Effect of Electronegativity and Magnetic Anisotropy of Substituents on C13 and H1 Chemical Shifts in CH3X and CH3CH2X Compounds

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Effect of Electronegativity and Magnetic Anisotropy of Substituents on C13 and H1 Chemical Shifts in CH3X and CH3CH2X Compounds*

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An investigation has been made of the major contributions which make up the relative chemical shifts in CH_3X and CH_3CH_2X compounds. In order to obtain more detailed information, both the carbon and hydrogen chemical shifts were measured. The carbon shifts were obtained by measuring natural abundance C^{13} resonances in the pure liquids; the H^1 resonances were measured on gaseous samples to avoid solvent effects. The results reveal surprisingly large contributions to both C^{13} and H^1 shifts arising from magnetic anisotropy effects of the X substituent. In CH_3X compounds, the contribution to the proton shifts is negative while that to the C^{13} shifts is positive. In CH_3CH_2X compounds, these effects contribute to the resonance shifts of carbon and hydrogen nuclei in both the methylene and methyl group. When such contributions are allowed for, an approximate correlation with the electronegativity of X can be obtained, indicating that inductive effects, together with anisotropy effects, account for the major part of the relative chemical shifts in these molecules. The quantitative determination of inductive parameters of substituents from chemical shift data is, however, somewhat limited. The presence of a large magnetic anisotropy within the molecule also affects the nuclear resonance shifts of neighboring molecules and gives rise to a "solvent dilution shift"; for the C^{13} resonance of CH_3I this amounts to 7.3 ppm.

I. INTRODUCTION

IN simple alkyl-substituted compounds, the chemical shifts of the α carbon, as well as those of the protons bonded to it, may be expected to be directly related to the inductive effects of the substituent. A simple relationship of this kind would be of great value in molecular structure determinations by nuclear magnetic resonance methods. However, previous attempts[1-6] to relate the measured chemical shifts in alkyl-X compounds with the electronegativity of the X substituent have been only partially successful, and a general systematic correlation with electronegativity was not found possible. Thus, for example, in halogen-substituted ·compounds, the observed shifts frequently bear no apparent relationship to the inductive effects of the halogen substituents. In the methyl halides, the proton resonances appear to follow the expected trend with electronegativity, the protons in CH_3Cl being less shielded than in CH_3I. However, this trend is completely reversed in the isopropyl halides.[4] Similar anomalies have been observed in F^{19} and C^{13} resonances of halogen-substituted compounds[1,6,7] and it is therefore apparent there are other major contributions to the chemical shift which completely obscure the inductive effects. These contributions have not been satisfactorily ex-

plained; they have been variously attributed to partial double-bond character of the C—X bond,[1,5] to diamagnetic anisotropy of the C—C bond and possibly also of the C—X bond,[5] and to repulsion effects.[7] The present work was undertaken in an attempt to obtain a better understanding of the chemical shifts in alkyl-substituted compounds generally. The measurements were largely confined to CH_3X and CH_3CH_2X compounds, and in order to obtain more detailed information, both C^{13} and H^1 resonance shifts were measured.

II. EXPERIMENTAL RESULTS

1. Proton Resonances

Since proton resonance shifts are peculiarly sensitive to solvent effects,[8] it was essential for the present purpose to obtain the "isolated molecule" shift for each compound. This can be achieved most directly by carrying out the measurements in the gaseous state. By the use of vacuum techniques, the samples were condensed into 5 mm o.d. Pyrex glass tubes. The amount of sample used in each case was measured so as to yield a pressure of 5 atm when completely vaporized. Methane gas was also added to each sample tube to a partial pressure of 5 atm. This provided the internal reference signal for the chemical shift measurements. The latter were carried out in the usual way by superimposing the sideband of the signal being measured on that of the reference methane, exact superposition having been determined by maximizing the signal amplitude on the paper recorder on slow back-and-forth traversals of the signal. The sideband (modulating) frequency was measured by a frequency counter. While these procedures are generally capable of greater precision, the accuracy of

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[1] L. H. Meyer and H. S. Gutowsky, J. Phys. Chem. **57**, 481 (1953).
[2] B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc. **77**, 3977 (1955).
[3] A. L. Allred and E. G. Rochow, J. Am. Chem. Soc. **79**, 5361 (1957).
[4] A. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc. **80**, 1728 (1958).
[5] A. A. Bothner-By and C. Naar-Colin, Ann. N. Y. Acad. Sci. **70**, 833 (1958).
[6] P. C. Lauterbur, Ann. N. Y. Acad. Sci. **70**, 841 (1958).
[7] G. V. D. Tiers, J. Am. Chem. Soc. **78**, 2914 (1956).

[8] A. D. Buckingham, T. Schaefer, and W. G. Schneider, J. Chem. Phys. **32**, 1227 (1960).

