A STUDY OF THE CHEMICAL SHIFTS OF SIMPLE HYDROCARBONS

AND THEIR HALOGENATED DERIVATIVES

Frank E. Hruska

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To My Parents

Who lacked college degrees

But not the wisdom and generosity to guarantee mine.

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ABSTRACT

A linear correlation with Q is found for the shifts
of protons or fluorines placed <u>ortho</u> or <u>cis</u> to the
substituent in monosubstituted benzenes, ethylenes, propenes,
monofluorobenzenes, and perfluorobenzenes. The substituent
X corresponds to H, F, Cl, Br, I, and Q equals P/Ir^3 where P
is the polarizability of the C-X bond, r is the C-X bond
length, and I is the first ionization potential of atom X.
The correlation is useful for predicting some as yet unknown
shifts in the above compounds. The significance of this
correlation is discussed in an inconclusive manner. The
interpretation of Q suggests a substantial contribution to
the proton chemical shift in unsaturated compounds from the
paramagnetic term in Ramsey's formulation of chemical shifts.

The chemical shift of the proton in the 1- (or α-)
position in 1- substituted propenes is discussed in the light
of current shielding theories. The observed trends are not
readily accounted for by a van der Waals, magnetic anisotropy,
electric field or inductive interaction with the substituent
nor by a combination of interactions. It is suggested that

the α-proton shifts may be accounted for by a combination of inductive and Q-type interactions but no strong support can be given for this suggestion.

The methyl proton shifts cannot be accounted for by current theories of magnetic shielding. The energy barriers to the internal rotation of the methyl group in ethane and in halogenated propenes are discussed. The magnitudes of these barriers suggest the presence of a substantial interaction between the substituent and the methyl protons which should be reflected in a considerable range of methyl proton shifts in cis 1-halopropenes. No such range is observed. A suitable explanation for these shifts cannot be put forth.

The solvent effects on the shifts of some 1-halopropenes are discussed. The solvent effects in benzene provide evidence for the presence of a dipole-induced dipole interaction between solute and solvent molecules but suggest that a dispersive interaction between solute and solvent is also important.

Evidence is given for the formation of weak hydrogen bonds between acetone and the 1- (or α-) and 2- (or β-) protons of 1-halopropenes. It is suggested that the acetone shift of the α-proton is due primarily to hydrogen bonding whereas the acetone shift of the β-proton is due to approximately equal

contributions from hydrogen bonding and reaction field effects.

A linear correlation exists between the proton shifts of some alkyl chlorides and some hydrocarbons and the occupation numbers of the hydrogen 1s orbitals in the C-H bonds. The occupation numbers are those given by the self-consistent group orbital and bond electronegativity method. The application of this correlation to the prediction of starting values for occupation numbers, to the derivation of bond anisotropies in ethylene and acetylene, and to the prediction of hydrogen-bonded shifts of C-H protons is discussed. The correlation suggests that the proton shift in these instances is a function mainly of the local electron density.

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CHAPTER I

INTRODUCTION

1-1   Introduction to Chemical Shifts*

For a fixed value of the radiofrequency field there
is a value of the main magnetic field at which a bare proton
will resonate. This field is given by

$$H = \frac{2\pi\nu}{\gamma} \qquad\qquad 1.1$$

where ν is the frequency of the radiofrequency field and γ
is the gyromagnetic ratio of the proton. Fortunately the
resonant field of chemically combined protons is not a
function of ν and γ alone but in addition chemical structure
has a small but interesting effect. This results from the
magnetic screening of the nucleus by the extranuclear electrons
and by neighbouring nuclei. Thus the field which must be
applied in order that the resonance condition be satisfied
will vary from molecule to molecule. These secondary magnetic

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*Treatments of chemical shift theory can be found in a number
 of textbooks (1).

fields at the nucleus (except those due to spin-spin coupling) are proportional to the applied field strength. If ΔH is the difference between the applied field (H_o) and the actual field at the nucleus (H), then

$$\frac{\Delta H}{H_o} = \frac{H - H_o}{H_o} = \text{constant} = \sigma \qquad 1.2$$

The constant σ is called the shielding constant and is a function of the electronic environment of the resonant nucleus.

For the sake of convenience some resonant field other than that of a bare nucleus is used as a reference. The standard for proton resonances, for example, is the resonant field of the methyl protons of tetramethylsilane (TMS). Then a unitless parameter δ, called the chemical shift, is defined by

$$\delta = \frac{H_s - H_r}{H_r} \qquad 1.3$$

where H_s and H_r are the resonant fields for a particular nucleus in the sample under investigation and for the reference nucleus, respectively. Using 1.1, equation 1.3 can be re-written more conveniently as

$$\delta \text{ (ppm)} = \frac{\Delta \nu \times 10^6}{\text{oscillator frequency in c/s}} \qquad 1.4$$

where $\triangle \nu$ is the separation in c/s of the resonant positions of the sample and reference. The sideband technique of calibrating NMR spectra makes 1·4 a convenient definition of δ .

The foremost problem confronting NMR spectroscopists lies in the understanding of the nature of the electric and magnetic fields which are manifest in the chemical shift. This perplexing problem resolves itself into measurement of σ and δ *, followed by interpretation of σ in terms of present knowledge of molecular structure.

1-2   Theoretical Evaluation of the Chemical Shift

Fifteen years have elapsed since the classic observation of the chemical shift phenomenon in the ethyl alcohol spectrum (2). Since then many approaches to its evaluation have been tried, each with its own merits and shortcomings. Summaries of the main attempts are given below.

A) Approach of Lamb

Lamb (3) attempted the first evaluation of nuclear screening in terms of the electron density about the nucleus.

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* σ and δ are related by the expression $\delta = (\sigma_s - \sigma_r) \times 10^6$ where s and r refer to sample and reference.

The effect of a uniform external magnetic field $\underline{H}$ on an electron in a spherically symmetric orbital is to induce a component of angular velocity along the direction of $\underline{H}$ (4). This angular frequency is given by

$$w = \frac{eH}{2mc} \qquad\qquad 1.5$$

where w is the angular, or Larmor precession frequency, e and m are the electronic charge and mass, respectively, and c is the velocity of light. At the nucleus a diamagnetic secondary field is produced. Extending this idea to a spherically distributed electron density, it was shown that the shielding constant was given by

$$\sigma = \frac{4\pi e^2}{3mc^2} \int_{0}^{\infty} r \rho(r)\,dr \qquad\qquad 1.6$$

where r is the distance from the nucleus to a point where the electron density has the value $\rho(r)$ (4). Lamb's equation 1.6 is limited in that it is strictly valid only for atoms in an S state. It requires that the electrons be free to move in circular paths about $\underline{H}$; in molecules this freedom does not exist (4).

B) Approach of Ramsey

Since the Lamb formulation was useful only for atoms which experienced a spherical electrical potential, Ramsey (5) put forth a more general expression for the magnetic shielding of nuclei in molecules. Using perturbation theory Ramsey could express the over-all shielding as a sum of two terms (4).

$$\sigma = \sigma_L + \sigma_P . \qquad\qquad 1\cdot7$$

The first term, in its expanded form, is similar to the Lamb expression. The integral in $1\cdot6$ is now taken over all electrons in the molecule. Physically it corresponds to what the shielding would be if the whole electronic structure revolved about the nucleus in question with the Larmor precession frequency. The second or paramagnetic term effectively corrects for the hindrance to the free diamagnetic circulation. In quantum mechanical terms, this hindrance corresponds to a mixing of excited electronic states with the ground state of the molecule.

Slichter (6) presents an equivalent but somewhat different approach. He breaks down the calculation of σ into two parts:

1. the determination of the electric currents produced

   in the molecule by the external magnetic field and

2. the calculation of the magnetic field at the resonant

   nucleus produced by these currents.

It is useful to consider the total current density as having

a diamagnetic current associated with the ground state and

a paramagnetic current associated with the excited states

(6). These currents flow in concentric circles but in

opposite directions and have opposite effects on σ --the

diamagnetic currents increase σ while the paramagnetic

currents decrease σ . The paramagnetic contribution is

relatively large if the excited states are readily accessible,

that is, if the excitation energies are small. For example,

Newell (7) finds σ_L = 32.5 ppm and σ_p = -5.6 ppm for the

hydrogen molecule, where the excitation energies are

relatively large.

C) Other Approaches to an Interpretation of the Chemical Shift

In 1954 Saika and Slichter (8) took the next important

step in the formal theory of chemical shifts by suggesting

that the overall nuclear screening could be subdivided into

three separate contributions:

1. The diamagnetic shielding by the electrons centered on the nucleus in question, σ_D.

2. The paramagnetic correction for these electrons due to lack of spherical symmetry in their distribution, σ'.

3. The combined effects of diamagnetic and paramagnetic currents on other atoms, σ_0. σ_0 may be either positive or negative.

Theory indicates that variations in the paramagnetic contribution are the dominant cause of fluorine-19 (8) and carbon-13 (9) chemical shifts. The range of fluorine* shifts is 875 ppm. (11) and 225 ppm for carbon* shifts (12). For all nuclei except protons σ_0 is relatively unimportant (12). Proton shifts in common organic compounds have an approximate range of 20 ppm. (13) while σ_0 may contribute as much as 2 ppm. (14); it is felt that variations in the diamagnetic term are the dominant factors in proton resonance while variations in the paramagnetic term are expected to make much smaller contributions (15).

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*The isotopes with mass number 13 and 19 are to be understood for carbon and fluorine.

Pople, Bernstein and Schneider (16) suggest a fourth contribution arising from the magnetic fields of interatomic currents. It is of particular importance for aromatic molecules in which the pi electrons are delocalized in the ring but it has been suggested that interatomic flow of electrons through the sigma bond framework of the cyclopropane ring may explain the unusually high proton resonant fields in these compounds (17). An indication of the size of this contribution is given by the work of Waugh and Fessenden (10); they estimate a low field or paramagnetic proton shift of 1.5 ppm. due to the ring current in benzene.

Karplus and Das (18) use LCAO theory and Ramsey's equation to express the magnetic shielding in terms of three localized bond parameters - ionic character, hybridization and double bond character. Application of their formulation to substituted fluorobenzenes provides an approximate explanation of the available experimental fluorine shifts and permits the rough prediction of shift values for other compounds. In ortho-difluorobenzenes anomalous fluorine shifts (the "ortho effect") are observed and explained in terms of charge repulsion between the neighbouring fluorine atoms.

Lauterbur (19) and Spiesecke and Schneider (20)
suggest on empirical grounds that the shielding of a carbon
atom varies linearly with the corresponding pi-electron
density ρ. This leads to an expression for the chemical
shift relative to benzene $\Delta\sigma$:

$$\Delta\sigma = \alpha(\rho - 1) \qquad\qquad 1.8$$

where α is a positive constant with a value of about 160 ppm.
(21). Karplus and Pople (9) suggest that variations in the
diamagnetic contributions are too small to account for the
observed proportionality constant; circulations on other
atoms are not expected to contribute more than one or two
ppm. Thus the main contribution must originate in the local
paramagnetic term. They formulate an MO theory of carbon
shifts in conjugated molecules and demonstrate that there is
a significant local-charge dependence which agrees in sign
and order of magnitude with the experimentally established
correlation. The calculations are roughly borne out by the
measured shifts in some alternant hydrocarbons (9).

The proton resonance shift in aromatic molecules tends
to reflect the pi-electron density on the carbon atom to

which the proton is bonded (22). Schaefer and Schneider

(23) state that evidence exists for a simple linear

correlation between the shift δ and the local excess

charge $\Delta \rho$ on the bonded carbon atom.

$$\delta = k \Delta \rho \qquad\qquad 1.9$$

where δ is the proton shift relative to that in benzene

and k is a constant with a value of about 10 ppm. per

electron. They derive density distributions for eleven

aromatic species and find strong support for this simple

empirical correlation. There is evidence, however, that k

may vary considerably from system to system (58).

We may conclude that to this date the theoretical

calculations of chemical shifts show very roughly the

trends observed experimentally. These a priori calculations

of chemical shifts are subject to many approximations; exact

evaluations are possible only if the exact wave functions

are known but these are almost certain to elude chemists for

some time. It seems fair to say that current interpretations

of the voluminous NMR shift data leave much to be desired.

For this reason the empirical correlations described in

Chapters II and IV seem justified.

1-3 Semi-Empirical Approach to Chemical Shifts

The various factors influencing nuclear screening
have been divided into two main categories:

1) Intramolecular effects resulting from changes in
   the substituents in the molecule in which the
   resonant nucleus is found.

2) Intermolecular, or solvent, effects; variations in
   the magnetic and electric properties of the solvent
   may alter the nuclear screening. For example,
   hydrogen bonding to the solvent results in a para-
   magnetic proton shift.

Intramolecular effects only are considered here.
They are conveniently subdivided into (A) electronic, and
(B) magnetic effects. The former effects alter the electronic
density at the resonant nucleus while the latter result from
the magnetic fields of distant electronic currents.

A) Electronic Effects

The electronic effects are readily assigned to one of
three changes: (a) changes in the electron-withdrawing power
of substituents via inductive or mesomeric mechanisms, (b)
changes in permanent electric fields which are present as a

result of unsymmetrical charge distribution in polar bonds

and (c) changes in van der Waals forces. A brief discussion

of these shielding mechanisms follows.

(ai) The inductive effect

The electrostatic action transmitted via the bonds

in a molecule is referred to as induction. In the series

CH_3-X (X = I, Br, Cl, F) the electron density at the methyl

proton is expected to decrease gradually from X = I to X = F.

This is reasonable since the order is that of increasing

electronegativity (24). The diamagnetic contribution to the

proton shielding is reduced with a consequent low-field shift

of the resonant field. Spiesecke and Schneider (25) find

the proton shift in methyl fluoride 2.15 ppm. to low field of

that in methyl iodide. This paramagnetic effect is also

observed in the carbon resonances of the methyl halides where

a low-field shift of 98 ppm. is found by substituting fluorine

for iodine (25).

The inductive effect should decrease as the number of

intervening bonds increases. In the series CH_3-CH_2-X

(X = I, Br, Cl, F) the trend in the methyl shifts can no

longer be predicted on the basis of substituent electron-

withdrawing power and is in fact opposite to the trend found

in the methyl-X series (25). This indicates that if the inductive effect reaches the β-protons it is greatly attenuated and more than compensated for by factors operating in a sense opposite to that of electronegativity. The reversed trend is also observed in the β-carbon resonance (25).

It is reasonable to expect the resonance position of a nucleus to vary uniformly with the substituent electronegativity in those instances where the inductive effect is of primary importance. Such correlations of proton shifts were first observed by Shoolery (26) and Dailey (27). The internal chemical shift, $\delta(CH_3) - \delta(CH_2)$, in a variety of substituted ethanes was linearly related to the substituent electronegativity by the relation (27)

$$E_x = 0.695 \left[\delta(CH_3) - \delta(CH_2) \right] + 1.71 \qquad 1.10$$

where E_x is the Pauling electronegativity of the substituent X and the proton shifts are in ppm. Equation 1.10 predicts a zero internal shift for $E_x = 1.71$; this shift is zero in tetraethyl lead while $E_{Pb} = 1.8$ (25). It also predicts a negative internal shift for $E_x < 1.71$; in tetraethylsilane this shift is -0.33 ppm while $E_{Si} = 1.8$ (25).

Lauterbur (28) and Schneider (25) observe that within a group of closely related compounds carbon chemical shifts show a regular variation with Pauling electro-negativities. Extensive fluorine shift measurements on compounds of the type XF_n indicate a low-field displacement with increasing electronegativity of the central atom (29, 30). This implies two effects of increasing electronegativity, both leading to paramagnetic shifts (31): (a) a reduction in the electron density about the fluorine and (b) a decrease in the spherical symmetry about the fluorine nucleus with increasing covalency of the X-F bond.

(aii) The mesomeric effect

In unsaturated systems it is apparent that mesomeric interactions can lead to significant shifts. Substituents on the phenyl group with electron pairs which are conjugated with the ring alter pi-electron densities at the ortho and para positions. These changes induce secondary changes at the meta position; in general, the mesomeric interactions will disturb the entire electronic structure of an unsaturated system.

From his study of dissociation constants of substituted benzoic acids, Hammett (32) was able to assign σ_m and σ_p

values to various substituent groups which were related to
the ability of the substituent to alter electron density
at the meta and para carbon atoms. It is not surprising
that these σ constants correlate chemical shifts at meta
and para positions. Gutowsky (33) finds linear relationships
for fluorine shifts in monosubstituted fluorobenzenes which
fit the equations

$$\delta_m = -5.92\ \sigma_m \qquad\qquad 1.10$$

$$\delta_p = -17.9\ \sigma_p + 4.84 \qquad\qquad 1.11$$

The order of the σ_m values parallels that of
substituent electronegativity. Thus the primary mode of
substituent interaction at the meta position is thought to
be inductive in nature (34). Equation 1.14 below indicates
that at the para position the resonance interaction is
significantly more important than the pi-inductive interaction.

Taft (35) finds that equations 1.12 to 1.14 are capable
of reproducing observed fluorine shifts with greater accuracy
than can be achieved by single σ values.

$$\delta_m = -6.1\ \sigma_I + 0.5 \qquad\qquad 1.12$$

$$\delta_p - \delta_m = -18.8\ \sigma_R + 0.6 \qquad\qquad 1.13$$

$$\delta_p = -6.1\, \sigma_I - 18.8\, \sigma_R + 0.11 \qquad\qquad 1.14$$

The constants σ_I and σ_R are separated inductive and mesomeric reactivity parameters determined by Taft and co-workers (35, 37). Equations such as 1.14 are of doubtful value since they contain three adjustable variables, including the constant term (38).

Schneider (20) suggests three main objections to the use of Hammett and modified Taft constants as criteria for predicting chemical shifts:

1. The σ constants are derived from kinetic data on benzoic acids. Because of mutual interaction of the substituents the electronic effects experienced by the carboxyl group in meta-nitrobenzoic acid may be different from those experienced by a meta-hydrogen in nitrobenzene.

2. The parameters are properties of the transition state while shift measurements are made on molecules in the ground state. There is no reason to expect identical electronic structures in the two states.

3. Magnetic effects of the substituent are neglected.

b) The effect of electric fields from polar bonds

In addition to the inductive and mesomeric effects there is an electrostatic interaction which originates at the polar bonds in the molecule and operates through space or via the solvent molecules. These fields alter the electron density at various parts of the molecule and result in characteristic shifts. Buckingham (39) formulated a relationship between the electric field at a proton and the chemical shift contribution which arises. It is assumed that the effect of a field acting along a C-H bond is to increase or decrease the electron density about the proton. A field perpendicular to the C-H bond destroys the axial symmetry of the electron distribution; this reduction in symmetry increases the paramagnetic contribution with a consequent low-field shift.

Buckingham's equation is

$$\sigma_E = -aE_z - bE^2 \qquad\qquad 1.15$$

where E_z is the component of the electric field $\underline{E}$ acting along the C-H bond (E_z is positive if it withdraws electrons from the proton) and $\underline{a}$ and $\underline{b}$ are constants found to have the

values of 2×10^{-12} and 10^{-18}, respectively. The various

fields acting on the proton are evaluated by dipolar

expressions (40). Alternate treatments of this field

effect exist but each suffers from its approximate nature.

(See for example Dewar (41)).

Boden et al (42) determined the ortho-fluorine shifts

in monosubstituted perfluorobenzenes C_6F_5X (X = F, Cl, Br, I).

These shifts are accounted for by changes in the ionic and

double bond character of the C-F bond, calculated by the

method of Prosser and Goodman (43), with contributions from

the dipolar fields and van der Waals effects (see below).

c) The van der Waals effect

Buckingham et al suggest that the London dispersion

forces between solute and solvent (commonly referred to as

van der Waals forces) may cause significant low-field

chemical shifts in proton magnetic resonance. The effects

are always paramagnetic (44). Linder and co-workers (45)

found that no interaction other than the van der Waals needs

be invoked to explain the gas-to-solvent shifts of methane.

A low-field shift of 0.7 ppm was observed for methane in

methylene iodide (44). On this basis intramolecular proton

dispersion shifts as large as -1 ppm can be expected (46).

Raynes et al derive an expression for the mean-square of the fluctuating electric field at a distance r from a polarizable atom (47).

$$\bar{E}^2 = \frac{3\alpha I}{r^6} \qquad\qquad 1.16$$

α is the atomic static polarizability and I is a mean excitation energy, taken to be the ionization potential of the atom. Boden (42) uses 1·16 and Buckingham's expression 1·15 to evaluate the van der Waals fluorine shift in a study of the C_6F_5X series. (Appropriate a and b values for fluorine are used in 1·15). Intramolecular dispersion effects are not readily dealt with quantitatively. However, Yonemoto (69) has shown that the effect of a fluorine atom at $3\overset{\circ}{A}$ from a proton is not significant, but a chlorine atom at the same distance may deshield the proton by about 0.3 ppm. Qualitatively, the methyl proton shifts in halogenated methanes as well as α-proton, β-proton and β-carbon shifts in halogenated ethanes can be rationalized in this fashion (46).

