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Studies on the Nuclear Magnetic Resonance Spectra in Aliphatic Systems. I. Preliminary Discussions on the Chemical Shifts of Alkyl Derivatives

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Proton chemical shifts in alkyl–R compounds are examined with respect to substituent constants and following results are obtained.

1) α-^{1}H chemical shifts are linear with σ_i–0.25 σ_π except for nitro group of isopropyl-R series, CN and halogen group.

2) β-^{1}H chemical shifts are linear with σ_i.

These results indicate that 20% π-electronic together with 80% σ-electronic effect takes part in determining α-^{1}H chemical shifts, on the other hand β-^{1}H chemical shifts are dependent mainly on σ-electronic effect. The deviations observed for halogen and cyano groups indicate that induced current effects on α-^{1}H are diamagnetic in character.

The effective shielding constants and substituent electronegativities are also linear with σ_i–0.25 σ_π.

Introduction

Several works have already been carried out on the studies of aliphatic ^{1}H chemical shifts, and attempts have also been made to explain the above origins with respect to electronegativity, inductive effect and magnetic anisotropy of substituent groups, *etc.*[2,3] However, attempts to correlate the ^{1}H chemical shifts directly with inductive effect were unsuccessful, and it has been indicated that there are other contribution together with inductive effect.

In the present study, ^{1}H chemical shifts of alkyl–R (R=variable substituent) compounds have been examined in terms of substituent constant σ_i and σ_π[4] in order to investigate whether π- together with σ-electronic effect has taken part or not in determining ^{1}H chemical shifts.

Results and Discussion

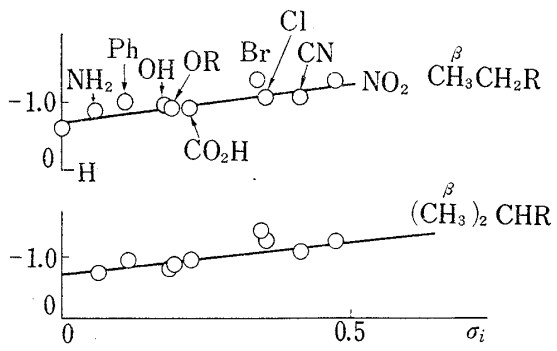

Fig. 1.[5] β-^{1}H Chemical Shift and σ_i

β-^{1}H Chemical Shifts[2,3] and Substituent Constants

As is illustrated in Fig. 1, β-^{1}H chemical shifts in above series are linear with σ_i. Consequently, it is concluded that they are controled mainly by σ-electronic effect of substituent group.

α-^{1}H Chemical Shifts[2,3] and Substituent Constants

Contrary to β-^{1}H shift, that of α-^{1}H does not show satisfactory correlation with either

1) Location: *Toneyama, Toyonaka, Osaka.*
2) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
3) J.R. Cavanaugh and B.P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
4) Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan* (*Pure Chemistry Section*), **86**, 873 (1965).
5) The number on the vertical axis indicates ^{1}H chemical shift (ppm) from CH_4 reference.