TABLE I. Proton chemical shifts of gaseous CH_3X and CH_3CH_2X compounds referred to CH_4 gas[a] (in cps at 60 Mc/sec).

| | CH_3X | | | CH_3CH_2X | | |
| | | | | | Proton shift (cps) | |
Compound	Temp (°C)	Proton shift (cps)	Compound	Temp (°C)	CH_2	CH_3
$CH_4(CH_3H)$	22	0				
CH_3F	22	−239.8	CH_3CH_2F	40	−253.7	−68.5
CH_3Cl	22	−162.6	CH_3CH_2Cl	113	−193.3	−77.5
CH_3Br	92	−138.9	CH_3CH_2Br	130	−187.3	−88.0
CH_3I	109	−111.0	CH_3CH_2I	168	−178.1	−99.6
$(CH_3)_2O$	22	−186.0	$(CH_3CH_2)_2O$	95	−197.7	−61.1
$(CH_3)_3N$	120	−121.7	$(CH_3CH_2)_3N$	150	−143.6	−53.9
$(CH_3)_4C$	110	− 49.5	$(CH_3CH_2)_4C$	220	− 76.0	−43.0
CH_3CH_3	22	− 45.0	$(CH_3CH_2)H$ $CH_3CH_2CH_2CH_3$	22 95	− 45.0 − 72.8	−45.0 −48.6
$(CH_3)_2S$	108	−114.1	$(CH_3CH_2)_2S$	170	−143.0	−66.2
CH_3CN	150	− 91.9	CH_3CH_2CN	155	−117.3	−64.6
$(CH_3)_2CO$	140	−109.1				
CH_3CHO	122	−107.6				
CH_3NO_2	166	−234.7				
$(CH_3)_4Si$	100	+ 8.0	$(CH_3CH_2)_4Si$	220	− 34.0	−54.0
$(CH_3)_4Ge$	120	0.0				
$(CH_3)_4Sn$	100	+ 6.0				
$(CH_3)_4Pb$	170	− 34.0	$(CH_3CH_2)_4Pb$	145	− 44.5	−44.5

[a] Positive shifts indicate higher proton screening than that of the reference proton; negative shifts, lower screening.

the present chemical shift measurements was about ±0.5 cps. The reason for this was that the reference methane signals were about four times as broad as those of most of the compounds measured, due to the smaller spin relaxation time of methane protons.[9] This permitted unambiguous assignment of the signals, but it limited the ultimate precision of the chemical shift measurements. (Use of ethane[9] instead of methane as the reference gas would overcome this difficulty).

The results of the chemical shift measurements are summarized in Table I. To bring about complete vaporization, the majority of the samples had to be heated above room temperature. The temperature at which the measurement was made in each case is shown. Heating of the samples in the spectrometer probe assembly was carried out as described previously.[10]

2. C¹³ Resonance Measurements

The carbon chemical shifts were obtained by measuring natural abundance C¹³ resonances, using dispersion mode and rapid passage conditions as described previ-

ously by Lauterbur.[11] A fixed measuring frequency of 15.1 Mc/sec was used. The sample container, illustrated in Fig. 1, consisted of two concentric, thin-walled spherical bulbs. The small inner bulb, 0.2 cc in volume, contained the reference liquid dimethyl carbonate enriched to 50% C¹³ in the carbonate group plus a small amount of Fe^{III} acetylacetonate. The latter served to shorten T_1 to yield a narrower line, making possible high-power audiomodulation for calibration purposes. The outer bulb, which contained the sample to be measured, had a volume of ~1.5 cc. The whole sample container assembly was aligned in a lathe and provided with a glass tip at its lower end to permit spinning of the sample within the rf coil. Because of the appearance of some "spinning noise", sample spinning did not significantly improve the over-all signal-to-noise ratio, but some line narrowing, about 20–25%, was realized and provided an improved resolution of closely spaced lines.

Since essentially rapid passage dispersion signals (with some saturation) are observed, the actual line position must be obtained from the mean of forward and reverse field sweeps. To minimize errors in line position caused by variations in sweep rate and saturation effects, the average of five forward and reverse sweeps

[9] The value of T_1 for methane gas, recently measured by M. Lipsicas-Lipschitz [Ph.D. thesis, University of British Columbia, Vancouver (1960)], is 0.02 sec, and that of ethane gas, 0.2 sec.
[10] W. G. Schneider, H. J. Bernstein, and J. A. Pople, J. Chem. Phys. 28, 601 (1958).
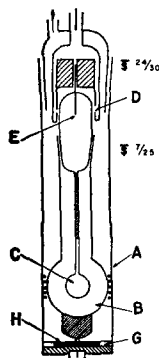[11] P. C. Lauterbur, J. Chem. Phys. 26, 217 (1957).

FIG. 1. Sample holder assembly. A, 15 mm rf coil insert; B, spherical sample container; C, inner sphere for reference liquid; D, small tangential blow-holes; E, 40 mil tungsten wire; G, Teflon ring; H, Bakelite bearing.

was normally taken. On this basis, the reproducibility of the final chemical shift measurements is about ± 5 cps or ± 0.3 ppm.

The samples were ordinarily measured in the form of the neat liquids, a condition imposed by the low (1%) natural abundance of C^{13}. This raises the question of possible influence of solvent effects on the chemical shifts so measured. Because the carbon shifts are generally at least an order of magnitude larger than the proton shifts in the same compounds, such effects may be expected to be relatively less important in carbon resonance measurements. To check this point, solvent dilution shifts were measured for two compounds for which such shifts may be expected to be largest. For reasons which will become apparent in the following section, the compounds chosen were CH_3I and CH_3Br. Using samples enriched to 72% in C^{13}, the neat liquid was placed in the inner sphere of the sample container, while the outer sphere contained a 5 mole-% solution in cyclohexane. The C^{13} resonance of the solution was displaced to high field relative to that of the neat liquid by 7.3 ppm for CH_3I and by 3.6 ppm for CH_3Br. (For comparison, the corresponding displacement of the proton resonance of CH_3I on dilution was found to be approx 0.5 ppm.) Figure 2 shows the C^{13} spectrum obtained for the CH_3I experiment, each C^{13} resonance line being split into a quartet by the three protons of the methyl group. Since spherical samples were employed, these results are not influenced by bulk susceptibility effects. It appears, therefore, that for molecules containing highly anisotropic groups local magnetic interactions may cause an appreciable shift of the C^{13} resonances well in excess of the accuracy of the measurements. For the remaining compounds measured, such effects may be expected to be much smaller, generally not exceeding 1 ppm and no corrections were attempted. The gaseous compounds, CH_3F and CH_4, which were isotopically enriched to 70% C^{13}, were measured in the form of a 5 mole-% solution in cyclohexane using the triplet C^{13} resonance of the solvent as a secondary reference.