B) Magnetic Effects

The intramolecular magnetic effects on nuclear magnetic shielding are understood in terms of the diamagnetic and

paramagnetic circulations induced by the applied magnetic field at points distant from the resonant nucleus. Theoretically, it is possible to evaluate the magnetic field due to these currents. On averaging over the random orientations of the molecule in the magnetic field these secondary fields will vanish unless the magnitudes of the induced currents are dependent on the orientation, that is, unless there exists a local anisotropy in the magnetic susceptibility of the distant electron group. The differences $X_{zz} - X_{xx}$ and $X_{zz} - Y_{yy}$ are called the anisotropies of the susceptibility tensor where the X_{ii} are the principal susceptibilities of the tensor. For molecules with a three-fold or higher principal axis there is only one anisotropy

$$\triangle X = X_{/\!/} - X_{\perp} \qquad\qquad 1.17$$

where $X_{/\!/}$ is the susceptibility along the principal axis and $X_{\perp}$ is the unique value perpendicular to it (48). Bond anisotropies are also defined by equation 1.17. Now, $X_{\perp}$ is an average of the two susceptibilities in directions perpendicular to the bond axis, i.e., $X_{/\!/} = X_{zz}$ and $X_{\perp} = 1/2 \; (X_{xx} + X_{yy})$.

McConnell (49) treats the problem of the long-range, or anisotropic, shieldings due to the distant electrons. He assumes that the secondary magnetic fields at the nucleus arise from a point dipole. His expression may be written as

$$\Delta \sigma = \frac{(1 - 3 \cos^2 \theta)\Delta X}{3R^3 N}$$ 1.18

where $\Delta \sigma$ is the contribution to the shielding of a nucleus, ΔX is the local anisotropy of the distant electrons, R is the separation between the resonant nucleus and the centre of the dipole while θ is the angle between the vector R and the dipole axis. N is the Avogadro number.

Spiesecke and Schneider (20, 25) assume that deviations of the proton and carbon shifts from electronegativity plots are rough estimates of this magnetic anisotropy effect. The deviations indicate that the C–X bond anisotropies (X = F, Cl, Br, I) are negative and become more so with increasing atomic number of X. Numerical values of bond anisotropies can be determined from experimental shifts using 1.18; these anisotropies can be used to make quantitative predictions of shifts in other compounds (50). For instance, Narisimhan and Rogers (51) suggest reasonable values of ΔX_{C-C} (1.50 x 10^{-6} to 3.0 x 10^{-6} cm3/mole) and ΔX_{C-H} (0.24 x 10^{-6} to

1.5×10^{-6} cm^3/mole) from a study of propane. Reddy and
Goldstein (52) apply their method of comparing proton
shifts with bonded carbon-hydrogen coupling constants;
they find Δ X$_{c-c}$ to be 10.0×10^{-6} cm^3/mole. A recent
review discusses such evaluations from a general viewpoint
(48).

The ring current effect is due to the unusually
large magnetic anisotropy of the aromatic pi electrons (48).
When the applied magnetic field is perpendicular to the
plane of the aromatic molecule, a large diamagnetic current
results; this current is greatly reduced when the field lies
in the plane of the molecule. MO calculations (53-55)
indicate that substituents may donate or withdraw at most 0.1
pi electron per carbon from the ring. This represents a 10%
change in the ring current; using the Waugh and Fessenden
value of 1.5 ppm for the ring current effect in benzene (10),
we can estimate a range of 0.15 ppm for proton shifts in
substituted benzenes.

There is some uncertainty as to the exact value of
the anisotropy of the benzene ring. Pauling (67) has
calculated this anisotropy classically. He assumes that
under the influence of the applied magnetic field the six

pi electrons are set into motion with the Larmor precession frequency in a superconducting current flowing about a circular loop. He assumes also that the other electrons contribute equally to the three principal components of the magnetic susceptibility while the ring current contributes only to the component along the axis perpendicular to the plane of the molecule. In other words his value of $\Delta X = -49.6 \times 10^{-6}$ cm^3/mole is attributed entirely to the ring current. This value is substantially smaller than the experimental value of -59.7×10^{-6} cm^3/mole (66). Hoarau (74) suggests that only part of the total anisotropy arises from the ring current. Significant contributions arise from the anisotropy of the σ bonds and from that due to the localized p pi electrons. Dailey (66) obtains a value of ΔX for benzene equal to -55.8×10^{-6} cm^3/mole by adding a quantum mechanical value of the ring current contribution (-33.3×10^{-6} cm^3/mole), the σ -bond contribution (-5.3×10^{-6} cm^3/mole) and the localized p pi-electron contribution (-17.2×10^{-6} cm^3/mole). This value is not very different from the experimental value.

Dailey et al (73) have measured the proton chemical shifts of protons in a series of condensed hydrocarbons such

as napthalene and anthracene and compared them with the
shifts calculated with the Pauling classical value of
-49.6×10^{-6} cm^3/mole for the benzene ring anisotropy.
The experimentally observed chemical shifts are
substantially smaller than the calculated values. The
two sets of results are, however, linearly related. Dailey
(66) concluded that the part of the diamagnetic anisotropy
which is effective in determining the chemical shift is
considerably less (about -31.2×10^{-6} cm^3/mole) than the
Pauling figure and is in fact near the figure obtained in
newer quantum mechanical calculations. The remaining
contribution to the total observed diamagnetic anisotropy,
if due entirely to the localized anisotropies, can be shown
to have a surprisingly small influence on the _relative_
chemical shifts for the condensed hydrocarbons considered
(66). Pople (68) has shown that the localized anisotropy
contributes about -0.7 p.p.m. to the shift of benzene _relative
to ethylene_. This contribution is subject to considerable
error but suggests that the Waugh and Fessenden value of -1.5
p.p.m. is not entirely attributable to the ring current.

Several difficulties arise in the evaluation of the
magnetic effects on proton shielding. They are:

a) McConnell's equation 1·18 has been shown to be

strictly valid only if the shielded nucleus is at

least six bond lengths from the anisotropic electrons

(48). Under these conditions the contribution will

be small and difficult to isolate (48).

b) The calculated magnetic field depends critically on

the position of the point dipole. In fact, slight

movement of the dipole may change the sign of the

shielding contribution. (See Appendix II).

c) Values of ΔX which depend on a separation of the

anisotropic shift from other contributions to the

observed shift may have a considerable range (48, 56).

Indeed some derived values of ΔX require that the

susceptibility along a C-C bond be paramagnetic.

This is absurd (48). Calculations of the anisotropy

of the benzene ring also indicate considerable

uncertainty in this value.

1-4   The Nature of the Problem

A vast amount of chemical shift data has been collected

but as yet there is little agreement as to the origin of these

shifts. This thesis attempts to explain the trends observed

in a limited number of compounds. In Chapter II an attempt

is made to correlate proton and fluorine shifts in some

unsaturated compounds with the ionization potential of the

halogen substituents. In Chapter III the α- and methyl

proton shifts of 1-halopropenes are discussed in terms of

the effects described in this chapter.* An attempt is also

made to improve on current theories of solute-solvent

interactions. In Chapter IV an attempt is made to correlate

proton shifts in substituted methanes and ethanes with the

calculated electron densities of the protons.

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*The 1-carbon which is attached to the halogen in the
 1-halopropenes is also referred to as the α-carbon. The
 2-carbon is then a β-carbon.

CHAPTER II

A NEW CORRELATION OF SOME OBSERVED SHIFTS
WITH MOLECULAR PARAMETERS

2-1 Need for Further Empirical Correlations

A new empirical correlation is presented here. It
correlates proton and fluorine shifts for ortho and cis
positions in monosubstituted benzenes, ethylenes and
perfluorobenzenes (Figure 2·1). The substituent X in all
cases is either halogen or hydrogen. A discussion and
criticism of current approaches to the explanation of these
shifts follows.

The observed proton shifts in the ortho position
correlate well with the para-proton shifts (57). This is
taken as evidence that the variation in the pi-electron
density at the carbon atom is the predominant effect
determining the shifts at these positions. Furthermore HMO
calculations of pi-electron density predict the observed
trends (58).

This ortho-para correlation is not found for iodo-,
bromo-, and chlorobenzenes (59). (Deviations are even more

FIGURE 2·1

The chemical shift of the underlined nucleus in each series

of compounds is used in the new correlation described in

this chapter.   The substituent X is either hydrogen or

halogen.
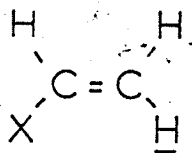
Vinyl-X
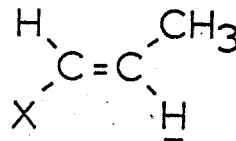
Trans
1-substituted
propene
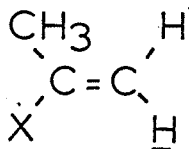
2-Substituted
propene
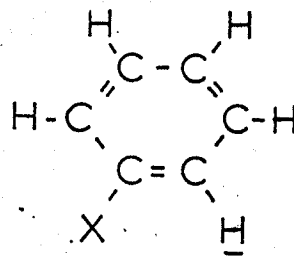
Monosubstituted
benzene
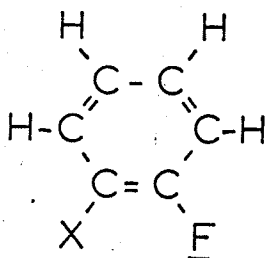
Ortho substituted
monofluorobenzene
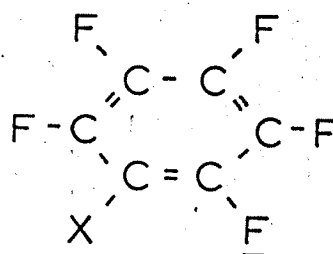
Monosubstituted
perfluorobenzene

pronounced when the ortho-carbon shifts are considered (58)).
The deviations are not accounted for by pi-electron density
calculations. Failure of the calculations to account for
these anomalies strongly suggests that factors other than
pi electrons become important in determining the observed
shielding in the ortho position (58).

Spiesecke and Schneider (25) conclude that the low-
field deviations of β-proton shifts in halogenated ethanes
from electronegativity plots could be explained on the basis
of the C-X bond anisotropy. Since the spatial relation
between halogen and ortho-proton on the benzene ring and
between halogen and β-proton in ethanes is similar, it
seemed logical to extend their explanation to the ortho-
proton (20). The deviations from electronegativity plots
on the one hand and those from pi-electron density calculations
on the other are indeed to low field (20, 58).

Several difficulties with the anisotropy model were
listed in Chapter I. Furthermore, use of the model leads to
a number of other inconsistencies (57):

1. If the magnetic anisotropy shifts at the ortho- and para-
   protons are calculated, equal contributions are predicted.
   However, because the para shift correlates with HMO

calculations this effect is assumed to be negligible at this position.

2. The size of the anisotropy shift should be the same regardless of the resonant nucleus. However, the anomalous fluorine shifts are twenty times larger than the analogous proton shifts (33, 42, 59).

For the above reasons the anisotropy model must be discounted as a suitable explanation for the ortho deviations.

Boden et al (42) suggest that a likely origin of the ortho effect is the presence of permanent and time-dependent (van der Waals) electric fields. The ortho-fluorine shift in the series C_6F_5X (X = halogen) are accounted for by use of the above fields (page 18). Schaefer et al (46) invoke van der Waals interactions to account for ortho-proton shifts in monosubstituted benzenes. The trend is to decreasing field with increasing size, and hence polarizability, of the halogen atom. Indeed the ortho-fluorine shifts show the same trend (Table 2·1, page 34).

If one attributes low-field deviations from electro-negativity or pi-electron density calculations to van der Waals forces, one assumes that those substituents which correlate must exert a van der Waals force which is linearly

related to the substituent electronegativity or to the electron density, or must exert no appreciable van der Waals force. There is no good reason for either assumption. (This also holds true for the anisotropy model (25)).

The β-proton shifts in the ethylenic compounds are not readily explained. These shifts decrease as the size of the halogen substituent increases (60). If a van der Waals interaction between the halogen and hydrogen were the main proton shielding mechanism at these positions, the larger effect at the more distant _trans_ proton remains unexplained. If the anisotropy in the magnetic susceptibility of the C-X bond were the predominant factor, equation 1·18 (with a negative sign for Δ X) would predict a trend opposite to that observed, that is, the β-proton resonances would be displaced to high field as the size of the halogen increases. Thus these proton shifts can not be satisfactorily explained by either of these two shielding mechanisms.

Mayo and Goldstein (60) find a rough correlation of vinyl halide proton shifts with the electronegativity of the halogen (after correction for C-X anisotropy). Points for the fluoride deviate by about 0.8 ppm in a range of 1.5

ppm. Unfortunately, the plots show diamagnetic shifts with increasing electronegativity. These shifts also correlate with μ/R where μ is the dipole moment of the C-X bond and R is the C-X bond length (60). At all positions diamagnetic shifts are observed with increasing μ/R; the dipole model predicts the exact opposite. De Wolfe and Baldeschwieler (61) do not attempt an explanation of the relative proton shifts in halogenated propenes.

2-2 The Q Correlation

As there appears to be no adequate theoretical model to explain these ortho- and cis shifts, an exact empirical correlation seems worthwhile. The halogens and hydrogen are suitable substituents for such correlations since considerable shift data is available. The substituent X and the resonant nucleus bear the same spatial relationship in each series (Figure 2·1, page 28), that is, they are separated by two single and one double bond and occupy cis positions with respect to the double bond. For this reason it is reasonable that an empirical correlation in one series should be manifest in a second series.

The proton and fluorine shifts indicated in Figure

2·1 are found to correlate with the quantity Q where Q is

given by

$$Q = \frac{P}{Ir^3},\qquad\qquad 2\cdot 1$$

P is the polarizability of the C-X bond, r is the C-X bond

length and I is the first ionization potential of X.

In Table 2·2 (page 35) the bond and atomic parameters

for X = H, F, Cl, Br and I are given. The ionization

potentials for the free atoms are taken since no data are

available on bond excitation energies. In Table 2·1 (page

34) are given the chemical shift values. The data were

selected with the criterion that, if possible, the shift

measurements were made in a common inert solvent for each

set and that an internal reference was used. In this way

solvent effects and bulk susceptibility corrections (44)

were small or non-existent.

A) Proton Shifts

In Figure 2·2a the ortho-proton shifts in C_6H_5X are

plotted versus Q. The largest deviations from linearity

are about 1.5 c/s in a range of 40 c/s. In Figure 2·2b the

TABLE 2·1

Chemical shifts* of protons and fluorines in ortho or cis positions to the substituent X in some conjugated molecules. The resonant nucleus is underlined.

X	o-C$_6$H$_5$X[a]	cis CH$_2$ = CHX[b]	cis CH$_2$ = CXCH$_3$	cis CHX = CHCH$_3$[e]	o-C$_6$H$_4$FX[i]	o-C$_6$F$_5$X[j]
H	0	-318.0[c]	-293.0[f]	-344.0[f]	0	-23.4
F	18.5	-281.5[d]	-264.0[k]	-317.9[g]	25.9	0
Cl	-1.2	-324.0[d]	-301.5[d]	-349.2[h]	2.7	-21.7
Br	-13.4	-345.0[d]	-316.7[h]	-365.2[h]	-5.5	-29.7
I	-24.0	-371.3[d]	-	-	-19.3	-43.1

a In c/s at 60 Mc/s in cyclohexane solution. Reference 20.
b In c/s at 60 Mc/s from tetramethylsilane in tetramethylsilane.
c Reference 14.
d Reference 60.
e In c/s at 60 Mc/s relative to internal tetramethylsilane.
f In carbon tetrachloride solution. Reference 89.
g Pure compound. Reference 113.
h In cyclohexane or tetramethylsilane solution. Reference 114.
i In ppm. Reference 33.
j In ppm. in carbon tetrachloride. Reference 42.
k In CCl$_3$ F solution. Reference 61.
* Positive sign indicates resonance to high field of the reference.

TABLE 2·2

Parameters for the C–H and C–halogen bonds

X	r_{C-X} (A°)[a]	P_{C-X} $(\times 10^{24}\ cm^3)$[b]	I_X $(\times 10^{12}\ ergs)$[c]	$Q = P/I r^3$ $(\times 10^{-14}\ ergs^{-1})$
H	1.09	0.645	21.8	2.28
F	1.30	0.633	27.8	1.04
Cl	1.70	2.604	20.8	2.55
Br	1.85	3.754	18.8	3.16
I	2.05	5.752	16.7	3.98

[a] Reference 110.

[b] Reference 111.

[c] Reference 112.

FIGURE 2·2

(a) The <u>ortho</u>-proton shift, δ , in c/s at 60 M c/s in

monosubstituted benzenes is plotted versus $Q = P/Ir^3$.

The shifts are relative to benzene.

(b) The shift, δ , of the proton <u>cis</u> to the substituent

in the vinyl-X compounds is similarly plotted. The

shifts are relative to internal tetramethylsilane (TMS).

Data are taken from Tables 2·1 and 2·2. The substituent

X is indicated by its chemical symbol.
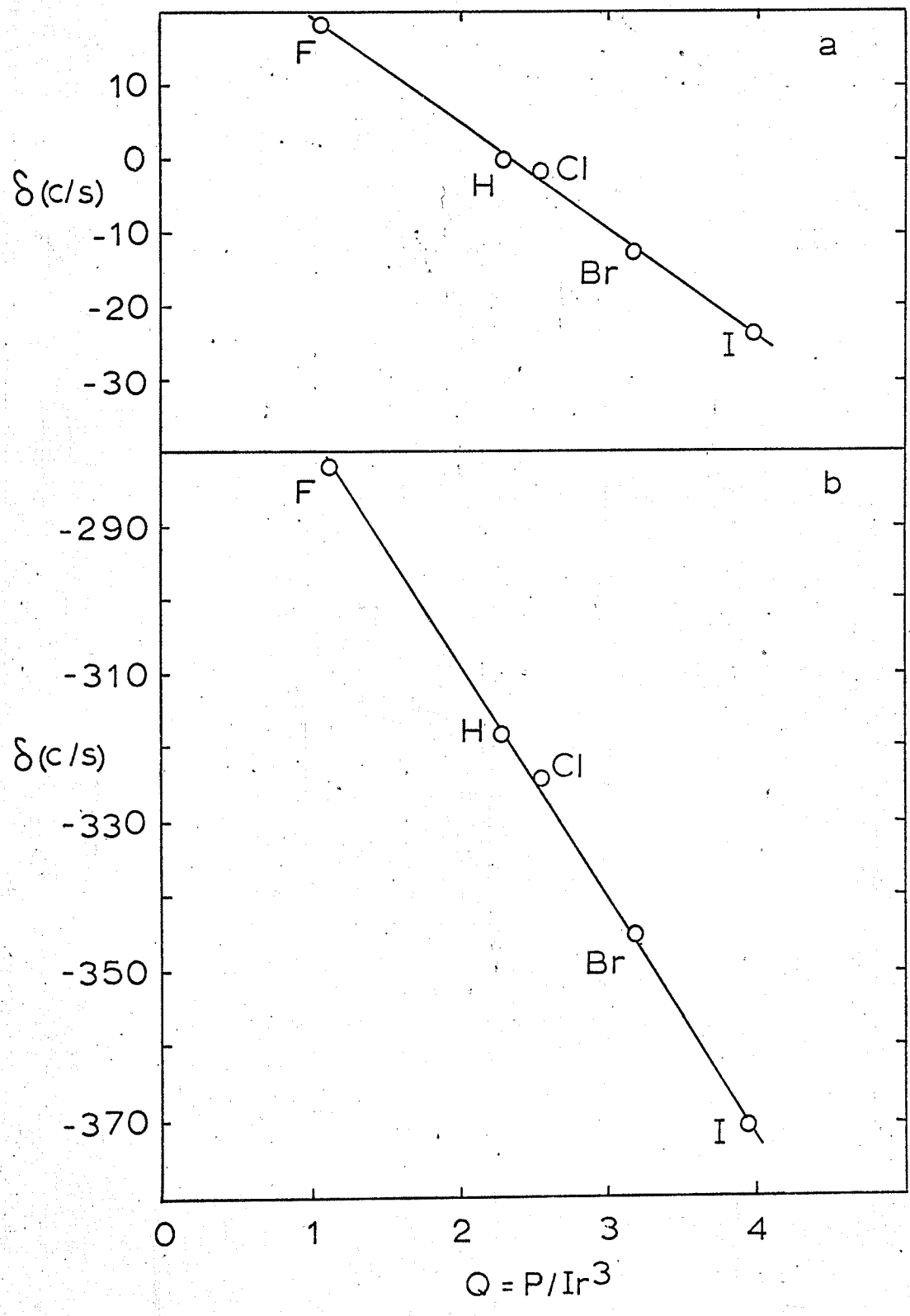
cis proton shifts in ethylene and the vinyl halides are
similarly plotted. The largest deviation is only 2 c/s in
a range of 90 c/s.

In Figure 2·3 the shift of the proton cis to the
substituent X in 1- and 2-halopropenes and in propene is
plotted versus the Q value of the substituent. Again a very
good straight line is obtained.

The above correlation plots can be used to predict
the unknown shifts of the iodopropenes. The points in
Figure 2·3 can be fitted by the method of least squares to
a straight line relationship between the shift δ and the Q
value of the substituent. The best straight line for the
1-substituted propenes is given by

$$\delta \text{ (c/s) } = -22.0 \times 10^{-14} \text{ Q} - 294.4 \qquad\qquad 2.2$$

The average deviation of the points from this line is only 0.9
c/s in a total range of 47.3 c/s (from X = F to X = Br). For
the 2-substituted propenes the best straight line is given by

$$\delta \text{ (c/s) } = -25.0 \times 10^{-14} \text{ Q} - 237.4 \qquad\qquad 2.3$$

The average deviation from this line is only 0.7 c/s in a
total range of 52.7 c/s. From the above equations the
predicted shifts are -382.0 c/s from TMS for 1-iodopropene and
-336.9 c/s from TMS for 2-iodopropene.

