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Studies on the Proton Magnetic Resonance Spectra in Aliphatic Systems. III.[1] On the $J_{C\text{-}H}$ of Alkyl Derivatives

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Several discussions have been extended on J_{C-H}, a_H^2 and ΔX of alkyl derivatives with respect to the substituent constants σ_i and σ_π, and showed that they were all linear with $\sigma_i-0.2\sigma_\pi$. This result, which is also accepted similarly in ^1H chemical shift, suggests that the state of hybridization of carbon atom is the dominant factor in determining the variation of J_{C-H}.

Introduction

Recently, several works have been reported on the elucidation of the physico chemical meaning of J_{C-H} in alkyl derivatives.[3] Formerly, Muller and Pritchard[4] have estimated the semi-empirical correlations among J_{C-H}, C–H bond length and electronegativity of substituent group, and moreover, Malinowski and his coworkers[5] have proposed numerous ζ (zeta) value of the substituent group and obtained the reliability of the simple additivity relationship of above parameter. But, the physico chemical meaning of the foregoing result and the origin of the variation of J_{C-H} are not completely clear at the present step. In this work, J_{C-H}, *s*-character and substituent parameter ΔX[6] of Me-R series have been examined with respect to the substituent constants σ_i and σ_π, and the physico chemical meanings of above parameters have been explored.

Discussion

$J_{C\text{-}H}$ of Me-R Series[6]

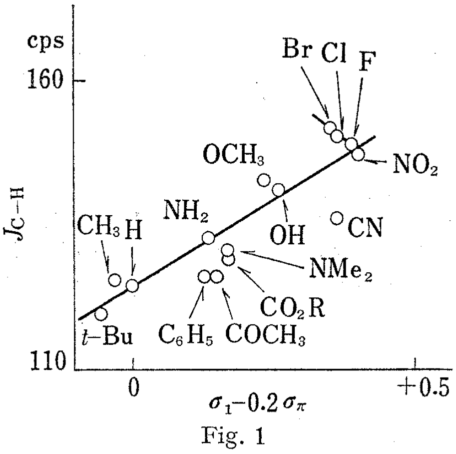

Fig. 1

J_{C-H} of Me-R series are linear with $\sigma_i-0.2\sigma_\pi$ (*cf.* Fig. 1), which signifies that J_{C-H} values are consist of 83.4% σ- and 16.6% π-electronic contributions.

In Table I, the contributions from both factors are summarised.

And, in our treatment, J_{C-H} for the molecules of the type CHXYZ can be predicted using the simple additive relation as below.

$$J_{C\text{-}H}=J_{C\text{-}H}(CH_4)+\sum J_{C\text{-}H}\Delta i+\sum J_{C\text{-}H}\Delta\pi \qquad (1)$$

The J_{C-H} value calculated from above equation

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[1] Part II: Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 2049 (1969).
[2] Location: *Toneyama 6-5, Toyonaka, Osaka.*
[3] J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy Pergamon," Vol. II, Chapter 12, Section 2, 1966.
[4] N. Muller and D.E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).
[5] E.R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961); E.R. Malinowski, L.Z. Pollara and J.P. Larmann, *J. Am. Chem. Soc.*, **84**, 2649 (1962).
[6] C. Juan and H.S. Gutowsky, *J. Chem. Phys.*, 37, 2198 (1962).

TABLE I

	J_{CH}	J_i	ΔJ_i	J_π	ΔJ_π
Me_4C	120	100	−4.2	20	−0.8
CH_4	125	104.2	0	20.8	0
C_2H_6	126	105	+0.8	21	+0.2
Acetone	126	105	0.8	21	0.2
MeC_6H_5	126	105	0.8	21	0.2
MeCOOH	130	108.4	4.2	21.6	0.8
Me_3N	131	109.2	5.0	21.8	0.8
$MeNH_2$	133	110.8	6.6	22.2	1.4
MeCN	136	113.4	9.2	22.6	1.6
MeOH	141	117.6	13.4	23.4	2.6
$MeOC_6H_5$	143	119.2	15.0	23.8	3.0
$MeNO_2$	147	122.5	18.3	24.5	3.7
MeF	149	124.2	20.0	24.8	4.0
MeCl	150	125	20.8	25.0	4.2
MeBr	152	126.7	22.5	25.3	4.5
MeOMe	140	116.7	12.5	23.3	2.5

Δ = deviations from CH_4 reference

(1) showed the complete agreement with that from Malinowski's ζ (zeta) value.[5,7,8] (*cf.* Table II)

TABLE II. Observed and Calculated J_{C-H} of Some Substituted CH_4 (cps)

	Observed	Calcd.
$CH_2(NMe_2)_2$	136.6	137
$CHCl_3$	209	200
$CH(OMe)_3$	186	170

s-Character a_H^2

Formerly, it is concluded that the magnitude of J_{C-H} between directly bonded nuclei depends mainly on the *s*-character of the C–H bond.[4,9]

