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DFT Calculations of ^{119}Sn Chemical Shifts Using Gauge-Including Atomic Orbitals and Their Interpretation via Group Properties

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Nonrelativistic DFT calculations of the ^{119}Sn chemical shift are presented for a large series of tetracoordinated Sn compounds, of the type $CH_3SnRR'R''$, where R, R′, R″ are halogens, alkyl, halogenated alkyl, alkoxy, or alkyl thio groups. The B3PW91 functional is used in conjunction with the IGLO III basis set. Leaving out compounds associating in solution and thus changing the Sn coordination, a correlation coefficient r^2 of 0.978 ± 0.023 is obtained between solvent NMR shifts and calculated values, with a slope of 0.984. These results indicate that this methodology yields excellent results both in the absolute and relative sense for the majority of the cases studied, where cancellation of errors (solvent and relativistic effects) occurs. The results were interpreted in terms of calculated electronegativity, hardness, and softness of the groups SnRR′R″, applying a methodology previously developed by us (*J. Phys. Chem.* **1993**, *97*, 1826) and using the 6-311++G** basis set for H, C, Cl, Br, O, and S and 3-21G for Sn and I. Sequences of group electronegativities and hardnesses could be rationalized via previously calculated or experimental first and second row atomic or functional group values reflecting the interplay of qualitative and quantitative changes in groups on the central Sn atom. The evolution of the ^{119}Sn chemical shift can be successfully interpreted on the basis of group electronegativities for groups introduced in the β position of the Sn atom, whereas changes in α position (i.e., groups directly bonded to Sn) turn out to be essentially hardness related, especially when changes in the row of the periodic table are involved.

1. Introduction

There is increasing interest in density functional theory (DFT) calculations to evaluate nuclear magnetic resonance (NMR) properties, due to the capability of these methods to include electron correlation at a favorable computational cost, as compared to traditional ab initio correlated methods (for a detailed account of density functional theory, see, for example, ref 1 and references therein). The DFT calculation of NMR properties has been the subject of many reviews;[2−4] moreover, it was also shown among others by the present authors that also electric properties can be obtained to a good accuracy[5−8] (for a detailed account, see again ref 1). A general review of the ab initio calculation of NMR shielding and indirect spin−spin coupling constants was recently provided by Helgaker et al.[9]

The application of DFT has been especially useful for those systems that cannot be easily and routinely treated by methods beyond the SCF type, such as large organic molecules or molecules containing transition metals. When going down in the periodic table, however, relativistic effects become increasingly important, and recently, under the impetus of Ziegler, efficient strategies have been developed to incorporate an adequate treatment of these effects, which have then been applied for nuclei up to ^{235}U,[10] ^{183}W, and ^{207}Pb.[11] In this paper, attention will be focused on the density functional calculation of ^{119}Sn chemical shifts using gauge-including atomic orbitals (GIAO).[9,12−14] In view of the vast amount of experimental literature data on these ^{119}Sn chemical shifts involving compounds of various types,[15,16] it could therefore be useful to assess this present day powerful nonrelativistic method in its performance in predicting/reproducing ^{119}Sn chemical shifts. The situation of this fourth row analogue of C is intermediate, lying at the borderline of main group and coordination chemistry. On the basis of the study by Ziegler et al. on chemical shifts of ^{125}Te,[17] one of the neighbor elements of Sn, it can be assumed that relativistic effects on these shifts may be minor (as opposed to absolute shieldings).

Despite the previously mentioned computational advances and the availability of a large number of experimental data,[15,16] only a few theoretical studies have been reported for ^{119}Sn nuclear shielding constants. Nakatsuji et al. published finite perturbation SCF level chemical shifts for $SnMe_{4-n}H_n$ ($n = 0-4$) and $SnMe_{4-n}X_n$ ($n = 0-4$ and X = Cl) and found values that agreed well with experiment.[18,19] They stated that the ^{119}Sn chemical shifts are mainly determined by the Sn valence p atomic orbital contribution to the paramagnetic term. In 1996, Nakatsuji et al. studied the spin−orbit effect on the magnetic shielding of the Sn atom in tin tetrahalides SnX_4 (X = Cl, Br, and I) and $SnBr_{4-n}I_n$ ($n = 1, 2, 3$).[20] They concluded that the calculated values without a correction for the spin−orbit interaction do not satisfactorily reproduce the experimental values of the

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chemical shifts when the halogen atom is heavy. They, however, found that the spin−orbit contribution due to the Sn atom was small.

De Dios calculated absolute shieldings for SnH_4, $SnCl_4$, and $SnMe_4$ using the HF/GIAO and SOS-DFTPT (sum-over-states density functional perturbation theory) methods, in combination with the IGLO II and IGLO III basis sets.[21] Moreover, he also presented shieldings using the hybrid B3PW91 functional, as likewise used by us in the present paper (vide infra). He concluded that, provided electron correlation is introduced in the calculations and large basis sets are used, the results approach the experimental values of the ^{119}Sn chemical shifts.

In the present work, DFT chemical shifts were computed for a large set of organotin compounds such as $SnMe_{4-n}H_n$, $SnMe_{4-n}X_n$, $SnMe_3R$, $Me_3SnCH_{3-n}X_n$, Me_3SnOR, and Me_3SnSR (with R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *s*-Bu, *t*-Bu, Ph, and X = F, Cl, Br, I). The shifts obtained are compared with the available experimental data and modeled using the concepts of group electronegativity and hardness.