FIGURE 2·3

The shift, δ , of the proton <u>cis</u> to the substituent X

in 1- and 2-substituted propenes is plotted versus

$Q = P/Ir^3$. The shifts are in c/s at 60 M c/s relative

to internal TMS. Arrowheads indicate the predicted

values for the iodo compounds. Data are taken from

Tables 2·1 and 2·2. The substituent X is indicated by

its chemical symbol.
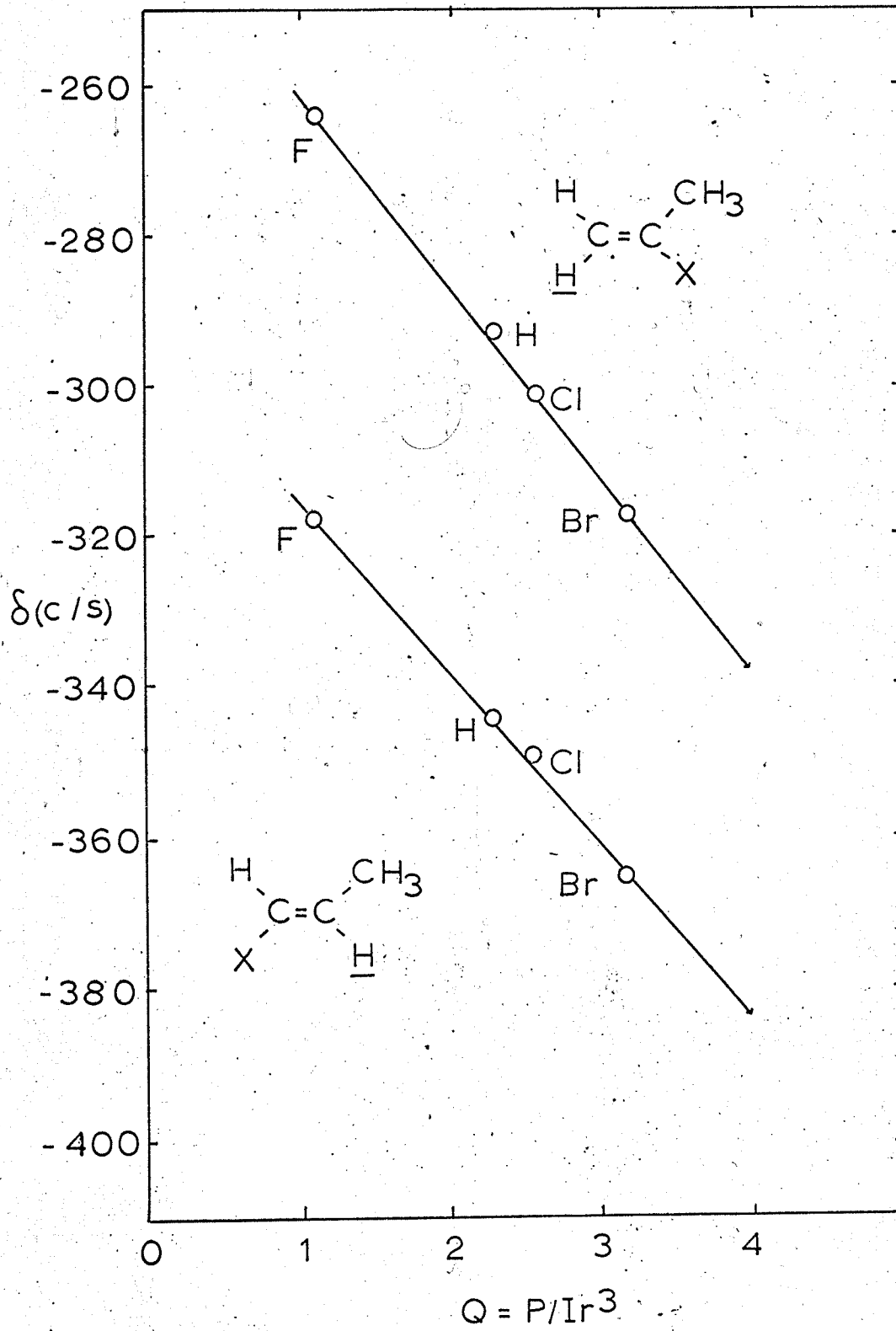
The cis and trans isomers of 1-iodopropene were prepared by the method described in Appendix I. NMR spectra were obtained for both isomers in a series of solutions, the results of which are given in Table 3·1. At this point the shift of the proton cis to the iodine (that is, the β-proton in the trans isomer) is of interest. This shift in TMS is -384.7 c/s, in good agreement with -382.0 c/s, the predicted value.

The 2-iodopropene was obtained from the Columbia Chemical Company as an impure mixture but was purified by gas chromatography as described in Appendix I. NMR spectra were obtained on a Varian DA-60 spectrometer equipped with an internal-lock system for 5 mole % solutions in carbon tetrachloride and in tetramethylsilane. The spectra were treated as first-order ARX_3 spectra in the notation of Pople, Bernstein and Schneider (127) where A and R correspond to the proton trans and cis to the iodine respectively and X_3 corresponds to the methyl protons. The results are given in Table 2·3.

The resonances at lowest field (centered at -350.8 c/s in TMS and -356.1 c/s in CCl_4) were readily assigned to the proton trans to the iodine on the basis of the observed coupling

TABLE 2·3

Proton Chemical Shifts* and Coupling Constants of 2-Iodopropene

Solution	Chemical Shifts			Coupling Shifts		
	A	R	X	J_{AR}	J_{AX}	J_{RX}
5% in TMS	-350.8	-332.7	-142.6	± 1.2	± 1.6	± 1.0
5% in carbon tetrachloride	-356.1	-335.2	-147.4	± 1.1	± 1.6	± 1.0

* Relative to internal TMS. A and R refer to the protons trans and cis to the iodine, respectively, and X refers to the methyl protons.

constants (J). The signs of the coupling constants cannot be obtained from a first-order analysis. However, the magnitudes are sufficient to allow an assignment to be made. The methyl couplings J_{AX} and J_{RX} are examples of "allylic" coupling constants. Experimental results and theoretical treatments of these coupling constants indicate that the interaction is larger if the coupled nuclei occupy cis rather than trans positions across the double bond, the difference being of the order of 0.5 c/s (88). Furthermore the value of the allylic coupling varies between 0 and 3 c/s. Since the larger repeated spacing common to the methyl proton resonances at highest field was repeated in the resonances at lowest field, these transitions were assigned to the proton cis to the methyl group. Therefore the chemical shift of the proton cis to the iodine (δ_R) is -335.2 c/s in carbon tetrachloride and -332.7 c/s in TMS. These values are in good agreement with the predicted value of -336.9 c/s.

B) Fluorine Shifts

In Figure 2.4a the ortho-fluorine shifts in ortho-substituted monofluorobenzenes are plotted versus Q. The average deviation of the points from the best straight line

FIGURE 2·4

(a) The chemical shift, δ , in ppm for the <u>ortho</u>-fluorine
in <u>ortho</u>-substituted fluorobenzenes is plotted versus
$Q = P/Ir^3$. The shift is relative to monofluorobenzene.

(b) The chemical shifts of the <u>ortho</u>-fluorine in mono-
substituted perfluorobenzenes are similarly plotted.
The shifts are relative to perfluorobenzene. The data
are taken from Tables 2·1 and 2·2. The substituent is
indicated by its chemical symbol.
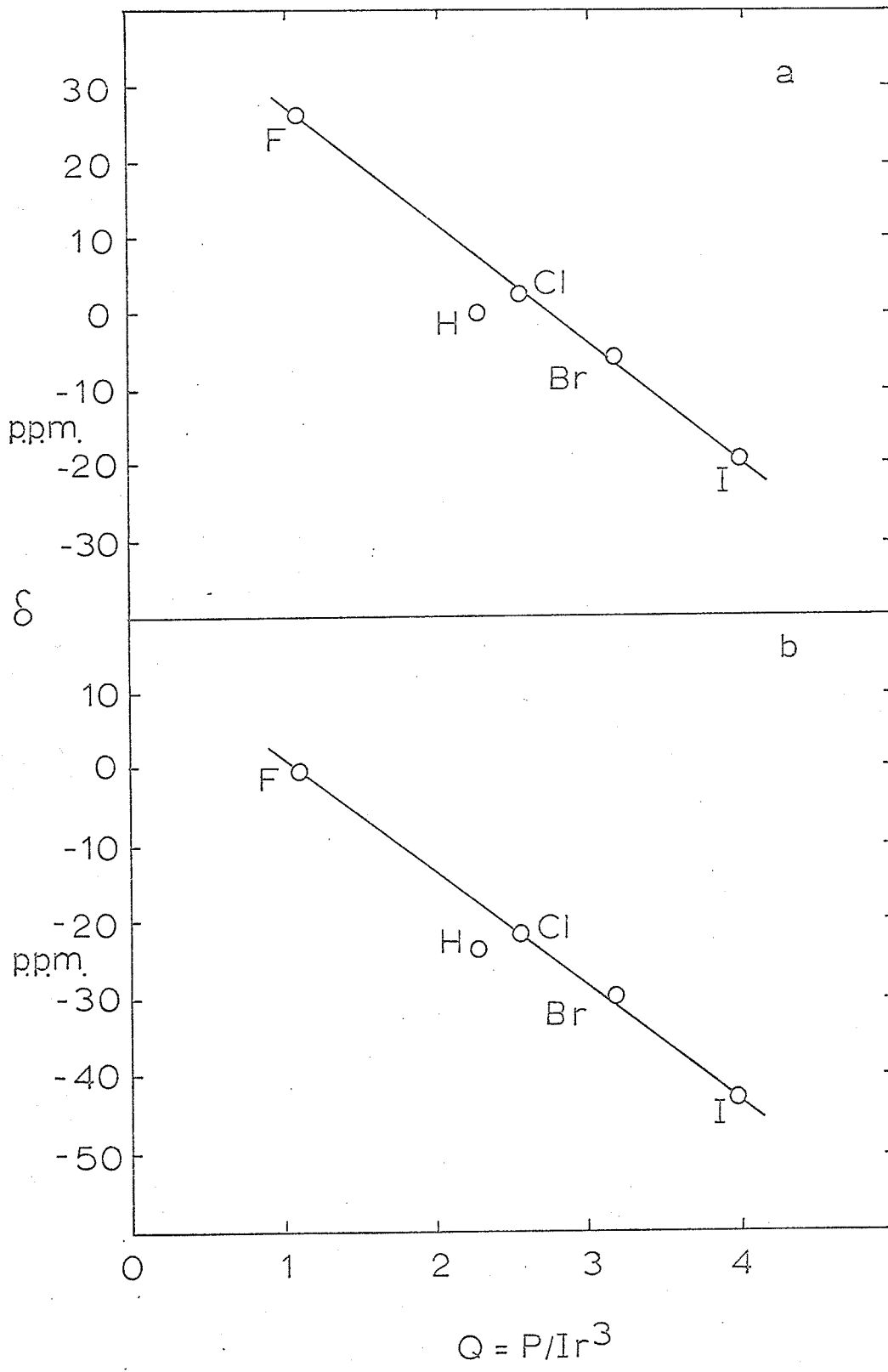
is only 2.2 p.p.m. in a total range of 45 p.p.m. The
point X = H has the largest deviation (-5.5 p.p.m.).

In Figure 2.4b the ortho-fluorine shifts in C_6F_5X
are plotted versus Q. A good straight line is obtained
once more with an average deviation of the points of only
1.8 p.p.m. in an over-all range of 43.1 p.p.m. The
deviation for the point X = H (-4.4 p.p.m.) is again the
largest. (Boden et al (42) who attempt to account for
these fluorine shifts using molecular orbital and electric
field calculations find a deviation of -23 p.p.m. for the
ortho shift in C_6F_5H). Part of the deviation of -4.4 p.p.m.
may be a result of the carbon tetrachloride solvent. Inter-
molecular van der Waals shifts in halogenated solvents are
particularly large in fluorine resonance and may amount to
8 p.p.m. (128). Since hydrogen is a small substituent it
may allow a closer approach of the solvent molecules to the
ortho-fluorine atoms, resulting in a large van der Waals
interaction at these positions. The deviation observed for
the point X = H is in fact to low field.

C) The Range of Observed Shifts

The range of observed shifts is as follows:

Proton Shifts

    ortho-proton in monosubstituted benzenes   0.7 p.p.m.

    cis proton in vinyl halides   1.5 p.p.m.

    cis proton in 1-substituted propenes   1.1 p.p.m.

    cis proton in 2-substituted propenes   1.2 p.p.m.

Fluorine Shifts

    ortho-fluorine in monosubstituted benzene   45 p.p.m.

    ortho-fluorine in perfluorobenzenes   43 p.p.m.

D) Discussion

    Pitcher et al (62) have reported the fluorine shifts
of a variety of fluorocarbon derivatives of metals. A large
shift to low field is found for the absorption by a CF_2 group
bonded directly to manganese, rhenium, iron or cobalt. It is
suggested that these screening effects are related to the
presence of low-lying excited states in the bonds between the
metals and the carbon atoms of the α-CF_2 groups, with the
result that the paramagnetic contribution to the screening
constants of the fluorine nuclei is substantially increased.
A similar mechanism suggests itself in the series studied here;
the ortho effect observed in fluorine shifts lies in an
increased paramagnetic term arising from smaller values of the

average excitation energy associated with fluorine atoms

ortho to a substituent. This is in accord with the

increasing magnitude of the effect as the substituent

increases in size. The proposal is therefore: the cis

and ortho-fluorine and proton shifts are dependent mainly

on the paramagnetic contribution to nuclear magnetic

shielding and for the substituents studied the variation

in this contribution is proportional to Q.

One rationalization of Q is as follows. The para-

magnetic contribution should be roughly inversely proportional

to a mean excitation energy $\triangle E$. Since $\triangle E$ is not known

the first ionization potential of the substituent X was used.

The quantity P/r^3 is then a factor which corrects for the use

of I in place of $\triangle E$.

There is some experimental justification for the use

of an ionization potential. Silfkin (63-65) has shown that in

a series of aromatic compounds there exists a linear relation-

ship between the first ionization potential and the energies

of the excited states of the molecule. For this reason the

use of I in place of $\triangle E$ may not be arbitrary. The use of

P/r^3 as a correction is admittedly difficult to rationalize

at the present time.

An attempt was made at correlating other shifts with Q. The chemical shifts of the proton trans to the substituent in monosubstituted ethylene are listed in Table 2·4 and plotted versus Q in Figure 2·5. A good straight line is obtained with an average deviation of the points of only 3·2 c/s in a range of 127.2 c/s.

A linear correlation with Q is also found for the chemical shift of the trans proton in 1- and 2-substituted propenes.* Once more straight lines are obtained for the available shifts listed in Table 2·4. The average deviation of the points for the 1-substituted propenes is 4.6 c/s in a range of 84.6 c/s; for the 2-substituted propenes the average deviation from the line is only 1.3 c/s in a range of 81.8 c/s. The correlation plots allow predictions to be made for the shifts of 1- and 2-iodopropenes. The predicted shift for the trans proton in 1-iodopropene is -403.6 c/s from TMS. The observed shift in Table 3·1 (for the β-proton in cis 1-iodopropene) is -367.1 c/s. The agreement is poor but no satisfactory explanation can be given for the discrepancy. The predicted shift for the 2-iodopropene is -361.0 c/s; the measured shift taken from Table 2·3 is -350.8 c/s in TMS and -356.1 c/s in carbon tetrachloride. The difference between

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*Figure 2·6

TABLE 2·4

Chemical shifts* of protons in the <u>trans</u> position
to the substituent X in some unsaturated molecules.

X	<u>trans</u> $C\underline{H}_2 = CHX$	<u>trans</u> $CHX = C\underline{H}CH_3$	<u>trans</u> $C\underline{H}_2 = CXCH_3$
H	-318.0^a	-344.0^c	-297.8^c
F	-258.5^b	-281.2^d	-248.8^f
Cl	-315.8^b	-344.8^e	-303.8^f
Br	-349.8^b	-365.8^e	-330.6^f
I	-387.0^b	–	–

* Of the underlined nucleus in c/s relative to internal TMS.

[a] In TMS. Reference 14.

[b] In TMS. Reference 60.

[c] Reference 89.

[d] Reference 113.

[e] Pure. Table 3·1.

[f] Reference 61.

FIGURE 2·5

The chemical shift, δ , of the proton <u>trans</u> to the

substituent X in vinyl-X compounds is plotted versus

$Q = P/Ir^3$. The shifts in c/s at 60 M c/s are relative

to internal TMS. Data are taken from Table 2·3. The

substituent is indicated by its chemical symbol.
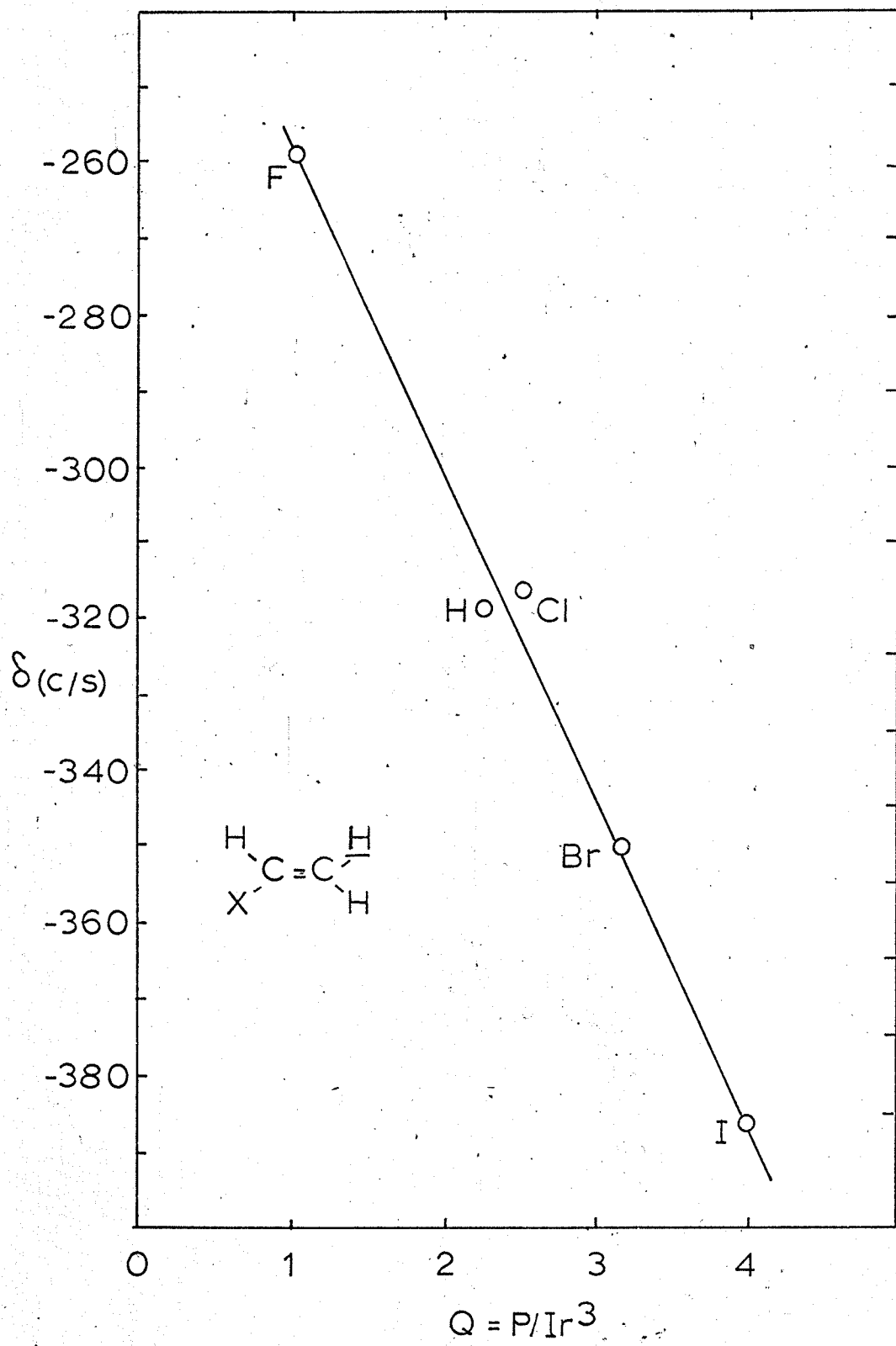
FIGURE 2·6

The chemical shift, δ , of the proton <u>trans</u> to the

substituent X in 1- and 2-substituted propenes is plotted

versus $Q = P/Ir^3$. The shifts in c/s at 60 M c/s are

relative to internal TMS. Data are taken from Table 2·3.