The complete results of the C^{13} resonance measurements are summarized in Tables II, III, and IV. Table V shows the measured carbon-hydrogen spin-coupling constants for the CH_3X compounds. For comparison,

some previous values reported by Lauterbur[11] are also listed, together with the values obtained by Muller and Pritchard[12] by measuring "C^{13} satellite lines" in the corresponding proton resonance spectra.

III. INTERPRETATION OF RESULTS

1. Magnetic Model for Alkyl-X Compounds

The nuclear screening by electrons of carbon and hydrogen nuclei in alkyl-X compounds are most conveniently considered as the sum of a number of local or "atomic" contributions, as discussed previously by Saika and Slichter,[13] Pople,[14] and McConnell[15]:

(i) Contributions arising from the electron charge distribution surrounding the nucleus being measured.

(ii) Contributions arising from the electron charge distributions of neighbor atoms in the molecule.

Both of these contributions may cause a diamagnetic or paramagnetic shift of the nuclear resonance. The diamagnetic part of contribution (i) arises from the total electronic charge distribution of the atom concerned, which depends in turn on the degree of hybridization of bonding orbitals and on the inductive effects of neighbor atoms. For the series of compounds being considered here, the degree of hybridization of the carbon orbitals may be regarded as approximately constant. Hence, there will be a diamagnetic contribution to the chemical shift related simply to the electronegativity of the X atom. In a CH_3X compound this effect will of course be greatest at the C atom and considerably attenuated at the H atoms, which are one bond further removed from the X substituent. The paramagnetic part of contribution (i) is generally small for protons.[16] For carbon atoms this contribution may be expected to
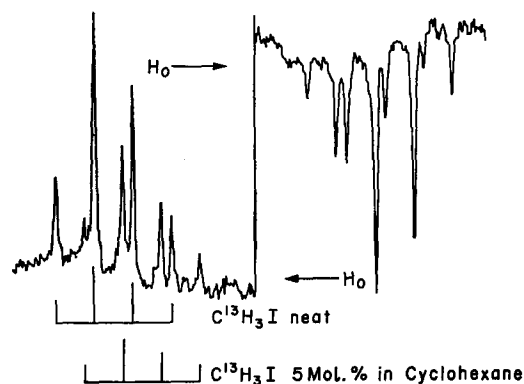
FIG. 2. C^{13} resonance spectrum of $C^{13}H_3I$ pure liquid, contained in inner sample bulb, and of $C^{13}H_3I$ diluted to 5 mole % in cyclohexane, which was contained in outer sample bulb. Forward- and reverse-sweep spectra are shown.

[12] N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 1471 (1959).

[13] A. Saika and C. P. Slichter, J. Chem. Phys. 22, 26 (1954).

[14] J. A. Pople, Proc. Roy. Soc. (London) A239, 541 (1957).

[15] H. M. McConnell, J. Chem. Phys. 27, 226 (1957).

[16] N. F. Ramsey, Phys. Rev. 78, 699 (1950).

Table II. C^{13} chemical shifts of CH₃X compounds. [Δν in cps referred to (CH₃O)₂C^{13}O and δ in ppm referred to benzene.][a]

Compound	Δν	δ	Compound	Δν	δ
CH₄	2404	130.8	(CH₃)₄Ge	2398	130.4
CH₃F	1234	53.3	(CH₃)₄Sn	2507	137.6
CH₃Cl	1996	103.8	(CH₃)₄Pb	2416	131.6
CH₃Br	2230	119.3	(CH₃)₂S	2078	109.2
CH₃I	2709	151.0	(CH₃)₂SO	1715	85.2
(CH₃)₂O	1475	69.3	CH₃NO₂	1507	71.4
(CH₃)₃N	1661	81.2	(CH₃)₂CO	1999	104
(CH₃)₄N⁺Br⁻ [b]	1530	72.9	CH₃CN	2301	124
(CH₃)₄C	1895	97.1	CH₃CHO	1925	99.1
(CH₃)₄Si	2377	129.0			

[a] C^{13} shift of benzene referred to (CH₃O)₂C^{13}O=28.4 ppm (benzene signal at high field).
[b] Measured in aqueous solution.

be much larger, although no quantitative estimate of its magnitude has been possible.