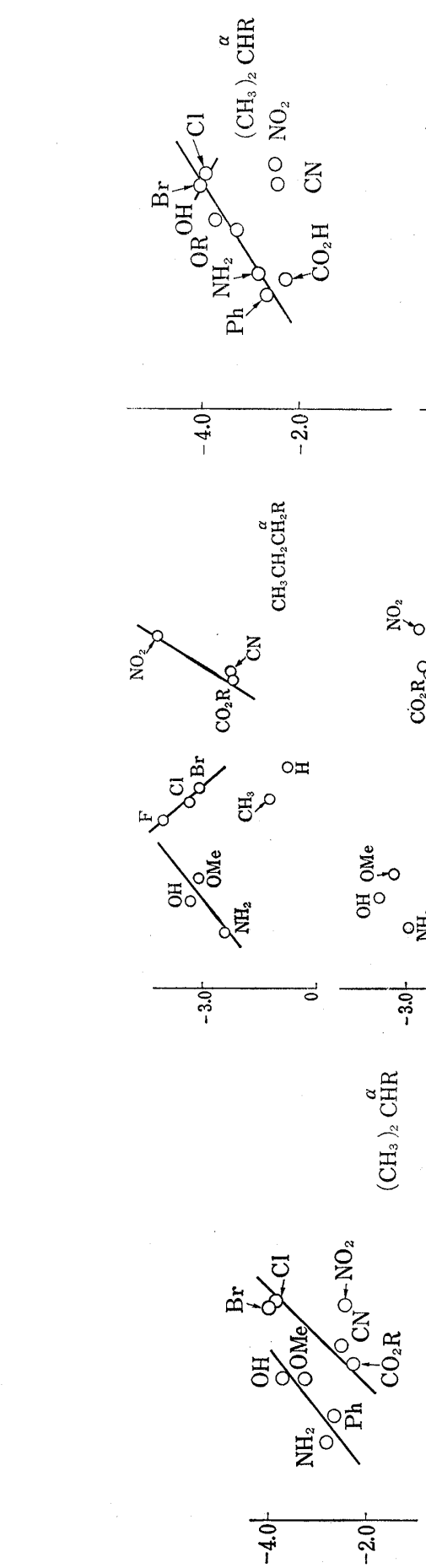

Fig. 2.[5] α-^{1}H Chemical Shift and σ_i

Fig. 3.[5] α-^{1}H Chemical Shift and σ_π

Fig. 4.[5] α-^{1}H Chemical Shift and $\sigma_i - 0.25\sigma_\pi$

σ_i or σ_π. As are shown in Fig. 2 and Fig. 3, electron-releasing, electron-attracting and halogen groups are not continuous with each other, although they are approximately linear in each group. However, it seems probable that σ_i correlate somewhat better than σ_π with α-^{1}H shift. Then, it can be assumed that σ-electronic effect has larger contribution than π-electronic effect. As is shown in Fig. 4, α-^{1}H chemical shifts are linear with modified substituent constant $\sigma_i - 0.25\ \sigma_\pi$ in any case except for NO_2 group of isopropyl-R series, CN and halogen group, which tends to high field shift in the following order, F<Cl<Br. If the origin of above deviation to high field is attributed to the magnetic anisotropy effect, the effect of induced current on α-^{1}H should be diamagnetic. The above assumption is opposed to the result observed from the correlation among α-^{1}H chemical shift and electronegativity,[2] showing the deviation to low field for halogen group.

At the present step, it is impossible to present a proper explanation for this deviation, and for which the study is now in progress.

Substituent Electronegativity[3,6] and $\sigma_i - 0.25\sigma_\pi$

In order to obtain some information about apparent discrepancy mentioned above, the correlation among substituent constant and substituent electronegativity was examined (*cf.* Fig. 5). As is shown in Fig. 5, substituent electronegativity has an approximately linear

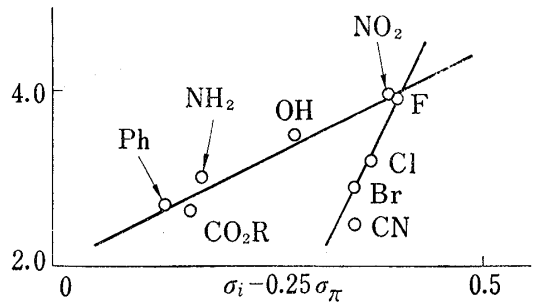

Fig. 5.[7] Substituent Electronegativity and σ_i–0.25 σ_π

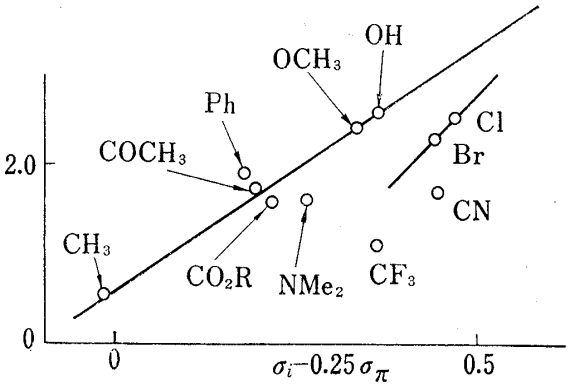

Fig. 6.[9] Effective Shielding Constant and σ_i–0.25 σ_π

correlation with σ_i–0.25 σ_π, except for halogen and CN group, therefore it can be recognized that so-called substituent electronegativity includes both σ- and π-electronic effect with same ratio as is observed in α-^{1}H chemical shift. However, the anomaly observed in halogen and CN group probably suggests that above two parameters are somewhat different in their physical meanings.

Effective Shielding Constant[8]

Shoolery's effective shielding constants, as is shown in Fig. 6, are also linear with σ_i–0.25 σ_π. Accordingly, the simple sum rule of effective shielding constant signifies the linear combination of both σ- and π-electronic effect of each substituent group.

6) B.P. Dailey and J.N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
7) The number on the vertical axis shows electronegativity scale.
8) J.N. Shoolery, "Technical Information Bulletin," **2**, No. 3, Varian Associates, Palo Alto, California, 1959.
9) The number on the vertical axis shows the scale of effective shielding constant (ppm).