The substituent is indicated by its chemical symbol.
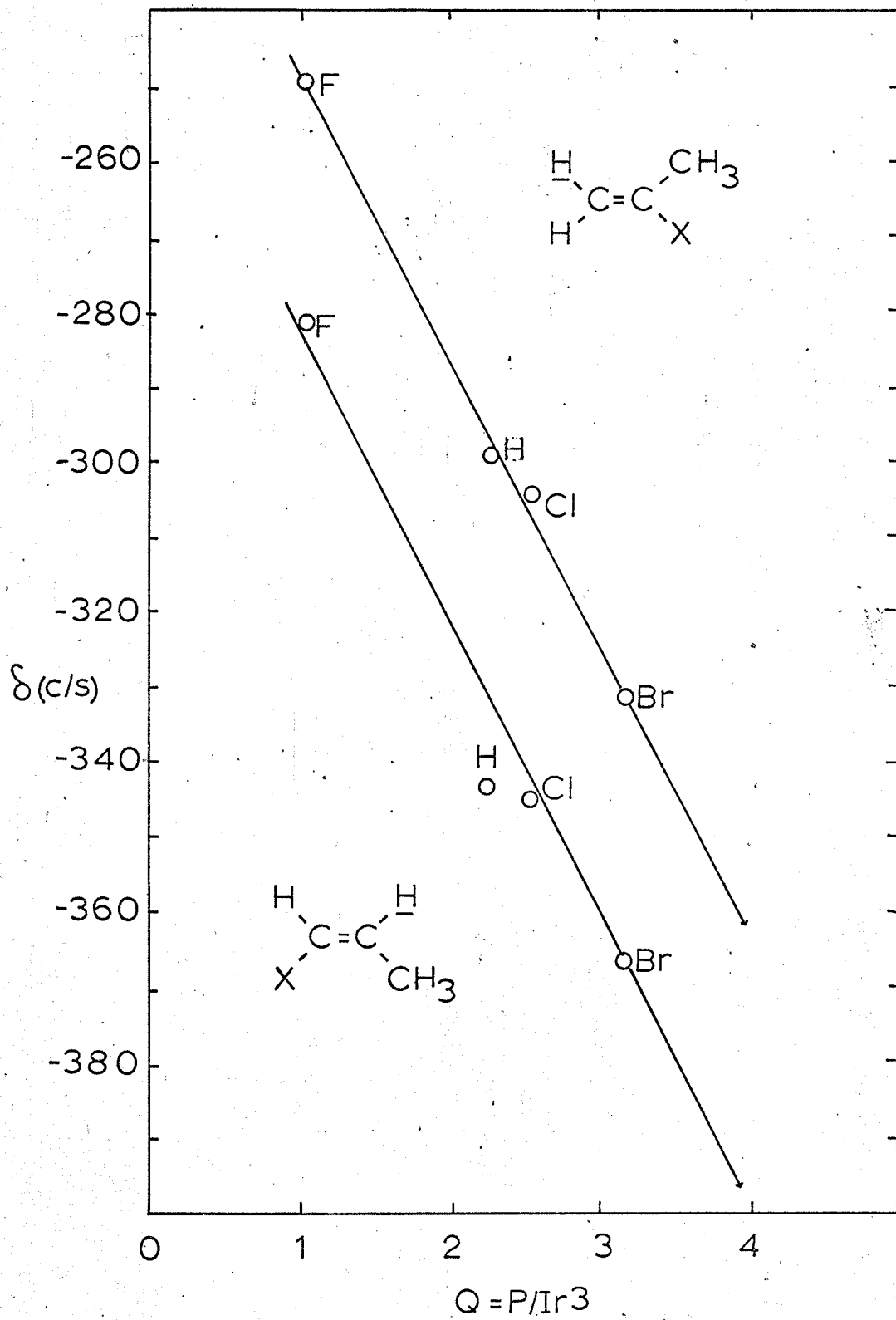
predicted and observed shifts is then 10.2 and 4.9 c/s for

the two solvents. Thus the agreement for the trans proton

shifts is not good whereas the agreement for the cis shifts

is satisfactory. Perhaps steric effects are the cause of

this discrepancy.

There is some evidence that the Q effect is transmitted

from the substituent to the β-proton via the pi electrons in

the double bond.

1. The pi-bond order in the vinyl compounds is to a first

   approximation twice that in the aromatic compounds.

   The ratio of the range of the cis proton shifts in the

   vinyl series to the range of the ortho proton shifts is

   2.25:1. Thus for these two instances the Q effect

   seems to be approximately proportional to the pi

   character of the intervening carbon-carbon bond.

2. The coupling mechanism between protons separated by more

   than three bonds in unsaturated molecules proceeds via

   the pi electrons. These long-range couplings are larger

   if the coupled nuclei are separated by the straightest

   "zig-zag" path (70). The Q effect in the vinyl series

   is found to be larger at the trans proton; indeed, the

   straighter zig-zag path separates the substituent and

the *trans* proton.

3. From their molecular orbital treatment of saturated
   hydrocarbons, Pople and Santry (71) conclude that the
   C-C bond in ethane has a small amount of double-bond
   character. The resonance position of the β-proton in
   ethyl - X (X = halogen) is shifted to low field as the
   Q value of the substituent increases.

2-3 Summary

In this chapter an attempt is made to correlate chemical

shifts of proton and fluorine nuclei situated in positions

ortho- or *cis* to a halogen or hydrogen substituent. These

shifts are not readily explained by the theories of magnetic

shielding which have been proposed. Electron density

calculations fail to explain anomalies in the aromatic compounds.

The use of van der Waals forces and bond anisotropies leads to

a number of inconsistencies. Inductive withdrawal of electron

density by the substituent predicts trends opposite to those

observed.

For the above reasons a search was made for a new inter-

pretation which could correlate these shifts with a greater

degree of success than has been had. It was found that one Q

value of the substituent could correlate both the proton

and fluorine shifts in a surprisingly large number of

compounds. Furthermore cis proton shifts are predicted

with some accuracy from the correlation plots. It is

suggested that the Q value is a measure of the paramagnetic

contribution from the substituent to the magnetic shielding

of the proton and that the effect is transmitted via the pi

electrons. The evidence for doing so, however, is not

strong.

There is some indication that the Q correlation is

more widely applicable than originally hoped. Smith and

Cole (72) find that ortho-proton shifts in ortho-disubstituted

benzenes correlate excellently with Q. The Q effect seems to

be additive in meta-disubstituted benzenes and seems to be

present, though greatly attenuated, in some saturated systems

but nothing definite can be said until more measurements are

made. A systematic study of substituted toluenes will be

carried out shortly.

CHAPTER III

CHEMICAL SHIFTS OF THE METHYL AND α-PROTONS OF HALOGENATED
PROPENES AND THEIR SOLVENT EFFECTS

3-1   Introduction

In Chapter II correlations with $Q = P/Ir^3$ were found

for the β-proton shifts in halogenated propenes. In this

chapter the α- and methyl proton shifts of cis and trans

halogenated propenes are discussed in the light of current

theories. Anisotropy, van der Waals, inductive and Q-type

interactions are considered. There has also been considerable

interest in the microwave spectra of halopropenes (77-83).

Of particular interest as far as the methyl proton shifts are

concerned are the accurate microwave measurements of the

energy barriers to internal rotation of the methyl group.

(The rotational barrier depends on the substituent. If this

dependence is a reflection of an electronic interaction between

the substituent and the methyl group, the methyl proton shifts

should also depend on the substituent).

The solvent effects of benzene and acetone on all proton

shifts of the 1-halopropenes are also discussed.

3-2 Experimental

The 1-bromopropene and 1-chloropropene were obtained
as mixtures of _cis_ and _trans_ isomers (with small amounts of
the 2-chloropropene) from the K and K Laboratories, Inc.
The 1-iodopropene was prepared as described in Appendix I.
The isomers were separated on a Wilkins Chromatograph (Model
A-90-P) using a six-foot copper column packed with 60-80 mesh
firebrick which had been coated to the extent of 20 wt.% with
Eastman Kodak tricresyl phosphate. The column, injector and
detector temperatures were, respectively, 90°, 115° and 150° C
for the 1-iodopropene, 65°, 90° and 150° C for the
1-bromopropene and 40°, 60° and 150° for the 1-chloropropene.

NMR spectra were obtained for the 1-halopropenes in
the pure form and in a variety of solvents. Spectroquality
acetone from Matheson, Coleman and Bell, tetramethylsilane
(TMS) from the Stauffer Chemical Company, Baker Analyzed carbon
disulfide and Fisher Certified benzene were used. The solutions
were generally about 10 mole % in 1-halopropene with 2 or 3
drops of added TMS for reference.

The spectra were measured at 60 M c/s on a Varian DP60

spectrometer. The probe temperature was about 20° C and was constant to within 1 C°. The solutions were contained in 5 mm O.D. sample tubes. Line positions were calibrated using sidebands from the internal reference TMS. Since the TMS sidebands were broadened when TMS was employed as the solvent, sidebands from an external reference (20 volume % benzene in carbon tetrachloride) were used for calibrating line positions. So that all shifts could be referred to the same reference, the relative position of the external reference and TMS solvent was measured. Line separations accurate to 0.05-0.15 c/s were obtained in this way. They are an average 6 to 10 measurements.

The spectra were analyzed by the ABX_3 effective-frequency method of Pople and Schaefer (84). The $\alpha-$, $\beta-$ and methyl protons are denoted by the letters A, B and X, respectively.

3-3 Results

In Table 3·1 are given the proton chemical shifts of the 1-halopropenes relative to internal TMS and the proton coupling constants. The shifts are probably accurate to 0.1-0.3 c/s while the couplings are accurate to 0.1 c/s. Sample spectra of the cis and trans 1-iodopropenes are shown. In Figure 3·1 the observed spectrum of cis 1-iodopropene in benzene is shown. The spectrum of this isomer calculated from

TABLE 3.1

Proton Chemical Shifts and Coupling Constants

of Cis and Trans 1-Halopropenes

cis 1-chloropropene

Solution*	Chemical Shifts[+] c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	-355.6	-339.9	-101.3	7.1	-1.8	6.7
10% in benzene	-342.7	-320.8	- 89.7	7.0	-1.8	6.8
10% in acetone	-368.4	-353.7	-103.4	7.0	-1.8	6.8
20% in carbon disulfide	-357.8	-344.9	-104.0	7.1	-1.8	6.6
neat#	-358.4	-344.8	-102.8	7.0	-1.8	6.6

TABLE 3·1 (continued)

trans 1-chloropropene

Solution*	Chemical Shifts+ c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	-351.1	-347.7	- 97.6	13.1	-1.7	6.9
10% in benzene	-335.5	-337.4	- 74.3	13.2	-1.8	7.0
45% in benzene	-342.2	-341.7	- 84.1	13.2	-1.9	6.9
10% in acetone	-364.9	-354.6	-101.3	13.2	-1.8	7.0
15% in carbon disulfide	-351.9	-348.1	-101.7	13.1	-1.9	7.2
neat	-354.2	-350.5	- 99.1	13.3	-1.8	7.2

cis 1-bromopropene

Solution*	Chemical Shifts+ c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	-365.3	-361.6	-101.6	7.0	-1.7	6.5
10% in benzene	-350.0	-339.9	- 88.2	7.0	-1.6	6.5
20% in benzene	-352.1	-342.5	- 89.7	6.9	-1.7	6.6
35% in benzene	-354.3	-346.2	- 91.7	7.0	-1.6	6.6
10% in acetone	-376.6	-373.9	-103.0	6.9	-1.8	6.6
neat	-367.5	-365.8	-102.1	7.0	-1.4	6.5

TABLE 3.1 (continued)

trans 1-bromopropene

Solution*	Chemical Shifts$^+$ c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	−356.9	−364.3	− 97.0	13.5	−1.8	7.0
10% in benzene	−339.0	−351.3	− 71.6	13.4	−1.7	7.3
10% in acetone	−369.3	−371.0	−101.0	13.3	−1.8	7.0
neat	−359.4	−366.7	− 99.2	13.4	−1.5	7.2

cis 1-iodopropene

Solution*	Chemical Shifts$^+$ c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	−369.4	−367.1	−100.7	7.5	−1.6	6.4
10% in benzene	−354.0	−344.4	− 87.2	7.3	−1.4	6.5
10% in acetone	−378.3	−377.4	−102.7	7.2	−1.6	6.4

TABLE 3·1 (continued)

trans 1-iodopropene

Solution*	Chemical Shifts+ c/s			Coupling Constants c/s		
	A	B	X	J_{AB}	J_{AX}	J_{BX}
10% in TMS	-356.5	-384.7	- 98.3	14.4	-1.7	6.8
10% in benzene	-335.9	-370.0	- 71.8	14.2	-1.6	6.8
10% in acetone	-366.5	-391.3	-102.9	14.3	-1.7	6.8

* mole per cent.

+ negative sign indicates resonance to low-field of internal TMS. A = α, B = β, and X = methyl.

pure compound.

the shift and coupling parameters listed in Table 3·1 is

illustrated in Figure 3·2. In Table 3·2 the calculated

and observed line frequencies and intensities are given

for the cis isomer. The relative intensities observed

were estimated from peak heights. No estimation was made

for over-lapping peaks. In Figures 3·3 and 3·4 are

illustrated the observed and calculated spectra of trans

1-iodopropene in benzene. Calculated and observed line

frequencies and intensities are listed in Table 3·3.

Deviations between calculated and observed frequencies are

also tabulated. The deviations in calculated and observed

line frequencies are generally less than 0.1 c/s. The

deviations were larger for over-lapping peaks or for peaks

of low intensity. The line intensities are not readily

estimated. For this reason the agreement between observed

and calculated intensities seems satisfactory.

The coupling constants will not be formally discussed

here. They are tabulated, however, because they serve as a

confirmation of the analysis and the assignment of the cis and

trans isomers. The sign of J_{AB} cannot be determined from the

analysis. However it is almost certainly positive in both

cis and trans isomers (85, 86). In vinyl compounds the trans

FIGURE 3·1

Observed proton resonance spectrum of <u>cis</u> 1-iodopropene

in benzene (10 mole %). The spectrum was obtained at 60

M c/s on a Varian DP60 spectrometer. The direction of

increasing magnetic field (H) is indicated by the arrow.

A, B and X refer to the α-, β- and methyl protons respectively

The line positions (relative to internal TMS) and relative

intensities are given in Table 3·2.

61.

FIGURE 3·2

Proton resonance spectrum of <u>cis</u> 1-iodopropene in

benzene (10 mole %) calculated from the proton chemical

shifts and proton coupling constants listed in Table

3·1 The numbering scheme corresponds to that in

Table 3·1. A, B and X refer to the α-, β- and methyl

protons respectively. The direction of increasing

magnetic field (H) is indicated by the arrow.

TABLE 3.2

Comparison of Observed and Calculated

Spectrum of Cis 1-Iodopropene

AB region

Peak No.	Frequency[X]			Intensity	
	Calculated	Observed	Deviation	Calculated	Observed*
1	360.53	–	–	0.05	0.04
2	360.31	360.55	-0.24	0.68	0.79
3	359.24	359.28	-0.04	1.59	2.17
4	358.74	358.65	0.09	0.63	0.79
5	353.19	–	–	1.95	–
6	352.97	353.03	-0.06	1.32	–
7	352.83	352.53	0.30	1.95	–
8	351.90	351.89	0.01	4.41	–
9	351.40	351.31	0.09	5.37	–
10	349.48	349.44	0.04	5.37	5.49
11	345.49	–	–	0.05	0.00
12	343.82	343.71	0.11	4.41	3.36
13	342.14	342.06	0.08	0.63	0.51
14	337.61	337.79	-0.18	1.32	1.46
15	336.48	336.49	-0.01	1.59	1.58
16	330.27	330.37	-0.10	0.32	0.43

TABLE 3·2 (continued)

X$_3$ region

Peak No.	Frequency Calculated	Observed	Deviation	Intensity Calculated	Observed*
1	99.48	–	–	0.09	–
2	95.61	96.05	0.58	0.23	0.18
3	90.76	90.82	−0.06	1.00	0.94
4	90.22	90.23	−0.01	1.91	2.01
5	89.70	89.62	0.08	4.00	4.25
6	87.91	87.88	0.03	0.77	0.71
7	86.35	86.54	−0.19	0.77	0.71
8	84.56	84.79	−0.23	4.00	4.25
9	84.04	84.09	−0.05	1.91	2.01
10	83.50	83.44	−0.06	1.00	0.94
11	78.65	78.22	0.43	0.23	0.18
12	74.78	–	–	0.09	–

*Intensities were obtained from peak heights. Because of overlap lines 5-9 are not listed.

^{x}c/s to low field of TMS.

–Lines of low intensity were not observed and are indicated by a dash.

FIGURE 3·3

Observed proton resonance spectrum of _trans_ 1-iodopropene
in benzene (10 mole %). The spectrum was obtained at 60
M c/s on a Varian DP60 spectrometer. The direction of
increasing magnetic field (H) is indicated by the arrow.
A, B and X refer to the α-, β- and methyl protons
respectively. The line positions (relative to internal
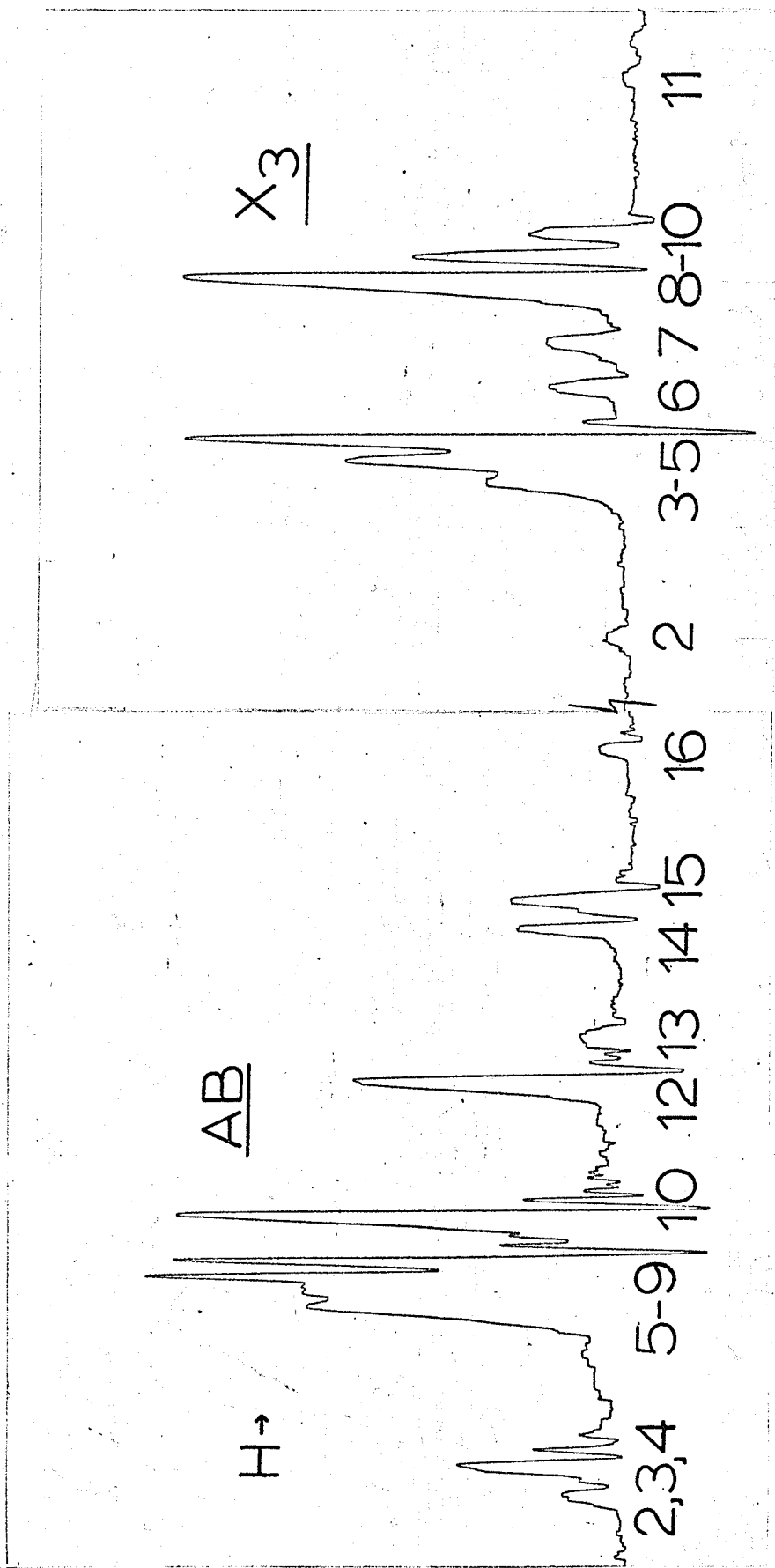TMS) and relative intensities are given in Table 3·3.
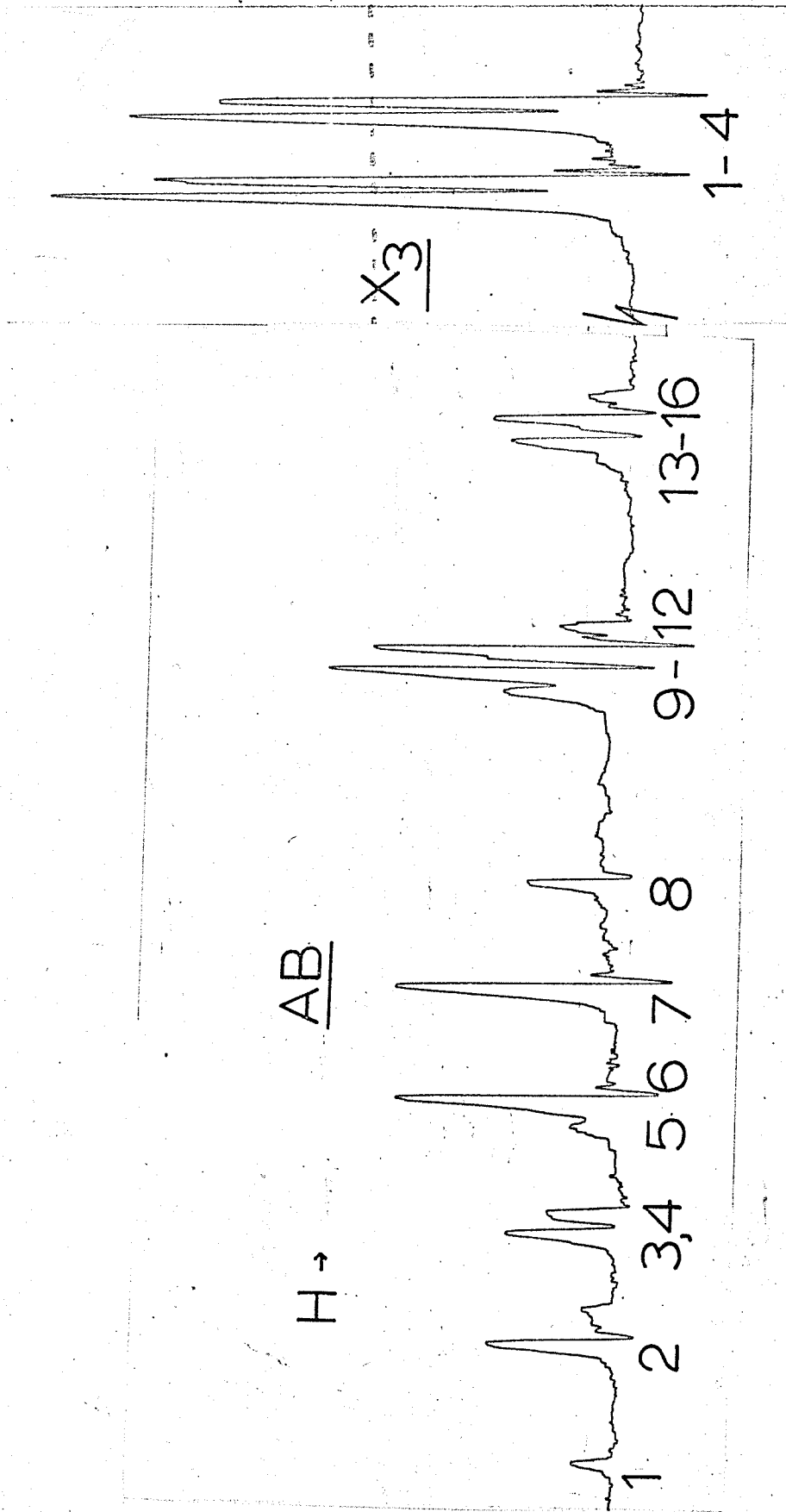
FIGURE 3·4

Proton resonance spectrum of trans 1-iodopropene in

benzene (10 mole %) calculated from chemical shifts

and coupling constants listed in Table 3·1. The

numbering scheme corresponds to that in Figure 3·3.

