*The Nuclear Magnetic Resonance Spectra of Olefinic Protons and the Substituent Effects. I. Systems of ω-Substituted trans-Styrenes and 1-Substituted trans-Propenes**

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Concerning the dependence of the magnetic resonance of olefinic protons on various features of chemical structures, several investigations have been reported, beginning in 1960[1]. Most of them, however, have failed in their attempts to derive some kind of smooth correlation between shifts and the nature of the substituents. The remaining problems center on the point of inquiring how the deviation of the chemical shifts of olefinic protons from values predictable on the basis of Dailey and Shoolery's proposition, which holds generally in the spectra of protons attached to the SP^3 carbon atom[2], can be elaborated and made consistent with the substituent effects by virtue of Hammett's relationship[3].

The present authors confirmed previously, from an inspection of the proton resonance spectra of series of α- and β-substituted methyl cinnamates, that some trends of correlation exist between the shifts of protons situated in the trans-position to the substituents and Hammett's substituent constants**. This finding may indicate that, if an olefinic part of a series of compounds were constructed in such a way that it might conjugate with another resonating group, such as a benzene ring or a hyperconjugative methyl group, the protons of this part of the structure, even though they were essentially of an olefinic nature, would show a similar nuclear magnetic behavior to that of benzene ring protons[3,4]. Therefore, they would be subject to the controlling effect of the series of terminal substituents in the sense of Hammett's relationship. Taking these considerations into account, the authors have attempted to investigate the proton resonance spectra of series of ω-substituted *trans*-styrenes and 1-substituted *trans*-propenes. This paper reports on the correlation between the chemical shifts of the olefinic protons of the two series of compounds mentioned above and the effect of terminal substituents considered from the viewpoint of Hammett's relationship.

Experimental

The nuclear magnetic resonance spectra of ω-substituted-styrenes were obtained with a Varian 4300-B high resolution spectrometer operating at 56.4 Mc., while a spectrometer operating at 60 Mc. was used for obtaining the spectra of 1-substituted propenes. The sample was dissolved in carbon tetrachloride of a 10 mol. per cent concentration, having been sealed in a glass tube, 5 mm. in outside diameter, which was spun in the magnetic field during the measurement. The absorption lines were measured by relating them with the resonance line of 2 mol. per cent cyclohexane added as an internal reference, while the frequencies of the lines were confirmed by the side band technique of controlled frequencies.

All the compounds are of a trans-configuration, but the spectral inspection has shown that some of them are contaminated by a small amount of cis-isomer. The styrene derivatives are as follows: Styrene, ω-chlorostyrene, ω-bromostyrene, ω-nitrostyrene, cinnamonitrile, l-phenylpropene, cinnamaldehyde, benzilideneacetone, cinnamoyl chloride, styryl acetate, methyl cinnamate, etc. Free cinnamic acid was also included. The synthesized compounds are of the following nature: ω-Nitrostyrene, m. p., 59~60°C; ω-chlorostyrene (cis), b. p., 199~199.5°C; n_D^{25} 1.5735, l-phenylpropene, b. p., 73~75°C under 14 mmHg; styryl acetate, b. p., 103~104°C under 6 mmHg. The cinnamonitrile prepared through the dry distillation of a mixture of cinnamic acid and lead rhodanide was fractioned into two parts. Of the products distilled, the first became crystalline upon standing for a long time and melted at 10°C, but the second distillate never did crystallize. The rest of the compounds were commercially obtained and purified***. The examined derivatives of propene are as

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1) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, **1960**, 2881; E. O. Bishop and R. E. Richards, *Mol. Phys.*, 3, 118 (1960); C. N. Banwell and N. Sheppard, ibid., 3, 351 (1960); W. Brügel, Th. Ankel and F. Krückeberg, *Z. Elektrochem.*, **64**, 1121 (1960).

2) B. P. Dailey and J. N. Shoorery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

3) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); R. W. Taft, Jr., ibid., **79**, 1045 (1957); R. W. Taft, Jr. and I. C. Lewis, ibid., **80**, 2436 (1957).