Contribution (ii) will affect the chemical shifts of both the carbon and hydrogen nuclei because of the so-called "neighbor-anisotropy effect," previously discussed by Pople[17] and McConnell.[15] This effect has its origin in the field-induced diamagnetic or paramagnetic circulation of electrons on the X atom (or C—X bond). The secondary field so produced will have a component at a neighboring nucleus being measured. If the mag-

Table III. C^{13} chemical shifts of CH₃CH₂X compounds. [Δν in cps referred to (CH₃O)₂C^{13}O and δ in ppm referred to benzene.[a]]

	CH₂		CH₃	
Compound	Δν	δ	Δν	δ
CH₃CH₃			2283	122.8
CH₃CH₂F	1175	49.4	2152	114.1
CH₃CH₂Cl	1777	89.3	2102	110.8
CH₃CH₂Br	1943	100.3	2064	108.3
CH₃CH₂I	2342	126.7	2022	105.5
(CH₃CH₂)₂O	1354	61.3	2114	111.6
(CH₃CH₂)₃N	1644	80.5	2164	114.9
(CH₃CH₂)₄N⁺Br⁻[b]	1578	76.1	2259	121.2
(CH₃CH₂)₄C	1993	103.6	2306	124.3
(CH₃CH₂)₄Si	2342	126.7	2279	122.5
(CH₃CH₂)₄Sn	2374	128.8	2206	117.7
(CH₃CH₂)₄Pb	2209	117.9	2132	112.8
(CH₃CH₂)₂S	1972	102.2	2134	112.9

[a] C^{13} shift of benzene referred to (CH₃O)₂C^{13}O=28.4 ppm (benzene signal at high field).
[b] Measured in aqueous solution.

[17] J. A. Pople, Proc. Roy. Soc. (London) A239, 550 (1957).

netization of the X atom (or group) is highly anisotropic in character, the component of the secondary field at a neighboring nucleus will not be averaged to zero by molecular rotations and will make a contribution to the measured chemical shift of this nucleus. The type of approximate molecular model, which is consistent with the experimental data, is schematically illustrated in Fig. 3 for the case of CH₃CH₂I. Since the C—I bond has cylindrical symmetry, free diamagnetic circulation of electrons occurs when the bond axis is oriented in the direction of the applied field H₀ [Fig. 3(a)]. Because of the large orbital radius of the iodine electrons, a large secondary field is generated which may be crudely represented by a magnetic point-dipole located in the C—I bond. The direction of the resulting local fields at each of the carbon and hydrogen nuclei, indicated in the figure, is such that the C^{13} resonance of the α carbon will be displaced very much to higher field, while that of the α protons and β protons, as well as the β carbon, will be displaced to lower field.

When the applied field is directed at right angles to the C–I bond, free diamagnetic circulation is highly hindered, so that in this orientation the resulting local fields are small. Thus averaging over all orientations will result in net displacements of the resonances as above. The diamagnetic anisotropy, $\Delta\chi = \chi_{||} - \chi_{\perp}$, where $\chi_{||}$ and $\chi_{\perp}$ are the magnetic susceptibilities para-

Table IV. C^{13} chemical shifts of methyl-substituted methanes. (δ in ppm relative to benzene)

Compound	Center carbon	Methyl carbon
CH₄	130.8	130.8
H₃CCH₃	122.8	122.8
H₂C(CH₃)₂	110.9	111.3
HC(CH₃)₃	103.9	103.9
C(CH₃)₄	101.1	97.1

TABLE V. C^{13}—H spin coupling constants in CH_3X compounds (in cps).

Compound	Present measurements	Lauterbur[11]	Muller and Pritchard[12]
CH_4	123		125
CH_3F	148		149
CH_3Cl	151		150
CH_3Br	154	153	152
CH_3I	151	151	151
$(CH_3)_2O$	138		
$(CH_3)_3N$	130		131
$(CH_3)_4N^+$	146		
$(CH_3)_4C$	124		124
$(CH_3)_4Si$	119	120	
$(CH_3)_4Ge$	126		
$(CH_3)_4Sn$	128	126	128
$(CH_3)_4Pb$	133		
$(CH_3)_2S$	136		
CH_4CH_3	127		126
$(CH_3)_2SO$	136		138
CH_3NO_2	155	137	147
$(CH_3)_2CO$	133	122	126
CH_3CN	134	136	136
CH_3CHO	128		127

llel and perpendicular to the bond axis, has a large negative value. For a simple magnetic point-dipole approximation, the resulting contribution to the screening constant σ is given by [15]

$$\Delta\sigma = (\Delta\chi/3R^3)(1-3\cos^2\theta), \qquad (1)$$

where R and θ define the position of the nucleus under consideration relative to the position of the point dipole and the bond axis, as indicated in Fig. 3. This simple approximation is only valid if $R \gg r$, where r is the orbital radius of the anisotropic group. For the larger halogen atoms, this condition is not fulfilled and a detailed quantum mechanical description[15] is necessary, although at present a quantitative treatment is not possible for relatively complex molecules. It may be noted from (1) that $\Delta\sigma$ is zero when θ is $54°45'$, and that it will be positive or negative depending on whether θ is larger or smaller than this value. However, it is not possible to predict *a priori* the sign of $\Delta\sigma$ for the α protons and the β carbon and β protons (the methyl group is assumed to be freely rotating) from the molecular geometry. Even assuming Eq. (1) to be approximately valid, the result depends on where the point dipole is to be located in the anisotropic group. However, the experimental data are consistent and leave little doubt that $\Delta\sigma$ is negative for all nuclei except the α-carbon atom.

Thus far, only the contributions to $\Delta\chi$ arising solely from diamagnetic electron circulation in the X substituent have been considered. In many compounds a comparable, or even greater, contribution to $\Delta\chi$ arises from paramagnetic electron circulation in the X substituent due to field-induced mixing of excited states. In the present example, because the C—X bond is cylindrically symmetrical, there will be a zero contribution to χ_{11}, but a large positive contribution to χ_1 [Fig. 3(b)]. Thus $\Delta\chi$ is very much enhanced. For substituents such as N, S, O, NO_2, HCO, etc., the magnetic anisotropy of X may be expected to be dominated by the paramagnetic contributions. On the other hand, if the electron distribution about the X atom is symmetric, as for example in the tetrahedral compounds, CH_4, $C(CH_3)_4$, $Si(CH_3)_4$, etc., $\Delta\chi$ is zero and the neighbor anisotropy effect is absent. According to the present model, for molecules of this type a simple correlation of the screening constants (chemical shifts) of C^{13} and H^1 nuclei with the electronegativity of the X substituent may be anticipated.

