USE OF A RELATIONSHIP BETWEEN $J(^{13}\text{C–H})$ AND τ TO EVALUATE ANISOTROPIC CONTRIBUTIONS TO τ-ANISOTROPIES IN THE τ-VALUES OF THE GROUP IV TETRAMETHYL DERIVATIVES

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INTRODUCTION

Since there is a relationship between the electron density about a proton and the local diamagnetic shielding, there have been many attempts[1–6] to establish a relationship between the proton chemical shifts, τ, of some simple alkyl substituted compounds CH_3X and C_2H_5X, and the electronegativities** of the substituents, X. The failure to establish such a correlation has been attributed[4,6,7] to the contribution of other factors to the chemical shifts, which obscure the contribution arising from the inductive effect upon the local electron density at the hydrogen atom. Hereafter, the shielding arising from the local electron density at the hydrogen atom will be designated as the local contribution and all other contributions to τ which arise from neighboring atoms will be designated as non-local. Since the non-local contributions are difficult to estimate, it is difficult to ascertain when an atom or group electronegativity can be obtained from a chemical shift. This uncertainty is illustrated by the differences in opinion[9–11] regarding the validity of determining a scale of electronegativities for the group IV elements from the chemical shifts of the tetramethyl derivatives of these elements.

By making use of a correlation[12,13] between the ^{13}C–H coupling constant, $J(^{13}\text{C–H})$, and τ, it is possible to determine when there are large non-local contributions to τ. In this article, large non-local contributions are shown to be present in $(CH_3)_4Ge$, $(CH_3)_4Sn$ and $(CH_3)_4Pb$; and, consequently, the proton chemical shifts cannot be used to predict the electronegativities of these elements. The $J(^{13}\text{C–H})$ *vs.* τ correlation can also be employed to show the magnitude and direction of the non-local contributions to the chemical shifts in the alkyl halides. In the discussion, necessary conditions are specified for determining electronegativities from chemical shifts.

EXPERIMENTAL

NMR spectra

$J(^{13}\text{C–H})$ and τ data were determined from spectra obtained on a Varian Model A-60 high resolution nuclear magnetic resonance spectrometer. τ-Values are obtained

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** As generally used in chemical shift correlations, electronegativities are based on some thermochemical scale, such as the Huggins scale[8].

from carbon tetrachloride solutions using tetramethylsilane as an internal standard. The ^{13}C present in natural abundance (1.1 %) produces satellite side bands which are symmetrically disposed about the main proton absorption. Coupling constants can be evaluated with an accuracy of at least ± 1 cps from these satellite bands. Samples of the pure liquids were examined for $(CH_3)_4Si$, $(CH_3)_4Ge$ and $(CH_3)_4Sn$. The spectrum of $(CH_3)_4Pb$ was obtained from an 85 weight-percent solution in toluene. It was shown that toluene does not effect the coupling constants for the silicon, germanium and tin compounds.

Materials

Tetramethyltin was prepared by a base-catalyzed redistribution reaction of trimethyltin chloride. *Tetramethylgermane* was prepared by the reaction of germanium tetrachloride and methylmagnesium chloride in di-*n*-butyl ether solution. *Tetramethylsilane*, reagent grade, was obtained from the Anderson Chemical Company and was used without purification. *Tetramethyllead* was obtained as an 85 weight-percent solution in toluene from the Ethyl Corporation.

RESULTS

The ^{13}C–H spin–spin coupling constants, $J(^{13}C–H)$, determined for the tetramethyl derivatives of the group IV elements are listed in Table 1 along with the electronegativity values reported for the central element by Allred and Rochow[9], $E_{(A,R)}$ and by Pritchard and Skinner[14], E.

TABLE 1

$J(^{13}C–H)$ COUPLING CONSTANT DATA FOR $M(CH_3)_4$ COMPOUNDS AND REPORTED ELECTRONEGATIVITIES FOR M

M	$J(^{13}C–H)$ (*cps*)	*E*	$E_{(A,R)}$
C	124 ± 1	2.5–2.6	2.60
Si	119 ± 1	1.8–1.9	1.90
Ge	124 ± 1	1.8–1.9	2.00
Sn	128 ± 1	1.8–1.9	1.93
Pb	134	1.8	2.45

The values for the coupling constants in Table 1 are in good agreement with the values 126 cps and 120 cps reported[19] for $(CH_3)_4Sn$ and $(CH_3)_4Si$, respectively. Subsequent to the completion of our studies, coupling constants for the compounds in Table 1 were reported[6] from measurements of the ^{13}C spectra. Because of inherent difficulty in obtaining reproducible ^{13}C spectra, Lauterbur[19] has attached rather large error limits (± 3 cps) to coupling constants obtained by this procedure. [^{13}C results: $(CH_3)_4Si$, 119 cps; $(CH_3)_4Ge$, 126 cps; $(CH_3)_4Sn$, 128 cps; and $(CH_3)_4Pb$, 133 cps.]

