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Proton Chemical Shifts in Nuclear Magnetic Resonance Spectra of Some Vinyl Compounds*

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La ĥemia ŝoviĝo de protonmagneta resona spektro de *styrene* estas duon-empire kalkulita, de konsidero de jenaj faktoroj : (i) π-ringa kurento-efiko, (ii) magneta anisotrop-efiko de najbaraj karbonaj atomoj, (iii) loka kontraŭmagneta ŝirmado de la hidrogena atomo, kaj (iv) efiko de parta ringa kurento. La konformiĝo de la kalkulado kun la mezurado ŝajnas al mi entute kontenta.

Kelkaj diskutoj pri la β-protona ŝoviĝo de ***vinyl halides***, kaj la rilato de protonaj ŝoviĝoj kaj elektronaj densecoj ankaŭ estas faritaj.

I. Introduction

If we examine the nuclear magnetic resonance (NMR) spectra of a given species of nucleus in various chemical environments, either in different molecules or in different chemical positions in the same molecule, there will be a corresponding set of different values of the shielding constant. So, magnetic resonance will occur in a different part of the spectrum for each chemically distinct position. This displacement of a signal for different chemical environments due to variations in shielding constant is referred to as a "chemical shift".

Phenomena of the chemical shift were first observed in 1950, (1) and then a number of important applications in various branches of chemistry and chemical physics developed widely. (2)

The general expression of nuclear shielding in molecules was first derived by Ramsey. (3) Using the usual perturbation theory, he calculated the total energy of electrons in a uniform external magnetic field and in a secondary magnetic field induced by the nuclear magnetic moment of a nucleus located at the origin, from which he picked up the terms of interactions of the magnetic moment with the external magnetic field. And he obtained the following shielding constant for the case of the external field in z direction :

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$$\sigma_{zz}=\frac{e^2}{2mc^2}\int\frac{x^2+y^2}{r^3}\rho\,d\tau+\frac{e^2h^2}{8\pi^2m^2c^2}\sum_{n\neq0}\frac{1}{E_n-E_0}\times$$

$$\left[(0\,|\sum_j\frac{\partial}{\partial\phi_j}|\,n)(n\,|\sum_k r_k^{-3}\frac{\partial}{\partial\phi_k}|\,0)+(0\,|\sum_k r_k^{-3}\frac{\partial}{\partial\phi_k}|\,n)(n\,|\sum_j\frac{\partial}{\partial\phi_j}|0)\right], \quad (1)$$

where 0 and n represent the ground and the excited electronic states respectively, and E_n-E_0 is the excitation energy, ϕ is the azimuthal angle for rotation about the z axis.

This is Ramsey's formula and the mean shielding constant is obtained by averaging over all directions. The first term in the formula is similar to the Lamb formula for the atom (4) and the second term corresponds closely to the paramagnetic term in the Van Vleck equation for the magnetic susceptibility. (5)

To evaluate the second term precisely, it would be necessary to have detailed knowledge of the energies and wave functions of all the excited electronic states.

The Ramsey formula is not suitable for the calculation of the shielding constants in any molecules. The principal dififculty lies in the fact that, for a large molecule, both terms become large and cancel each other. In order to make comparative studies of a series of related compounds, a theory wherein the total shielding is divided into local contributions was developed by Saika and Slichter. (6) They suggested that the shielding could be approximately divided into separate atomic contributions, and divided the total shielding into three parts:

(i) The diamagnetic correction for the atom in question.
(ii) The paramagnetic correction for the atom in question.
(iii) The contribution from other atoms.

Neglecting the effect (iii), because variations in the local paramagnetic term are the dominant cause of fluorine chemical shift, they evaluated the fluorine chemical shift of the partly ionic molecule HF relative to the non-ionic molecule F_2, to be 625 ppm, which is compared with the observed value of 1,400 ppm. (7)

The mathematical basis of this division into atomic currents has been discussed by Pople (8) and McConnell. (9) Moreover, Pople (10) suggested that the division proposed by Saika and Slichter does not take account of the possible magnetic effects of interatomic currents in which electrons flow from one atom to another, and that the interatomic currents can make a significant contribution to proton chemical shifts, and he completed the division of the shielding constant by adding the effect (iv):

(iv) The contribution from interatomic currents.

In the case of the proton magnetic resonance, the effect (ii) which is the dominant cause of fluorine chemical shift, would have little contribution to the shift, because the ground electronic state for hydrogen atom is spherically symmetric. Therefore the effects (iii) and (iv) become relatively large and can not be neglected compared with other effects.

A theory was proposed by Pople(8),(11) for evaluating the shielding constant including the effects (iii) and (iv). For the estimation of the effect (iii), he divided up the contribution from other atoms into the atomic current on each atom, and treated the magnetic moment, induced by the atomic current, as a point dipole, and he described the effect (iv) by a simple classical model(12) of free electrons on a wire, in aromatic compounds.

By Pople' s theory, it was possible to study concretely the proton chemical shift, and the ground for wide applications of the chemical shift to chemistry and chemical physics was given. Thereafter, there appeared many theoretical works on the ring current effect,(13) the polar effect, (14) and the bond anisotropy. (15) And also, a study extended Pople's theory to the fluorine chemical shift was published. (16)

In this paper, a semiempirical evaluation of the proton chemical shift of styrene based mainly on the Pople theory is presented, and some considerations on the β-proton shift in vinyl halides are made. At last, the correlation of the proton chemical shift and the electron density is discussed.

II. The Proton Chemical Shift of Styrene

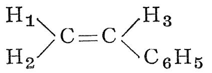
§ 2-1. Experimental Results

NMR spectra of styrene were obtained with JNM-3 type high-resolution NMR spectrometer of Japan Electron Optics Laboratory Co., Ltd, and the resonance frequency for protons is 40 Mc.

The results of the chemical shift were published previously,(17) and are represented in Table I with other reported values. (18)-(20)

TABLE I. Proton dhemical shifts of styrene.

Protons*	Proton chemical shifts $(H-H_1)/H_1$ppm			
H_1	0.00	0.00	0.00	0.00
H_2	−0.50	−0.52	−0.55	−0.50
H_3	−1.50	−1.50	−1.55	−1.48
Hring		−2.05	−2.05	
Ref.	(17)	(18)	(19)	(20)

* Protons are labeled according to the system  $(H_1)(H_2)C{=}C(H_3)(C_6H_5)$.

§ 2-2. Theoretical Considerations

a. The pi-ring-current effect

It is very often reported that the chemical shifts in aromatic compounds are able to be successfully interpreted by considering the contribution of the pi-ring currents induced by an externally applied magnetic field.

Therefore, the contribution of the pi-ring-current effect to the proton chemical shift of styrene is evaluated at first. Methods for calculating this effect were proposed by many workers,(13) and we adopted some of them.

First, the dipolar approximation proposed by Pople (10), (13a) was used, in which the contribution of induced pi-ring currents to the shift is approximated by the effect of the magnetic dipole located at the center of the ring.

If a magnetic field H is applied perpendicularly to the aromatic ring, the electrons circulate with angular frequency $eH/(2\pi mc)$, leading to a current of j

$$j = 3e^2H/(2\pi mc). \qquad (2)$$

And then the current j is replaced by a magnetic dipole μ_d at the center of the ring and perpendicular to it:

$$\mu_d = -3e^2a^2H/(2mc^2), \qquad (3)$$

where e and m are the electronic charge and mass, respectively, a is the radius of the ring and c is the light velocity. The direction of this moment will be such as to lead to a diamagnetic moment opposed to the primary field H. For the proton at the distance R from the center of the ring, there will be the following contribution to the shielding constant,

$$\mu_d/(HR^3) = -3e^2a^2/(2mc^2R^2), \qquad (4)$$

Averaging over all directions of H, the resultant contribution is

$$\sigma^{\pi} = -e^2a^2/(2mc^2R^2). \qquad (5)$$

A direct method of calculating the field at any point was formulated by Mcweeny, (13d) based on the London theory, (21) and it is easily applied even to large molecules.

