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THE *geminal* TIN—PROTON COUPLING CONSTANT: A COMMENT

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Summary

By consideration of typical examples and the general form of the contact contribution, it is shown that care must be exercised in basing conclusions on the *geminal* tin—proton coupling constant.

Introduction

The *geminal* coupling constant $^2J(\mathrm{SnH})$ between the tin isotopes which have a magnetic spin $I = 1/2$ and the methyl protons in methyltin compounds of the general form $\mathrm{Me}_{4-n}\mathrm{SnX}_n$ varies with the nature of the substituent X and the number of substituents n, as shown in Fig. 1. Kaesz [5,11] was the first to interpret the change of $^2J(\mathrm{SnH})$ in the series where X = Cl, H, by putting $^2J(\mathrm{SnH}) = q \cdot \%s(\mathrm{SnC})$, where $\%s(\mathrm{SnC})$ is the s-character of the tin orbital used in the tin—methyl bond, and q is a constant. This linearity was an extension of the empirical relationship, found by Shoolery [12], between the one-bond coupling constant $^1J(^{13}\mathrm{CH})$ and the s-character of the carbon orbital used in the C—H bond: $^1J(^{13}\mathrm{CH}) = t \cdot \%s(\mathrm{CH})$. However, Kaesz emphasized that this linearity was only an empirical correlation, without a theoretical basis; this has been confirmed by calculations performed by Gutowsky [13], who concluded that the contact contribution to $^1J(\mathrm{CH})$ can be written as $^1J(\mathrm{CH}) = J_0 \cdot \%s(\mathrm{CH})$, where J_0 can be considered to be constant owing to the compensation of two factors, but that in the case of the analogous coupling between silicon and hydrogen, $^1J(\mathrm{SiH})$, J_0 is no longer constant.

According to Gutowsky [13], the linear relationship between $^1J(\mathrm{CH})$ and $\%s(\mathrm{CH})$ explained the additive change of this coupling constant, i.e. $^1J[\mathrm{CH}_{4-n}\mathrm{X}_n] = {}^1J[\mathrm{CH}_4] + n\Delta_x$. About this time Bent's rule was formulated [14], stating that in $\mathrm{MY}_n\mathrm{Z}_m$ the orbital of M which is used in the bond with the least electronegative

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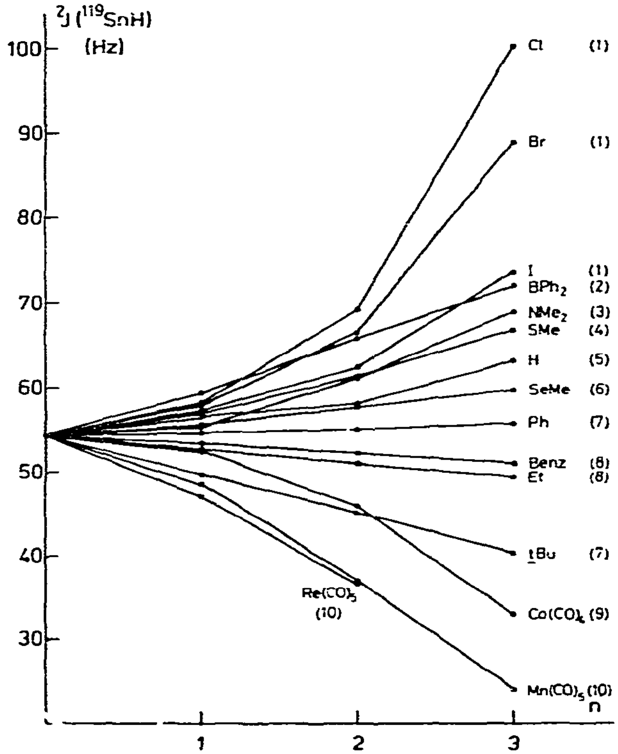