** Results and discussions are to be discussed in Part II of this series.

4) Y. Yukawa, Y. Sakai and K. Kabazawa, *Memories of Scientific and Industrial Research, Osaka Univ.*, **17**, 185 (1960); Y. Yukawa and H. Yamada, lecture given at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

*** Products of Tokyo Kasei Kogyo Co., Ltd., and Wako Pure Chemical Industries, Ltd.

follows: 1-Bromopropene (b. p., 59∼60°C), 1-phenylpropene (already mentioned), crotonyl chloride (b. p., 124∼125°C), methyl crotonate (b. p., 119∼120°C), crotonaldehyde (b. p., 104∼105°C), crotonitrile (b. p., 118∼119°C) and 1-nitropropene (b. p., 94∼95°C under 8 mmHg).

Results

The spectra of olefinic protons with regard to substituted styrenes belong to the simple AB-type, with the exception of those of styrene and cinnamaldehyde. Substituted propenes give the spectra corresponding to the system of 5 nuclei, ABX_3, and crotonaldehyde has a system of ABX_3Y. The chemical shifts obtained by analysis of the spectra are summarized in Table I. The coupling constants will be discussed later.

Discussion

Whipple et al. investigated the substituent effects on the chemical shifts of olefinic protons. They claim that, although the trends of the vinyl proton shifts in 2-substituted propenes are qualitatively consistent with inductive and mesomeric effects attributable to substituents, no precise correlation exists between the shifts and Hammett's constants for substituents[5].

Meanwhile Taft investigated to secure a correlation between the nuclear magnetic resonance shifts of fluorine atoms in mono- and di-substituted fluorobenzenes and Hammett's σ-constants. Taft found that the σ-value leads to a fairly good correlation with the fluorine nuclear shielding constants, $\delta^{F}{}_{m}$ and $\delta^{F}{}_{p}$[3]. The olefinic part in the system examined by Whipple et al. indeed conjugates with the methyl group, but this conjugation will be somewhat disintegrated by the introduction of a second substituent. Therefore, the direct application of the relationship advanced by Taft would not necessarily be suitable for the results obtained for systems of a poorer stabilization due to such cross-conjugation, and any correlations of σ_p would probably be missed. In the case of the compounds here investigated ($RCH_A=CH_BX$, R: C_6H_5 or CH_3), on the other hand, the olefinic bond conjugates not only with the aromatic ring or the methyl

TABLE I. PROTON CHEMICAL SHIFTS OF ω-SUBSTITUTED *trans*-STYRENES AND 1-SUBSTITUTED *trans*-PROPENES, $RCH_A=CH_BX$

Chemical shifts in τ-values, ±0.05 p. p. m.

Substituent X	R: C_6H_5			R: CH_3		
	δ_{H_A}	δ_{H_B}	δ_{Ph-H}	δ_{H_A}	δ_{H_B}	δ_{CH_3-H}
H	3.35	3.36	2.77	4.27[d]	5.04[d]	8.26[e] 8.28_7
Cl	3.46[a]	3.80[a]	2.79[a]	4.16[d]	4.12[d]	
Br	3.12	3.30	3.79	3.92	4.05	8.16
NO_2	2.08	2.49	2.52	2.78	3.05	
CH_3	3.76	3.76	2.82	4.75[d]	4.75[d]	8.26[d]
CHO	2.57	3.35	2.60	3.21	3.97	7.95
CO_2H	2.28[b]	3.61[b]	2.50[b]	2.93[f]	4.20[f]	
CO_2CH_3	2.43	3.69	2.63	3.13	4.24	8.01
COCl	2.20	3.41	2.64	2.81	3.91	7.98
$COCH_3$	2.55	3.35	2.64			8.00
CN	2.68 2.97[a]	4.23 4.62[a]	2.65	3.32	4.69	8.19[d]
C_6H_5	3.01[c]	3.01[c]	2.73[c]	3.76	3.76	8.12
$OCOCH_3$	2.23 2.65[a]	3.72 4.43[a]	2.80			

a) The values presumably attributable to the cis-isomer.

b) The data were obtained on previous occasions.

c) The values were adopted from Tiers' table (G. van D. Tiers, "Characteristic NMR Shielding Values for Hydrogen in Organic Compounds", Part I, Central Research Department, Minnesota Mining and Manufacturing Co., Minneapolis, Minnesota, 1958).

d) Measurement was performed under the conditions reported by Bothner-By et al. and by Reddy et al. A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). Cf. Ref. 8.

e) Adopted from the monograph: J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959).

f) The values were obtained from measurement with the glacial acetic acid solution owing to the low solubility of the compound in carbon tetrachloride.