III. Comparison with Experiment

A. CH_3X *Compounds*

Figure 4 shows the proton chemical shifts of CH_3X compounds plotted against the electronegativity of the X substituents.[18] Compounds in which the neighbor anisotropy effect is appreciable will give rise to points in this plot which deviate from the simple electronegativity correlation line. This is particularly striking for the compounds CH_3I, CH_3Br, CH_3Cl, and $(CH_3)_2S$, for which the deviations are negative, in agreement with the assumed model. The deviation of the points from the correlation line may be taken as a relative measure of the neighbor-anisotropy contribution.
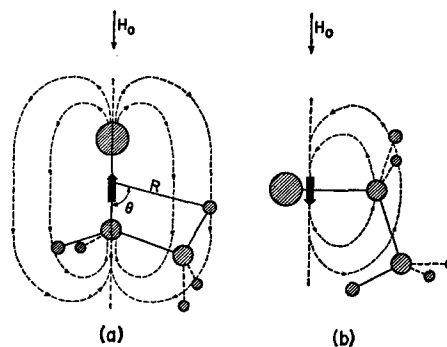
Figure 5 shows the corresponding plot of the C^{13}

FIG. 3. Magnetic fields in CH_3CH_2I induced by the applied field H_0.

[18] Electronegativities used are so-called "best values" compiled by D. E. Pritchard and H. A. Skinner, Chem. Rev. 55, 745 (1955). They differ little from the original Pauling scale [L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960)].

resonances.[19] Here the neighbor-anisotropy effect causes positive deviations conforming with the model (Fig. 3). The anisotropy contributions to the carbon resonance is relatively much larger than to the protons in the same compound, which are 1 bond further removed from the anisotropic center. In the compounds $(CH_3)_3N$, $(CH_3)_2O$, and CH_3F, for which no appreciable anisotropy contributions to the proton shifts were apparent, there is a considerable contribution to the C^{13} shift.[20]

As would be anticipated, the largest neighbor-anisotropy contribution, amounting to 54 ppm, occurs in CH_3I. This satisfactorily accounts for previous observations[11,21] that the largest C^{13} screening constants tend to occur in compounds in which iodine atoms are bonded to carbon. This is further supported by the C^{13} measurements of a series of methyl- and halogen-sub-
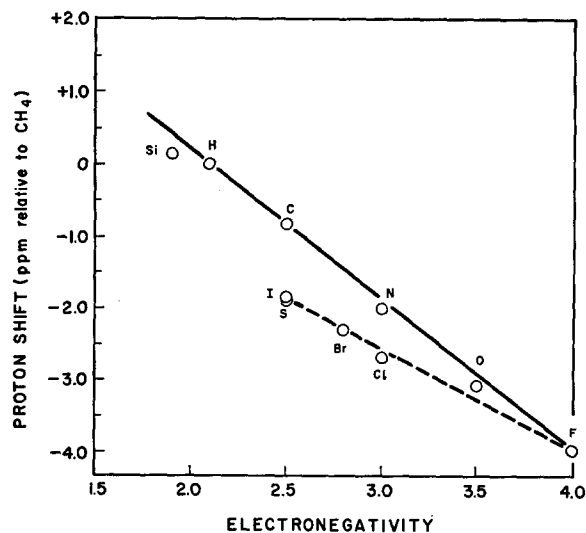

FIG. 5. The C^{13} chemical shifts of CH_3X compounds plotted against the electronegativity of X.

atom, it may be anticipated that, as the H atoms of methane are successively replaced by these substituents, the C^{13} resonance would be progressively displaced to lower field (lower screening). The measurements show this trend is approximately followed with methyl and Cl substitution, but the trend is reversed with increased Br substitution and is completely contrary with I substitution. These results are satisfactorily interpreted in terms of an increasing neighbor-anisotropy contribution to the carbon shift as more halogen atoms are added to the molecule. As the size of the halogen atom increases and it electronegativity decreases, the anisotropy con-

FIG. 4. Proton chemical shifts of CH_3X compounds vs the electronegativity of X. (The X substituent is identified in each case.)

stituted methanes shown in Fig. 6. In this plot some measurements reported by Lauterbur[6] have been included. Since the methyl group and the halogen atoms, Cl, Br, and I, are each more electronegative than the H

[19] The electronegativity correlation line in this plot is obviously not as well established as in the corresponding proton plot. Lauterbur[6] has previously pointed out a nearly linear correlation of the C^{13} resonances of tetramethyl compounds with the electronegativity of the central atom. The inclusion of the $(CH_3)_4N^+$ ion in such a correlation may be questioned. The fact that its C^{13} resonance falls near the correlation line is surprising in itself. The small positive deviation of the CH_4 point appears real. If the correlation line were made to pass through the CH_4 and $C(CH_3)_4$ points, the indicated anisotropy contribution for CH_3F would then obviously be much too large. The correlation line shown in Fig. 5 gives the best overall consistency with the experimental data, but its approximate nature must be emphasized.