Fig. 1. ^2J(SnH) versus n in $Me_{4-n}SnX_n$.

substituent has the highest *s*-character. These two rules have frequently been used in the study of the *geminal* tin—proton coupling constant; if one assumes that $^2J(SnH) = q \cdot \%s(SnC)$, one must expect that in Me_3SnX the $\%s(SnC)$ and consequently $^2J(SnH)$ increases with increasing electronegativity of X (Bent), and that in $Me_{4-n}SnX_n$ $^2J(SnH)$ varies additively (Gutowsky): $^2J[Me_{4-n}SnX_n] = {^2J}[Me_4Sn] + n \cdot \Delta'_x$. Exceptions to both rules have been noted, e.g. (*i*) in Me_3SnCH_2Ph $^2J(SnH)[CH_3]$ is smaller than in Me_4Sn *, although the benzyl radical is considered as more electronegative than the methyl group, (*ii*) $^2J(SnH)$ varies additively only when X = alkyl (Fig. 1).

The observation of such deviations and other anomalies has prompted some authors to invoke other effects, such as $p_\pi \rightarrow d_\pi$ bonding in addition to the contact contribution. We will first mention a few typical examples taken from the literature, and comment subsequently.

Examples

(*i*) In the ethyltin halides, $^2J(SnH)$ increases following the sequence I < Br < Cl, whereas the variations of the *vicinal* coupling constant are smaller and do

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* $^2J(^{119}SnH)$ = 52.9 Hz for Me_3SnCH_2Ph and 54.3 Hz for Me_4Sn [8].

not show a general trend. As ^2J(SnH) does not vary additively in the series $Et_{4-n}SnX_n$, Lorberth [1] concluded that the contact term is insufficient and that the electron orbital and dipole—dipole contributions play an important role; ^3J(SnH), on the contrary, could be mainly determined by the contact contribution, which would, however, be too complicated to be written as a function of %s(SnC).

(*ii*) To explain the same facts in the same compounds, Van der Kelen concluded that the *geminal* coupling constant is mainly influenced by the contact contribution [15]; according to this author the small variation of the *vicinal* coupling constant is due to a complementary contribution of the electron orbital term, which would counteract the contact contribution.

These two examples illustrate the important disagreement surrounding interpretation of tin—proton coupling constants.

(*iii*) McFarlane [16] compared ^2J(SnH) and ^1J(SnC) in some methyltin compounds; as the curve relating both coupling constants did not pass through the origin, McFarlane concluded that one of the coupling constants is not solely determined by the contact contribution, which he considered to be proportional to %s(SnC).

(*iv*) The fact that in many ethylmetal compounds the *vicinal* metal—proton coupling constant is larger than the *geminal* has been attributed to a complementary contribution of the dipole—dipole term, which would have a sign opposite to that of the contact contribution and have a greater influence on ^2J(MH) than on ^3J(MH) [17].

(*v*) The deviation from the additivity in $Me_{4-n}SnCl_n$ has been interpreted by Taddei [18] as evidence for the existence of a $p_\pi \rightarrow d_\pi$ bond formed between the electron pairs on chlorine and the empty 5d orbitals of tin.

(*vi*) Holloway [19] found it necessary to introduce other contributions to explain a difference of 20 Hz (resp. 35 and 55 Hz) for the *geminal* coupling constants between tin and the diastereotopic methylene protons in t-BuPhISn-CH_2CMe_2Ph.

