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SPIN—SPIN COUPLING CONSTANTS IN ORGANOMETALLIC DERIVATIVES

I. A SEMI-EMPIRICAL APPROACH TO THE STUDY OF $(d\text{—}p)\pi$ CONTRIBUTION TO BONDS IN ORGANOSTANNANES

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Summary

The contact term contributions to direct ^1J(Sn—H) and long-range ^2J(Sn—H) coupling constants in methylchlorostannanes and methylhydrides have been calculated in the one-electron MO approximation employing extended Hückel wave functions. The AO basis set for the different atoms is that given by Clementi, while for tin an analytical form of 5*s* and 5*p* orbitals was derived from Herman and Skillman digital tables. Calculations were performed with and without *d* orbitals (Slater type) on the tin AO set, and the behaviour of calculated coupling constants in relation to *d* orbital energy and contraction was explored. The results show that for tetramethylstannane and tin hydride the coupling constants are unaffected by *d* orbital participation, while for mixed methyltinhydrides and methylchlorostannanes a dependence is found on the form of *d* orbital employed. The analysis of MO combinations and energy levels provides an indication of the mechanism involved in the participation of *d* orbitals of tin to bonding, but difficulties are encountered when flexibility criteria are introduced into the method in order both to compute the coupling constants resulting from the different redistribution of orbitals and their energies when different bonding situations are present. A study of the dependence of calculated coupling constants on geometrical parameters shows that small changes in bond lengths and bond angles give large intervals of indeterminacy of the computed quantities, thus indicating that the choice of selected geometries is of the utmost importance if, in order to achieve a more quantitative description of the coupling constants in organometallic derivatives, higher levels of sophistication are introduced into the computation methods.

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Introduction

In recent years there have been many studies of the high resolution nuclear magnetic resonance of organotin derivatives. The studies were carried out at the frequencies of ^{1}H, ^{13}C and ^{119}Sn and a large number of short- and long-range coupling constants $J(^{117,119}\text{Sn—H})$, $J(^{117,119}\text{Sn—}^{13}\text{C})$ and chemical shifts of these nuclei have been reported for derivatives containing different organic groups and halogens directly bonded to tin.

While correlation of chemical shift data with chemical structure and bonding patterns is still full of problems, owing to the large number of effects that act intra- and inter-molecularly on the screening of a nucleus, the situation for spin—spin coupling constants seems more promising, for the coupling pattern seems, at least approximately, to be related to the stereochemistry of the molecule [1,2]. For organometallic derivatives it has been shown [3] that a rough correlation exists between the dihedral angle and $J(\text{Hg—H})_{\text{vic.}}$ in mercury derivatives of cyclic organic compounds. More generally, it has been reported that coupling constants between an element M with spin 1/2 in a substituted organic derivative R—M and a proton are roughly proportional to the corresponding proton—proton coupling constants involving the same bond pattern in the parent R—H molecule. This has been shown for metal-substituted benzenes [4,5] containing thallium and mercury, heterocyclic derivatives [6—9] of tin, lead and mercury and was recently discussed more generally for several classes of organometallic derivatives [10]. The results have been interpreted [10] in the light of the widely-accepted suggestion that the contribution to the total observed coupling constant from the Fermi contact term is greater than the dipolar and orbital contributions. The approximate contributions of the three terms have been estimated [11] for proton—proton coupling constants, and the results show that J(contact) is at least ten times greater than the other terms and so the same could be thought to be true for J(M—H), at least in those derivatives for which correlations with structurally related J(H—H) can be found. These correlations also imply that, in addition to the magnetic quantities of the M nuclei (i.e. gyromagnetic ratios), the proportionality constant must contain [10] a term which describes the bonding pattern between coupled nuclei and which does not change dramatically over all the R—M and R—H derivatives. This was verified [10] in derivatives in which the element M is symmetrically substituted with n R groups, n being the valency of element M, while deviations are found when different R groups are bonded to M, these deviations being particularly marked when halogens are also bonded to M, in $R_{n-i}MHal_i$ compounds.