A, B and X refer to the α-, β- and methyl protons

respectively. The direction of increasing magnetic
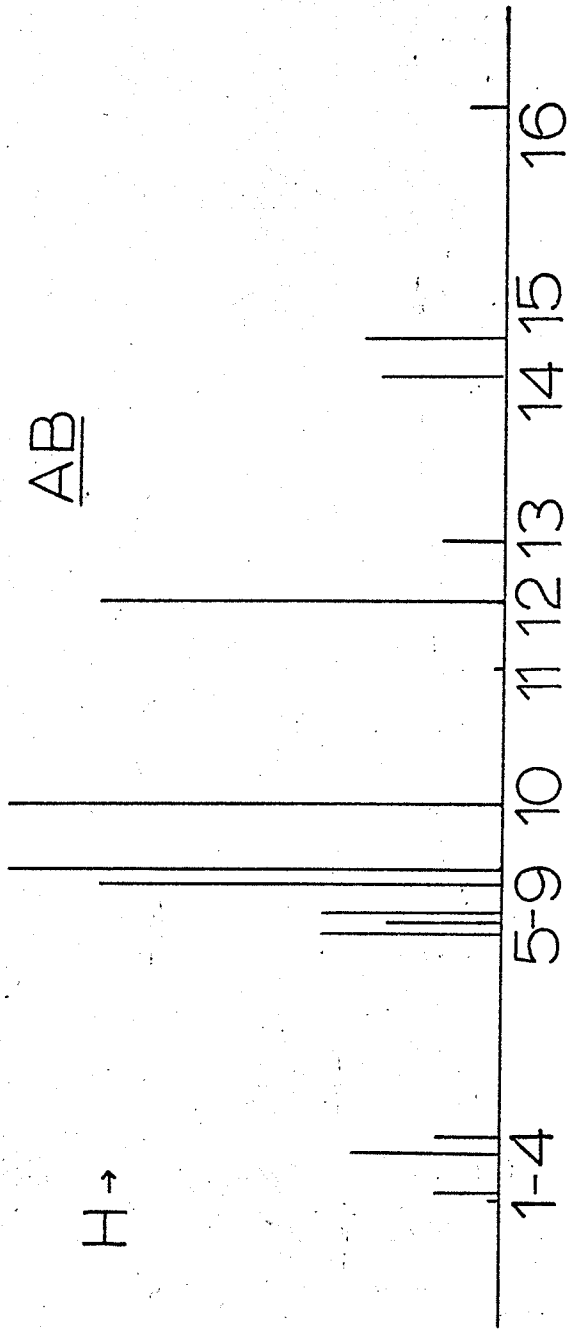
field (H) is indicated by the arrow.
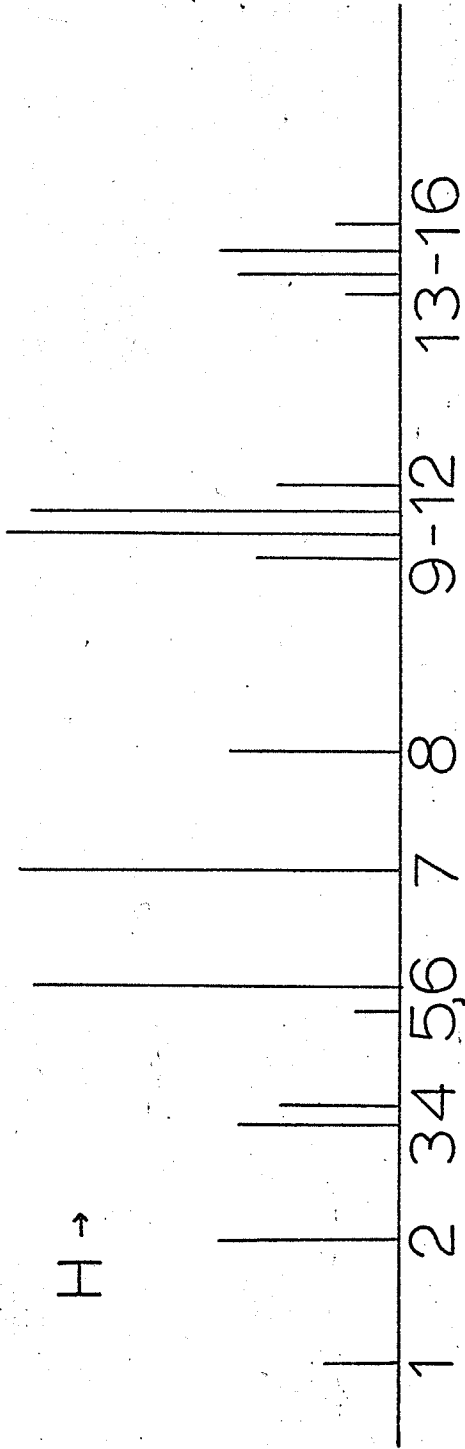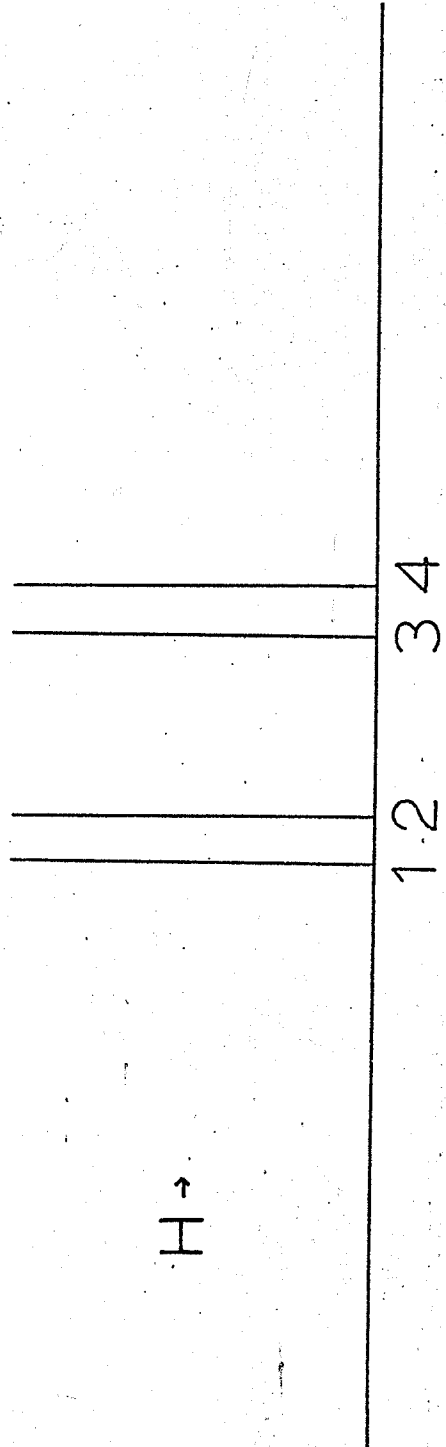
TABLE 3·3

Comparison of Observed and Calculated

Spectrum of <u>Trans</u> 1-Iodopropene

AB Region

Peak No.	Frequency Calculated	Observed	Deviation	Intensity Calculated	Observed
1	388.44	388.45	-0.01	0.71	0.71
2	381.83	381.74	0.09	1.95	2.14
3	375.36	375.42	-0.06	1.71	1.89
4	374.19	374.31	-0.12	1.29	1.22
5	369.06	369.05	0.01	0.45	0.61
6	367.60	367.59	0.01	4.05	3.67
7	361.13	361.11	0.02	4.29	3.72
8	354.86	354.84	0.02	1.55	1.28
9	343.35	343.34	0.01	1.55	1.43
10	342.26	342.32	-0.06	4.29	4.59
11	340.95	341.01	-0.06	4.05	3.93
12	339.54	339.53	0.01	1.29	1.02
13	329.12	329.15	-0.03	0.45	0.56
14	328.03	328.04	-0.01	1.71	2.09
15	326.72	326.73	-0.01	1.95	2.35
16	325.31	325.22	0.09	0.71	0.71

TABLE 3·3 (continued)

X$_3$ Region

Peak No.	Frequency			Intensity	
	Calculated	Observed	Deviation	Calculated	Observed
1	75.70	75.73	-0.03	4.00	4.60
2	74.41	74.40	0.01	4.00	3.88
3	69.21	69.21	0.00	4.00	4.14
4	67.92	67.90	0.02	4.00	3.37

coupling is 6-10 c/s larger than the cis and varies

between 10 and 25 c/s (87). The cis and trans isomers

can be assigned solely on the basis of the magnitude of

the J_{AB} spacing which is repeated a maximum of eight times

in the AB portion of the spectrum. From the analysis J_{AX}

and J_{BX} can be shown to have opposite signs but their signs

relative to J_{AB} cannot be obtained in this way. However,

J_{AX} is an example of an allylic coupling which varies between

0 and 3 c/s and is generally negative (88). Spin-decoupling

techniques have shown that J_{AB} and J_{BX} are of the same sign

while J_{AX} has the opposite sign (61).

3-4 Discussion of the α-proton Chemical Shifts

A. Inductive and electric field effects

In Figure 3·5 the α-proton shifts of the cis and trans

1-halopropenes are plotted versus the electronegativity of the

halogen. The α-proton shifts are -382.5 c/s and -386.1 c/s

from TMS for the cis and trans 1-fluoropropenes, respectively

(61). In propene itself this proton shift is -292.5 c/s for

the cis series of compounds and -297.8 c/s for the trans series

(89).

FIGURE 3·5

The α-proton chemical shifts, δ , of <u>cis</u> and <u>trans</u>

$CH_3CH = CHX$ and $CH_2 = CHX$ are plotted versus the

Pauling electronegativity, E, of the substituent X.

The shifts are in c/s at 60 M c/s from internal TMS

and the negative sign indicates resonance to low

field of the reference.
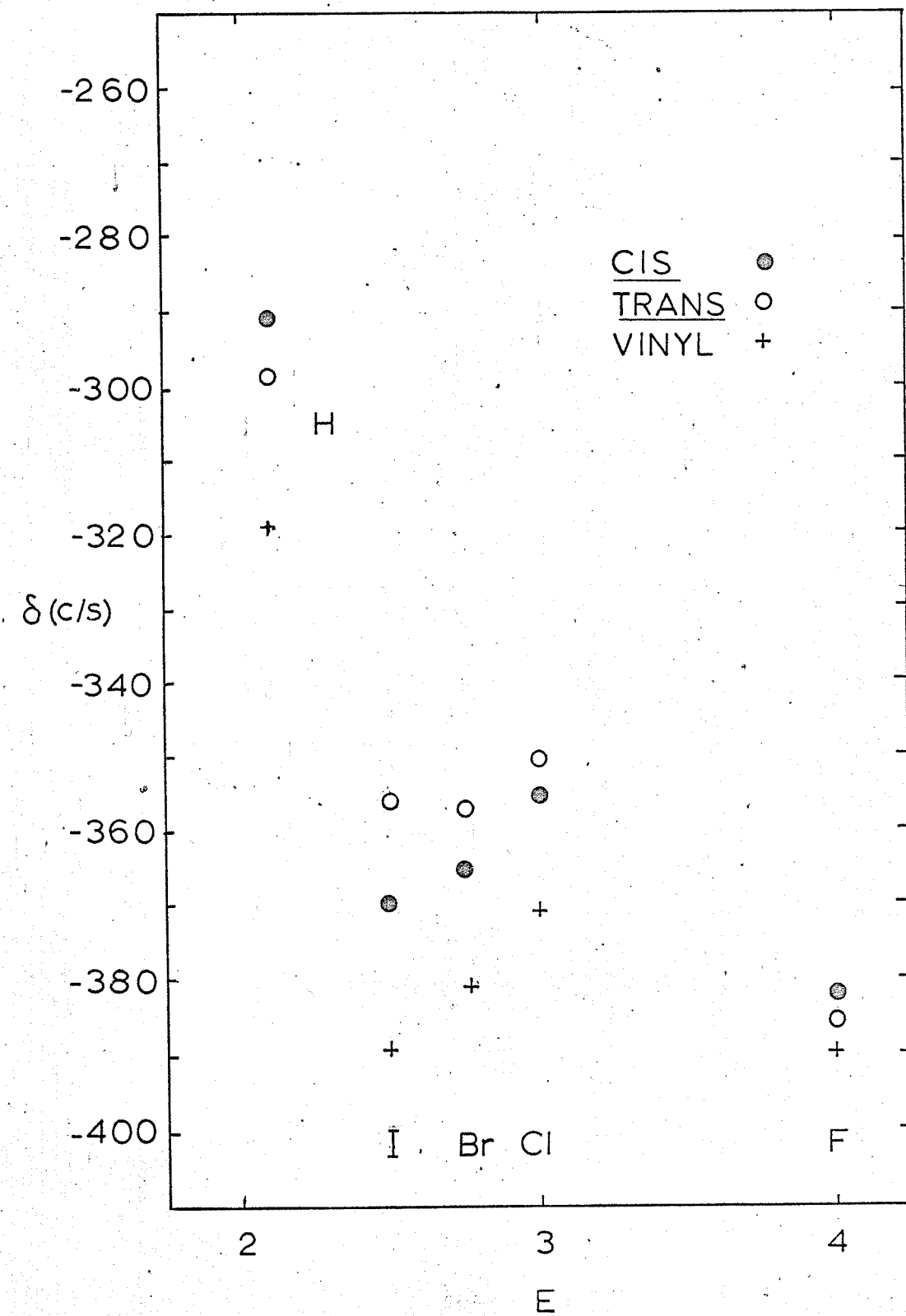
The shift measurements on propene and the
1-fluoropropenes were carried out on the pure compounds
at 60 M c/s. The proton shifts (from Table 3·1) for the
1-chloro-, 1-bromo- and 1-iodopropenes in TMS are plotted.
Also plotted for comparison purposes are the α-proton
shifts in vinyl halides at infinite dilution in TMS (60)
and the shifts of ethylene in a 5% solution in TMS (14).

It is obvious that the inductive effect alone is
not able to explain the trends observed in Figure 3·5. A
gradual displacement to low field from X = H to X = F is
expected if the inductive effect were the predominant
factor at this position.

Mayo and Goldstein fail, after correction for the
anisotropy in the magnetic susceptibility in the C-X bond,
to find in the vinyl halides a simple dependence on halogen
electronegativity in the order expected (60). They also plot
the α-proton shifts versus μ/R where μ is the dipole moment
of the C-X bond and R is the C-X bond length. The quantity
μ/R is expected to be at best only a rough index of the
change transferred (60). A rough correlation was observed.
However, a high-field shift was observed with an increase in
μ/R whereas the electric field of the C-X bond is expected
to withdraw electrons from the α-hydrogen and to cause low-

field shifts.

B. The van der Waals Effect

A van der Waals interaction with the halogen cannot be the sole source of the variations in the α-proton chemical shifts. In the cis, trans and vinyl series this shift in the fluoride is to low field of that in the iodide (see Figure 3.5). Since the atomic polarizability increases with the size of the atom, the reverse should be the case. In the trans 1-halopropenes there is little variation for the chloride, bromide and iodide while a 60 c/s high-field shift in propene (X = H) and a low-field shift of 30 c/s in the fluoride are observed. If the α-proton shifts were due mainly to a van der Waals interaction with the halogen, the above observations would be surprising.

C. Anisotropy Effects

Anisotropy in the magnetic susceptibility of the C-X bond cannot reproduce the observed trends. Δ X for a carbon-halogen bond is presumably negative and increases with the atomic number of the halogen (20, 46). Equation 1.18 predicts a high-field anisotropic contribution which should be largest for X = I and should decrease in the order X = I

> X = Br > X = Cl > X = F (52, 60). Clearly this is not

the case. Furthermore the α-proton for X = H is 60 to 80

c/s to high field of that for X = I.

D. Q Effects

The logical conclusion is that several factors are

important in determining the shift at the α-position. A

quantitative separation of the contributions to the shielding

is virtually impossible at the present time. Furthermore a

fourth contribution suggests itself. This is a Q-type inter-

action between geminal nuclei. Spiesecke and Schneider (20)

observe that the α-proton shifts in methyl and ethyl halides

correlate well with electronegativity of the halogen. The

most obvious difference (other than hybridization) between

the α-carbon in saturated and in unsaturated compounds is

the presence of a pi electron on the latter. If the

interpretation of Q in Chapter II is correct, a Q-type

interaction transmitted by this electron is possible.

Qualitatively the distribution of points in Figure 3·5 can be

explained with the assumption that large contributions to the

shielding arise from the inductive and Q contributions. For

instance the electronegativity and Q are relatively small for

hydrogen. Hence the points for X = H are to high field.
Large low-field contributions from Q could reverse the
order of the points for I and Br relative to that for Cl.
The point for F is always at lowest field because of a
large inductive effect which compensates for the small
value of Q. The points in Figure 3·5 can be adequately
fitted to an equation in E and Q (where E is the electro-
negativity of the halogen substituent) of the form

$$\delta = a + bE + cQ \hspace{3cm} 3·1$$

where δ is the shift relative to TMS and a, b and c are
constants. Equations such as 3·1 are of doubtful value
unless the constants can be evaluated theoretically and
shown to agree with the experimental values. Until that time
this approach is purely speculative. The neglect of
anisotropy and van der Waals forces is perhaps unjustified.
Furthermore, the relative positions of the points in Figure
3·5 can be rationalized equally well if large contributions
from induction and dispersion only are postulated.

3-5 Discussion of the Methyl Proton Shifts

The methyl proton shifts (in c/s from internal TMS)
of the cis and trans 1-halopropenes and propene are given in

Table 3·4. The methyl shifts of propene and the

1-fluoropropenes are for the pure compounds while those

of the 1-chloro-, 1-bromo- and 1-iodopropenes are for 10%

solutions in TMS. The shifts in the inert solvent TMS

are more desirable because medium effects are minimized.

Certainly all the shifts should be measured under these

conditions. However, it can be seen in Table 3·1 that the

difference in methyl shifts for the 1-chloro- and

1-bromopropenes in the pure state and in TMS solvent never

exceeds 1.5 c/s. A fair estimation of the medium effect

makes the methyl shifts in propene and the fluoropropenes

about 1 c/s less negative. This change will certainly not

alter the following discussion from which few definite

conclusions can be drawn in any case.

A. Inductive Effects

Since the methyl protons in the 1-fluoropropenes are

found at highest field, an inductive effect at the methyl

protons cannot be an important factor. This effect is not

expected to be important since the substituent and the

resonant protons are separated by three single bonds and one

double bond. In the ethyl halides the inductive effect on

TABLE 3.4

Methyl Proton Chemical Shifts[#] in $CH_3CH = CHX$

Substituent X	cis series	trans series
H[∓]	− 99.7	−99.7
F[x]	− 95.7	−89.8
Cl*	−101.3	−97.6
Br*	−101.6	−97.0
I*	−100.7	−98.3

[#] in c/s relative to internal TMS. The negative sign indicates resonance to low field.

[∓] pure compound. ref. 89.

[x] pure compound. ref. 61.

[*] 10% in TMS. Table 3.1.

proton shifts is of minor importance at the β-proton which is three bonds from the substituent (20).

B. The van der Waals Effect

If a van der Waals effect at the methyl protons predominated two trends would be observed:

1. The methyl shift in the cis isomer would be to low field of that in the analogous trans isomer. This is observed in the halogenated propenes. However, the difference in shifts is largest in the 1-fluoropropenes (5.9 c/s) and smallest in the 1-iodopropenes (2.4 c/s), an unexpected result since the iodine should have the largest effect.