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[5] E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **82**, 3010 (1960).

group, but with substituent X in a uniform direction. Consequently, the olefinic proton, H_A, of these compounds seems to be shielded by substituent X in a sharper and more characteristic way than may be the case in the system of Whipple. It may be reasonable, therefore, to apply Hammett's relationship to the τ-values of H_A. It is true, on the other hand, that the influence of substituents on the resonance absorption may be subject also to the anisotropy of the magnetic susceptibility of bonding axes in substituent groups, the diamagnetic anisotropy arising from a long range shielding exerted by the benzene ring and other substituents. Indeed, Spiesecke and Schneider, who studied the resonance spectra of mono-substituted benzenes, assumed that the shifts due to ortho-protons are controlled by the polar nature of substituents as well as by the disturbing factors of the diamagnetic anisotropy of substituents and other magnetic effects(6). The disturbing factors, however, may be seen as not very considerable from an inspection of Fig. 1, which illustrates that the shifts for ortho-protons correlate practically with those of para-protons, at least so far as the substituents, OCH_3, H, F, Cl, Br, CHO and NO_2, are concerned. This fact implies that the cis-proton chemical shifts in the ω-styrene and 1-propene systems are governed mainly by the polar substituent effects.

Figure 2 shows the relationship between the τ-values of H_A of these compounds and Hammett's constants, σ_p. The value of the resonance line of H_A in stilbene, adopted from Tiers' table, may be lowered by the long-range shielding effect of the benzene ring. As the lowering of the shift by the benzene ring, situated in the cis-position to H_A, is estimated as about 0.05 p. p. m., the τ-value of H_A may be corrected to 3.51 p. p. m.(7) In Fig. 2 the corrected value is used. The value observed with ω-chlorostyrene is tentatively assumed to be attributable to the cis-isomer, but the value may not differ considerably from that of trans-isomer(1). As for the cinnamo- and crotonitriles, the cyano group exerts on the neighboring cis-proton, H_A, a positive shielding contribution due to the bond anisotropy around its triple bond axis(8). In the case of crotonitrile, the magnitude of this diamagnetic shielding of the cis-proton has been calculated by Reddy et al. to be as much as +0.287 p. p. m., and that of the geminal proton, as +1.11 p. p. m.(9) In plotting the value of the H_A of cinnamonitrile, it is assumed that a positive shielding of the cyano group would give an exaggeration of about the same order as in the case of crotonitrile. The groups, $COCH_3$ and possibly CO_2CH_3, may have the same kind of anisotropic shielding effect. That an anisotropic shielding effect of some magnitude should not be ignored in computing the substituent effects

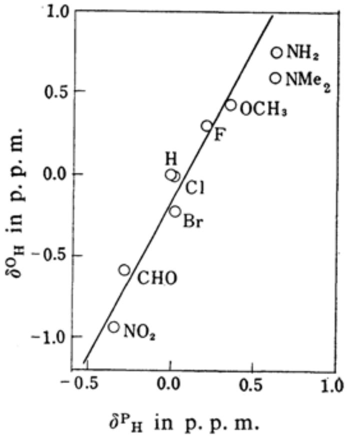

Fig. 1. The correlation between the chemical shifts of ortho- and para-protons in mono-substituted benzenes. The data are cited from Ref. 6 and are accommodated for comparison by taking the benzene proton shift as the point of reference.

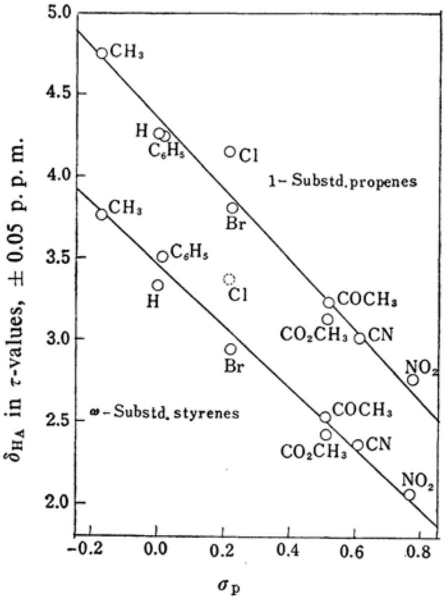

Fig. 2. The cis-proton chemical shifts, plotted vs. Hammett's substituent constants, σ_p.