This suggests either that a different bonding mechanism is operating when halogens or other elements with electron pairs are bonded to M or that the other terms, namely dipolar and orbital, make different contributions to the total spin—spin coupling constant in alkylhalogenoderivatives than in derivatives with four M—C bonds. These considerations apply particularly in the case of tin derivatives, and the ample documentation allows a more systematic analysis of the results.

The first hypothesis seems better able to explain deviations from empirical correlations, since the experimental trend of coupling constants J(Sn—H) and

J(Sn—C), which are higher in $R_{4-i}SnHal_i$ than in R_4Sn compounds and increase with the number of halogen atoms, has been rationalized [12,13] in terms of $(d\text{—}p)\pi$ interactions between d empty orbitals of tin and lone-pairs in p orbitals of halogens. It is commonly accepted that d orbitals in tin are usually too diffuse and high in energy to contribute appreciably to bonding [14] in organotin compounds with four carbon to tin bonds. When halogens are attached to tin, however, the polarity of the Sn—Hal bond makes the tin atom more positive, and the d orbitals, which are contracted and stabilised as a result, are thus able to interact with p orbitals of the halogen atom. In fact, changes in the nuclear effective charge have a greater effect on the energy of d orbitals than they do on that of s and p orbitals [14,15]. The back-bonding taking place reinforces the tin to halogen bond in a synergic process which increases the π character of the bond, leaving the 5s orbital of tin more free to contribute to the bond to carbon. This increase in the s character of the tin to carbon bond in alkylhalogenostannanes would appear to be responsible for the enhancement of the long-range coupling constant J(Sn—H).

We have now carried out semi-empirical calculations of the coupling constant J(Sn—H) in tetramethylstannane, tin hydride, methyltinhydrides and methylchlorostannanes, in order not only to provide a more quantitative proof of the empirical interpretation of spin—spin coupling constants but also to arrive at a better description of the bonding characteristics in these systems. An approach to the semi-empirical description of long-range coupling constants based on molecular geometry is also described.

Method of calculation

We took into account only the contribution made by the contact term expressed in the one-electron MO approximation given by Pople and Santry [16].

$$J(\mathrm{A\text{—}B}) = -(16\,\pi\beta h/3)^2\,\frac{\gamma_A\gamma_B}{h}\sum_{i}^{\text{occ.}}\sum_{j}^{\text{unocc.}}(E_j-E_i)^{-1}\sum_{\lambda,\mu,\nu,\sigma}c_{i\lambda}c_{j\mu}c_{j\nu}c_{i\sigma}$$
$$\times\,\langle\phi_\lambda|\delta(r_A)|\phi_\mu\rangle\langle\phi_\nu|\delta(r_B)|\phi_\sigma\rangle \qquad (1)$$

All Dirac integrals were retained in the calculations. We used the LCAO-MO scheme of the extended Hückel (EHMO) approximation [17], having tested it previously [18] against other semi-empirical approaches and found that it seems to afford a better description of spin—spin coupling constants in small organic molecules [18] and organometallic derivatives [10]. Also, owing to its great flexibility, the method enables changes in parametrization bases and different sets of atomic orbitals to be tested. Furthermore, it has been used in recent papers [19,20] in evaluation of coupling constants in organometallic derivatives of tin, lead and mercury with encouraging results.