2. The methyl shifts in the trans isomers should be fairly constant but should suffer increased displacements to low field as the halogen increases in size in the cis isomers. Except for 1-fluoropropene the trans shifts are roughly constant but the cis series does not show the expected trend.

The natural conclusion to be drawn from these observations is that van der Waals forces are of secondary importance in determining the shielding of the methyl protons.

C. Electric Field and Anisotropy Effects

Most certainly these effects would fail to explain the trends, or lack of trends, in methyl proton shifts.

D. Resonance Interaction

There exists one possible explanation for the anomalies. Fluorine is generally believed to have the ability to donate electrons mesomerically, that is, resonance structures with doubly-bonded fluorine atoms make significant contributions to the overall molecular structure. This mesomeric donation of electrons increases the effective electron density about the β-carbon atom. The net effect is to reduce the electron-donating power of the methyl group and to increase the magnetic shielding of these protons. Indeed the shifts in the 1-fluoropropenes are considerably higher than those in the other compounds. The constancy of methyl shifts in propene and in 1-chloro-, 1-bromo- and 1-iodopropene requires all other shielding mechanisms to be small or to cancel in each case. The probability of this occurring is negligible.

The resonance interpretation fails, however, to explain

the larger effect in the <u>trans</u> 1-fluoropropene. Furthermore the increase in charge at the β-carbon will also increase the shielding of the β-proton which now should not correlate with Q as it does (Chapter II).

E. Energy Barriers to Internal Rotation

The constancy of the methyl proton shifts appears even more mysterious if the energy barriers to the internal rotation of the methyl group are considered. A brief discussion of the origin of these barriers in ethane and in the halopropenes follows.

(a) The origin of the barrier potential in ethane

The potential barrier in the ethane molecule is 2.7 - 3.0 kcal/mole (90). The attempts to determine the origin of this barrier have been varied and inconclusive.

Mason and Kreevoy (91) use a simple model based on a van der Waals interaction between the hydrogen atoms on adjacent carbons to account for the barrier. Lassettre and Dean (92, 93) suggest that the barrier arises from a quadrupolar electrostatic interaction of the C-H bonds. Oosterhoff (94) considers both dipolar and quadrupolar interactions. The right order of magnitude was found by

attributing a large dipole moment of 0.7 D to the C-H
bonds.

In 1957 Wilson (90) reviewed the theoretical and
experimental progress in the evaluation of the barrier
potential in ethane and concluded that the van der Waals
interpretation was not correct. For instance, substitution
of a single fluorine for a hydrogen atom raises the barrier
only slightly while substitution of a second fluorine in
the α position lowers it. Wilson concluded that the barrier
was an inherent property of the axial (C-C) bond and not
due in any substantial measure to direct forces between the
attached atoms. Two years later Pauling (95) developed a
simple valence-bond theory of the potential barrier in
ethane. Qualitative agreement with experiment provided
support for his theory that the barriers were not a property
of the axial bond but resulted from exchange interactions
of the C-H bonds which were dependent on the relative
orientations of the two methyl groups.

Perhaps partly as a consequence of the failure of the
nonbonded interactions to account for the size of the barrier
attention has shifted to more complex wave functions
utilizing d and f hybridization, excited valence-bond

structures and electronic correlation (96 and references therein). Recently Wyatt and Parr (97) stated that their quantum-mechanical argument "isolated, identifies and confirms" the source of the internal-rotation barrier in the ethane molecule. Their conclusions are:

1. Repulsion by the protons favors the staggered conformer by 5 kcal/mole.

2. Interactions between the electron density about the protons produces a barrier of 2 kcal/mole favoring the eclipsed conformer.

3. The net result is a barrier of 3 kcal/mole, in excellent agreement with the experimental values.

(b) The origin of the barrier potential in halopropenes

Microwave spectra have been obtained for propene, cis and trans 1-fluoro- and 1-chloropropene and 2-fluoro- and 2-chloropropene. The barriers to methyl rotation have been measured and tabulated by Unland et al (83). Table 3·5 is taken from their work. Some interesting trends are observed. As the size of the 2-substituent increases the barrier increases whereas an increase in size of the cis halogen substituent decreases the barrier. The size of the

TABLE 3·5

Comparison of Barriers to Internal Rotation
in Propene and the 1- and 2-Halopropenes

	Compound	Barrier (cal/mole)	Reference
	$CH_3CH = CH_2$	1978	77
trans	$CH_3CH = CHF$	2200	78
cis	$CH_3CH = CHF$	1060	79
	$CH_3CF = CH_2$	2440	80
trans	$CH_3CH = CHCl$	2170	84
cis	$CH_3CH = CHCl$	620	82
	$CH_3CCl = CH_2$	2671	83

trans halogen substituent has a small effect only on the barrier.

Beaudet and Wilson (79) suggest an explanation for the lowering of the barrier in cis 1-fluoropropene with respect to the trans isomer. The more stable conformation of the methyl group is not known but they assume that it is staggered with respect to the 2-, or β-proton. (This is the case in propene (98)). Having knowledge of all inter-atomic distances (Figure 3.6) Beaudet and Wilson suggest that the atomic separations are such that repulsive inter-action between the cis 1-fluoro substituent and the methyl protons increases the energy of both the staggered and eclipsed conformers but the increase is larger for the lower-energy (staggered) conformer. A net decrease in the barrier results. As the size of the cis substituent increases this effect is enhanced. In this way the trend in the cis series is rationalized. Presumably the 2-substituent has the opposite effect on the eclipsed and staggered conformers of the 2-halopropenes.

The interactions producing the energy barriers in the halopropenes are of the order of 1-2 kcal/mole and vary by about 1.5 kcals in the cis 1-halopropenes. Hydrogen

FIGURE 3·6

Staggered and eclipsed conformers of <u>cis</u> 1-fluoropropene.
The separations in $\overset{\text{O}}{\text{A}}$ between the methyl protons and the
β-proton are indicated. The values are taken from

reference 79.

2.55 Å

STAGGERED

2.49 Å

2.35Å

ECLIPSED

2.93Å
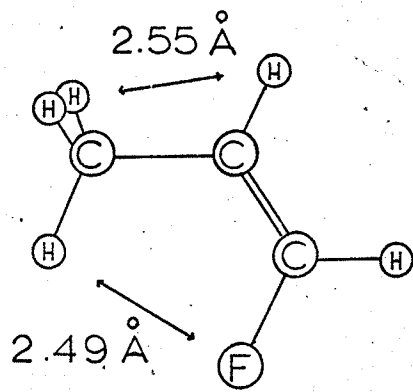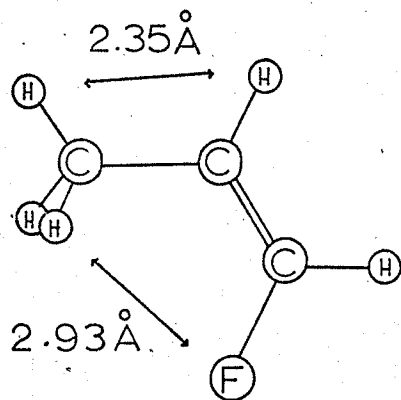
CIS 1-FLUOROPROPENE

bonds with energies around 5 kcal/mole result in proton

shifts amounting to several ppm. (99) and in considerable

C-H stretching-frequency shifts in the IR spectra of

molecules (100). Therefore it is not unreasonable to

expect considerable methyl proton resonance shifts. However

the entire range of these shifts is only 0.10 ppm in the

cis series where the variation in the barrier potential is

large and 0.15 ppm in the trans series where the barrier is

nearly constant. Thus, contrary to expectations, no

correlation between barrier heights and proton shifts exists

in the cis and trans 1-halopropenes.

The methyl proton shifts in the 2-halopropenes are

more strongly dependent on the halogen substituent (61).

The trend is to decreasing field with increasing substituent

size. Furthermore the available barrier heights show a

gradual trend here. If a van der Waals interaction were

important both trends would be compatible if the methyl

proton-fluorine interaction stabilizes the staggered conformer

with respect to the eclipsed conformer.

The complete series of halopropenes is now available.

Microwave measurements on the bromine and iodine derivatives

will prove interesting. The cis 1-iodopropene should show

an extremely low barrier potential while the 2-iodopropene

should show a value in the vicinity of 3 kcal/mole.

3-6 <u>Discussion of the Solvent Effects on the Proton
Shifts of the 1-halopropenes</u>.

A. Introduction

Solvent or medium effects on chemical shifts are

well known in NMR. These effects may be either diamagnetic

or paramagnetic depending on the nature of the medium. The

most widely discussed solvent shifts are those observed upon

formation of hydrogen bonds and those observed in aromatic

media. Buckingham <u>et al</u> (44) discuss the medium effects of

rod-shaped molecules such as carbon disulfide; these arise

primarily from the anisotropy in the magnetic susceptibility

of the solvent molecule and give rise to small low-field

shifts in the solute molecule. In Table 3·1 we see that the

proton shifts in <u>cis</u> and <u>trans</u> 1-chloropropene are displaced

to low field relative to their values in the inert solvent

TMS. However we are concerned primarily with the hydrogen-

bond and aromatic shifts which are discussed below.

(a) Introduction to Hydrogen Bonding

In all cases the proton resonance is displaced to

low field upon formation of a hydrogen bond, the only

exceptions to this behavior being connected with association

to some aromatic molecules (101). The principal contributions

to the shift were suggested by Pople et al (101). The two

general effects are:

1. The proton experiences a magnetic field due directly

   to the currents induced in the electron-donor atom

   and if this has a nonzero average over all directions,

   there will be a net contribution to the proton

   chemical shifts.

2. The presence of the electron-donor atom disturbs the

   electronic structure of the proton. The electric

   field of the donor atom tends to draw the proton away

   from its electrons and consequently reduces the electron

   density in its immediate vicinity.

   In cases where hydrogen bonds are expected to be

strong, low-field shifts amounting to 1 ppm can be expected

(102).

(b) Aromatic Solvents

   The large high-field shifts in proton resonance

observed when a solute is dissolved in an aromatic solvent

are also well known (103, 104). The solvent effects are

readily explained on the basis of the large anisotropy in the magnetic susceptibility of the benzene molecule (103). A magnetic field H_O applied normal to the ring induces a circular current which generates a secondary magnetic field opposed in direction to that of the applied field (Figure 3·7a). This can be approximated very crudely by a dipole placed at the centre of the ring. The dipolar lines of force oppose the field above and below the ring. When chloroform, for example, is dissolved in benzene a weak hydrogen bond is formed with the pi electrons (Figure 3·7b). Ordinarily hydrogen bonding results in a low-field shift. However, while hydrogen bonded to the benzene, the chloroform proton finds itself in a region where diamagnetic shielding by the ring-current effect is large. As a result a large high-field proton shift is observed for chloroform.

Acetonitrile experiences a high-field shift of 1 ppm. relative to neopentane when both are dissolved in benzene (103). Neither solute is expected to hydrogen bond (100). Schneider (103) suggests that this is evidence for a specific interaction, other than hydrogen bonding, between the polar CH_3CN and the benzene molecules. He interprets the

FIGURE 3·7

(a) The direction of the ring current induced in benzene
by a field H_O perpendicular to the plane of the
molecule is indicated by the arrows. The magnetic
effect of this current is approximated by an arrow
at the centre of the ring with the magnetic lines of
force illustrated by the dashed lines.

(b) The hydrogen bond between chloroform and the benzene
pi electrons is shown.

(c) The mutual orientation of acetonitrile and benzene
as a result of dipole-induced dipole interaction is
illustrated. The direction of the electric dipole
in acetonitrile and the induced dipole in the benzene
molecule are given by the arrows, the negative ends
of which are at the arrowheads.
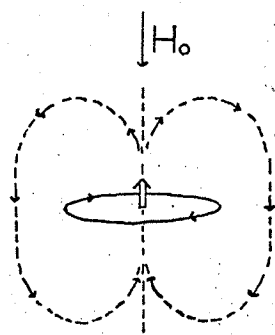
(a)
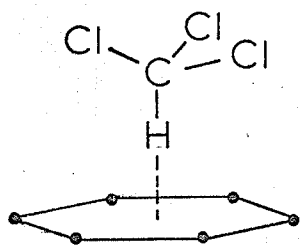
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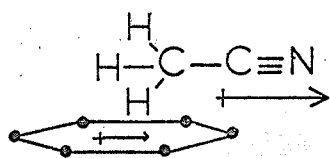
(c)

interaction in terms of a dipole-induced dipole interaction resulting in a preferred orientation in which the positive end of the molecule (the methyl group) lies above the benzene ring while the negative end (the cyano group) is repelled by the pi electrons (Figure 3·7c). If there were no specific interaction between the benzene and acetonitrile molecules involving a preferred mutual orientation of these molecules, i.e., if the system were completely random, both the neopentane and acetonitrile would experience the same environment. To a first approximation both would be affected in the same way by the magnetic anisotropy of the benzene molecule. The observed net high-field shift for the acetonitrile led Schneider to conclude that this preferred mutual orientation existed.

Schneider (103) also cites evidence for a mutual orientation of vinyl-X molecules with benzene. Presumably the interaction is similar to that mentioned above. The polar vinyl-X induces a moment in the benzene resulting in an attraction between the two molecules. Again a high degree of specificity is evident since the _trans_ proton experiences the largest solvent shift while the _cis_ proton experiences the smallest solvent shift. Schneider interpreted

this as a greater tendency for the trans proton to be
located above the ring while the polar X group tends to
lie off the ring (103). The effect of benzene on the
proton shifts of the vinyl-X solutes was as large as 1
ppm for 5 mole % solutions.

B. Effect of Benzene on the Proton Shifts in the 1-Halopropenes

TMS is a nonpolar solvent and for this reason will
exert only weak van der Waals forces on the solute molecules.
Since TMS was used as an internal reference in all instances,
the difference between a given resonance in benzene and TMS
solutions is a measure of the specific interaction between
the solute and the benzene molecule. In Table 3·6 are
tabulated these differences for each of the protons. (A
similar approach was used by Schneider for his study on
vinyl-X compounds (103)).

Some interesting trends are observed.

1. In the cis isomers the proton trans to the substituent
   (β) is most strongly affected by the benzene while the
   protons cis to the substituent (methyl) are the least
   affected. In the trans isomers, the protons trans to
   the substituent (methyl) are most strongly affected

TABLE 3·6

Solvent Effects on $CH_3CH = CHX$ - Benzene Shifts*

δ (benzene) $-$ δ (TMS) for 10% solutions

	Proton		
	α	β	methyl
X(cis)			
Cl	13.0	19.5	11.6
Br	15.0	22.1	13.4
I	15.5	22.7	15.5
X(trans)			
Cl	15.6	10.3	23.3
Br	18.0	13.1	25.4
I	20.6	14.7	26.5

* in c/s from Table 3·1. The positive sign indicates that the resonance in benzene is at high field.

while the <u>cis</u> proton (β) is the least affected.

This trend is identical to that observed by Schneider

in a study of vinyl-X compounds (103). This indicates

that the electron-rich halogen tends to avoid the

benzene ring.

2. The sum of the benzene shifts for each 1-halopropene

is larger for the <u>trans</u> isomer than it is for the <u>cis</u>

isomer. The dipole moments of the <u>cis</u> and <u>trans</u>

isomers of 1-chloro- and 1-fluoropropene are known

from microwave measurements (78, 79, 81, 82). The

dipole moments of the 1-bromopropenes are also

available (105). In each case the dipole moment of

the <u>trans</u> isomer is larger than that of the <u>cis</u> isomer.

If the sum of the benzene shifts is a measure of the

extent of mutual orientation of the 1-halopropene and

the benzene molecules, the larger value for the <u>trans</u>

isomer can be taken as evidence for Schneider's dipole-

induced dipole model. (But see below).

3. The benzene shifts at all positions increase for a

given series as the size of the halogen substituent

increases. Measurements indicate that the dipole

moments of the propenes (except the 1-fluoro isomers)

increase in the opposite order, that is, the relative

order can be predicted from the electronegativities

of the substituents. These increases in the benzene

shifts are surprising if Schneider's dipole-induced

dipole interpretation is correct.

Hruska, Bock and Schaefer (106) conclude that an

unmodified dipole-induced dipole model used for the alkyl-X

and vinyl-X shifts in benzene is not quite compatible with

their measurements on cis and trans dichloro- and dibromo-

ethylene. It was noted that the aromatic shifts of the

dibromoethylenes were slightly larger than the shifts of

the corresponding dichloroethylenes. Even more surprising

was the fact that the nonpolar trans molecule experienced

aromatic shifts almost as large as the cis isomer. A mutual

polarization of the solute and solvent via a dispersion

interaction was suggested as an explanation of these anomalies.

A simple van der Waals, or dispersion, interaction ordinarily

leads to a low-field displacement (44) but in these instances

it was assumed to lead also to a mutual orientation of solute

and solvent. Since the dipole moment is larger for the cis

dichloroethylene than for the cis dibromoethylene, the

larger benzene-shift values for the latter indicate that the

dispersion interaction is more important than the polar
interaction. The same conclusion can be drawn from the
large values of benzene shifts for the nonpolar trans
dihaloethylenes.

A similar dispersion effect can be invoked to
explain the substituent effect on the benzene shifts in
the 1-halopropenes. The dipole moments of cis and trans
1-iodopropenes are not yet available but we can assume
from the trends in the vinyl halides (105) that they will
be less than those of the corresponding 1-bromopropenes.
That the benzene shift at each position increases with the
size, and polarizability, of the substituent indicates that
the dipole-induced dipole interaction is of secondary
importance for the 1-halopropenes, as also seems to be the
case in the dihaloethylenes.

C. Effect of Acetone on the Proton Shifts in the 1-Halopropenes

The acetone shifts, δ (acetone)$-\delta$ (TMS), for the 10%
solutions given in Table 3.1 have been evaluated and listed
in Table 3.7. The trends observed are now discussed.

1. The acetone shifts of the methyl protons are small in
both the cis and trans isomers of each 1-halopropene.

TABLE 3·7

Solvent Effects on $CH_3CH = CHX$ - Acetone Shifts*

δ (acetone) - δ (TMS) for 10% solutions

	Proton		
	α	β	methyl
X(<u>cis</u>)			
Cl	-12.8	-13.7	-2.1
Br	-11.3	-12.4	-1.3
I	- 8.9	-10.3	-2.0
X(<u>trans</u>)			
Cl	-13.0	- 6.9	-3.6
Br	-12.4	- 6.7	-4.0
I	-10.1	- 6.6	-4.6

* in c/s from Table 3·1. The negative sign indicates that the resonance in acetone is at low field.

Pople et al (107) list hydrogen-bond shifts for a
number of simple hydrides. These shifts are zero
for methane and ethane indicating that the methyl
protons have little, or no, tendency to form
hydrogen bonds. Allerhand et al (100) cite IR
evidence that a single electron-withdrawing group
attached to an sp^3-hybridized carbon is not
sufficient to make proton donors of the hydrogens
attached to this carbon. If three withdrawing
groups are present on an sp^3-carbon strong hydrogen
bonds may be formed. Paterson and Cameron (102)
observe a hydrogen-bond shift of 0.9 ppm. for
chloroform in acetone.

In the 1-halopropenes only a single electron-
withdrawing group (-CH = CHX) is attached to the
sp^3-carbon. The small methyl acetone shifts indicate
the absence of any significant hydrogen-bond formation.
The small values can be attributed to dispersion forces
or to the anisotropy in the magnetic susceptibility of
the solvent molecules (44).

2. The acetone shifts of the α-proton, the largest of
which is 12.8 c/s (0.22 ppm), are small compared to

In the East Arm, the largest numbers and biomass occurred during sample period V. The East Arm was largely dominated by crustaceans that did not reach their maximum until late in the summer. The dominant dipteran was Microtendipedes (Table XII) which also occurred most frequently toward autumn. The large ephemeropteran, Hexagenia, reached its maximum during a similar period. The cumulative effect produced by similar life cycles was largely responsible for the autumn maximum.

Analyses of variance has indicated that benthic biomass and numbers along a transect did not vary significantly through the summer of 1963 (Tables IX and X). This would suggest that when one group of animals was large or small, abundant or absent, another group was in a complimentary relationship. Only slight evidence of this is given by Big Wave Bay and East Arm results (Figure 8). In Big Wave Bay, for example, as the Mollusca and Diptera increased and then decreased in numbers, the crustaceans and oligochaetes usually decreased and then increased. The reason for this is unknown. A certain degree of inter-specific intolerance may exist. If this is true, decreases would appear as such mainly because of dispersion of some organisms to less favourable habitats. Even some of the dynamic groups, such as the Ephemeroptera and Trichoptera, would generally tend to produce equal levels of biomass.

This is surprising because the α-proton is expected
to be more acidic. The anomaly can be rationalized
by postulating a considerable contribution to the
shifts from the electric reaction field of the polar
1-halopropene molecules. A short review of this
phenomenon follows. (See also 39, 44, 106).

The electric field associated with a polar molecule
polarizes the surrounding medium. This polarization which
is proportional to the magnitude of the dipole and depends
on the dielectric constant of the medium gives rise to a
secondary, or reaction, field. This secondary field further
polarizes the solute molecule and hence will be manifest in
a chemical shift. A useful model for evaluating the
secondary field is the Onsager approach which represents the
polar molecule by a sphere with a point dipole at the centre
and represents the medium by a continuum (109). Buckingham's
equation 1·15 is useful for estimating the effect of an
electric field on the shift of a proton bonded to carbon. If
the Onsager expression for the reaction field is substituted
into 1·15, the reaction field effect σ_R is given approximately
by

$$\sigma_R = -a\mu\cos\theta \qquad\qquad 3\cdot2$$

where $\underline{a}$ is a constant for a given solution, μ is the

dipole moment of the molecule and θ is the angle between

μ and the C-H bond direction. This contribution to the

shielding is zero if $\theta = 90°$, positive if $\theta > 90°$ and

negative if $\theta < 90°$.