In the method proposed by McWeeny, the usual LCAO perturbation theory is generalized to take account of the imaginary perturbation due to an external magnetic field, and the induced field at a point is then calculated by inserting a test dipole, adopting approximations due to London, and using the perturbation theory to evaluate a coupling energy. The results are as follows, which differ somewhat from those obtained by Pople,

$$\sigma^{\pi} = 2\beta(2\pi e/hc)^2S^2/a^3(-1/9)(\mu/R^3), \qquad (6)$$

where, β is the resonance integral, e, the electronic charge, h, Planck constant, c, light velocity, S, the area of the aromatic ring, a, the carbon-carbon bond length, and R is the distance from the center of the ring in units of a. μ is a dipole moment and $\mu \rightarrow 1$ for large R, that is the induced moment may be regarded as a point dipole at large distances, but the correction factor must in general be added:

$$\mu = 1 + (9/8)R^{-3} + (843/128)R^{-4} + \cdots\cdots. \qquad (7)$$

Instead of a magnetic dipole in Pople's theory, Waugh and Fessenden (13b) considered the magnetic field which actually arises from n electrons circulating in a loop of radius a. In the usual cylindrical coordinates ρ and z, expressed in units of a, the component of this field normal to the plane of the ring was given by

$$H_z = \frac{\mathrm{I}k}{4\pi c a \rho^{1/2}}\left[K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2}E(k)\right], \qquad (8)$$

K and E are the complete elliptic integrals and the modulus k is expressed by

$$k^2 = 4\rho/[(1+\rho)^2+z^2]. \qquad (9)$$

I is a superconducting current flowing in a ring having a radius equal to that of the benzene ring,

$$I = ne^2H/(4\pi mc). \qquad (10)$$

If the average projection of H_z on the applied magnetic field was taken into account, the results is

$$\sigma = ne^2B_0/(24\pi mc^2 a), \qquad (11)$$

$$B_0 = \frac{1}{2\pi\rho^{1/2}}\left[K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2}E(k)\right], \qquad (12)$$

It is well known that the pi-electron cloud does not have its maximum density in the plane of the carbon atoms, but its maximum density exists rather in two doughnut-like rings, one on each side. The spacing of these rings is not known but is probably of the order of 1A. (22)

We carried out the evaluation of the ring current effect by the similar model of two circular loops. (23) Since the current flowing in a single loop is

$$I = 3e^2H/(4\pi mc), \qquad (13)$$

the secondary field on the z axis, $H'(z)$, is given by

$$H'(z) = \frac{3e^2a^2}{2mc^2}H\left\{\left[(z+d)^2+a^2\right]^{-\frac{3}{2}} + \left[(z-d)^2+a^2\right]^{-\frac{3}{2}}\right\}, \qquad (14)$$

where, a is the radius of the ring and $2d$ is the separation of two doughnut-like rings. If the scalar potential of the secondary field H' is put as

$$\phi = \sum_{n=0}^{\infty} A_n P_n(\cos\theta) r^{-(n+1)}, \qquad (15)$$

the secondary field on the z axis ($r=z$, $\theta=0$), derived from this potential, must equal to $H'(z)$. So, we expanded both fields in terms of z and determined the coefficients of ϕ, A_n, and derived the general expression for the secondary field, $-\partial\phi/\partial r$. The result was the following and this is in accord with Pople's expression,$^{(13a)}$ if only the first term is taken for the case of large distance,

$$\begin{aligned}-\sigma^{\pi}=\frac{3e^2a^2}{mc^2}\Big[&P_2(\cos\theta)r^{-3}+(6d^2-3a^2/2)P_4(\cos\theta)r^{-5}\\&+(15d^4-45a^2d^2/2+15a^4/8)P_6(\cos\theta)r^{-7}\\&+(-105a^2d^2+105a^4d^2/2-35a^6/16)P_8(\cos\theta)r^{-9}\\&+\cdots\cdots\cdots\Big].\end{aligned}\tag{16}$$

In the case of styrene, $\theta=\pi/2$ and C-H distance is 1.09A, and C-C distances are assumed from the bond-order calculated by simple LCAO method as C=C distance in the vinyl group : 1.36 A ; C−C distance between the vinyl and the phenyl groups : 1.47 A, and $a=1.39$A. The separation of two circular loops, $2d$, is taken as 0.9 A,$^{(13b)}$ 0.7 A,$^{(22)}$ and 1.28 A.$^{(13c)}$ With McWeeny's model, the values of the resonance integral β from −20 to −40 Kcal/mol were used and it is said that the observed values of the resonance energy for benzene are −36∼−41 Kcal/mol.$^{(24)}$ Using the above models, we evaluated the contribution of the pi-ring-current effect to the proton chemical shifts in styrene, and the results are summarized in Table II.

In Table II, it is shown that an order of magnitude of proton shifts is qualitatively interpreted by the pi-ring-current effect, but for H_3, the quantitative agreement between the observed value and the theoretical estimate is not satisfactory.

b. Magnetic anisotropy of neighboring carbon atom.

If the electronic currents in a molecule are divided into atomic contributions in the manner proposed by Saika and Slichter,$^{(6)}$ the proton magnetic moment is likely to experience a considerable magnetic field due to local circulations in the atom to which it is bonded. The simple way to estimate the magnitude of such an effect, that is the effect (iii) of Saika and Slichter, is to replace the currents on the other atoms by point magnetic dipoles at the center of atoms, which is the way adopted by Pople$^{(11)}$ and McConnell.$^{(9)}$

We calculated the secondary field due to the currents on the neighboring carbon atom in styrene, according to Pople's consideration.$^{(11)}$ The anisotropy of the local susceptibility on an atom can be separated into an anisotropy of the purely diamagnetic part (corresponding to the simple rotation with the Lamor frequency) and the paramagnetic part arising from the mixing of the ground state with excited electronic states by the magnetic field. In most atoms, the distribution of electrons is not likely to be very non-spherical, so it is expected that most of the anisotropy will arise from the paramagnetic part. Therefore, we evaluated the magnetic susceptibility due to the paramagnetic current on the neighboring carbon atom for vinyl function in general.

Each atom has labeled according to Fig. 1, and delocalized pi-LCAOMO's and localized sigma-LCAOMO's adopted in the present treatment were written as following.

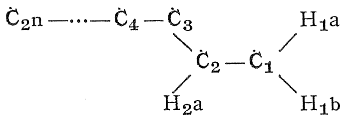


Fig. 1.

TABLE II The contribution of the ring-currents to the proton chemical shift of styrene.

Model		Proton chemical shift (ppm)			
		H_1	H_2	H_3	Hring
Point dipole approx.(13a)		0.00	−0.28	−0.35	−0.43
Two doughnuts-like loops (Eq. (16))	d = 0.00 A	0.00	−0.37	−0.47	−2.40
	d = 0.35 A	0.00	−0.34	−0.43	−1.97
	d = 0.45 A	0.00	−0.33	−0.41	−1.72
	d = 0.64 A	0.00	−0.29	−0.36	−1.19
McWeeny(13 d)	β = − 20 Kcal/mol	0.00	−0.26	−0.33	−2.01
	β = − 30 Kcal/mol	0.00	−0.38	−0.49	−3.02
	β = − 40 Kcal/mol	0.00	−0.51	−0.66	−4.02

Delocalized π-orbitals :

$$\psi_{\pi 1}=c_{11}\phi_1+c_{21}\phi_2+\cdots \quad \cdots+c_{2n1}\phi_{2n}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\psi_{\pi n}=c_{1n}\phi_1+c_{2n}\phi_2+\cdots \quad \cdots+c_{2nn}\phi_{2n} \tag{17}$$

$$\psi'_{\pi 1}=c'_{11}\phi_1+c'_{21}\phi_2+\cdots \quad \cdots+c'_{2n1}\phi_{2n}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\psi'_{\pi n}=c'_{1n}\phi_1+c'_{2n}\phi_2+\cdots \quad \cdots+c'_{2nn}\phi_{2n},$$

where c_{ri} is the coefficient of $2p_z$ orbital of the r-th carbon atom, ϕ_r, in the i-th occupied orbital, and the prime denotes those of unocupied pi-Mo's.