DISCUSSION

A new scale of electronegativity has been proposed for the Group IV elements which is based essentially upon the trends in the relative proton chemical shifts for the corresponding tetramethyl derivatives[9]. It is generally conceded that in a qualitative sense the term electronegativity should be employed to represent nuclear attraction for the bonding pair of electrons. Both the Mulliken and Jaffe approaches to determining electronegativities imply this. Consequently, the effect of orbital overlap on charge distribution is not included in the concept of electronegativity. Two objections to the interpretation of the chemical shift data of the Group IV tetramethyl derivatives in terms of electronegativities have been offered[10]:

(*a*) There may be non-local (*i.e.*, neighboring atom) contributions to the relative chemical shifts.

(*b*) The inductive effect of the substituent M in the compounds $(CH_3)_4M$ will be dependent not only on the electronegativity of M but also on the C–M bond energies,

TABLE 2

^{13}C–H COUPLING CONSTANTS AND PROTON CHEMICAL SHIFTS FOR SELECTED COMPOUNDS

Code	*Compound*[a]	$J(^{13}C–H)$	τ[e] *(ppm)*
1	$(C\underline{H}_3)_4C$	124[b]	9.10
2	$(C\underline{H}_3)_4Si$	119	10.000
3	$(C\underline{H}_3)_4Ge$	124	9.87
4	$(C\underline{H}_3)_4Sn$	128	9.94
5	$(C\underline{H}_3)_4Pb$	134	9.29
6	$C_6\underline{H}_6$	126[b]	9.12
7	$(C\underline{H}_3)_2NH$	132[b]	7.65
8	$(C\underline{H}_3)_3N$	131[b]	7.876
9	$(C\underline{H}_3CH_2)_2O$	125	8.84
10	$C\underline{H}_3CH_2OH$	125	8.83
11	$C\underline{H}_3OH$	141[b]	6.622
12	$(C\underline{H}_3)_2O$	139	6.67
13	$C\underline{H}_3OC_6H_5$	143[b]	6.266
14	1,4-dioxane	142[c]	6.43
15	$C\underline{H}_3NO_2$	147[b]	5.722
16	$(C\underline{H}_3O)_3B$	143[c]	6.470
17	$C\underline{H}_3CCl_3$	134[b]	7.28
18	$C\underline{H}_3F$	149[b]	5.74
19	$C\underline{H}_3Cl$	150[b]	6.95
20	$C\underline{H}_3Br$	152[b]	7.32
21	$C\underline{H}_3I$	151[b]	7.843
22	$C\underline{H}_3CO_2H$	130[b]	7.933
23	$(C\underline{H}_3)_2CO$	126[b]	7.914
24	$(C\underline{H}_3O)_2CO$	147[c]	6.23
25	$(C\underline{H}_3)_2NC_6H_5$	135[c]	7.096
26	$(C\underline{H}_3)_3CCH_3$	126[b]	8.299
27	$C\underline{H}_3CHO$	127[b]	7.830
28	$C\underline{H}_3CN$	136[b]	8.029
29	$(C\underline{H}_3)_2S$	138[c]	7.92
30	$(C\underline{H}_3)_2SO$	138[b]	7.50

[a] Coupling constants, $J(^{13}C–H)$, and chemical shifts, τ, for protons underlined. [b] Ref. 15. [c] Ref. 16. [d] Ref. 17. [e] Values taken from ref. 18 with the exception of values 1–5.

the average values for which are[20]: C–C 82.6 kcal/mole; C–Si[21], 76.0; C–Sn 54: C–Pb, 31. It was proposed[10] that the weaker the C–M bond is the more *s* character the carbon atom will employ in the C–H bonds. Since there is a fixed number of *s* and *p* bonding orbitals on the carbon atom there will be a corresponding increase in the amount of *p* character in the carbon hybrid employed in the M–C bond in this series. As proposed earlier[10], the increase in *p* character for the larger elements results from the decreased strength of the M–C bond and can be interpreted in terms of a competition among the four bonds on carbon for the amount of carbon *s* orbital available. Stronger C–H bonds form and more effective overlap results as the amount of *s* character[22] in the hybrid orbitals employed by carbon increases ($sp > sp^2 > sp^3$). A similar increase in energy would be expected for the M–C bond with increase in *s* character of the carbon hybrid. However, for atoms (M) with large covalent radii the change in energy of the M–C bond with change in hybridization would be less steep than for atoms with smaller orbitals, and a lower energy results when more of the *s* orbital is used in the bond to hydrogen. Since the carbon electronegativity depends on its hybridization[22] (the more *s* character, the more electronegative), the relative chemical shifts should be influenced by this effect. For example, since the lead–carbon bond is weak, carbon will employ more *s* character in the bonds to the proton, and *carbon* will be more electronegative toward proton in $(CH_3)_4Pb$ than in $(CH_3)_4Sn$. *Carbon* electronegativity depends upon factors other than the electronegativity of the central element.