In cis 1-chloropropene the dipole moment is almost

perpendicular to the α C-H bond ($\theta = 85°$, $\cos\theta = 0.09$)

(82). In cis 1-fluoropropene this is also the case

($\theta = 80°$, $\cos\theta = 0.17$) (79). It is not unreasonable

to assume that this angle is also large in cis 1-bromo-

and cis 1-iodopropene. Hence the reaction field effect

at the α-proton in the cis isomers is small. The angle

between the β C-H bond and the dipole moment in cis 1-chloro-

propene is small ($\theta = 34°$, $\cos\theta = 0.83$). Hence the

β-proton will experience a relatively large low-field

contribution σ_R from the reaction field. From the work of

Hruska et al (106) an estimate of 7-10 c/s to low field can

be made for this effect at the β-position, from the known

values of the dipole moments of the cis 1-halopropenes. If

this interpretation is correct the acetone shift at the

α-proton is due primarily to hydrogen-bond formation while

the acetone shift of the β-proton consists of significant contributions from the reaction field as well as hydrogen bonding.

This hypothesis can be readily tested with the available data in Table 3·7. In the _trans_ isomer both the α C-H and β C-H bonds are nearly perpendicular to the dipole axis (78, 81). In this case the reaction field is expected to be small at both positions. Clearly the acetone shift of α-proton which experiences no reaction-field effect in either isomer is almost constant. The acetone shift of the β-proton has been reduced by 4.8 to 6.8 c/s in the _trans_ isomer. This reduction presumably is due mainly to the reaction-field effects.

The reduction of the acetone shift at β-proton in the _trans_ isomer relative to that in the _cis_ may be due in part to steric hindrance to hydrogen bonding by the halogen placed _cis_ to the β-proton. However this cannot be the major factor since the reduction is least (4.8 c/s) for the largest substituent iodine and largest (6.8 c/s) for the smallest substituent. This result is compatible with the reaction-field interpretation but not with steric hindrance.

The reaction-field effect may also account partially

for the acetone shift of the methyl protons. However,

estimates would be difficult to make because of the

rotation of the methyl group. Furthermore the shifts

are small and difficult to treat in any conclusive manner.

3-7 Conclusions

The α-proton of the 1-halopropenes dissolved in TMS

are discussed in terms of inductive, van der Waals,

anisotropic and Q-type interactions with the halogen

substituent. However no simple explanation can be given

for the trends observed. This proton is strongly affected

by several factors but neither a quantitative nor suitable

qualitative separation of contributions can be made. The

methyl proton shifts are also unexplainable by current

theories of shielding. The constancy of methyl proton

shifts in the cis 1-halopropenes is made more surprising

by the observation that the barriers to the internal

rotation of the methyl group vary considerably.

Solvent effects are also discussed. Evidence is

cited for considerable dispersion interaction between the

1-halopropene and benzene molecules. Furthermore this

interaction appears to be more important than the dipole-

induced dipole interaction. Aromatic solvent effects
should be useful in identifying the cis and trans isomers
of ethylenic compounds.

Evidence is also cited for the formation of weak
hydrogen bonds by the ethylenic protons. The acetone
shift of β-protons is qualitatively explained by postulating
roughly equal contributions from hydrogen bonding and from
the reaction field of the polar 1-halopropenes. The acetone
shifts of the α-proton are assumed to be due mainly to the
formation of weak hydrogen bonds.

CHAPTER IV

A LINEAR CORRELATION OF PROTON CHEMICAL SHIFTS WITH THE
OCCUPATION NUMBER OF THE HYDROGEN 1s ORBITAL

4-1 Introduction

It is generally accepted that the paramagnetic
contribution in the Ramsey formulation is small for protons
because of the large excitation energies of the wave functions
centered on the hydrogen. However, if the interpretation of Q
is correct, significant variations in this term are possible
for protons in unsaturated systems. On the other hand,
proton shifts in saturated systems might still reflect changes
in the diamagnetic contribution to the proton magnetic
shielding. Evidence for this is found in a linear correlation
which exists between proton shifts of some alkyl halides and
some hydrocarbons and the occupation number of the hydrogen
1s orbital in the C-H bond. The occupation number is defined
as the effective electronic charge (which may be non-integral)
in a given orbital. A similar correlation between the charge
on the carbon atom and the carbon shift in the chloromethanes

has already been pointed out (115).

Recently, the self-consistent group orbital and bond electronegativity method has been employed to calculate the orbital charge distributions in some hydrocarbons and aliphatic chlorides (115). The calculation of the charge distributions begins with a chemically reasonable value of the occupation number for one orbital and then iterates to a self-consistent charge distribution. The calculated occupation numbers are used in the correlation.

4-2   The Correlation with Occupation Number

In Table 4·1 the occupation numbers, n, of the hydrogen orbitals in a number of hydrocarbons and aliphatic chlorides are presented, as are the proton shifts relative to internal tetramethylsilane for 5% solutions in carbon tetrachloride and cyclohexane. In a few cases the solvent was chloroform or tetramethylsilane. Ideally, the proton shifts in the gas phase are required to eliminate solvent effects (44) but these are not available for most of the compounds in Table 4·1. The most extensive data are for carbon tetrachloride solutions although cyclohexane is preferable as a solvent.

TABLE 4.1

Hydrogen-Orbital Occupation Numbers and Proton Shifts for

some Hydrocarbons and Alkyl Chlorides

Compound*	$n^{\dagger}$	Chemical shift in:		Hydrogen-bond shift at 27 C
		$CCl_4{}^{\ddagger}$	$C_6H_{12}{}^{\ddagger}$	
CH_3Cl	0.936	186	172	—
CH_2Cl_2	0.888	318	309	—
$CHCl_3$	0.843	436	426	516
$\underline{CH}_3CH_2Cl$	0.968	90	83	—
$CH_3\underline{CH}_2Cl$	0.926	211	205	—
$CH_3C\underline{H}Cl_2$	0.890	352	346	—
$\underline{CH}_3CHCl_2$	0.955	134	118	—
CH_2ClCH_2Cl	0.923	222	215	—
CH_3CCl_3	0.943	165	158	—
$\underline{CH}_2ClCHCl_2$	—	236	229	262
$CH_2ClC\underline{H}Cl_2$	—	344	337	409
$\underline{CH}_2ClCCl_3$	—	257	250	—
$CHCl_2CHCl_2$	0.870	356	347	416

* Protons in question are underlined.

† Occupation numbers in units of electrons are from
reference 115.

‡ Chemical shift in c/s at 60 Mc/s to low field of
internal TMS; referense 117.

‖ TMS solvent; reference 52.

TABLE 4.1 (continued)

| Compound[*] | n[†] | Chemical shift in: | | Hydrogen-bond shift at 27 C |
		CCl_4[‡]	C_6H_{12}[‡]	
$CHCl_2CCl_3$	—	257	359	—
CH_4	0.985	—	15[‖]	—
$\underline{C}H_3CH_2CH_3$	0.981	55[‖]	—	—
$(CH_3)_4C$	0.980	56[†]	—	—
C_2H_2	0.881	110[⊥]	96[#]	—
C_2H_4	0.931	320[⊥]	318[·]	—

△ $CDCl_3$ solvent; reference 118.

† Reference 119.

⊥ Reference 120.

TMS solvent; reference 121.

· Reference 14.

In Fig. 4·1 the proton shifts in carbon tetrachloride are plotted versus n. For the alkyl chlorides there is a linear correlation and the shielding decreases with the occupation number of the hydrogen 1s orbital. The proportionality constant is 46 ± 1 ppm per electron, as compared to 27 ppm calculated for the shielding in the hydrogen molecule (7). In the alkyl chlorides the hydrogen orbital is probably much less diffuse and this would lead to a higher value for the proportionality constant. However, the matter may be more complex.

The shifts of the methyl protons in propane and neopentane also fall very near the correlation line in Fig. 4·1.

In Fig. 4·2, the proton shifts in cyclohexane are plotted versus n. Again a linear correlation is noted for the alkyl chlorides. The slope of the line is nearly the same as that in Fig. 4·1, but is slightly displaced to high field. Here the methane shift (measured in tetramethylsilane) deviates strongly to high field from the extended correlation line. If the correlation line held it would indicate $n = 0.996$ for the hydrogen orbital in methane and $n = 1.002$ for the hydrogen orbital in tetramethylsilane (obtained by

FIGURE 4.1

The proton shifts, δ , in c/s at 60 Mc/s of some hydrocarbons
and alkyl chlorides in carbon tetrachloride plotted versus
the occupation number in units of electrons, n, of the
hydrogen 1s orbital. Negative shifts indicate resonance
to low field of the reference TMS.

FIGURE 4.2

The proton shift, δ, in c/s at 60 Mc/s of some hydrocarbons

and alkyl chlorides in cyclohexane plotted versus the

occupation number in units of electrons, n, of the

hydrogen 1s orbital. Negative shifts indicate a

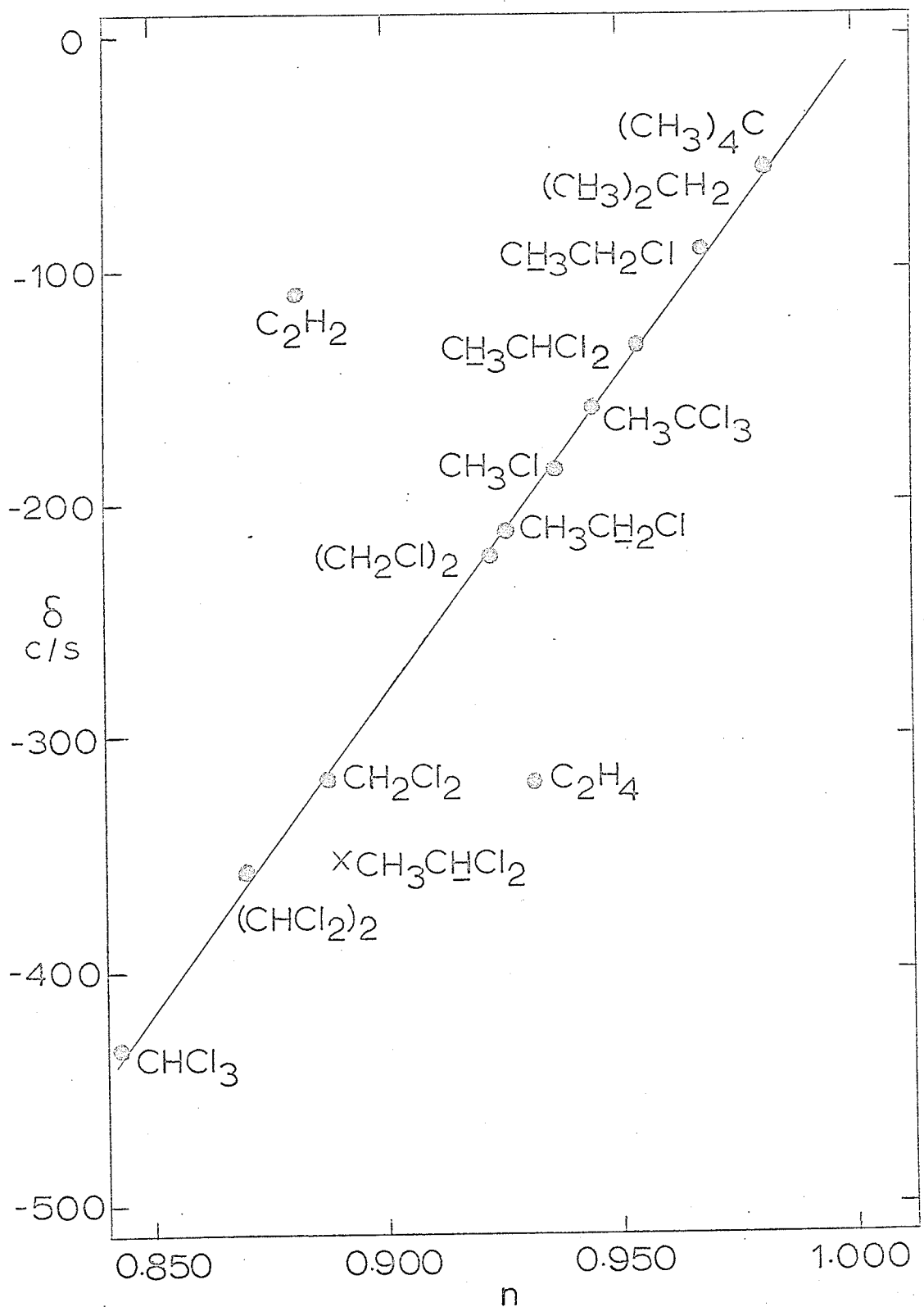resonance to low field of the reference TMS.
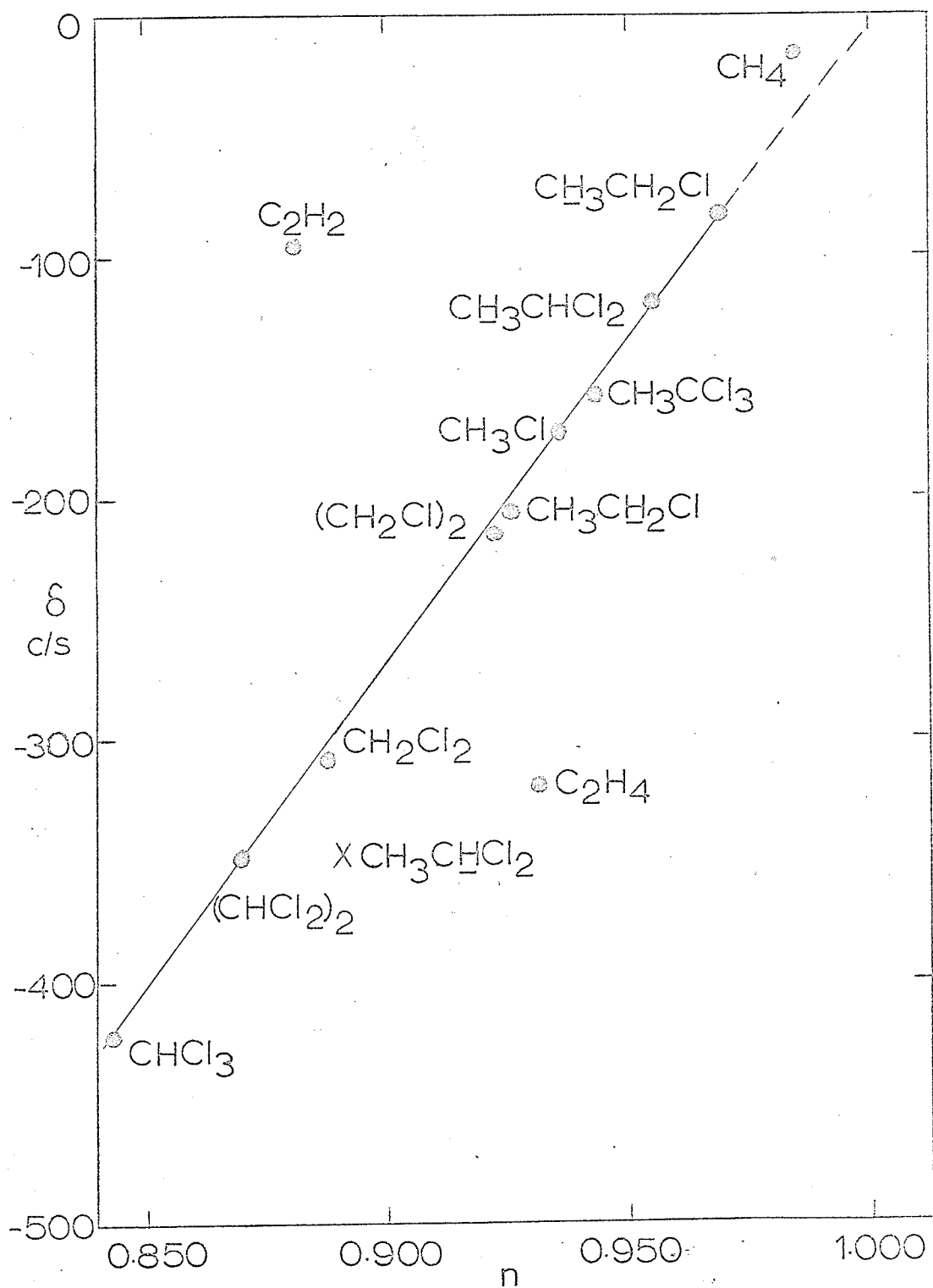
extrapolating to zero shift). Silicon is expected to

donate charge to the methyl group.

4-3 Application of the Linear Correlation

A) Prediction of n from Proton Shift

For three chlorinated ethanes in Table 4·1 the

occupation numbers are not yet calculated but they can be

obtained from Figs. 4·1 and 4·2. The predicted n values

from the two plots agree to within 0.001 units and are

$n(CHCl_2-CH_2Cl) = 0.916$; $n(CHCl_2CH_2Cl) = 0.876$; $n(CCl_3CH_2Cl) =$

0.909; $n(CCl_3CHCl_2) = 0.868$. The proton shift would seem to

present a reasonable value for n and also serves as a check

on the calculation. As an example, the proton shift of the

methyl proton in 1,1-dichloroethane indicates n = 0.871

instead of the calculated n = 0.890. The latter is marked

as a cross in Figs. 4·1 and 4·2 and is the only 1 out of 10

that deviates significantly from the correlation line.

In order to test the correlation plots the proton

shifts of the gases neopentane (C_5H_{12}), thiomethyl alcohol

and methane were measured in either cyclohexane or carbon

tetrachloride. The occupation numbers of these protons have

been calculated (115). Solutions in carbon tetrachloride or

cyclohexane were prepared in a vacuum system.   The

concentration of the dissolved gas was between 1-5 mole

per cent, estimated roughly from the NMR peak intensities.

The NMR spectra were obtained on a Varian DP 60 spectrometer

operating at 60 megacycles.   Line positions were calibrated

by the side-band technique using internal TMS as a reference.

The neopentane and methane spectra consisted of a single line.

The chemical shift is given directly by this line position.

The thiol spectrum was considerably more complicated but was

readily analyzed as an AB_3 system (A = S$\underline{H}$ and B_3 = C$\underline{H}_3$).   A

simplified approach to the analysis has been given by Diehl

(116).

The measured proton chemical shifts relative to internal

TMS are listed in Table 4.2.   The predicted occupation numbers

corresponding to these shifts were obtained from either Fig.

4.1 or 4.2, depending on the solvent used.   The occupation

numbers calculated by the self-consistent group orbital and

bond electronegativity method are taken from reference 115.

The units of n are electrons.

TABLE 4·2

Occupation Numbers Calculated and Predicted from

Proton Shifts in Units of Electrons

Solute	Solvent	Proton Shift (c/s from TMS)	n(predicted)	n(calculated)
CH_4	cyclohexane	−11.1	0.996	0.985
CH_4	carbon tetrachloride	−14.1	0.998	0.985
C_5H_{12}	cyclohexane	−55.4	0.981	0.980
$C\underline{H}_3SH$	carbon tetrachloride	−122.6*	0.958	0.980
$CH_3S\underline{H}$	carbon tetrachloride	−63.8*	0.980	0.972

*shift of underlined protons.

The agreement is good only in the case of neopentane.
The deviations in the thiol are interesting in that they are
of opposite sign. If the anisotropy in the magnetic
susceptibility of the C-S bond is larger than that of the
C-C bond, this can be rationalized very simply by evaluating
the geometric factor $1-3\cos^2\theta$ at the $C\underline{H}_3$ and $S\underline{H}$ positions.
A scale diagram of thiomethanol was drawn using the bond
lengths and bond angles listed in Interatomic Distances (110).
The origin of the dipolar field was placed at the electronic
centre of the C-S bond. Then the angle factor is positive at
the S-H proton and negative at the methyl protons. The sign
of the C-S bond anisotropy is not known but the deviations
indicate that it is positive. The hazard in using McConnell's
equation (1.18) for quantitative measurements have been
pointed out; for this reason only qualitative estimates have
been attempted.