Localized σ-orbitals:

$$\begin{aligned}
\psi_{\sigma 1a} &= a_{1a}h_{1a}+b_{1a}\chi_{1a}\\
\psi_{\sigma 1b} &= a_{1b}h_{1b}+b_{1b}\chi_{1b}\\
\psi_{\sigma c} &= b_{1c}h_{1c}+b_{2c}\chi_{2c}\\
\psi_{\sigma 2a} &= a_{2a}h_{2a}+b_{2a}\chi_{2a}\\
\psi_{\sigma 2b} &= b_{2b}\chi_{2b}+b_{3b}\chi_{3b}\\
\psi'_{\sigma 1a} &= a'_{1a}h_{1a}+b'_{1a}\chi_{1a}\\
\psi'_{\sigma 1b} &= a'_{1b}h_{1b}+b'_{1b}\chi_{1b}\\
\psi'_{\sigma c} &= b'_{1c}\chi_{1c}+b'_{2c}\chi_{2c}\\
\psi'_{\sigma 2a} &= a'_{2a}h_{2a}+b'_{2a}\chi_{2a}\\
\psi'_{\sigma 2b} &= b'_{2b}\chi_{2b}+b'_{3b}\chi_{3b},
\end{aligned} \tag{18}$$

where h_{1a}, h_{1b}, and h_{2a} are ls-orbitals of H_{1a}, H_{1b} and H_{2a}, respectively, and three sp^2-hybridized orbitals for C_1 are given by

$$\begin{aligned}
\chi_{1a} &= \frac{1}{\sqrt{3}}(2s)_1+\frac{1}{\sqrt{6}}(2p_x)_1+\frac{1}{\sqrt{2}}(2p_y)_1\\
\chi_{1b} &= \frac{1}{\sqrt{3}}(2s)_1+\frac{1}{\sqrt{6}}(2p_x)_1-\frac{1}{\sqrt{2}}(2p_y)_1\\
\chi_{1c} &= \frac{1}{\sqrt{3}}(2s)_1-\sqrt{\frac{2}{3}}(2p_x)_1.
\end{aligned} \tag{19}$$

Three sp^2-hybridized orbitals for C_2 are

$$\begin{aligned}
\chi_{2c} &= \frac{1}{\sqrt{3}}(2s)_2+\sqrt{\frac{2}{3}}(2p_x)_2\\
\chi_{2a} &= \frac{1}{\sqrt{3}}(2s)_2-\frac{1}{\sqrt{6}}(2p_x)_2-\frac{1}{\sqrt{2}}(2p_y)_2\\
\chi_{2b} &= \frac{1}{\sqrt{3}}(2s)_2-\frac{1}{\sqrt{6}}(2p_x)_2+\frac{1}{\sqrt{2}}(2p_y)_2.
\end{aligned} \tag{20}$$

An sp^2-hybridized orbital for C_3 which perticiptates C_2-C_3 sigma-bond is

$$\chi_{3b} = \frac{1}{\sqrt{3}}(2s)_3+\frac{1}{\sqrt{6}}(2p_x)_3-\frac{1}{\sqrt{2}}(2p_y)_3. \tag{21}$$

The wave functions for the ground states are expressed by the Slater determinant,

$$\begin{aligned}
\Psi_0 = \left[(2n+10)!\right]^{-\frac{1}{2}}\cdot\sum_{p}\,(-1)^p p\,\psi_{\sigma 1a}(1)\,\alpha(1)\cdot\psi_{\sigma 1a}(2)\,\beta(2)\cdots\\
\cdots\psi_{\pi n}(2n+10)\,\beta(2n+10).
\end{aligned} \tag{22}$$

The excited states are constructed by promoting a single electron from an occupied to an unoccupied molecular orbital.

Using the method of evaluation adopted by Pople, (8) the local paramagnetic susceptibilities due to paramagnetic currents on carbon atoms C_1 and C_2, for the case of the external magnetic field is in x, y and z directions, respectively, are given by

$$
\begin{aligned}
\chi_1{}^{x} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[(b'_{1a})^2\sum_i^{\mathrm{occ.}}\frac{(c_{1i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 1a'}}+(b'_{1b})^2\sum_i^{\mathrm{occ.}}\frac{(c_{1i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 1b'}} \\
& +(b_{1a})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{1k})^2}{(\triangle E)_{\sigma 1a\rightarrow\pi k'}}+(b_{1b})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{1k})^2}{(\triangle E)_{\sigma 1b\rightarrow\pi k'}}\Big] \\
\chi_1{}^{y} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[\frac{1}{3}(b'_{1a})^2\sum_i^{\mathrm{occ.}}\frac{(c_{1i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 1a'}}+\frac{1}{3}(b'_{1b})^2\sum_i^{\mathrm{occ.}}\frac{(c_{1i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 1b'}} \\
& +\frac{4}{3}(b'_{1c})^2\sum_i^{\mathrm{occ.}}\frac{(c_{1i})^2}{(\triangle E)_{\pi i\rightarrow\sigma c'}}-\frac{4}{3}(b'_{1c}b'_{2c})\sum_i^{\mathrm{occ.}}\frac{c_{1i}c_{2i}}{(\triangle E)_{\pi i\rightarrow\sigma c'}} \\
& +\frac{1}{3}(b_{1a})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{1k})^2}{(\triangle E)_{\sigma 1a\rightarrow\pi k'}}+\frac{1}{3}(b_{1b})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{1k})^2}{(\triangle E)_{\sigma 1b\rightarrow\pi k'}} \\
& +\frac{4}{3}(b_{1c})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{1k})^2}{(\triangle E)_{\sigma c\rightarrow\pi k'}}-\frac{4}{3}(b_{1c}b_{2c})\sum_k^{\mathrm{unocc.}}\frac{c'_{1k}c'_{2k}}{(\triangle E)_{\sigma c\rightarrow\pi k'}}\Big] \\
\chi_1{}^{z} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[\frac{2}{3}\frac{(b'_{1b}b_{1a})^2}{(\triangle E)_{\sigma 1a\rightarrow\sigma 1b'}}+\frac{2}{3}\frac{(b'_{1a}b_{1b})^2}{(\triangle E)_{\sigma 1b\rightarrow\sigma 1a'}} \\
& +\frac{2}{3}\frac{(b'_{1a}b_{1c})^2}{(\triangle E)_{\sigma c\rightarrow\sigma 1a'}}+\frac{2}{3}\frac{(b'_{1c}b_{1a})^2}{(\triangle E)_{\sigma 1a\rightarrow\sigma c'}} \\
& +\frac{2}{3}\frac{(b'_{1b}b_{1c})^2}{(\triangle E)_{\sigma c\rightarrow\sigma 1b'}}+\frac{2}{3}\frac{(b'_{1c}b_{1b})^2}{(\triangle E)_{\sigma 1b\rightarrow\sigma c'}}\Big]
\end{aligned}
\tag{23}
$$

