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THE GEMINAL TIN—PROTON COUPLING CONSTANT. INFLUENCE OF X IN R_3SnCH_2X AND $R_3SnCH_2CH_2X$, AND OF THE Sn—C—H ANGLE

BERTHA DE POORTER
Vrije Universiteit Brussel, Algemene en Organische Scheikunde (TW), Pleinlaan 2, B-1050 Brussel (Belgium)

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Summary

By use of examples taken from the literature, it is shown that the influence of an α-substituent on the geminal tin—proton coupling constant follows the expected trend, so that the theory developed by Pople for ^2J(HH) can also be used to explain the changes of ^2J(SnH).

Introduction

In the past fifteen years many publications have dealt with variations of the geminal tin—proton coupling constant with the nature or number of the substituents in series such as $Me_{4-n}SnX_n$ ([1] and refs. cited). In contrast, there has been no systematic study of how ^2J(SnH) is influenced by a change in the nature of the carbon atom between tin and the coupled hydrogen. Schmidbaur [2] observed an increase of ^2J(SnH) on replacing a proton by a trimethylsilylgroup in $(CH_3)_4Sn$ (Table 2) and explained this in terms of the rehybridization of the bridging carbon. Van der Kelen [3] compared ^2J(SnH) in $(CH_3)_3SnX$, $(CH_3CH_2)_3SnX$ and $(XCH_2)_3SnX$ with X = Br, Cl and found that ^2J(SnH) decreased in the sequence $(CH_3)_3SnX > (CH_3CH_2)_3SnX > (XCH_2)_3SnX$. He suggested that the large decrease of ^2J(SnH) is caused principally by a decrease of the electron density around the hydrogen nucleus, rather than by an increase of the polarity of the Sn—C bond. For van der Kelen this could also explain why the coupling constant between tin and the methylene protons in R_3SnCH_2Ph is always larger than between tin and the methyl protons in R_3SnCH_3, since he postulates that the π-system of the phenyl ring is delocalized towards tin, causing the electron density round the methylene protons to increase. According to Mitchell [4] the large value of ^2J(SnH) in allyltin compounds and the lower value in compounds in which the α-carbon has as substituent an electronegative group, is probably caused by steric factors.

As can be seen in the Tables 1—4 the variation of ^2J(SnH) due to a change of the nature of α-carbon is rather large, even in some cases causing a sign inversion. In the next section we try to explain these trends qualitatively by comparing ^2J(SnH) with the geminal proton—proton coupling constant in analogous compounds.

Discussion

A. The geminal proton—proton coupling constant (Pople's model)

Any change in the nature of the carbon atom in a methylene group leads to a change in the geminal proton—proton coupling constant. These variations of ^2J(HH') have been explained qualitatively by Pople by means of a MO theory [5]. This author considers the CH_2 group as an isolated entity with C_{2v} symmetry, and describes it in terms of 4 MO's, two of which are bonding:

$$\Psi_1 = c_{1h} \cdot h + c_{1h'} \cdot h' + c_{1\sigma} \cdot \sigma(C)$$

$$\Psi_2 = c_{2h} \cdot h - c_{2h'} \cdot h' + c_{2p} \cdot p_y(C)$$

where $h \equiv 1s(H)$, $h' \equiv 1s(H')$, $\sigma(C)$ is a combination of $2s(C)$ and $2p_z(C)$; by symmetry $c_{1h} = c_{1h'}$, $c_{2h} = c_{2h'}$. Similarly the two antibonding MO's can be written:

$$\Psi_3 = c_{3h} \cdot h + c_{3h'} \cdot h' - c_{3\sigma} \cdot \sigma(C)$$

$$\Psi_4 = c_{4h} \cdot h - c_{4h'} \cdot h' - c_{4p} \cdot p_y(C)$$

Of these four MO's, Ψ_1 and Ψ_3 are symmetrical relative to the symmetry plane, Ψ_2 and Ψ_4 are antisymmetrical. If, for instance, electrons are witdrawn from the symmetrical orbital Ψ_1, c_{1h} and $c_{1h'}$ are reduced, causing the other symmetrical orbital Ψ_3, to become more hydrogen-like, i.e. the magnitude of c_{3h} and $c_{3h'}$ increases. What has now to be assessed is the effect this has on

$$^2J(\mathrm{HH'}) = -\frac{1}{h}\left(\frac{16\pi\beta h}{3}\right)^2 \gamma_{\mathrm{H}}^2 |1s_{\mathrm{H}}(\mathrm{o})|^4 \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} (\epsilon_j - \epsilon_i)^{-1} c_{ih} c_{jh} c_{ih'} c_{jh'}$$

By considering the changes of the coefficients and by taking into account the relative energy differences of the four MO's, Pople [5] comes to the following conclusions:

(a) Increasing the *s*-character of the carbon orbitals causes a positive change in ^2J(HH').

(b) Withdrawal of electrons from the symmetrical orbital causes a positive shift in ^2J(HH').