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6) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

7) C. E. Johnson, Jr. and F. A. Bovey, ibid., **29**, 1012 (1958).

8) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon, London (1959), p. 59.

9) G. S. Reddy, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

of halogens, may probably be illustrated from the departure of their plots from the correlation line in Fig. 2.

Generally, the decrease of free energy in the reactions of benzene derivatives changes under the influence of a substituent in such a way that the parameters of the inductive and resonance interactions, σ_I and σ_R, which are inherent to the substituent, may act independently of each other. Since the nuclear magnetic shielding is also supposed to be affected by these two parameters independently, as in the reactions of benzene derivatives, the shielding constants may be expressed by the equation of the general form, $\delta=\alpha\sigma_I+\beta\sigma_R$. The coefficients, α and β, are measures of the susceptibility with which the inductive and resonance influences are called upon to function. Taft has suggested that the relation of the proton shielding might best be described by the equation, $\delta_H=0.40\sigma_I+0.70\sigma_R$[3]. As is shown in Fig. 3, this equation is applicable to the data presented here with regard to styrene and 1-propene derivatives. The linearity of its correlation with the observed shifts is a little improved compared with that obtained from σ_p alone. The σ_I and σ_R values and their combination according to Taft's equation are listed in Table II.

From the existence of a certain correlation between the cis-proton shifts of these olefinic compounds and Hammett's σ-values, the same kind of correlation may be expected among the shifts of those protons situated at the corresponding positions of the systems which have a similar conjugation structure,—cis-proton shifts, here investigated, ortho-proton shifts of mono-substituted benzenes[6], and β-proton shifts of 4-substituted pyridine 1-oxides[10]. In Fig. 4, the fairly clear correlations among them may be observed. This suggests that, in these systems, the modes of the transmittance of substituent effects are essentially similar. These modes would be not only peculiar to the benzene nucleus, but also inherent in the structures of carbon skeltons, which constitute the expanded conjugation systems with certain restricted conditions. To

TABLE II. THE SUBSTITUENT CONSTANTS

Substituent	σ_I[a]	σ_R[c]	$0.40\sigma_I+0.70\sigma_R$
CH_3O	+0.23	−0.50	−0.26
F	+0.50	−0.44	−0.11
CH_3	−0.05	−0.13	−0.11
C_6H_5	+0.10	−0.09	−0.02
H	0.00	0.00	0.00
Cl	+0.47	−0.24	+0.02
Br	+0.45	−0.22	+0.03
I	+0.38	−0.10	+0.08
CO_2R[d]	+0.30[b]	+0.20	+0.26
CN	+0.58[b]	+0.07	+0.29
$COCH_3$	+0.27	+0.25	+0.29
NO_2	+0.63	+0.15	+0.36

a) Evaluated by Taft.
b) Revised by Taft and Lewis, cf. Ref. 3.
c) Calculated from the values of σ_p according to the equation: $\sigma_R=\sigma_p-\sigma_I$. The values of σ_p are cited from the paper of Jaffe's. Cf. *Chem. Revs.*, **53**, 216 (1953).
d) The value is applicable to both H and alkyls.

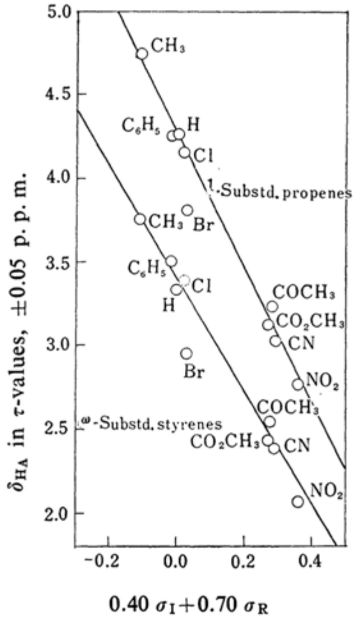

Fig. 3. The cis-proton chemical shifts, plotted vs. substituent parameters, $0.40\sigma_I+0.70\sigma_R$.