$$
\begin{aligned}
\chi_2{}^{x} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[(b'_{2a})^2\sum_i^{\mathrm{occ.}}\frac{(c_{2i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 2a'}}+(b'_{2b})^2\sum_i^{\mathrm{occ.}}\frac{(c_{2i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 2b'}} \\
& -b'_{2b}b'_{3b}\sum_i^{\mathrm{occ.}}\frac{c_{2i}c_{3i}}{(\triangle E)_{\pi i\rightarrow\sigma 2b'}}+(b_{2a})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{2k})^2}{(\triangle E)_{\sigma 2a\rightarrow\pi k'}} \\
& +(b_{2b})^2\sum_k^{\mathrm{unocc}}\frac{(c'_{2k})^2}{(\triangle E)_{\sigma 2b\rightarrow\pi k'}}-b_{2b}b_{3b}\sum_k^{\mathrm{unocc.}}\frac{c'_{2k}c'_{3k}}{(\triangle E)_{\sigma 2b\rightarrow\pi k'}}\Big] \\
\chi_2{}^{y} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[\frac{4}{3}(b'_{2c})^2\sum_i^{\mathrm{occ.}}\frac{(c_{2i})^2}{(\triangle E)_{\pi i\rightarrow\sigma' c}}-\frac{4}{3}b'_{2c}b'_{1c}\sum_i^{\mathrm{occ.}}\frac{c_{1i}c_{2i}}{(\triangle E)_{\pi i\rightarrow\sigma' c}} \\
& +\frac{1}{3}(b'_{2a})^2\sum_i^{\mathrm{occ.}}\frac{(c_{2i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 2a'}}+\frac{1}{3}(b'_{2b})^2\sum_i^{\mathrm{occ.}}\frac{(c_{2i})^2}{(\triangle E)_{\pi i\rightarrow\sigma 2b'}} \\
& -\frac{1}{3}b'_{2b}b'_{3b}\sum_i^{\mathrm{bocc.}}\frac{c_{2i}c_{3i}}{(\triangle E)_{\pi i\rightarrow\sigma 2b'}}+\frac{4}{3}(b_{2c})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{2k})^2}{(\triangle E)_{\sigma c\rightarrow\pi k'}} \\
& -\frac{4}{3}b_{2c}b_{1c}\sum_k^{\mathrm{unocc.}}\frac{c'_{1k}c'_{2k}}{(\triangle E)_{\sigma c\rightarrow\pi k'}}+\frac{1}{3}(b_{2a})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{2k})^2}{(\triangle E)_{\sigma 2a\rightarrow\pi k'}} \\
& +\frac{1}{3}(b_{2b})^2\sum_k^{\mathrm{unocc.}}\frac{(c'_{2k})^2}{(\triangle E)_{\sigma 2b\rightarrow\pi k'}}-\frac{1}{3}b_{2b}b_{3b}\sum_k^{\mathrm{unocc.}}\frac{c'_{2k}c'_{3k}}{(\triangle E)_{\sigma 2b\rightarrow\pi k'}}\Big] \\
\chi_2{}^{z} = {} & \frac{e^2h^2}{8\pi^2m^2c^2}\Big[\frac{2}{3}\frac{(b'_{2b}b_{2a})^2}{(\triangle E)_{\sigma 2a\rightarrow\sigma 2b'}}+\frac{2}{3}\frac{(b'_{2a}b_{2b})^2}{(\triangle E)_{\sigma 2b\rightarrow\sigma 2a'}} \\
& +\frac{2}{3}\frac{(b'_{2a}b_{2c})^2}{(\triangle E)_{\sigma c\rightarrow\sigma 2a'}}+\frac{2}{3}\frac{(b'_{2c}b_{2a})^2}{(\triangle E)_{\sigma 2a\rightarrow\sigma' c}} \\
& +\frac{2}{3}\frac{(b'_{2b}b_{2c})^2}{(\triangle E)_{\sigma c\rightarrow\sigma 2b'}}+\frac{2}{3}\frac{(b'_{2c}b_{2b})^2}{(\triangle E)_{\sigma 2b\rightarrow\sigma c'}}\Big],
\end{aligned}
\tag{24}
$$

where sums over i and k are over all occupied and unoccupied orbitals and $(\triangle E)_{i\rightarrow j}$ is the energy for the excitation $i\rightarrow j$.

Then, we require the average value of the paramagnetic shielding constant over the three directions x, y and z in the molecule. If the applied field H makes and angle θ_x with the C-H bond line for x direction and so on, then the average paramagnetic shielding at the proton due to induced paramagnetic susceptibilities at the carbon atom is

$$\sigma^{anis}=-\frac{1}{3R^3}\left[\chi^x(3\cos^2\theta_x-1)+\chi^y(3\cos^2\theta_y-1)+\chi^z(3\cos^2\theta_z-1)\right], \qquad (25)$$

where R is the C-H internuclear distance.

In the case of styrene, internuclear distances were assumed to be the values used previously, and an angle HCH is put as 120°, because the values based on the measurement are not available. The calculated paramagnetic susceptibilities using the atmic values assumed above, LCAO's obtained by Yonezawa et al (25) and eqs. (23), (24), are shown in Table III. Thus, the calculated results of the contribution of the paramagnetic currents on carbon atoms to the shielding constants of protons were obtained as shown in Table IV. Hereafter, for simplicity, protons H_{1b}, H_{1a} and H_{2a} in Fig. 1 are denoted by H_1, H_2, and H_3, respectively.

In Table IV, the differences of proton chemical shifts due to the magnetic anisotropy of carbon atoms are shown to be -0.05 ppm for H_2 and -0.11 ppm for H_3 referred to H_1 as 0 ppm.

c. Local diamagnetic shielding of the hydrogen atom.

The contribution of local diamagnetic currents on the hydrogen atom itself can be estimated from the Lamb formula(4)

$$\sigma^{dia}=\frac{e^2}{3mc^2}\int\frac{\rho}{r}d\tau, \qquad (26)$$

where ρ is the electron density of the electrons associated with the hydrogen atom and is represented approximately by

TABLE III. The calculated paramagnetic susceptibilities at each carbon atom when the applied field is in x y and z directions, in units of $(eh/2\pi mc)^2$.

Carbon atoms \ Field directions	x	y	z
C_1	0.0692	0.0940	0.0431
C_2	0.0644	0.0889	0.0401
C_3	0.0709	0.0756	0.0370

TABLE IV. The contribution of the paramagnetic current to the proton chemical shift of styrene (in ppm, referred to H_1).

Carbons \ Protons	H_1	H_2	H_3
C_1	0.000	0.000	3.032
C_2	0.000	0.000	−2.925
C_3	0.000	−0.05	−0.218
Total	0.000	−0.05	−0.11

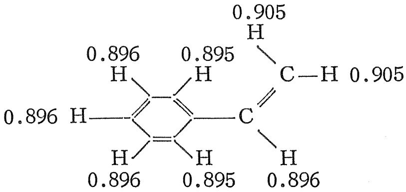
$$\rho = q_H \psi_{1s}^2, \tag{27}$$

where q_H is the total sigma-electron density of the hydrogen atom, and ψ_{1s} is 1s-atomic orbital. The integral is then easily evaluated

$$\sigma^{dia} = \frac{q_H e^2}{3mc^2 a_0} \cdot \delta = 17.8\delta \cdot q_H \times 10^{-6}, \tag{28}$$

where a_0 is the Bohr radius and δ is the effective nuclear charge in a hydrogen-like 1s-wave function.

The total sigma-electron density of the sigma-skeleton was evaluated by a delocalized LCAOMO calculation for saturated compounds.(29) The calculated electron densities of hydrogen atom in styrene were



Hence taking the coefficient of q_H, 25 tentatively, eq. (28) gives the lower field shift of about 0.25 ppm of H_3 resonance referred to H_1 and H_2 resonances.

d. The partial ring-current effect

A method of estimating the contribution of partial ring-currents on side chains to the shift, was given by Pople(13c).

As the value of the overlap integral of pi-orbitals between C_2—C_5 and C_2—C_4, is about 0.04 and that of C—C bond in the aromatic ring is about 0.25, the value of the resonance integral $m\beta$ ($m=0.16$) was assumed for C_2—C_5, C_2—C_4.

Following Pople, we obtained the ratio of the ring current of the phenyl group in styrene to that of benzene as shown in Table V, and the currents in the benzene ring and in the side-chain ring are given as follows:

$$J_B=\frac{8\pi^2\beta e^2H}{h^2c}\left\{2\times0.05128\,S_B+2\times0.00408\,S_\triangle\right\}$$
$$J_\triangle=\frac{8\pi^2\beta e^2H}{h^2c}\left\{-2\times0.00134\,S_B+0.00408\times2\,S_\triangle\right\}, \tag{29}$$

where S_B and $S_\triangle$ are areas of the benzene and the side-chain rings, respectively. The ratios of currents in side-chain rings to those or benzene are given as shown in Table VI.

Finally, if m is overestimated to be m=0.2, the contribution to the proton shift of the ring-current in side-chains of styrene is 0.03 ppm for H_3 and for H_2, 0.01 ppm.

§ 2-3. Results and Discussion

The proton chemical shifts of styrene have to be interpreted by considering additively various effects estimated above. The calculated and observed results for the proton shifts of styrene are summarized in Table VII. Table VII shows that the agreement of the calculated shifts with the observed values is fairly good but, quantitatively, it is not satisfactory, especially for the H_3 proton shift.