Discussion

We discuss only the contact contribution, which is generally considered to be the most important when one of the coupled nuclei is a proton [20]. The contribution of this term to the tin—proton coupling constant can be written as [20]:

$$J(\mathrm{SnH}) = -\frac{1}{h}\left(\frac{16\pi\beta h}{3}\right)^2 \gamma_{\mathrm{H}}\gamma_{\mathrm{Sn}}|1s_{\mathrm{H}}(0)|^2|5s_{\mathrm{Sn}}(0)|^2 \sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}} (\epsilon_j-\epsilon_i)^{-1} c_{is_{\mathrm{Sn}}} c_{is_{\mathrm{H}}} c_{js_{\mathrm{Sn}}} c_{js_{\mathrm{H}}} \tag{1}$$

where $|1s_H(0)|^2$ and $|5s_{Sn}(0)|^2$ are the density of the valence electrons at a distance zero from resp. the hydrogen and the tin nucleus; ϵ_i is the energy of the occupied molecular orbital ψ_i; ϵ_j is the energy of the unoccupied molecular orbital ψ_j; c_{is_A} is the coefficient of the valence s electron of atom A in the MO ψ_i defined by the LCAO form:

$$\psi_i = \sum_{\mu} c_{i\mu}\phi_\mu \qquad (\phi_\mu = \text{atomic orbital})$$

Note that $^2J(\mathrm{SnH})$ can also be written in the valence bond formalism, as developed by Karplus [21], but as in the MO treatment no simple relation appears between the coupling constant and the hybridization of the tin orbitals.

In order to predict how J will vary on changing the substituents on tin, we must know the influence of X on the electron density at the nuclei, on each individual energy level ϵ and on the different coefficients of the atomic orbitals. Therefore we will discuss successively the variation of $|5s_{\mathrm{Sn}}(0)|^2$ and the sum

$$\sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} (\epsilon_j - \epsilon_i)^{-1} c_{is_{\mathrm{Sn}}} c_{is_{\mathrm{H}}} c_{js_{\mathrm{Sn}}} c_{js_{\mathrm{H}}} \ ;$$

we will assume $|1s_{\mathrm{H}}(0)|^2$ to be constant.

(a) *The electron density at the tin nucleus.* According to Perkins and Wall [22] this factor increases when the electron population P_{5s} and/or the effective nuclear charge $Z_{\mathrm{eff}}(5s)$ increase. An electronegative substituent causes a decrease of P_{5s} and an increase of $Z_{\mathrm{eff}}(5s)$, the former being the most important according to their calculations; e.g. $|5s_{\mathrm{Sn}}(0)|^2$ would diminish with 15% from $\mathrm{Me_4Sn}$ to $\mathrm{Me_2SnCl_2}$, while $^2J(\mathrm{SnH})$ increases with 20%. This would mean that the electron density change is not the major cause of the variation of $^2J(\mathrm{SnH})$.

(b) *The electron density summed over the molecular orbitals.* It is necessary to define the energy of each occupied and unoccupied MO and the coefficients of the AO's $1s_{\mathrm{H}}$ and $5s_{\mathrm{Sn}}$. This is a task not yet performed for organotin compounds, but it is clear from eq. 1 that only those MO's contribute to $J(\mathrm{SnH})$ in which the coefficients of $5s_{\mathrm{Sn}}$ and $1s_{\mathrm{H}}$ are non zero. Because of symmetry considerations, $c_{5s_{\mathrm{Sn}}}$ is different from zero only in the totally symmetrical MO's, so that for a molecule with a given symmetry we can determine the number of terms in the sum. We calculated this for four typical molecules, the symmetry of which is shown in Table 1, 2nd column; the atomic orbitals we took into consideration are the tin 5s and 5p, the carbon 2s and 2p, the hydrogen 1s orbital, and

TABLE 1

DETERMINATION OF THE NUMBER OF TERMS THAT HAVE TO BE SUMMED IN ORDER TO CALCULATE $^2J(\mathrm{SnH})$ (MO formalism) IN SOME TYPICAL METHYLTIN COMPOUNDS