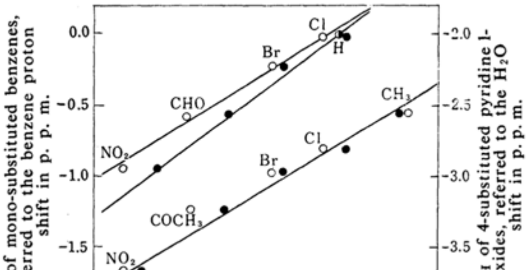

Fig. 4. The chemical shifts of ortho-protons of mono-substituted benzenes (Ref. 6) and of β-protons of 4-substituted pyridine 1-oxides (Ref. 10), plotted vs. the cis-proton chemical shifts of 1-substituted propenes (○) and ω-substituted styrenes (●) with respect to non-substituted ones respectively.

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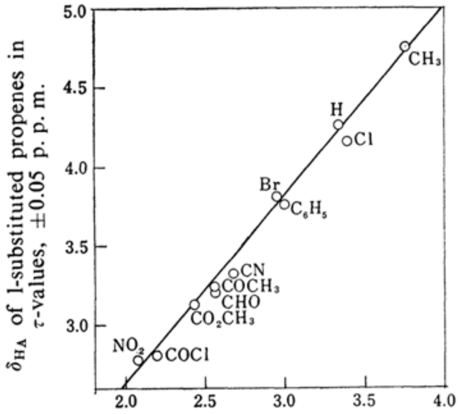
[10] A. R. Katritzky and J. M. Lagowsky, *J. Chem. Soc.*, **1961**, 43.

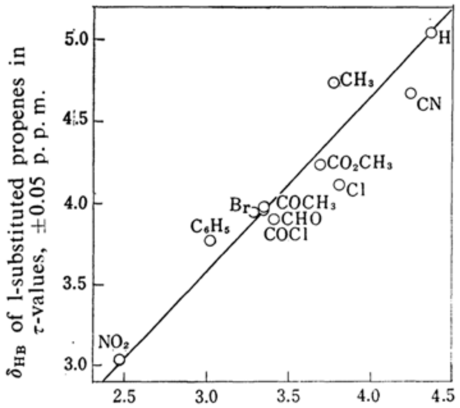
the conditions correspond the constancy of the parameters, α and β.

Figures 5 and 6 illustrate the correlations of the chemical shifts of two sets of protons with each other for styrene and 1-propene derivatives. The former relates with those of cis-protons (H_A), and the latter, with those of geminal protons (H_B). It is clear that the correlation for cis-protons is excellent. Any straightforward correlation of geminal proton shifts has been discernible neither with the electronegativity of the first atom of substituents nor with Hammett's constants. The reasons for this will be clear from an observation of the two figures. It is worthy of brief mention, however, that the geminal proton shifts for compounds, the substituent of which is hydrogen itself, are located in the highest region of the field in both series. This probably arises form the lower electronegativity of hydrogen compared with that of the first atoms in other substituents.



δ_{H_A} of ω-substituted styrenes in τ-values, ±0.05 p. p. m.

Fig. 5. The correlation of the cis-proton chemical shifts between ω-substituted styrenes and 1-substituted propenes.



δ_{H_B} of ω-substituted styrenes in τ-values, ±0.05 p. p. m.

Fig. 6. A comparison of the chemical shifts of geminal protons for ω-substituted styrenes and 1-substituted propenes.

Summary

High resolution proton magnetic resonance spectra of ω-substituted *tsans*-styrenes and 1-substituted *trans*-propenes have been observed and discussed from the viewpoint of substituent effects. The chemical shifts of protons located at the cis-position to substituents depend roughly upon Hammett's σ_p constants and presumably correlate better with the combination of potential inductive and resonance parameters, namely $0.40\,\sigma_I + 0.70\,\sigma_R$, proposed by Taft.

These results suggest that the chemical shifts of olefinic cis-proton may be computed from the viewpoint of the polar nature of the substituents, though the diamagnetic anisotropy and the long-range shielding effect of the substituents must be carefully considered side by side.

When the chemical shifts of protons situated at corresponding positions of structure in several systems are compared, a fairly good correlation is observed among them. This fact implies that the modes of the transmittance of substituent effects is similar in these systems.

The nature of the substituent effects on the chemical shifts of geminal protons is, however, very complicated and might be out of consonance with both the electronegativity and the available substituent parameters.

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