There will be discussions on some points. In the first place, for estimate of the diamagnetic shielding of the hydrogen atom, we tentatively adopted the effective nuclear charge for 1s-atomic orbital of the hydrogen atom in a molecule larger than unity ($\delta\sim1.4$), but the phisical foundation for this assumption is not so clear. The discussions on these points shall be appeared again in an article on the electron density and the shift.

TABLE V. The ratios of ring-currents in styrene and in benzene.

m	0	0.16	0.20
Jstyr. / Jbenz.	0.9193	0.9252	0.9493

TABLE VI. The ratios of the current of side-chains of styrene to that of benzene.

m	0	0.16	0.20
$J_\triangle$ / Jbenz.	0	0.0056	0.0141

Secondly, it is usually accepted that the styrene-molecule is in the same plane, but the information about the molecular plane of styrene was not able to be obtained. In stilbene derivatives, the possibility of twist of aromatic ring was discussed by Katayama et al.,(26) therefore we estimated the contribution of the twist of aromatic ring in styrene to the proton shift.

Adopting the model of two circular loops, the proton shift due to the effect of twist of the aromatic ring was evaluated as functions of the angle of twist for various loop separations and the results are shown in Fig. 2, in which φ means the angle of the ring about C_2—C_3 axis and the values of the shifts are relative to those of H_1.

TABLE VII. The calculated and observed proton chemical shifts (in ppm) of styrene.

Protons Effects	H_1	H_2	H_3
π–ring–currents*	0	−0.34	−0.43
Carbon–anisotropy	0	−0.05	−0.11
Looal diamag. shielding	0	0	−0.25
Partial ring–currents	0	−0.01	−0.03
Total	0	−0.40	−0.82
Observed values**	0	−0.50	−1.50

* Eq. (16) with d=0.35A. ** Ref. (17)-(20).

In Fig. 2, it is clearly seen that as the twisting angle of the aromatic ring becomes larger, the spectrum of H_2 is appeared at considerable higher field that of H_3. This is contrary trend to the observation and it seems to be acceptable that the molecule of styrene is in the same plane.

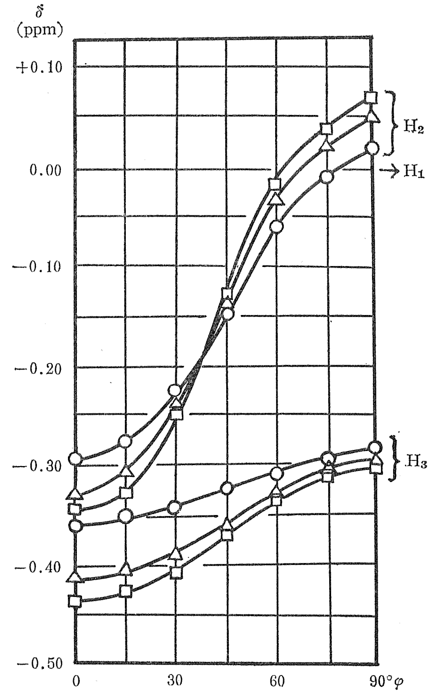


Fig. 2. Proton chemical shifts due to the effect of twist of the aromatic ring plane in styrene.
□ : d=0.35A, △ : d=0.45A, ○ : d=0.64A.

III. The β-Proton Shift of Vinyl Compounds

In the case of styrene, the chemical shift of beta-proton was able to be interpreted by considering the effect of pi-ring-currents, but for the chemical shift of alpha-proton, the quantitative agreement of the theoretical shift and the observed value was not necessarily good. Now, we consider the chemical shifts of beta-proton in some vinyl compounds.(27)

§ 3-1. Experimental values

The proton chemical shifts of some vinyl compounds were reported by Banwell et al(20) and Jackman et al,(28) which we adopted here. The results are shown in Table VIII.

There are two types of values of proton chemical shifts. One is the type that the resonance spectra of H_2 appear at lower field than the resonance field of H_1, to which $CH_2=CHF$, $CH_2=CHCl$ and $CH_2=CH\ C_6H_5$ belong. The other type is that the resonance field of H_2 is higher than that of H_1, to which $CH_2=CHCN$, $CH_2=CBrCH_3$ and $CH_2=CH\ Br$ belong. We referred these types to "styrene type" and "vinyl-bromide type", respectively.

§ 3-2. The Electron Density

The sigma-electron densities of vinyl compounds were reported by Fukui et al,(29) which are shown in Fig. 3. By these densities it is possible to interprete the trend that H_3 is resonated at lower field than that of other protns.

Secondly, the pi-electron densities of vinyl halides were also given by the same authors.(29) The results are shown in Fig. 4.

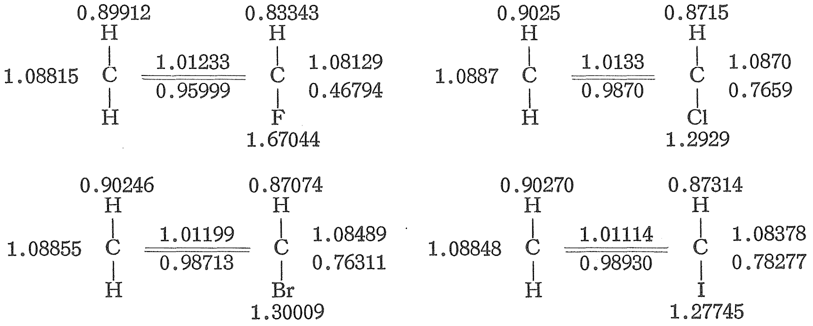


Fig. 3. The sigma-electron densities of vinyl halides.(29)

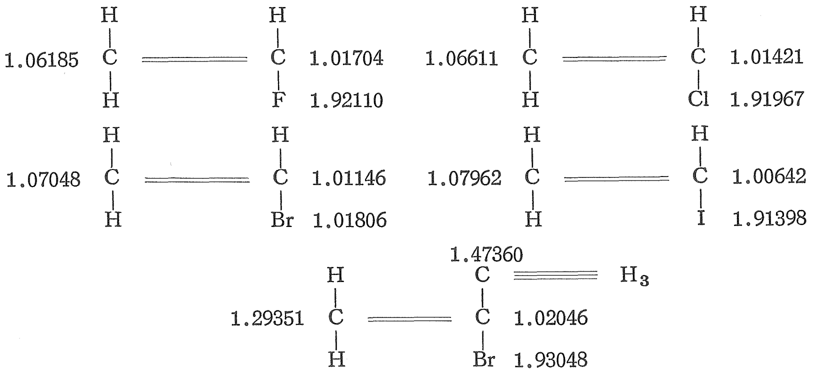


Fig. 4. The pi-electron densitites of vinyl halides.(29)

§ 3-3. The Magnetic Anisotropy of the Halogen Atom

According to Pople's formulation,(8) the contribution of the magnetic anisotropy of halogen atoms is given by

$$\chi^{x}{}_{l\to\pi}=\left(\frac{eh}{2\pi mc}\right)^{2}\sum_{j}^{unocc.}\frac{(c_X{}^{j})^{2}}{(\triangle E)_{l\to j}}. \tag{30}$$

$$\chi^{y}{}_{\sigma\to\pi}=\left(\frac{eh}{2\pi mc}\right)^{2}\left[\sum_{j}^{unocc.}\frac{1}{(\triangle E)_{\sigma\to j}}\left\{a^{2}(c_X{}^{j})^{2}+\sqrt{\frac{2}{3}}\,ab\,c_C{}^{j}c_X{}^{j}\right\}\right.$$
$$\left.+\sum_{i}^{occ.}\frac{1}{(\triangle E)_{i\to\sigma'}}\left\{(a')^{2}(c_X{}^{i})^{2}+\sqrt{\frac{2}{3}}\,a'b'c_C{}^{i}c_X{}^{i}\right\}\right], \tag{31}$$

$$\chi^{z}{}_{l\to\sigma}=\left(\frac{eh}{2\pi mc}\right)^{2}\frac{(a')^{2}}{(\triangle E)_{l\to\sigma'}}; \tag{32}$$

$$\sigma=-\frac{1}{3R^{3}}\left[\chi^{x}(3\cos^{2}\theta_x-1)+\chi^{y}(3\cos^{2}\theta_y-1)+\chi^{z}(3\cos^{2}\theta_z-1)\right], \tag{33}$$

where χ^{x}, for instance, is the paramagnetic susceptibility on the halogen atom induced by the applied external field in x direction, and l, π and σ mean lone-pair, pi- and sigma-orbitals, respectively, and LCAOMO's were written as

$\psi_\pi=\sum_j c_C{}^{j}\phi_C+\sum_j c_X{}^{j}\phi_X$	(unoccupied)
$\psi_\pi{}'=\sum_i c_C{}^{i}\phi_C+\sum_i c_X{}^{i}\phi_X$	(occupied)
$\psi_\sigma=a\phi_X+b\phi_C$	(bonding)
$\psi_\sigma{}'=a'\phi_X+b'\phi_C$	(antibonding)

The magnetic susceptibilities induced by the applied field H are calculated by Eqs. (30), (31) and (32) as shown in Table IX, and the beta-proton shifts of vinyl compounds due to these induced susceptibilities are given in Table X. Table X shows that the magnetic anisotropy of the halogen atom influences more diamagnetically on H_1 than H_2.