(c) Withdrawal of electrons from the antisymmetrical orbital causes a negative shift in ^2J(HH').

As the withdrawal of electrons from the symmetrical orbital corresponds to the inductive effect of an α-substituent and withdrawal from the antisymmetrical orbital to the hyperconjugative effect of an α-substituent and the inductive effect of a β-substituent, Pople can explain qualitatively the generally observed trends, which are [5]:

(1) ^2J(HH') becomes more positive as the hybridization of carbon becomes more *s*-like.

(2) Attachment of an electronegative group X to the CH_2 group causes a positive shift of $^2J(HH')$.

(3) The presence of a π-electron system on the CH_2 group causes a negative shift of $^2J(HH')$.

(4) Introduction of an electronegative group β to the CH_2 group causes a negative shift of $^2J(HH')$.

B. The geminal tin—proton coupling constant

It is interesting to see whether this model can be used to the geminal tin—proton coupling constant. We consider the $SnCH_2$ group as an isolated entity; if we do not take into account an eventual asymmetry of Sn or X, $SnCH_2X$ belongs to the C_s point group, where the only element of symmetry is the plane bisecting the H—C—H' angle. We can thus construct the following bonding MO's:

$$\Psi_a = c_{ah} \cdot h + c_{ah'} \cdot h' + c_{a\sigma} \cdot \sigma(C) + c_{a\sigma'} \cdot \sigma'(\mathrm{Sn})$$

$$\Psi_b = c_{bh} \cdot h + c_{bh'} \cdot h' + c_{bp} \cdot p_y(C) - c_{b\sigma'} \cdot \sigma'(\mathrm{Sn})$$

$$\Psi_c = c_{ch} \cdot h - c_{ch'} \cdot h' + c_{cp} \cdot p_z(C)$$

where $\sigma'(\mathrm{Sn}) = a \cdot 5s(\mathrm{Sn}) + \sum_{i=x,y,z} b_i \cdot 5p_i(\mathrm{Sn})$, and $\sigma(C)$ is a combination of $2s(C)$ and $2p_x(C)$.

As the geminal tin—proton coupling constant can be formulated as following:

$$^2J(\mathrm{SnH}) = {}^2J(\mathrm{SnH'}) = \frac{-1}{h}\left(\frac{16\pi\beta h}{3}\right)^2 \cdot \gamma_{\mathrm{Sn}}\gamma_{\mathrm{H}}|1s_{\mathrm{H}}(o)|^2\,|5s_{\mathrm{Sn}}(o)|^2 \cdot \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} (\epsilon_j - \epsilon_i)^{-1} c_{is(\mathrm{Sn})}c_{is(\mathrm{H})}c_{js(\mathrm{Sn})}c_{js(\mathrm{H})}$$

and as $c_{cs(\mathrm{Sn})} = 0$, it is clear that the contribution of Ψ_c to $^2J(\mathrm{SnH})$ is zero, and that only Ψ_a and Ψ_b have to be considered in the following discussion.

In Ψ_a the sign of the coefficients of $1s(H)$ and $5s(\mathrm{Sn})$ are the same *, just as in Ψ_1 the signs of $1s(H)$ and $1s(H')$ are equal; in contrast, in Ψ_b and Ψ_2, the coefficients of the s-orbitals of the coupled nuclei have the opposite sign. Just as in Pople's system, we can consider the energy of Ψ_b, ϵ_b, to be higher than ϵ_a, as in Ψ_a the carbon atom uses partly its 2s orbital. The same concordance exists between the antibonding MO's. This means that our system is qualitatively similar to Pople's; we can thus adopt his conclusions. However, one difference must be kept in mind, namely that γ_{Sn} is negative and γ_{H} positive, which causes the algebraic sense of a change of $^2J(\mathrm{SnH})$ to be opposite to this of $^2J(HH')$. We can thus expect the following trends:

(1) $^2J(\mathrm{SnH})$ becomes more negative as the hybridization from carbon changes from sp^3 to sp^2;

(2) an electronegative group on CH_2 leads to a negative shift of $^2J(\mathrm{SnH})$;

(3) a π-electron system on CH_2 leads to a positive shift of $^2J(\mathrm{SnH})$;

(4) an electronegative group in the β position makes $^2J(\mathrm{SnH})$ more positive.

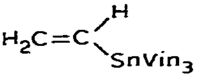
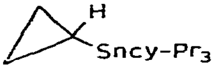
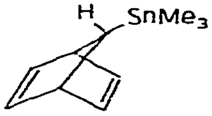
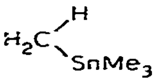
Let us now consider the experimental data:

1. Change of the carbon hybridization or of the Sn—C—H angle

There are few data for comparison available, because the sign of $^2J(\mathrm{SnH})$ is

TABLE 1

INFLUENCE OF THE Sn—C—H ANGLE ON ^2J(SnH)

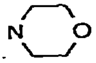
Compound	$^2J(^{119}$SnH) (Hz)	Reference
	−99.06	6
	−26.92	7
	21.0 [a]	8
	+54.3	9, 10

[a] The sign of this coupling constant has not been determined.

often not determined and as with cyclic systems, this coupling constant is sometimes not measured at all because of the complexity of the spectra. In Table 1 we list some typical examples of organotin compounds for which we can more or less estimate the Sn—C—H angle.