[20] The direction and relative magnitudes of the C^{13} shifts in these compounds parallel the corresponding proton shifts of the hydride molecules, NH_3, H_2O, and HF, for which anisotropy contributions have been calculated theoretically. (See reference 17.)
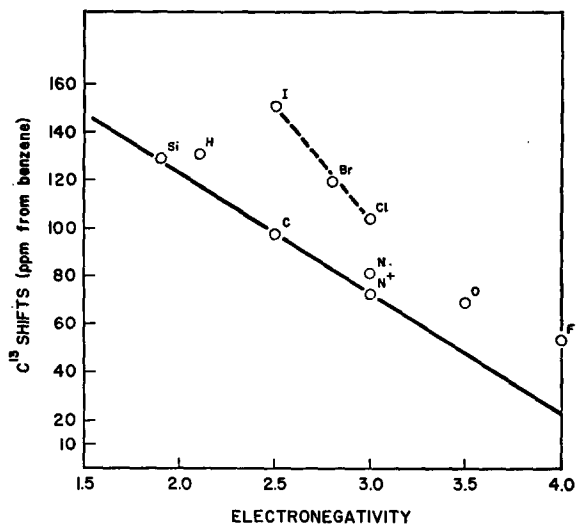
[21] C. H. Holm, J. Chem. Phys. **26**, 707 (1957).

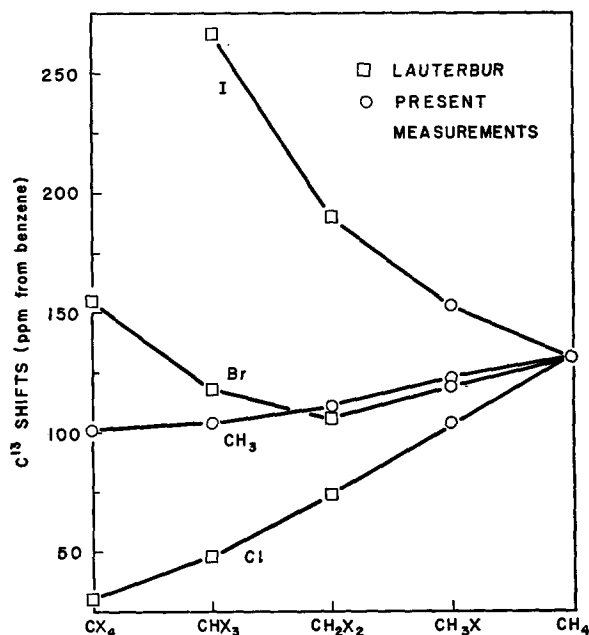
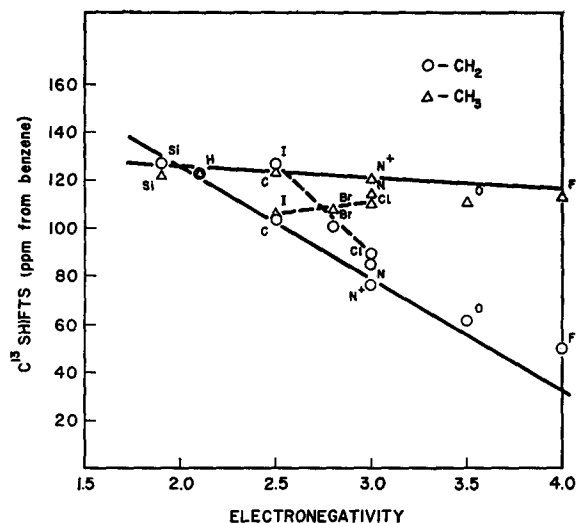FIG. 6. The C^{13} chemical shifts of some substituted methanes.

FIG. 7. The C^{13} chemical shifts of CH_3CH_2X compounds plotted against the electronegativity of X.

tributions to the carbon screening constants dominate those arising from electronic inductive effects.

B. CH_3CH_2X Compounds

The C^{13} and H^1 chemical shifts of both the methylene and methyl groups of a series of CH_3CH_2X compounds plotted against the X electronegativity are shown in Figs. 7 and 8. As may be expected, the results for the α carbon and the α protons are very similar to those of the CH_3X compounds, and the slopes of the electronegativity correlation lines are similar. However, the actual magnitudes of the shifts of the α carbon and α protons are somewhat less than those of the corresponding CH_3X compounds. This is a result of the greater electronegativity of the CH_3 group as compared to an H atom, the CH_3CH_2X compound being regarded as resulting from the replacement of an H atom in the corresponding CH_3X compound by a CH_3 group. From Figs. 4 and 5, the resonance shift to be expected by this replacement is -0.67 ppm for protons and -8.0 ppm for C^{13}. The measured results (cf. Tables I, II, and III) scatter considerably from these values, and to this extent quantitative correlations of the present type break down.

As in the results for the CH_3X compounds, magnetic anisotropy contributions of the X substituent are evident in the plots shown in Figs. 7 and 8. These are particularly prominent in ethyl chloride, bromide, and iodide, for which the individual points have been joined by dotted lines. For the α carbon and α protons, the deviations from the correlation line are similar to those for the CH_3X compounds, being to high field for the C^{13} resonances and to low field for protons. Of particular interest, however, is the definite indication of magnetic anisotropy contributions at both the β carbon and β protons (methyl group). Since the inductive effects of

the X substituent are largely absent at the methyl group, the dotted line joining the proton resonances for the β protons of ethyl chloride, bromide, and iodide has a negative slope, the anisotropy contribution decreasing in the order $I > Br > Cl$. This is also the case for the β-carbon resonances, and it is to be noted particularly that both the β-carbon and β-proton resonances are displaced to low field, in agreement with the assumed model. Moreover, because the anisotropy contribution causes a high-field shift of the α-carbon resonance, and a low-field shift of the β-carbon resonance, the dotted lines in Fig. 7 joining the points for these resonance shifts actually cross; thus in CH_3CH_2I, the α-carbon resonance appears at higher field than that of the β carbon.