§ 3-4. The Effect of Dipolar Field

A method of estimating the effect of the bond moment on the proton chemical shift was formulated by Buckingham.(14) In his formulation, the effect on the proton chemical shift is given by

$$\triangle\sigma=-2\times10^{-12}E_z-10^{-18}E^{2}, \tag{34}$$

where E_z is the component in the bonding direction of the electric field E due to the dipole moment of the molecule or the bond.

TABLE VIII. β-proton shifts (in ppm) of vinyl compounds. (20), (28)

Compounds	$CH_2=CHF$	$CH_2=CHCl$	$CH_2=CHBr$	$CH_2=CHI$	$CH_2=CBrCH_3$	$CH_2=CHCH_3$
$(H_2\text{-}H_1)/H_1$	-0.34	-0.08	$+0.15$	—	$+0.2$	$+0.1$

TABLE IX. The inducad magnetic susceptibilities in the halogen atom (in units of $e^2h^2/4\pi^2m^2c^2$).

X	F	Cl	Br	I
χ^x	0.0077	0.0045	0.0089	0.0111
χ^y	0.0580	0.0546	0.0686	0.0833
χ^z	0.0641	0.0570	0.0661	0.0808

TABLE X. The proton chemical shifts (in ppm) due to the magnetic anisotropy of the halogen atom.

	$CH_2=CHF$	$CH_2=CHCl$	$CH_2=CHBr$	$CH_2=CHI$	$CH_2=CBrCH_3$
H_1	0.1726	0.1273	0.1259	0.1334	0.1283
H_2	0.0208	0.0546	0.0709	0.0871	0.0756

Now, this effect for vinyl bromide was evaluated as an example. If the bond moment $\mu=1.48\times10^{-18}$ esu is located at the midpoint of C-Br bond, Eq. (34) results,

$$\triangle\sigma(H_2)=-0.287 \text{ ppm}, \qquad \triangle\sigma(H_1)=-0.184 \text{ ppm},$$

and therefore

$$\delta=(H_2-H_1)/H_1=-104 \text{ ppm}.$$

Next, if the dipole moment of the molecule, $\mu_{mol}=1.41\times10^{-18}$ esu, is in the line connecting the midpoints of C-Br bond and C-C bond, the relation of the proton chemical shift and the position at which the dipole moment located is as shown in Fig. 5. In Fig. 5, R means the distance from the midpoint of C-Br bond.

§ 3-5. The Anisotropy of C-H Bond.

A formulation of estimating the effect of the anisotropy of bonds on the proton chemical shift was given by McConnell.(15a)

According his expression, the chemical shift due to the bond anisotropy $\triangle\chi$ is described as

$$\sigma=\frac{\triangle\chi}{R^3L_0}(1-\cos^2\theta), \qquad (35)$$

where L_0 is the Avogadro's number and R the distance between the proton and the midpoint of C-H bond.

By calculations, Eq. (35) is reduced to

$$\sigma(H_1)=-0.038\triangle\chi,$$

$$\sigma(H_2)=+0.025\triangle\chi. \qquad (36)$$

Values of the bond anisotropy reported by Narasimhan et al (^{15b}) are

$$\triangle\chi_{C-H}=+0.24\sim1.5 \text{ ppm}$$

$$\triangle\chi_{C-C}=1.48\sim2.95 \text{ ppm}$$

$$\triangle\chi_{C-H}<\triangle\chi_{C-C},$$

and then Eq. (36) results

$$\delta_{C-H}=(H_2-H_1)/H_1=-0.015\sim-0.095 \text{ ppm},$$

$$\delta_{C-C}=(H_2-H_1)/H_1=0.093\sim0.186 \text{ ppm},$$

$$|\delta_{C-H}|<|\delta_{C-C}|.$$

It is expected that the proton shifts of propyrene which are the vinyl bromide type are interpreted by the effect of the C-C bond anisotropy because of $\triangle\chi_{C-H}<\triangle\chi_{C-C}$.

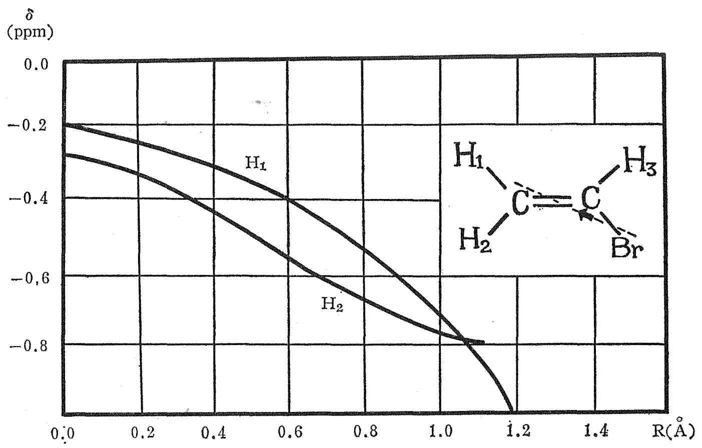


Fig. 5. The proton chemical shift of vinyl bromide due to the dipole moment of the molecule.

§ 3-6. The Results and Discussion

Of the effects evaluated above, the effect of the bond anisotropy was small compared with the other effects, and so this contribution was neglected, and the effect due to the dipolar field was assumed to be the same value, −0.1 ppm, for all compounds in question. Then, the final results of the proton chemical shift in the compounds become as tabulated in Table XI.

All the effects considered here bring the spectra of the proton H_1 to lower field. Except the case of vinyl bromide, theoretical proton shifts agree qualitatively, or at least in trends, with the observed shifts.

For vinyl bromide, it may be considered that if 4p-atomic orbital deformes, the effect of the magnetic anisotropy becomes larger.

IV. The Chemical Shift and the Electron Density

It is believed that the proton chemical shift is closely related to the total sigma-electron density of the hydrogen atom. The close relations between them were reported in paraffins,(30) alcohols,(31) vinyl compounds,(27) benzene derivatives(32) and halomethanes.(33)

§ 4-1. The Electron Densities

According to Ramsey's theory(3) of the chemical shift, it can be said that the variation of the sigma-electron density on a hydrogen atom by unity produces the shift of the proton spectra of 17.8ppm (cf. Eq. (28)). Therefore, if the main cause of the proton chemical shift is the electron density and the other effects are small, then the linear correlation between the proton shift and the electron density must be obtained and the constant of proportionality is expected to be about 17.8 ppm/electron.

In reality, however, the linear correlation of the same value of gradient 17.8 ppm/electron is not necessarily obtained in various compounds. The correlation of the proton chemical shifts and the sigma-electron density is graphically shown for vinyl halides in Fig. 6, where ethylene is adopted as reference.

TABLE XI. Calculated and observed shifts (in ppm) of β-protons of some vinyl compounds.