Molecule	Symmetry of molecule	Symmetry of MO's	Number of totally symm. MO's	Nature of symm. bonding MO's	Number of terms in sum
$\mathrm{Me_4Sn}$	T_d	$4A_1 + 2E + 2T_1 + 6T_2$	4	1(C—H) 1(Sn—C)	4
$\mathrm{Me_3SnX}$	C_{3v}	$8A_1 + 2A_2 + 8E$	8	2(C—H) 1(Sn—C) 1(Sn—X)	16
$\mathrm{Me_2SnX_2}$	C_{2v}	$8A_1 + 2A_2 + 6B_1 + 4B_2$	8	2(C—H) 1(Sn—C) 1(Sn—X)	16
$\mathrm{MeSnX_3}$	C_{3v}	$6A_1 + 4E$	6	1(C—H) 1(Sn—C) 1(Sn—X)	9

the orbital with which the substituent X forms the bond with tin: this means that 32 AO's have to be combined to form as many MO's in the case of Me_4Sn, 26 AO's for Me_3SnX, 20 for Me_2SnX_2 and 14 for $MeSnX_3$. With the character tables we then determined the symmetry of these molecular orbitals (column 3); in column 4 can be found the number of totally symmetrical MO's, half of which are bonding. The nature of these totally symmetrical bonding MO's have also been determined with the character tables (column 5); it is important to remember, however, that in all these MO's $c_{5s_{Sn}}$ and c_{1s_H} are in principle not zero. The number of terms in the sum is then the number of pairs that can be made with one occupied MO and one unoccupied MO, which is equal to: (number of totally symmetrical MO's/2)^2 (column 6).

The change of the sum with X and n in $Me_{4-n}SnX_n$ is caused by a variation of each individual MO, and, in the case of n, also by the variation of the number of terms; this means that one cannot predict this change, not even qualitatively, as both the energy levels and the coefficients change. Moreover one has to keep in mind that the sign of the terms can as well be positive as negative.

We now return to examples *i—vi*.

(*i*, *ii*) As the contact contribution is not proportional to %*s*(SnC), there is no reason to expect an additive variation of ^2J(SnH), so that it does not make much sense to introduce the electron orbital and/or dipole—dipole terms in order to explain deviations from this additivity, especially as it is as difficult to say how these two contributions vary. Neither is the smallness of the *vicinal* coupling constant variations for favor of the electron orbital term, as compensations of positive and negative terms in the sum are highly probable.

(*iii*) Even if the contact mechanism were the only one contributing to ^2J(SnH) and ^1J(SnC), they would not be zero at the same time, as

$$\sum_i \sum_j (\epsilon_j - \epsilon_i)^{-1} c_{is_{Sn}} c_{is_H} c_{js_{Sn}} c_{js_H} \qquad \text{and} \qquad \sum_i \sum_j (\epsilon_j - \epsilon_i)^{-1} c_{is_{Sn}} c_{is_C} c_{js_{Sn}} c_{js_C}$$

do not have to be zero simultaneously.

(*iv*) From eq. 1 it is clear there is no reason why the *geminal* coupling constant should be larger than the *vicinal*, as it is impossible to predict the value of the sum.

(*v*) $p_\pi \rightarrow d_\pi$ Bonding has been invoked frequently to explain unexpected observations in organotin chemistry. Since it is impossible at present to define the effect of this back donation on ^2J(SnH), it cannot be used to explain the non additivity.

(*vi*) The observation of different coupling constants between tin and the two diastereotopic hydrogens can be explained qualitatively in terms of the contact contribution: as soon as two protons H and H' are diastereotopic, the coefficients c_{1s_H} and $c_{1s_{H'}}$ in each MO are different, so that J(SnH) must be different.

Conclusion

The linear relationship between the *geminal* tin—proton coupling constant and the *s*-character of the tin orbital has frequently been used, but also misused. Consideration of the general expression of the contact contribution shows that theory does not require this linearity so that it is not surprising an observation cannot be explained by means of this oversimplified relation, and deviations from it cannot be taken as evidence for electron orbital or dipole—dipole contributions, $p_\pi \rightarrow d_\pi$ back donation etc.

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