310. [e] Taken from C. Heathcock, Can. J. Chem., **40**, 1865 (1962). [f] Taken from R. E. Hess, C. K. Haas, B. A. Kaduk, C. D. Schaeffer, Jr., and C. H. Yoder, Inorg. Chim. Acta, **5**, 161 (1971). [g] N. Inamoto, S. Masuda, Y. Tamura, and K. Tori, unpublished results. [h] This study. [i] Taken from ref 8.

The magnitudes of $J_{^{13}C-C-H}$ for the meta and para derivatives correlated very well with the Hammett σ_m and σ_p constants,[6] respectively. The slopes (ρ) and correlation coefficients (r) for each series are also listed in Table 3. The results with $J_{^{13}C-C-H}$ in the ortho-isomers were rather surprising, the $\rho_o(J_{C-C-H})$ values being abnormally small, although the available data on ortho-isomers are limited to the four substituents. The $J_{^{13}C-C-H}$ values in various systems are known to be very sensitive to the bonding situation of the two carbon atoms or to the configuration between the proton and substituents.[10] Therefore, the slight change in the formyl group by ortho-steric effects[5] may decrease the substituent effects on $J_{^{13}C-C-H}$.

The $J_{^{13}C-H}$ and $J_{^{13}C-C-H}$ values were measured from ^{13}C-H satellite spectra recorded on a Varian A-60A spectrometer at a sweep rate of 0.5 Hz per sec using about 30% (w/v) solutions of the benzaldehydes in the three solvents. Calibration of the charts was carried out by the usual side-band technique.

Table 2. The $J_{^{13}C-H}$ values for the formyl group and the $J_{^{13}C-C-H}$ values involving the formyl proton in substituted benzaldehydes (±0.2 Hz)

Substituent	$J_{^{13}C-H}$				$J_{^{13}C-C-H}$			
	neat	CCl_4	$CDCl_3$	$(CD_3)_2CO$	neat	CCl_4	$CDCl_3$	$(CD_3)_2CO$
None	174.2 (173.7)[b] (174.0)[c]	173.2	174.3	174.9	24.0 (24.2)[d]	24.6	24.1	24.2
4-NO_2		a	179.2	181.4		a	25.3	24.8
4-CN		a	178.8	181.0		a	25.2	25.1
4-Br		175.2	176.0	178.0		24.9	24.7	24.8
4-Cl		174.4	175.9	177.7		25.2	24.6	24.9
4-Me	173.2	172.1	173.0	174.1		24.2	23.8	24.1
4-OMe	172.9 (173.0)[c]	171.3	173.8	174.9	23.9 (24.1)[d]	24.4	23.9	24.1
4-OH		a	a	172.3		a	a	23.9
4-NMe_2		168.2	168.8	169.0		23.7	23.0	23.6
3-NO_2		179.5	180.3	181.2		26.2	26.0	25.9
3-Br	177.7	176.1	176.8	178.9	25.0 (25.1)[d]	25.5	24.8	25.2
3-Cl	178.0 (177.5)[b]	176.4	176.9	178.6	24.9 (25.0)[d]	25.3	25.0	25.2
3-Me	173.8	172.8	173.6	174.6	23.9 (24.2)[d]	24.4	23.7	24.0
3-OMe	175.2	173.9	174.4	175.3	24.3	24.5	24.3	24.4
2-NO_2		191.8	192.0	192.2		25.6	25.2	25.2
2-Cl	182.7 (182.8)[b]	182.7	183.1	183.1	23.8 (23.6)[d]	23.6	23.3	23.8
2-Me	173.5	173.3	173.5	174.1	23.5 (23.4)[d]	23.6	23.1	23.5
2-OMe		179.9	180.2	180.0		22.7	22.1	22.8

[a] Unobtainable because of low solubility. [b] Taken from ref 3. [c] Taken from ref 4.

[d] Taken from ref 5.

Table 3. The ρ values and correlation coefficients (r) for the $J_{^{13}C-H}$-σ and $J_{^{13}C-C-H}$-σ relationships in substituted benzaldehydes

Compounds	Solvent	$J_{^{13}C-H}$-σ		$J_{^{13}C-C-H}$-σ	
		ρ (Hz)	r	ρ (Hz)	r
3- and 4- XC_6H_4CHO	CCl_4	7.21 [a]	0.987	1.37 [a]	0.939
	$CDCl_3$	6.72 [a]	0.983	1.71 [a]	0.953
	$(CD_3)_2CO$	7.88 [a]	0.985	1.29 [a]	0.864
4-XC_6H_4CHO	CCl_4	6.28 [b]	0.993	1.26 [b]	0.931
	$CDCl_3$	6.39 [b]	0.991	1.47 [b]	0.991
	$(CD_3)_2CO$	7.87 [b]	0.987	0.95 [b]	0.927
3-XC_6H_4CHO	CCl_4	8.68 [c]	0.995	2.37 [c]	0.980
	$CDCl_3$	8.41 [c]	0.987	2.73 [c]	0.987
	$(CD_3)_2CO$	9.12 [c]	0.989	2.62 [c]	0.981
2-XC_6H_4CHO	CCl_4	23.7 [c]	0.981	2.30 [b]	0.848
	$CDCl_3$	23.3 [c]	0.985	2.49 [b]	0.877
	$(CD_3)_2CO$	21.6 [c]	0.984	2.00 [b]	0.917

[a] Against σ_p and σ_m. [b] Against σ_p. [c] Against σ_m.

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