Compounds	Calculated shifts	Observed shifts(20)
$CH_2 = CHF$	−0.25	−0.34
$CH_2 = CHCl$	−0.17	−0.08
$CH_2 = CHBr$	−0.16	+0.15
$CH_2 = CHI$	−0.14	—
$CH_2 = CBrCH_3$	−0.15	+0.2
$CH_2 = CHCH_3$	+0.07	+0.1

On the other hand, for aromatic compounds, the proton chemical shifts were connected with the pi-electron densitites on the adjacent carbon atom, and attempts of obtaining the pi-electron densities from the observed proton chemical shifts were appeared.

In the work of Fraenkel et al,(34) the proton chemical shifts of $C_5H_5^-$ and $C_7H_7^+$ were interpreted by the electrostatic interactions between the charge localized in the pi-orbital of the carbon atom and the electrons in the C-H bond, and utilizing the results, the charge distributions of other aromatic systems were determined from the proton chemical shifts.

In their paper, it was assumed that the important contribution to the proton chemical shift is the charge on the carbon atom to which the hydrogen bonded, and that the variations of the charge-effect containing the total charge on the hydrogen atom, the diamagnetic anisotropy of the carbon atom and the paramagnetic current on the excess pi-electrons q, Then, the "charge shift" $\delta(q)$ of the aromatic hydrogen was given by

$$\delta(q)=aq, \tag{37}$$

and a constant a was determined empirically to be about +10 ppm/electron.

Similar works were published by some authors(35) and the values of a ranging from +10 to +15 ppm/electron were obtained.

§ 4-2. The Chemical Shift and the σ-π Interaction

In the sigma-electron densities used previously, the effect of pi-electrons was taken no account of. But the effect of pi-electrons on the proton chemical shift was discussed for the aromatic system by some workers, as mentioned above. Therefore, we calculated the sigma-electron densities into which the effect of pi-electrons was taken and discussed the correlation of the chemical shifts of the alpha-proton in vinyl halides with the modified sigma-electron densities.

Now, for the sigma-pi interaction, the "ω-technique"(36) was proposed by Wheland and Mann(37). They proposed that the value of the Coulomb integral α should be linearly related to the charge q and

$$\alpha_r=\alpha_0+\omega(1-q_r)\beta_0, \tag{38}$$

where, ω is a dimensionless parameter whose value may be so chosen as to give best agreement with experiment.

Using this method, it has been shown that the calculated dipole moments for hydrocarbons were improved (38) and the energy values for organic cations were refined.(39) The values proposed for the empirical parameter ω have ranged from 0.33 to 1.8, and the value $\omega=1.4$ seems now to be desirable.

We employed also this technique for calculating the modified sigma-electron densities, that is,

$$\alpha^{\sigma}=\alpha^{\sigma}_{0}+\omega(1-q^{\pi})\beta^{\sigma}_{0}. \tag{39}$$

This expression means that when many pi-electrons exist, the sigma-electrons are reduced by means of the electron repulsion. If $q^{\pi}=1$, $\alpha^{\sigma}=\alpha^{\sigma}_{0}$, but if $q^{\pi}<1$, the Coulombic attraction to the nucleus is increased.

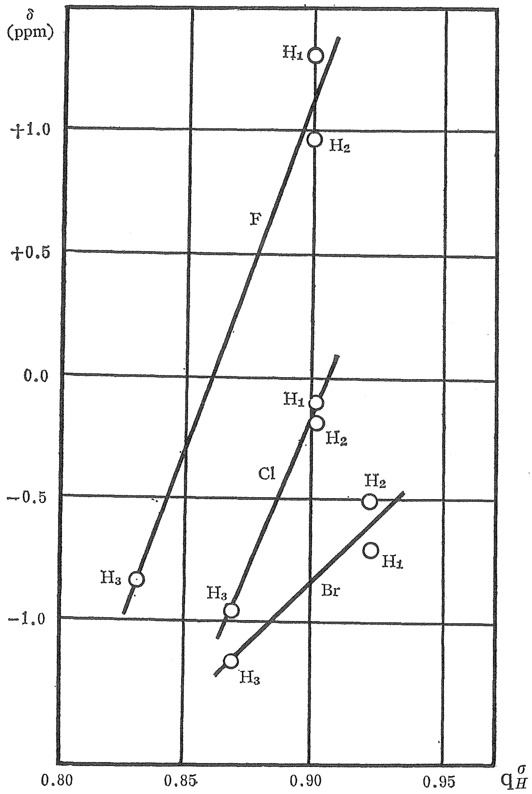


Fig. 6. The proton chemical shift δ in ppm and the sigma–electron density $q_{H^{\sigma}}$ for vinyl halides.

In order to calculate the sigma-electron densities of vinyl halides, the parameters shown in Table XII were chosen and the obtained sigma-electron densities employing the ω-technique, Eq. (39), are shown in Table XIII.

With the sigma-electron densities in which the effect of pi-electrons was considered, the chemical shifts of alpha-protons, H_1 and H_3, of vinyl halides were discussed. Here, the following two effects were evaluated:

TABLE XII. Parameters used in the claculation of sigma-electron densities of vinyl halides.
$\alpha_H=\alpha-0.2\beta;\beta_{CC}=\beta$ (adjacent), 0.38β(own); $\beta_{CH}=0.94\beta$.

X	α	$\omega=1.0$	$\omega=1,5$
F	α_{C_1}	$\alpha-0.062\ \beta$	$\alpha-0.093\ \beta$
	α_{C_2}	$\alpha-0.017\ \beta$	$\alpha-0.026\ \beta$
	α_F	$\alpha+0.779\ \beta$	$\alpha+0.819\ \beta$
Cl	α_{C_1}	$\alpha-0.066\ \beta$	$\alpha-0.099\ \beta$
	α_{C_2}	$\alpha-0.014\ \beta$	$\alpha-0.021\ \beta$
	α_{Cl}	$\alpha+0.380\ \beta$	$\alpha+0.420\ \beta$
Br	α_{C_1}	$\alpha-0.070\ \beta$	$\alpha-0.105\ \beta$
	α_{C_2}	$\alpha-0.011\ \beta$	$\alpha-0.017\ \beta$
	α_{Br}	$\alpha+0.332\ \beta$	$\alpha+0.373\ \beta$
I	α_{C_1}	$\alpha-0.080\ \beta$	$\alpha-0.120\ \beta$
	α_{C_2}	$\alpha-0.006\ \beta$	$\alpha-0.009\ \beta$
	α_I	$\alpha+0.286\ \beta$	$\alpha+0.329\ \beta$

TABLE XIII. The sigma-electron densities for vinyl halides.

X	H	Sigma-electron densities		
		$\omega=0$	$\omega=1.0$	$\omega=1.5$
F	H_1	0.89912	0.93450	0.93657
	H_2	0.89912	0.93450	0.93657
	H_3	0.83343	0.84605	0.84561
Cl	H_1	0.90250	0.93330	0.94874
	H_2	0.90250	0.93330	0.94874
	H_3	0.87150	0.87583	0.87843
Br	H_1	0.90246	0.93480	0.95104
	H_2	0.90246	0.93480	0.95104
	H_3	0.87084	0.87247	0.87416
I	H_1	0.90270	0.93934	0.95771
	H_2	0.90270	0.93934	0.95771
	H_3	0.87314	0.87165	0.87173

(i) The magnetic shielding due to the electrons on the hydrogen atom, —— this effect was evaluated by the Lamb's corrections, Eq. (28),

$$\sigma^{dia}=17.8.\ \delta.\ q_H\ (\mathrm{ppm}). \qquad (28)$$

(ii) The magnetic anisotropy of the halogen atom, —— for this effect only paramagnetic currents were considered and the results obtained previously were used, that is Eqs. (30), (31), (32) and (33).

The calculated proton chemical shifts due to these two effects are shown in Table XIV. In the table, it was indicated that if $\omega=0$, the trend of magnitudes of the calculated shifts is parallel to that of the observed, but the absolute values of calculated values are small compared with the observed shifts, and also that if $\omega=1.0$ or 1.5, the trend of magnitudes of the calculated shifts is contrary to that of the observed, but the absolute values of the calculated shifts approach to the observed values.

In the assumption employed in the calculation, however, there will be some argument. For instance, it seems to be over-estimation to assume ω to be 1.0 or 1.5 and it should be noted that in the present step, the method is not self-consistent in the sense of no considering the effect of pi-electrons affected by sigma-electrons.