A further feature of the plots shown in Figs. 7 and 8 is that the correlation lines for α and β protons, and for α and β carbons, cross at an electronegativity value near 2.0. Such a crossing may be expected if the inductive effects of the substituent influence the α nuclei, but not those of the methyl group. Actually the correlation line for the methyl resonances of both C^{13} and H^1 shows a small residual slope. It is not possible to say whether this arises from residual inductive effects or magnetic anisotropy effects. As a result of the crossing-over of the two correlation lines, the proton and carbon resonances of the methyl group should lie at lower field than those of the methylene group when the effective electronegativity of the X substituent is less than 2.0. This was first observed experimentally in the proton resonance of tetraethyl lead and triethyl aluminum by Baker.[22] Similar results were observed in the present measurements for the C^{13} resonances of tetraethyl Si, Sn, and Pb.
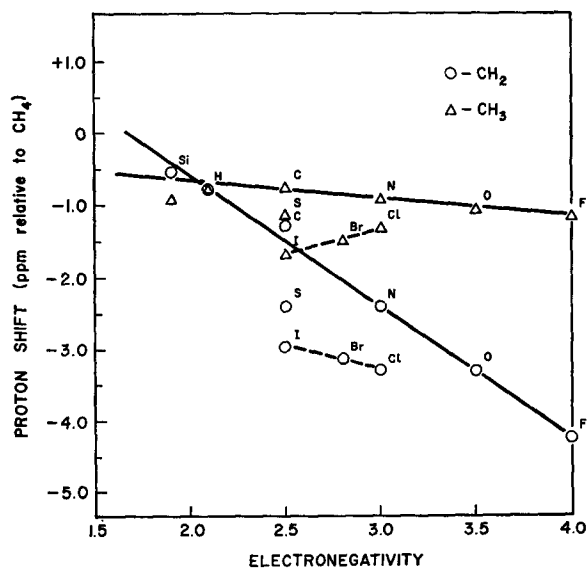

FIG. 8. The H^1 chemical shifts of CH_3CH_2X compounds plotted against the electronegativity of X.

[22] E. B. Baker, J. Chem. Phys. 26, 960 (1957).

The proton data for the ethyl compounds shown in Fig. 8 afford some insight into the empirical relation previously proposed by Dailey and Shoolery[2]:

Electronegativity of $X = 0.695 \ (\delta_{CH_3} - \delta_{CH_2}) + 1.71.$ (2)

Here $(\delta_{CH_3} - \delta_{CH_2})$ is the difference in chemical shift between the protons in the methyl and methylene groups. This formula, which also predicts a cross-over (at electronegativity 1.71), has been moderately successful for a variety of substituents, although its physical basis has remained obscure. The constants of the equation were fitted using only the data of the four ethyl halides (X = F, Cl, Br, I.). However, it is evident from Fig. 8 that for these compounds there are large anisotropy contributions to the proton shifts which are not present in other ethyl compounds. It is also apparent that the anisotropy contributions to δ_{CH_3} and δ_{CH_2} in the ethyl halides are in the same direction and of comparable magnitude. Thus, on taking the difference $(\delta_{CH_3} - \delta_{CH_2})$, these effects are largely cancelled. The approximate validity of Eq. (2) would appear to rest on this fortuitous cancellation.

C. Methyl and Ethyl Compounds of Group IV Elements

The C^{13} and H^1 resonance shifts of the tetramethyl and tetraethyl compounds of C, Si, Ge, Sn, and Pb are listed in Tables I, II, and III. Since magnetic anisotropy contributions to the central atom should be absent in the C^{13} and H^1 shifts, it was originally intended to employ the latter to establish the effective electronegativities of Si, Ge, Sn, and Pb relative to that of carbon. Attempts to employ proton resonances in this manner have been previously reported by Allred[23] and by Brown and Webster.[24] However it was not found possible to establish a wholly self-consistent set of values from both C^{13} and proton resonances from correlation plots such as those shown in Figs. 4 and 5. The individual results, together with those of previously reported values are listed in Table VI. The discrepancy is largest for the higher members in the series, Sn and Pb. In the alkyl compounds of these metals it would appear the proton and carbon shifts are altered in a different manner by the central atom. This is borne out by the fact that in tetraethyl lead the proton shifts in the methyl and methylene groups are equal (within experimental error), whereas the corresponding C^{13} shifts differ by 5.1 ppm. Moreover, the spin-coupling constant of the protons in the CH₃ group with the lead nucleus (Pb²⁰⁷) is considerably larger than that of the protons in the CH₂ group,[22] indicative of rather unusual bonding orbitals.

[23] A. L. Allred and E. G. Rochow, J. Inorg. & Nuclear Chem. 5, 269 (1958).
[24] M. P. Brown and D. E. Webster, J. Phys. Chem. 64, 698 (1960).

TABLE VI. Electronegativity data of group IV elements.

| | From H^1 resonances | | | | |
	Present data	Allred and Rochow	From C^{13} resonances	Pritchard and Skinner	Pauling[a]
C	2.60	2.60	2.5	2.5–2.6	2.6
Si	2.03	1.90	1.9	1.8–1.9	1.8
Ge	2.1	2.00	1.85	1.8–1.9	1.8
Sn	2.05	1.93	1.72	1.8–1.9	1.8
Pb	2.35	2.45	1.82	1.8	1.8

[a] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1960).