The AO basic set employed is that given by Clementi [21], while for the tin atom Herman and Skillman [22] digital tables relative to 5s and 5p orbitals were converted in analytical form as least-squares combinations of Slater-type orbitals [23]. When the external 5d orbital of tin was introduced into the calculation it was given the form of a Slater-type orbital and the orbital exponent

TABLE 1

EXPERIMENTAL AND CALCULATED COUPLING CONSTANTS IN ORGANOSTANNANES (Hz)

Compound		Experimental	Method A	Method B	Method C	Method D	Method E	Method F	Method
SnH_4	$^1J(Sn-H)$	−1930 [a]	−2334.56	−2334.56	−2334.56	−2334.56	−2334.56	−2334.56	−2334.56
CH_3SnH_3	$^1J(Sn-H)$	−1852 [b]	−1904.46	−1937.32	−1904.05	−1902.54	−1939.16	−1913.32	−1816.37
	$^2J(Sn-H)$	62.0 [c]	65.74	57.21	66.48	66.83	56.96	63.90	114.72
$(CH_3)_2SnH_2$	$^1J(Sn-H)$	−1758 [b]; −1797 [a]	−1546.19	−1620.66	−1563.87	−1551.73	−1620.13	−1586.63	−1380.34
	$^2J(Sn-H)$	58.6 [a]	59.35	53.91	59.07	59.53	53.85	57.64	75.65
$(CH_3)_3SnH$	$^1J(Sn-H)$	−1744 [a]	−1242.33	−1355.94	−1291.30	−1255.73	−1351.16	−1326.63	−1091.40
	$^2J(Sn-H)$	56.5 [a]	56.34	53.73	55.95	56.29	53.73	55.38	59.89
$(CH_3)_4Sn$	$^2J(Sn-H)$	55.80 [d]	55.69	55.69	55.69	55.69	55.69	55.69	55.69
$(CH_3)_3SnCl$	$^2J(Sn-H)$	59.85 [d]	61.98	64.51	63.61	62.60	64.27	64.48	64.82
$(CH_3)_2SnCl_2$	$^2J(Sn-H)$	69.82 [d]	67.00	72.52	70.66	69.34	71.82	73.19	78.40
CH_3SnCl_3	$^2J(Sn-H)$	101.47 [d]	77.77	86.16	85.35	82.43	87.03	87.54	92.71

[a] Ref. 31, [b] Ref. 1, [c] Ref. 32, [d] Ref. 13.

evaluated with different approaches, as will be explained in the discussion.

The valence orbital ionization potentials (VOIP) were employed for the diagonal elements of the Hamiltonian matrix, obtained from Basch tables [24] for elements up to chlorine. For elements of higher periods the VOIP's were calculated following the method given by Basch [24] and employing the atomic tables [25]. For tin the values obtained are as follows: V(5*s*) = 14.23; V(5*p*) = 7.012; V(5*d*) = 1.90 e.V.

The off-diagonal elements are approximated by Cusach's expression [26], which was handled so as to retain invariance to rotation [26,27]. The bond distances employed are taken from the literature [28,29]. The Calculations were performed on a CDC CYBER 76 computing system.

Results and discussion

In order to explore the importance of *d* orbital participation in the bonds of organometallic compounds of tin, the one bond and two bond *J*(Sn—H) coupling constants were calculated for the following compounds.

$(CH_3)_nSnH_{4-n}$ $n = 0, 1, 2, 3, 4$

$(CH_3)_nSnCl_{4-n}$ $n = 1, 2, 3$

The values refer to the ^{119}Sn isotope.

As a first step the coupling constants were evaluated by excluding *d* orbitals from the AO set (method A). The results, reported in Table 1, show that the absolute sign is in agreement with the experimental observations and the coupling constants through two bonds calculated at this stage of approximation are close to the experimental values, an appreciable deviation being found only for methyltrichlorostannane. The gross trend is also reproduced for ^1J(Sn—H), even though the absolute values differ from the experimental values.