TABLE 2

^2J(SnH)[CHXY] IN $Me_3SnCHXY$ FOR VARIOUS X AND Y

X	Y	$^2J(^{119}$SnH)[CHXY] [a] (Hz)	Reference
H	H	54.3	9
H	CH_3	51.4	11
H	CH_2Ph	49.5 [b]	12
H	Cl	19.4 [b]	13
H	Br	18.0 [b]	13
Cl	Cl	15.0 [b]	13
Br	Br	13.2 [b]	13
H	$SiMe_3$	72.2	2
H	$SnMe_3$	60.3	14
H	OCH_3	16.2 [b]	15
H		28.8 [b]	15

[a] Except for Me_4Sn, the sign of this coupling constant has not been determined, but it is assumed to be positive in all cases. [b] Average value of $^2J(^{117}$SnH) and $^2J(^{119}$SnH).

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* The same reasoning is valid for H', as H and H' are considered to be equivalent.

TABLE 3

INFLUENCE OF A π-ELECTRON SYSTEM ON $^2J(SnH)[CHXY]$ IN $Me_3SnCHXY$

X	Y	$^2J(^{119}SnH)[CHXY]$ (Hz)	Reference
H	H	54.3	9
H	Ph	62.7	16
H	2-Pyridyl	62	17
H	Benzoyl	66	18
Ph	Ph	74.4	12

We see that in going from tetramethyltin (angle ~109°) to tetravinyltin (angle ~120°) there is a large negative shift of ^2J(SnH). The fact that the other substituents on tin do not remain the same cannot account for this dramatic fall in this coupling constant (see e.g. [1]), and so we can conclude that the expected trend is observed.

2. *Inductive effect of an α-substituent*

The data in Table 2 allow us to examine the influence of some substituents on the α-carbon. We can distinguish three classes of compounds in this series: (i) the substituents X, Y are less electronegative than C and H, e.g. Sn and Si: in these compounds $^2J(SnH) > 60$ Hz; (ii) the substituents are C or H: $^2J(SnH) \sim 50$ Hz; (iii) the substituents are more electronegative, e.g. Cl, Br, O, N: ^2J(SnH) is about 20—30 Hz.

Pople [5] pointed out that although an electronegative substituent leads to a positive change of $^2J(HH')$, this change is not a simple function of electronegativity. This seems to be true also in the case of ^2J(SnH). It can thus be concluded that once again ^2J(SnH) and $^2J(HH')$ behave similarly.

3. *Effect of a π-electron system on carbon*

It can be seen that in all the cases covered in Table 3, a π-system leads indeed to a positive shift of ^2J(SnH).

In the introduction we mentioned the explanation given by Van der Kelen [3] for the positive shift observed when the substituent is a phenyl group. For

TABLE 4

$^2J(SnH)$ IN $Ph_3SnCH_2CH_2Z$ [19]

Z	$^2J(^{119}SnH)$ (Hz)
CN	51.5
Ph	55.5
$C(OCH_3)=O$	56 [a]
OPh	63.5
$OC(CH_3)=O$	56
H	56.5 [b]

[a] Average value of $^2J(^{117}SnH)$ and $^2J(^{119}SnH)$. [b] In ref. 19 the values for $^2J(SnH)$ and $^3J(SnH)$ in this compound were interchanged.

his explanation to be true, it has to be accepted that the π-electrons are delocalized towards tin. As it is now established [20] that the opposite takes place in benzyltin compounds, our explanation, based on Pople's arguments, seems more logical.

4. A β-substituent

The only relevant data we could find in the literature are those for the series $Ph_3SnCH_2CH_2Z$ [19] (Table 4). This is the only case in which the expected trend is not observed. However, following Pople's theory, the influence of a β substituent depends largely on the dominant conformation. If a β substituent has the same effect on ^2J(HH') and ^2J(SnH), this would indicate that the gauche conformer is rather stable in $Ph_3SnCH_2CH_2Z$.

Conclusion

Either an electronegative group, a π-electron system bonded to the α carbon atom, or a change of the hybridization of this atom lead to a qualitatively similar change of ^2J(HH') in the CH_2 and ^2J(SnH) in the SnCH entity. In contrast, a β substituent does not have the expected influence on ^2J(SnH), and conformational factors may be important in this case. The results indicate that the theory devised by Pople for ^2J(HH') can also be used to explain the large changes of ^2J(SnH) which occur when the nature of the carbon atom between tin and the coupled hydrogen is changed.

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