D. C^{13} Resonances of Methyl-Substituted Methanes

Table IV shows the C^{13} chemical shifts for a series of methyl-substituted methanes, both for the central carbon atom and for the methyl groups. The latter results are shown plotted in Fig. 6. Replacement of an H atom by a CH₃ group causes the C^{13} resonance to be displaced to lower field by ~7–8 ppm. An exception to this occurs in C(CH₃)₄, for which the methyl C^{13} resonance occurs at lower field (by 4 ppm) than that of the central carbon atom. This appears as yet another instance where quantitative electronegativity correlations break down.

C. C^{13}–H^1 Spin-Coupling Constants in CH₃X Compounds

The carbon-hydrogen spin coupling constants in the CH₃X compounds (Table V) range from 119 to 155 cps. The values for the methyl halides are uniformly high (~150 cps). The reasons for these variations in coupling constants are not clear. Factors such as bond angle, bond length, and degree of ionicity of the C–H bond may each contribute to the spin-coupling constants.[25,26]

IV. CONCLUSION

The experimental data for alkyl-X compounds provide ample evidence that the major contributions to the C^{13} and H^1 chemical shifts in these compounds arise from the inductive and magnetic anisotropy effects of the X substituent. When the magnetic anisotropy contributions are allowed for, a reasonably good correlation with the electronegativity of the X substituent is possible. Except for series of closely related compounds, such correlations tend to be qualitative rather than quantitative, and appear inadequate for heavy metal atoms such as Sn and Pb. Effective group electronegativities of substituents, such as NO₂, CN, CHO,

[25] N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 1471 (1959).
[26] M. Karplus and D. M. Grant, Proc. Natl. Acad. Sci. U.S. 45, 1269 (1959).

CO, SO₂, etc., cannot be reliably determined by these methods without some knowledge of their magnetic anisotropy contributions. This imposes serious limitations on the nuclear resonance technique as a method of determining inductive parameters.

The magnetic anisotropy contributions to the C^{13} and H^1 resonance shifts of the α carbon and hydrogens, as well as to the β-carbon and hydrogen atoms, are rather large. Similar contributions are to be expected for the F^{19} resonances of compounds in which the hydrogen atoms are replaced by fluorine atoms. The anomalous F^{19} shifts observed by Meyer and Gutowsky[1] in the series of compounds of the type CH_xF_{4-x} and CCl_xF_{4-x}, as well as those observed by Tiers[7] in compounds of the type $CF_3CF_2CF_2CH_2X$ ($X=Cl$, Br, I), can be satisfactorily explained on this basis.

In a recent study, Cavanaugh and Dailey[27] have compared the proton resonance shifts of methyl-X, ethyl-X and isopropyl-X compounds. In the ethyl-X compounds the difference between the α- and β-proton shifts was found to give a good linear correlation with the electronegativity of X, in agreement with the earlier Dailey-Shoolery relation. On this basis it was concluded that any large influence due to magnetic anisotropy of the C–X group could be ruled out, and in this respect their interpretation is at variance with the present results. The observed differences in the proton shifts between the CH_3X compounds and that of the α protons in the corresponding CH_3CH_2X compounds was attributed by Cavanaugh and Dailey to a "C–C bond shift" arising in the latter compounds, the magnitude of which depends on X. The physical meaning of this shift is not clear. The difference in proton shifts in CH_3X and the α protons of CH_3CH_2X may be expected to arise primarily from the difference in electronegativity between the H atom and a CH_3 group. The value of this shift, as given by the difference in the CH_4 and CH_3CH_3 resonance shifts, is approximately 0.7 ppm. Appreciable deviations from this value are observed on comparing CH_3X compounds with the corresponding ethyl and iso-

propyl compounds. This may be taken as another indication that quantitative correlations based solely on inductive and magnetic anisotropy contributions are inadequate and that smaller contributions of other origin also contribute. This aspect has also been emphasized above in relation to the H^1 and C^{13} shifts of lead and tin tetra-alkyls, the C^{13} shifts of methyl-substituted methanes, and the C^{13}–H^1 spin coupling constants. Some or all of these effects may be considered to reflect the limitations (from a quantitative standpoint) of the assumed model, which regards the observed chemical shifts to be made up of local atomic contributions.

The magnetic interaction of neighboring molecules having large magnetic anisotropies gives rise to a "solvent dilution shift" in the nuclear resonance. This has been observed in both H^1 and C^{13} resonances. In CH_3I the dilution shifts are, respectively, 7.3 ppm for the C^{13} resonance and 0.5 ppm for the H^1 resonance. Thus the magnitude is considerably larger in the C^{13} resonance than in the H^1 resonance. A similar difference is evident if one compares the *intramolecular* magnetic anisotropy shift contributions. For example, in CH_3CH_2I the contribution to the α-proton resonance is about 1.5 ppm, while that of the β carbon atom (which is in a similar geometric position relative to the anisotropic group, although the C–C bond is longer than the C–H bond) is approximately 18 ppm. Thus, in its response to the *inter-* or *intra*molecular fields arising from the magnetic anisotropic group, it appears carbon behaves as though it had an effective "atomic" susceptibility about an order of magnitude greater than the hydrogen atoms in methyl iodide. This suggests the presence of an additional contribution which remains to be characterized.

ACKNOWLEDGMENTS

[27] J. R. Cavanaugh and B. P. Dailey, J. Chem. Phys. **34**, 1099 (1961). We are greatly indebted to the authors for communicating their results to us prior to publication.