Now, more reasonable ω-technique including the effects of all electrons was applied to vinyl halides. That is, for the halogen atom X, three electrons were taken into account and for the carbon atom, four electrons were considered, then

$$\begin{aligned} \alpha_H{}^\sigma &= \alpha_H{}^{\sigma 0}+\omega(1-q_H{}^\sigma) \\ \alpha_X{}^\sigma &= \alpha_X{}^{\sigma 0}+\omega(3-q_X{}^\sigma-q_X{}^\pi) \qquad (40) \\ \alpha_C{}^\sigma &= \alpha_C{}^{\sigma 0}+\omega(4-\Sigma q_C{}^\sigma-q_C{}^\pi) \end{aligned}$$

Here, $\omega=0.2$, was chosen because it becames evident that this value of ω is reasonable to interprete a phenomenon in ESR measurements in some compounds.(40) The calculated electron densities with $\omega=0.2$ and the theoretical and observed chemical shifts in which only two effects considered above were taken into account, are shown in Table XV.

In order to calculate the proton chemical shift, the effects of the magnetic anisotropy of the halogen atom and Lamb's shielding were evaluated, however, in the calculation of the magnetic anisotropy of the halogen atom, only the paramagnetic term was estimated and the diamagnetic term was not taken into account. The diamagnetic term intends to shift the spectra of H_1 to the higher field, and results more negative value of the chemical shift defined here. Thus the contribution of this term to the proton chemical shift is desirable for vinyl fluoride but undesirable for vinyl chloride and bromide (cf., Table XV). But, it seems probably that the contribution of the diamagnetic term is negligibly small for the present case.

TABLE XIV. The calculated α-proton chemical shifts using the electron densities obtained with the ω-technique.

Compds.	Effects	Calculated shifts			Observed
		$\omega = 0$	$\omega = 1.0$	$\omega = 1.5$	shifts (20)
$CH_2=CHF$	(i)	−1.1692	−1.5744	−1.6191	−2.14
	(ii)	0.4470	0.4470	0.4470	
	Total	−0.7222	−1.1274	−1.1721	
$CH_2=CHCl$	(i)	−0.5518	−1.0230	+1.2515	−0.86
	(ii)	0.2852	0.2852	0.2852	
	Total	−0.2666	−0.7378	+0.9663	
$CH_2=CHBr$	(i)	−0.5646	−1.1095	+1.3685	+0.46
	(ii)	0.2613	0.2613	0.2613	
	Total	−0.3033	−0.8482	+1.1072	
$CH_2=CHI$	(i)	−0.5252	−1.2049	−1.5305	—
	(ii)	0.2861	0.2861	0.2861	
	Total	−0.2401	−0.9188	−1.2444	

TABLE XV. The calculated sigma-electron densities (ω=0.2) and the α-proton chemical shifts, $(H_3-H_1)/H_1$ ppm.

Compounds	Electron densities		α-proton shifts	
	H_1	H_2	Calculated	Observed
$CH_2=CHF$	0.9242	0.8186	−1.4339	−2.14
$CH_2=CHCl$	0.9332	0.8773	−0.7084	−0.86
$CH_2=CHBr$	0.9334	0.8779	−0.7271	−0.46
$CH_2=CHI$	—	—	—	—

TABLE XVI. The sigma-electron densities (ω=0.2) and the proton chemical shift of vinyl halides.

Compounds	Sigma-electron densitites			Chemical shifts*		
	H_1	H_2	H_3	H_1	H_2	H_3
$CH_2=CHF$	0.9242	0.9242	0.8186	1.12_7	0.93_9	-1.28_7
$CH_2=CHCl$	0.9332	0.9332	0.8773	-0.23_7	-0.24_5	-1.25_5
$CH_2=CHBr$	0.9334	0.9334	0.8779	-0.82_6	-0.62_1	-0.42_1
$CH_2=CHI$	—	—	—	—	—	—

* Subtracted the calculated shift due to the magnetic anisotropy of the halogen atom from the observed value of the chemical shift.

Secondly, in the approximation used in the calculation of the magnetic anisotropy, p-orbitals are to be used, and so in the case of the chlorine or bromine atoms, sp or 4p-orbitals are treated in the calculation. Therefore, it is inferred that because the energy differences of sp or 4p-orbitals and d-orbital are small, the calculated anisotropy effect becomes to be doubtful. To improve the calculation, it may be a way to consider the hybridization of (spd).

The sigma-electron densities calculated with $\omega=0.2$ and the proton chemical shifts of vinyl halides are tabulated in Table XVI and graphed in Fig. 7. These data indicated that the gradient of the lines of the proton chemical shift versus the sigma-electron densities for each vinyl halide equals nearly to 20 ppm/electron density, which is compared with 17.8～27 ppm ($\delta=1\sim1.5$ in eq. (28)).

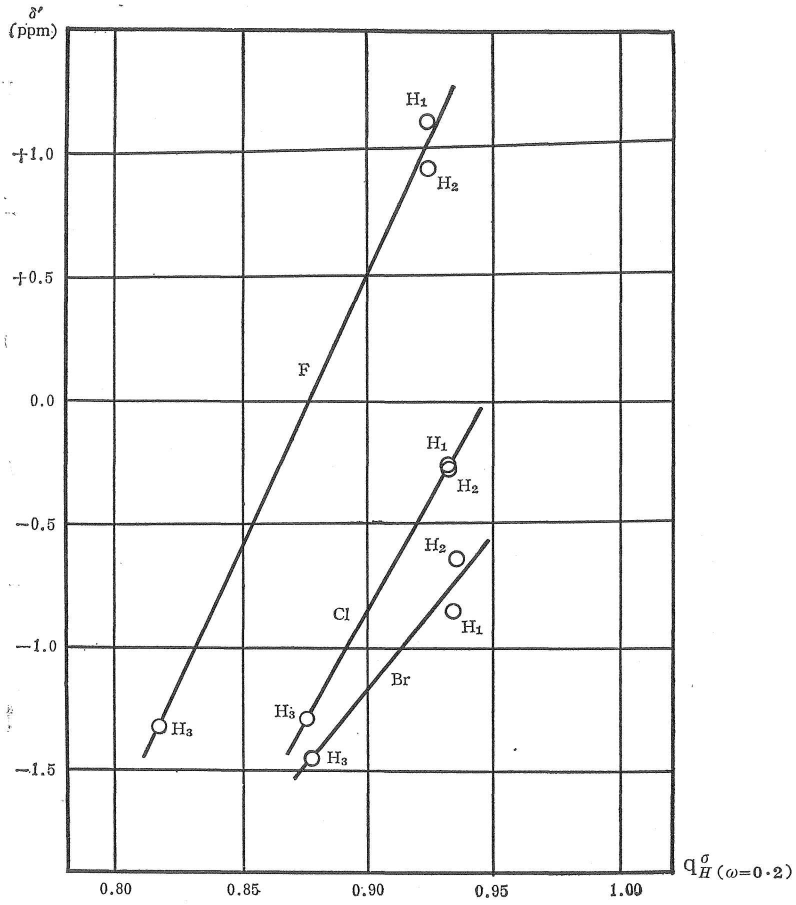


Fig. 7. Plots of the calculated sigma-electron densities versus the proton chemical shifts subtracted the calculated shifts due to the magnetic anisotropy of X from the observed shifts.

V. Conclusion

Various problems on the chemical shifts of styrene and vinyl halides were semi-empirically studied.

It is shown that the proton chemical shift of styrene is able to be interpreted by the effects of the induced currents in the aromatic ring, the magnetic anisotropy of the carbon atom and the local diamagnetic shielding of the hydrogen atom, and that the causes of the proton chemical shift of vinyl halides are mainly the effects of the magnetic shielding of electrons on the hydrogen and the paramagnetic anisotropy of the halogen.

It can be concluded from the arguments on the electron densities and the chemical shift, that if ω-technique is employed to calculate the sigma-electron densities, the relation of the calculated sigma-electron density with $\omega=0.2$ to the proton chemical shift is in good agreement with Lamb's expression.

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