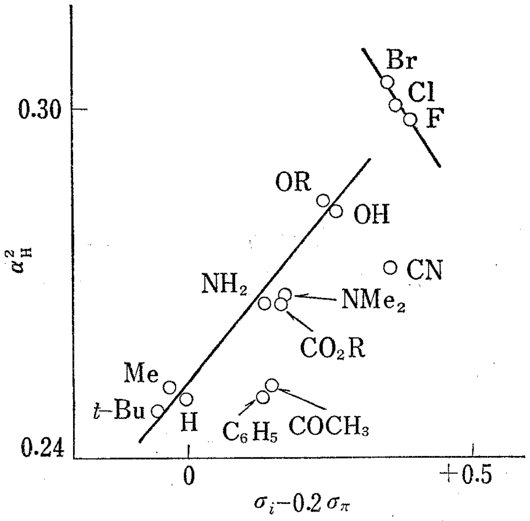

Fig. 2

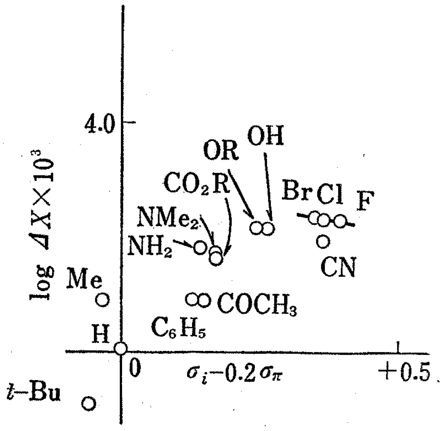

Fig. 3

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7) N. Muller and P.I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962).
8) S.G. Frankiss, *J. Chem. Phys.*, **67**, 572 (1963).
9) N. Muller and D.E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

But, in this section, a_{H}^{2}[6] has been shown to be linear with σ_i—0.2 σ_π (*cf.* Fig. 2).

Substituent Parameter ΔX[6]

In the similar way, as described in the preceding section, the substituent parameter ΔX is also correlated with σ_i—0.2 σ_π (*cf.* Fig. 3).

$J_{\mathrm{C\text{-}H}}$ and δC of Me-R Series

As described in the preceding section and in our previous paper,[1] both $J_{\mathrm{C-H}}$ and δC are linear with σ_i—0.2 σ_π and σ_i—0.25 σ_π, respectively. From these results, it is assumed, consequently, that they are correlative with each other.

Formerly, Goldstein and Reddy[10] have confirmed the linear relations among ^{1}H chemical shifts and $J_{\mathrm{C-H}}$ in ethylenic and heterocyclic systems.

This is because $J_{\mathrm{C-H}}$ is insensitive to the magnetic anisotropy effect, and when such effect operates, the deviation from the linear relation is expected.

In this work, both δC and δH[11] are correlated with $J_{\mathrm{C-H}}$, and linear relations among non-anisotropic H, Me and OMe groups[12] have been observed (*cf.* Fig. 4, 5).

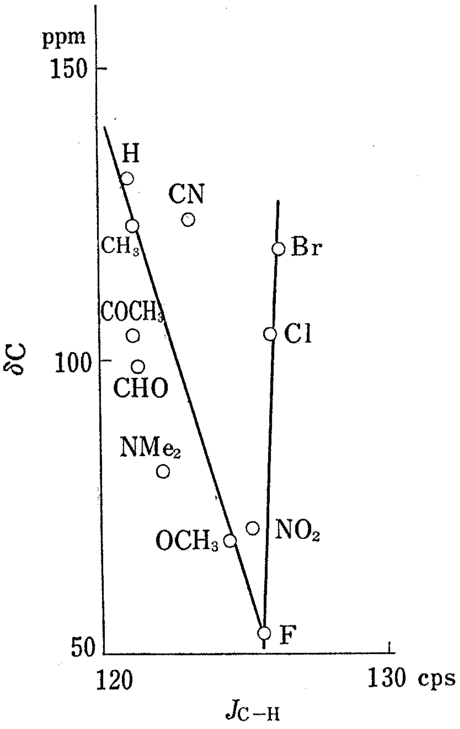

Fig. 4

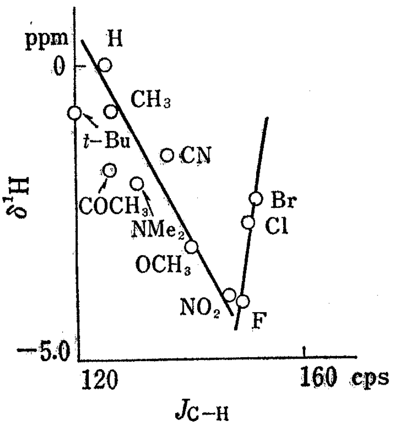

Fig. 5

From these observations,—similar result is also acknowledged in our previous study[13] — we are able to deduce that the contributions from the magnetic anisotropy effect of Cl, Br and CN groups are positive.

Conclusion

From above discussions, the following conclusions have been deduced.

1. Coupling constant $J_{\mathrm{C-H}}$, *s*-character a_{H}^{2} and substituent parameter ΔX are assumed to be dependent on the degree of hybridization of carbon atom.

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[10] J.H. Goldstein and G.S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962).
[11] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
[12] J.A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).
[13] Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **16**, 2120 (1968).

2. Malinowski's simple additive rule of zeta value for the estimation of J_{C-H} means the linear combination of both σ- and π-electronic contributions from CH_4 reference.

3. Magnetic anisotropy effect of Cl, Br and CN groups must be positive in alkyl derivatives.

4. In alkyl derivatives, chemical shifts δ^1H are linear with σ_i—$0.25\,\sigma_\pi$, whereas δC and J_{C-H} are with σ_i—$0.2\,\sigma_\pi$, except some substituent group with magnetic anisotropy effect. Then, it is assumed, consequently, that in this series both variations of δC and J_{C-H} are controled by the similar mechanism, and further work along this line is now being carried out from the quantum mechanical view point.