These objections were strenuously disclaimed in a subsequent article[11] and the interpretation became a matter of opinion. The differences could be resolved if carbon hybridization could be determined. This information can be obtained from $J(^{13}C\text{–}H)$. It has been shown[15,17] that ^{13}C–H coupling constants, $J(^{13}C\text{–}H)$, are related to the fraction of *s* character, ρ, employed by carbon in its bonds to hydrogen by the equation:

$$J(^{13}C\text{–}H) = 500\,\rho$$

$J(^{13}C\text{–}H)$ *data for* $(CH_3)_4M$ *compounds*

The coupling constant data in Table 1 indicate an increase in *s* character in the C–H bond with increasing size of the central element as earlier predicted[10] and as described in (*b*) above. Therefore the methyl *carbon* electronegativities in the series $(CH_3)_4M$ change in a manner which is not directly related to the electronegativity of the central element, and consequently, the electronegativities of these central elements cannot be deduced from τ.

The high coupling constant for $(CH_3)_4C$ should be discussed. There is no doubt that carbon is more electronegative than the other group IV elements. According to the concept of isovalent hybridization[24], increasing the electronegativity of the atom bonded to the methyl group will result in more *s* character in the C–H orbitals. In $(CH_3)_4C$, the high electronegativity of the central carbon results in the high $J(^{13}C\text{–}H)$ value as expected from isovalent hybridization arguments. If (as suggested by Allred and Rochow[11]) isovalent hybridization arguments account for the changes in the hybridization of the carbon atom for all the compounds in this series, the order of electronegativity (for the central atoms) indicated by the coupling constant data would then be Pb > Sn > C, Ge > Si. However, it does not appear necessary to postulate this unusual electronegativity scale to account for the trends in the $J(^{13}C\text{–}H)$ values. The isovalent hybridization argument is important when the central element is carbon but for the tetramethyl compounds of the remainder of the elements in this family if this effect does exist it is of minor importance. Instead, orbital overlap is the primary factor affecting the trend in $J(^{13}C\text{–}H)$ for $(CH_3)_4Si$, $(CH_3)_4Ge$, $(CH_3)_4Sn$ and $(CH_3)_4Pb$ and this effect obscures any electronegativity differences that may exist.

It is interesting to point out that in the series of compounds $CH_3\text{–}X$, where X is a halogen, electronegativity decreases and the effectiveness of orbital overlap also decreases as the atomic number increases. The two effects counteract one another and the $J(^{13}C\text{–}H)$ values vary only slightly in this series*.

The correlation of $J(^{13}C\text{–}H)$ with τ

Having substantiated the arguments in (*b*) above, it was of interest to examine the problem of non-local contributions to the proton shift. This problem is of significance not only for the Group IV tetramethyl derivatives but in the interpretation of any chemical shift data.

It has been shown[23] that a linear relationship exists between the electronegativity of the carbon atom and the *s* character of the hybrid employed by carbon, ρ:

$$EN \text{ of carbon} = k\rho$$

Therefore, the $^{13}C\text{–}H$ coupling constants which measure carbon hybridization $[J(^{13}C\text{–}H) = 500\,\rho]$ can be used as a direct measure of the relative electronegativity which *carbon* exhibits toward hydrogen in substituted methyl compounds.

$$EN \text{ of carbon} = k'\,J(^{13}C\text{–}H)$$

The local contribution to the chemical shift is a function of carbon electronegativity. Therefore if non-local contributions are absent, constant, or vary linearly with electronegativity in a series of compounds:

$$\tau = f[J(^{13}C\text{–}H)]$$

The data for some CH_3X compounds, in which X is either a first row element or a saturated functional group in which the methyl carbon is bonded to a first row element, were selected to determine empirically the relationship of J and τ. It was felt that these compounds best satisfied the requirements specified above for non-local contributions. The data are plotted in Fig. 1. Within the required limit of accuracy, the relationship is linear. The direction of the slope of this line is that predicted from isovalent hybridization arguments. $J(^{13}C\text{–}H)$ becomes larger as the electronegativity of X increases.

The data for the methyl halides clearly deviate from this line. Since changes in the carbon electronegativity from both overlap and electronegativity effects are incorporated into the $J(^{13}C\text{–}H)$ values, it can be concluded that the methyl protons in these compounds are actually *more shielded* than would be expected on the basis of the electronegativity which the carbon atom exhibits toward hydrogen. The deviations increase regularly with the atomic number of the halogen atom and the pattern, on

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* The orbital overlap effect for the methyl halides has been discussed by Muller and Pritchard[15].

the basis of the model proposed by Bothner-By and Naar-Colin[3], indicates that paramagnetic anisotropic effects dominate the non-local contributions to the proton chemical shifts in these compounds.