B) Hydrogen-Bond Shifts

As n decreases the C-H bond becomes more polar and is
expected to hydrogen bond more strongly with a proton acceptor.
In Fig. 4·3 the four known hydrogen-bonded proton shifts
in dimethyl sulfoxide are plotted versus the occupation number

FIGURE 4.3

Hydrogen-bond shifts (of the underlined hydrogen atom) in dimethylsulfoxide, δ , plotted versus the occupation number in units of electrons of the hydrogen 1s orbital, n.
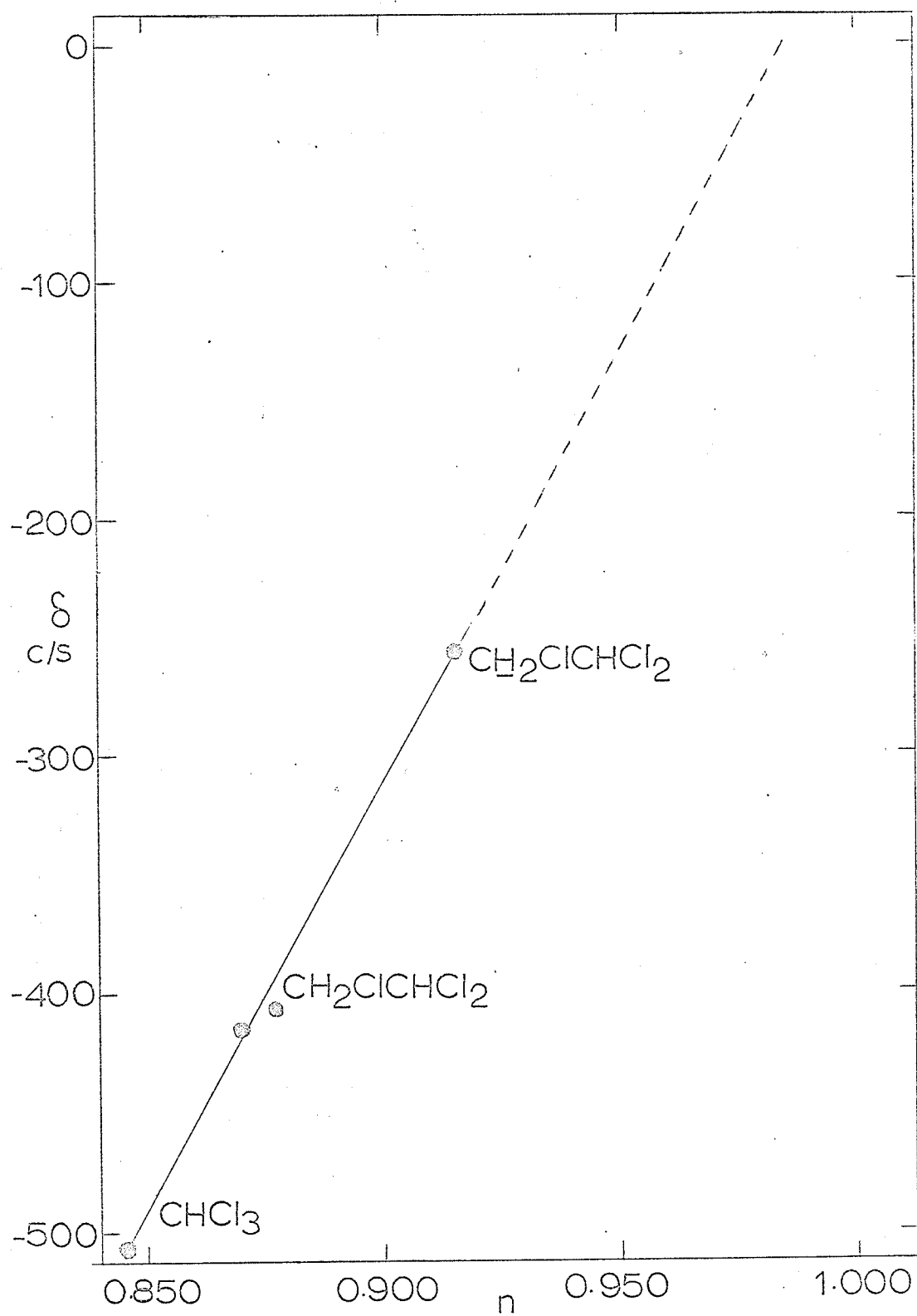
of the hydrogen orbital in the C-H bond. The shifts were

obtained by the method of Huggins, Pimentel, and Shoolery

(122). There appears to be a linear correlation for this

restricted number of values. For two of the points in Fig.

4·3 the n values were obtained from the plots in Figs. 4·1

and this suggests that correlations of this sort will be

useful in hydrogen bond studies by proton resonance.*

C) Estimates of Bond Anisotropies

In view of the considerable anisotropies attributed

to C-C and C-Cl bonds (52,123), the linear correlations in

Figures 4·1 and 4·2 are perhaps unexpected unless they happen

to be equivalent to the C-H bonds in this respect. For

example, two points on the line in Figure 4·1 are $\underline{H}-C{\overset{\diagup H}{\underset{\diagdown Cl}{-}}}Cl$

and $H-C{\overset{\diagup Cl}{\underset{\diagdown Cl}{-}}}Cl$. Replacement of a hydrogen by a chlorine

is certainly expected to reduce the occupation number of the

remaining proton. However, unless the C-H and C-Cl bond

anisotropies are equal, the chloroform proton is expected to

experience a larger anisotropic shielding effect and hence

is not expected to correlate with occupation numbers. The

underlined protons in $\underline{H}-C{\overset{\diagup H}{\underset{\diagdown Cl}{-}}}Cl$ and $\underline{H}-C{\overset{\diagup CH_3}{\underset{\diagdown Cl}{-}}}Cl$ also correlate

with occupation numbers. The occupation number of this proton

should be increased because of the larger electron-donating

---

*Furthermore a zero hydrogen-bond shift is predicted for methane.

power of the methyl group. The calculated values in Table 4·1 indicate that this is so. However, unless the C-H and C-C bond anisotropies are equal correlation with occupation numbers is not expected. The presence of the correlation suggests that the C-H, C-C and C-Cl anisotropies are equal. If they are all small this condition is satisfied.

In their review of anisotropy Pople and Bothner-by (48) state that little theoretical justification exists for some of the large values of C-C and C-H bond anisotropies. They show that C-C values greater than 4.5×10^{-6} cm^3/mole are absurd. Furthermore their listed values of C-H anisotropies are never larger than 3.0×10^{-6} cm^3/mole. Schaefer et al (46) estimate a C-Cl value of 5×10^{-6} cm^3/mole. Perhaps the apparent cancellation of anisotropic effects is not too surprising.

Whatever the explanation it is instructive to consider the ethylene and acetylene proton shifts. On the assumption that the deviations of these shifts from the lines in Figs. 4·1 and 4·2 are a measure of the anisotropy contribution of the double and triple bonds, one calculates $\Delta\delta = 3.8$ ppm. for acetylene and $\Delta\delta = -2.1$ ppm. for ethylene. These contributions are of the right sign and compare with

$\triangle \delta$ = 4.0 ± 0.5 p.p.m. for acetylene derived by the method proposed by Reddy and Goldstein (121) for the empirical estimation of anisotropy effects through the use of directly-bonded carbon-hydrogen coupling constants. The ratio of the values for the two compounds is -1.9, in rough agreement with that calculated from molecular orbital theory (124).

4-4 Conclusion

The linear correlation between the proton shift in alkyl chlorides and some saturated hydrocarbons and the occupation number of the hydrogen orbital in C-H bond suggests its application in predicting starting values for occupation numbers in the iterative process for the calculation of charge distributions in molecules; in deriving bond anisotropies in some cases while, at the same time, casting doubt on some current values for others; and in predicting hydrogen-bonded shifts in equilibrium studies by proton magnetic resonance. The ability to predict occupation numbers was tested with little success. In only one case out of five did the value predicted from shift measurements agree with that calculated. However several occupation numbers are now available for some bromo derivatives of methane and ethane.

A linear correlation is apparent here though the correlation line is not coincident with that for the chloro derivatives. Since none of the compounds listed in Table 4·2 contain chlorine they are perhaps members of some other correlation plot and for this reason accurate values of their occupation numbers cannot be predicted from Figs. 4·1 and 4·2.

The excellent correlations in this chapter indicate that the proton chemical shifts in some simple hydrocarbons and their chloro derivatives reflect changes in the local electron density of protons in saturated hydrocarbons. If this is the case variations in the local paramagnetic contribution to proton shielding in these simple compounds are not important.

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APPENDIX I

Preparation of <u>Cis</u> and <u>Trans</u> 1-Iodopropene

A) <u>Starting Materials</u>

(1) 1-Bromopropene*: K and K Laboratories, Inc.   This

   commercial product contains <u>cis</u> and <u>trans</u> isomers and

   a small amount of 2-bromopropene.

(2) Di-n-butyltin dichloride (practical)*: Eastman

   Organic Chemicals.

(3) Tetrahydrofuran: Fisher Certified Reagent.

(4) Magnesium (powdered, 70-80 mesh)*: Fisher Scientific

   Company.

(5) Iodine (resublimed reagent A.C.S.)*: Baker and Adamson

   Laboratory Chemical.

(6) Ammonium chloride*: Mallinckrodt Chemical Works.
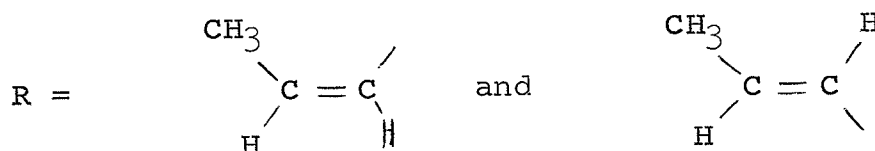
(7) Diethyl ether*: Fisher Scientific Company.

_____

*Used without further purification.
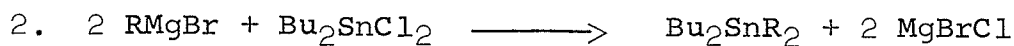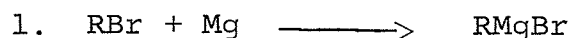
B) Purification of Tetrahydrofuran

Since the 1-iodopropene was prepared via a Grignard reagent, purification was necessary. One liter of tetrahydrofuran (THF) was refluxed over calcium hydride for more than 24 hours and distilled into a flask containing lumps of sodium. To this was added 10-20 mgs of recrystallized naphthalene and the flask was fitted to the reflux condenser of a vacuum system. With the pressure-release valve open refluxing was continued until the sodium-naphthalene complex was formed, characterized by the appearance of a dark green colour. (The complex is destroyed by a slight trace of water). The THF was then distilled under vacuum to a storage bulb which kept the liquid from contact with the atmosphere.

C) Procedure

The proposed reaction scheme for the preparation is as follows (125):

$$R = \begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown \\ H \end{array} \qquad \text{and} \qquad \begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C = C \begin{array}{c} H \\ \diagup \\ \diagdown \end{array}$$

Bu =   n - butyl radical

1. RBr + Mg ———————> RMgBr

2. 2 RMgBr + Bu$_2$SnCl$_2$ ———————> Bu$_2$SnR$_2$ + 2 MgBrCl

3. Bu$_2$SnR$_2$ + 2 I$_2$ ———————> Bu$_2$SnI$_2$ + 2 RI

The amounts of materials used were such as to make the solution of RMgBr about 1.5 M; very dilute or very concentrated solutions were deemed undesirable. Thus about 150-200 mls dry THF, 38 grams of the mixed bromopropene and 8 grams of magnesium were measured out. (A slight excess of magnesium was used).

The apparatus was set up as in Figure 1. The reaction was started with a small amount of magnesium and 1-bromopropene mixture dissolved in about 25 mls of THF. The reaction started after one hour of vigorous stirring, proceeding with considerable foaming.

When the reaction had subsided, the remainder of the magnesium was flushed into the reaction flask with the remaining THF. The 1-bromopropene was added dropwise with stirring, care being taken to keep heating and foaming at a minimum.

A saturated solution was prepared by dissolving about 37 grams of di-n-butyltin dichloride in dry THF. (This weight

FIGURE 1

Apparatus used in the preparation of <u>cis</u> and <u>trans</u>

1-iodopropene.

A. 500 ml. three-neck round bottom flask.

B. Condenser.

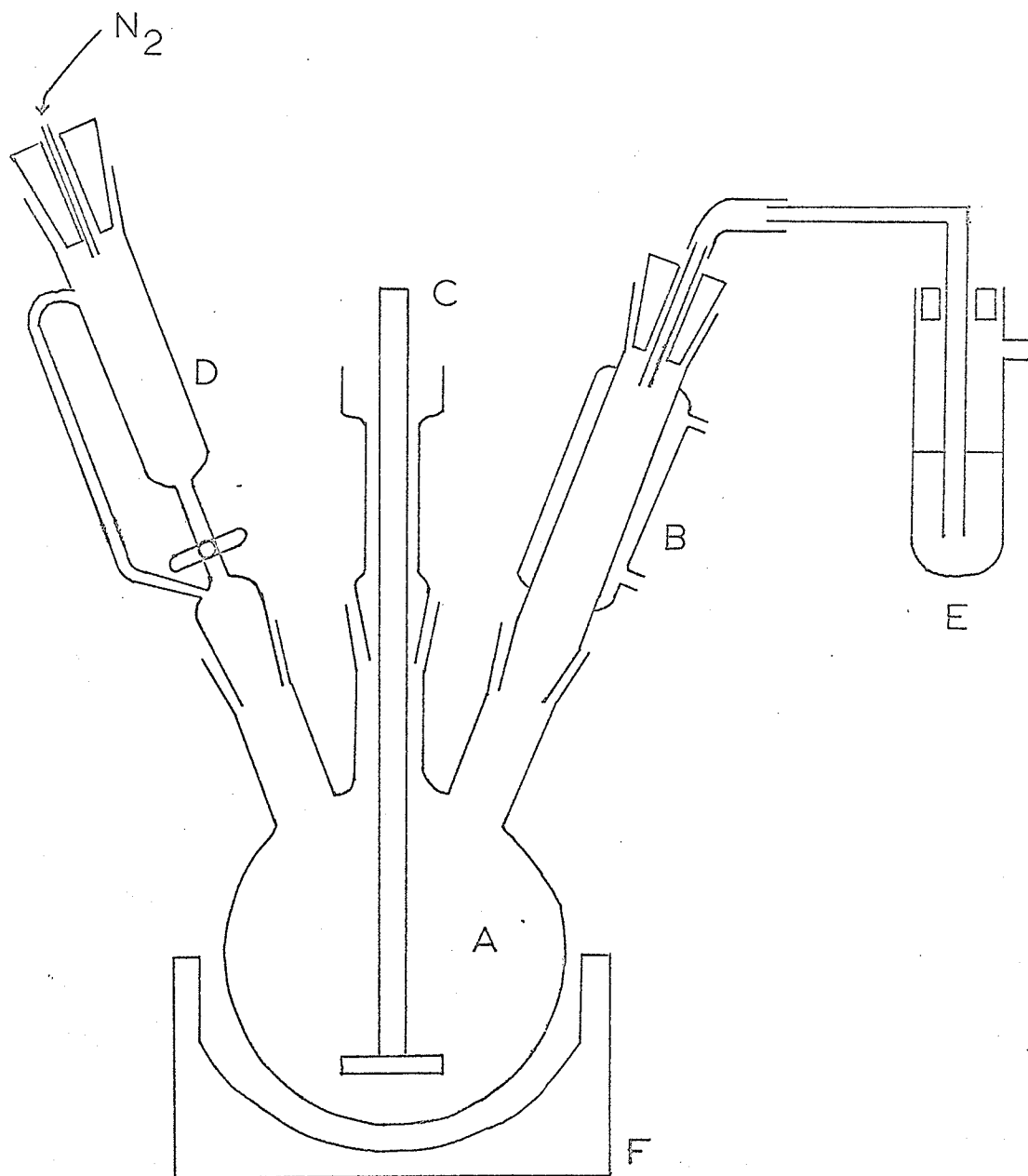C. Mercury seal stirrer driven by electric motor.

   (Paraffin oil was used in the seal).

D. Pressure equalizing separatory funnel.

E. Test tube with paraffin oil used to indicate the

   N_2 flow rate. The N_2 gas was passed through the

   system in order to provide an inert atmosphere

   above the reaction. The N_2 was bubbled slowly at

   about 20-25 mls. per minute.

F. Heating mantle.

of the tin compound was about 25% under the theoretical

amount required. An excess of RMgBr at this stage was

originally thought to be advantageous; however, now it is

felt that stoichiometric quantities are preferable). The

saturated solution was added to the reaction flask and the

reaction mixture was refluxed overnight at approximately

45° C.

After refluxing most of the THF was drawn off under

vacuum. (Bu_2SnR_2 has a low vapor pressure and is not

appreciably lost). Approximately 100 mls. of ethyl ether

which need not be exceedingly dry were added. (The

subsequent step involves addition of water to the system;

since THF is miscible with water while ethyl ether is not,

two easily separable layers will be formed if THF is replaced

by ether). A saturated solution of ammonium chloride in 25

mls. of water was added dropwise with stirring. Magnesium

halides were precipitated in this step. (Tin halides can be

precipitated by passing dry ammonia into the reaction mixture

(125) but it was found that this step could be safely by-passed).

Since Bu_2SnR_2 is not volatile, the low-boiling solvent

and impurities can be drawn off in a vacuum system. At this

stage there should be approximately 38 grams of Bu_2SnR_2. The

next step involved cleavage of the Sn-R bond with iodine.

About 15 grams of iodine were weighed out; this amount

will remove 1/2 R per Bu_2SnR_2.* The iodine was added slowly

to the ice-cooled Bu_2SnR_2. This step proceeds rapidly as

indicated by the decolorization of the iodine. The solution

was transferred to a vacuum system and the volatile

iodopropenes were drawn off. The solution remaining was

again treated with iodine in an attempt to retrieve more

iodopropene which may be expected to be contaminated with

increasing amounts of n-butyl iodide. Initially about 5 grams

of final product were isolated, indicating a 50% yield.

The impure iodopropenes were chromatographed on a

Wilkins chromatograph (Model A-90-P). A six-foot copper

column packed with 60-80 mesh firebrick coated to twenty

weight-per cent with tricresyl phosphate was used. The

boiling points of the iodopropenes were estimated to be

about 90° C. Therefore the column was kept at 90° C. The

injector and detector were at 115° C and 150° C, respectively.

Good separation of the isomers was obtained using 40 μl

injections and a helium flow-rate of 60-70 mls/min. The

_____

*By keeping this tin compound in excess the formation of
 butyl iodide is suppressed. However subsequent treatments
 with iodine yielded iodopropenes of comparable purity.

separated isomers were collected in NMR tubes immersed in acetone cooled by liquid air and stored over dry ice.

A mixture of the 1-iodopropene was sent for micro-analysis.* The results of the analysis are tabulated in Table I.

The analysis is in good agreement with the formula $CH_3CH = CHI$.

Proton resonance studies were further confirmation of the preparation (see Chapter III). Calculated and observed spectra are given in Figures $3 \cdot 1 - 3 \cdot 4$. From the magnitudes of the coupling constants, chemical shifts and solvent effects, it is fairly certain that the preparation was successful.

---

* Geller Laboratories,
  P. O. Box 6400,
  Charleston, W.Va. 25302

TABLE I

Microanalysis of 1-iodopropenes

	Trial				Average	Calculated*
	1	2	3	4		
% carbon	21.24	21.26	21.07	–	21.19	21.45
% hydrogen	2.89	2.77	3.10	–	2.92	3.00
% iodine	–	–	75.71	75.50	75.61	75.55
molecular weight	–	–	170.00	167.00	168.00	167.98
hydrogenation number	–	–	0.97	0.99	0.98	1.00
% tin	–	–	0.41%	–	0.11	

*From the formula, $CH_3CH = CHI$

APPENDIX II

In Chapter I McConnell's treatment of magnetic

anisotropy effects in proton magnetic resonance was

discussed briefly. It was noted that the dipolar

approximation used in the derivation of equation 1·18 is

accurate only if the shielded nucleus is at least 6 bond

lengths from the anisotropic electron distribution. In

addition to this defect equation 1·18 is unable in certain

instances to determine even the sign of the contribution

to nuclear magnetic shielding. This second difficulty

arises in the placement of the origin of the magnetic

dipolar field.

The positioning of the origin of the dipolar field

has been rather arbitrary. It has been placed at atomic

centres (125) and at the midpoints of bonds (52). Since the

anisotropy in the magnetic susceptibility is a property of

the electrons in a chemical bond, positioning the origin at

the electronic centre of gravity is also reasonable. It is

shown here that, in fact, diamagnetic or paramagnetic

contributions from the magnetic anisotropy of a given C-X

bond are predicted depending on the choice of the origin. The vinyl-X compounds where X is a halogen or hydrogen are used to illustrate this second difficulty.

The C-X bond in vinyl-X compounds is expected to have an anisotropic effect on the shielding of the proton cis to the substituent. For a given value of ΔX, the anisotropy in the magnetic susceptibility of the C-X bond, the sign of the shielding contribution depends on the factor $(1-3 \cos^2\theta)$ where θ is the angle between the vector drawn from the origin to the cis proton and the C-X bond direction. Scale diagrams of the vinyl-X compounds were drawn from the available data in reference 110 and θ was obtained to within 1° with a protractor. The values of θ and the corresponding angle factors are given in Table II. They are evaluated at each of the three suggested origins.

In all instances except X = H the sign of the shielding of the cis proton when the origin is placed at the substituent is opposite to that when the origin is placed at the centre of the bond. For X = Br and X = I opposite signs are obtained if the origin is placed at the midpoint of the C-X bond or at the electronic centre. Therefore it is felt that the arbitrariness in the placement of the origin of the dipolar field can be a

TABLE II

Value of θ and $1-3\cos^2\theta$ for the proton cis

to the substituent X in vinyl-X compounds

	Origin					
Substituent	X		Midpoint of C-X bond		Electronic centre of gravity of C-X bond	
	θ(degrees)	$1-3\cos^2\theta$	θ(degrees)	$1-3\cos^2\theta$	θ(degrees)	$1-3\cos^2\theta$
H	59	0.16	72	0.72	80	0.91
F	53	-0.08	69	0.60	64	0.39
Cl	47	-0.40	63	0.34	56	0.04
Br	45	-0.50	62	0.28	49	-0.30
I	42	-0.68	59	0.16	45	-0.50

serious defect in the use of equation 1·18 for estimating

absolute values of the contribution to magnetic shielding

from bond anisotropies. However the angle factors are seen

to increase in the same fashion no matter where the origin.

For this reason equation 1·18 may perhaps be useful in

predicting trends in proton shifts in molecules of similar

geometry if other effects are negligible, absent or readily

estimated.