When 5*d* orbitals (Slater-type with the orbital exponent obtained according to the CNDO/2 approximation [30]) are included in the valence AO basic set of tin (method B) the calculated coupling constants for SnH_4 and $Sn(CH_3)_4$ remain unchanged, while those of the other derivatives, and particularly that of methyltrichlorostannane, are noticeably affected. The inclusion of *d* orbitals in an AO basic set usually produces two effects: a polarization effect which does not affect [33] the electronic charge of the atom, since it causes only a redistribution of the electrons in the new *spd* set and an electron transfer effect from the doubly-occupied orbitals of an electronegative neighbour element and empty *d* orbitals [34]. SCF calculations on the entity of the latter effect were reported for phosphorous compounds [35] and proved that the inclusion of *d* orbitals enhances $(d—p)\pi$ bonding even though polarization effects are still evident. An "ab initio" exploration of *d* orbital participation in bonding was also conducted for chlorosilanes [36]. Differences in electron densities show that the inclusion of *d* orbitals in the set of AO's of chlorine or silicon gives the same electron transfer between the two atoms, but in terms of orbital contribution it can be deduced that the inclusion of *d* orbitals on the silicon AO set results in an electron transfer from chlorine to silicon.

In our calculations, inclusion of 5*d* orbitals on tin results in an increase of the positive charge on this atom, while higher values in calculated coupling constants are found for the chlorostannanes. No information can be obtained regarding the second-order contraction and stabilization of *d* orbitals, since the method of computation does not afford an internal consistency of orbital energies. The increase of the positive charge on tin can be related to a decreased contribution by tin AO orbitals to MO's: the redistribution of the AO orbitals does not affect the coupling constants of symmetrical molecules (SnH_4 and $Sn(CH_3)_4$) but a different redistribution in the asymmetrical derivatives gives a different weight in the MO combinations to the orbitals of the different groups bonded to tin, and thus different changes for ^1J(Sn—H) and ^2J(Sn—H) are calculated. For the hydrides the result is a reduction in the difference between ^1J(Sn—H) in SnH_4 and H_3SnCH_3, which is considerably greater than that found experimentally; on the other hand, the theoretical and experimental findings in respect of ^2J(Sn—H) differ considerably. Probably an optimization of 5*s* and 5*p* orbitals is necessary in the different hydrides, even though this could be partially accomplished by introducing a suitable form of 5*d* orbitals. Furthermore, the Sn—H bond distances are expected to vary somewhat in the $(CH_3)_{4-n}SnH_n$ compounds, and small differences in bond distances lead to large changes in calculated coupling constants, as will be shown later. The inclusion of *d* orbitals also leads to an increase in the positive charge on the tin atom in chlorostannanes, and the electronic population of *d* orbitals increases with the number of halogen atoms (about 0.1 e for each halogen atom). It is not clear whether this is only a polarization effect or whether the electrons are transferred from chlorine to the *d* orbitals of tin, for the chlorine atoms also become more negative. The *P*(5*s*—2*s*) orbital-orbital bond-order for Sn—C also increases slightly in the molecules examined, except in the case of symmetrical derivatives, as shown in Table 2.

When a less contracted form of 5*d* orbitals is employed, by assigning to the orbital exponent a value obtained following Burns rules [37] and allowing for s^2pd configuration at tin, the results obtained are those indicated under method C. Apart from the fact that for SnH_4 and $(CH_3)_4Sn$ the coupling constants remain unchanged; in the other cases the values obtained are midway between those obtained with and without *d* orbitals on tin (method A and B, respectively). The same behaviour is also found for atomic and overlap populations. This is not unexpected if it is accepted that any contribution to MO combinations by *d* orbitals must depend on their degree of contraction. Accordingly, we set out to obtain a set of AO's of tin to be employed in evaluating the coupling constants in organostannanes containing also halogens or other elements with electron pairs, in order to simulate changes of coupling constants in different coordinations at the tin atom or in the chemical reactivity of tin compounds.

We therefore assumed the orbital exponent of *d* orbitals to be dependent on the electron charge on 5*s* and 5*p* orbitals of tin according to the following approximations:

$$\zeta = (5.65 - 1.4125 \sum_{s,p} Z)/4 \qquad (2)$$