It is also seen (Fig. 1) that in the tetramethyl derivatives of the Group IV elements, as in the methyl halide series, there are paramagnetic contributions to the shielding of the proton which increase with atomic number. Since the distribution of the electrons about the Group IV element in the tetramethyl derivatives is symmetrical (at least in the ground state of the molecules), there should be no magnetic anisotropic effect arising from the circulation of electrons about the Group IV element.

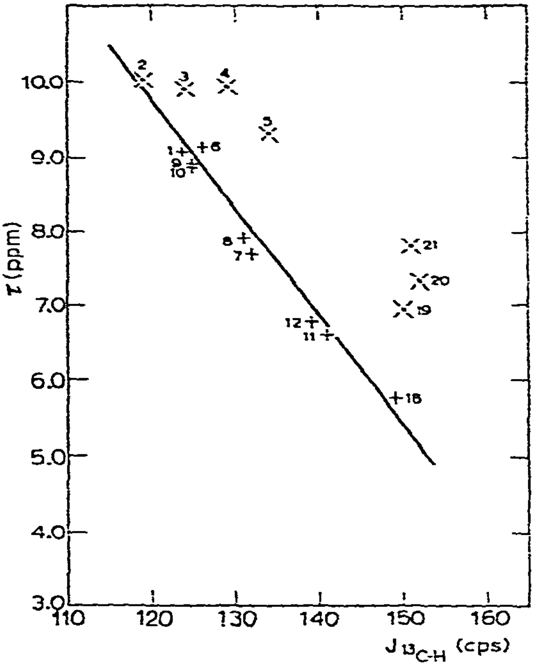

Fig. 1. The relationship between $J(^{13}C\text{–}H)$ and τ. + Points used to establish the relationship; numbers correspond to the code in Table 2.

However, since the distribution of electrons about the *carbon atom* is not symmetrical due to the non-equivalence of the four carbon hybrid orbitals, the paramagnetic contribution can be attributed to the anisotropy of the carbon atom*.

The paramagnetic anisotropy of the carbon atom would be expected to shift the proton resonance to high field as is seen in Fig. 1. This paramagnetic *shielding* effect might be expected to increase as the C–M bond energy decreases. Since the C–M bond energy *decreases* in the series, Si > Ge > Sn > Pb, and since the carbon electronegativity *increases* in the series, $(CH_3)_4Si < CH_3)_4Ge < (CH_3)_4Sn < (CH_3)_4Pb$, a partial cancellation of the two effects with respect to the range of proton chemical shifts

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* Pople[32] has shown that, for the molecules $MH_n(NH_3, H_2O$ and HF), the diamagnetic circulation of electrons about the atom M should not appreciably affect the shielding of the proton but that the paramagnetic contribution (arising from the anisotropy of the atom M) to the shielding of the proton is significant.

should be observed. The total range of chemical shifts *observed* for the tetramethyl derivatives is less than the range which might be *expected* from a consideration of the range of ^{13}C–H coupling constants. For the observed coupling constant range of 15 cps a range of 2 ppm for τ is predicted from the slope of the line in Fig. 1 but a range of only 0.9 ppm is observed.

The existence of large non-local contributions, (*a*) above, and varying X–C overlap, (*b*) above, in this series of compounds makes it difficult to obtain electronegativities from chemical shift data. Both of these requirements must be satisfied whenever one attempts to evaluate electronegativities from proton chemical shift data.

The relationship in Fig. 1 affords a means of determining the existence of appreciable non-local contributions to the proton chemical shifts. Data on other compounds are presented in Table 2 for this purpose. It most probably will not be valid to compare quantitatively the deviation from this line with calculated anisotropies because the compounds used to establish this line may all contain non-local contributions which are constant or vary linearly with electronegativity. The line can be used to detect the presence of an unusual large non-local contribution as was done in this article.

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SUMMARY

A linear relationship is reported between ^{13}C–H spin–spin coupling constants, $J(^{13}\text{C–H})$, and proton chemical shifts, τ, for a restricted series of methyl derivatives. The existence of this relationship is rationalized and the relationship is employed: (*a*) to justify an earlier interpretation of the chemical shift data for the tetramethyl derivatives of the group IV elements; (*b*) to conclude that the chemical shift data cannot be employed to evaluate electronegativities of the central group IV element in these compounds; (*c*) to aid in evaluating the anisotropic contributions to the chemical shifts of the methyl halides and other compounds. The ^{13}C–H spin–spin coupling constants indicate that the hybridization of the methyl carbon atom in the tetramethyl derivatives of the group IV elements changes with the effectiveness of central element–carbon overlap.

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