The methodology used (isolated gas phase molecules considered at a nonrelativistic level) obviously contains simplifications. However, cancellation of corrections due to various factors may be expected as we concentrate on shifts (i.e. differences of shielding values) and not on shieldings themselves (cf. the above-mentioned study by Ziegler on ^{125}Te shifts).

Only in the case of compounds in which Sn is directly bonded to heavy atoms (Br and I) relativistic effects might play a decisive role in view of Nakatsuji's results indicating that spin−orbit terms are very important. The spin−orbit contribution is indeed very sensitive to the atomic number of the atoms directly coordinated to the metal. So ^{119}Sn shieldings can be underestimated when heavy halogen atoms (Br, I) are bonded directly to the tin atom, but when the halogen is not attached directly to the tin atom, the effect can be expected to be minor.

The effect of the solvent on the other hand can be considered to be negligible as long as one considers noncoordinating solvents, e.g., CH_2Cl_2 (as is the case for the experimental studies with which the values are compared). Only if a change in coordination is to be expected, a breakdown in the compensation of errors is expected to occur.

Transferability is one of the basic concepts in chemistry; considering molecules as being built up from blocks transferable from one molecule to another is of fundamental importance when ordering and interpreting the immense amount of data concerning structure and reactivity functional group properties, and this permits us to quantify this building block ansatz. Among properties, group electronegativity is one of the first discussed and most thoroughly investigated properties with a variety of scales presented from the 1960s on (for a comprehensive review, see ref 22). These scales, just as those for atomic electronegativities, were derived starting from experimental data such as bond vibrational data[23] and inductive parameters,[24] among others, due to the lack of a sharp definition the electronegativity concept itself. An important breakthrough is the definition of electronegativity, by Iczkowski and Margrave,[25] as the negative of the derivative of the energy E of a system with respect to the number of electrons N, later identified with the negative of the chemical potential by Parr and co-workers,[26] within the context of density functional theory.[27] The latter step offered the possibility for nonempirical calculations of atomic, group, and molecular electronegativities.[28,29]

A similar evolution, however, only starting in the 1960s, is seen for the concepts of hardness and softness introduced by Pearson.[30] Only after identification by Parr and Pearson[31] themselves of the atomic or molecular hardness as the second derivative of the energy with respect to the number of electrons, and the softness as its inverse, the way to a parameter-free evaluation was paved.

The evaluation of group electronegativities, hardness, and softness values has until now essentially concentrated on groups containing first, second, and third row atoms[32−36] and has been of great use to, among others, the presents authors,[28,29] when applying the hard and soft acids and bases theory[37] and the electronegativity equalization principle,[38] e.g., when studying acidity and basicity sequences both in the gaseous phase and in solvent.[39−43] In this paper we consider the extension of our computational approach for group electronegativity, hardness, and softness as developed in ref 28 to functional groups containing tin. The methodology of group electronegativity, hardness, and softness can indeed be applied to tin compounds without any fundamental changes, as relativistic effects may still be expected to be relatively small and probably are canceled out in the evaluation of these quantities which is no longer the case for fifth and higher row elements. Peregudov and his group have done studies on this kind of compound,[44−49] their approach being, however, less in line with our previous contributions and concentrating on large groups.

2. Computational Details

2.1. Chemical Shifts. All magnetic property calculations were performed using the B3PW91 functional,[50,51] combined with the IGLO III basis set[52] (for the elements H, O, Cl, and S) and the IGLO II basis set[52] (for the elements Sn, Br, and I), both for the full geometry optimizations (The Cartesian coordinates of the equilibrium geometries of all the molecules studied in this work can be obtained from the authors upon request.) of each compound and the NMR calculations. The latter were performed using the gauge-invariant atomic orbital (GIAO) technique.[9,12−14]

2.2. Group Electronegativity and Hardness. A detailed discussion about the calculation of hardness, softness, and electronegativity can be found elsewhere,[27] and only the relevant expressions used for the evaluation of these quantities expressions are given below. The global hardness (η), softness (S), and electronegativity (χ) are calculated within DFT as follows:

$$\eta \approx \frac{\mathrm{IE} - \mathrm{EA}}{2} \qquad (1)$$

Softness is the inverse of hardness

$$S = \frac{1}{2\eta} \qquad (2)$$

The electronegativity is defined as

$$\chi = \frac{\mathrm{IE} + \mathrm{EA}}{2} \qquad (3)$$

where IE and EA are vertical ionization energy and electron affinity of the systems, respectively.

We use the expressions 1−3 as working equations to calculate the group electronegativity, hardness, and softness.[28,29]

For a group G (e.g., the CH_3 group[28] or SnH_3 in the present work), the corresponding (neutral) radical was considered in the geometry the group usually adopts when being part of a molecule and not in the equilibrium geometry of the isolated radical. The CH_3 radical, for example, is therefore considered in a pyramidal geometry and not in the planar geometry it adopts in an individual molecule. Within this option, standard bond

TABLE 1: Calculated Absolute Shieldings σ (ppm) and Chemical Shifts (ppm), Together with the Experimental Shifts (ppm)[15]

		δ	
molecule	σ	calcd	expl
$Sn(CH_3)_4$	2527	0	0
$Sn(CH_3)_3Cl$	2379	148	164.2
$Sn(CH_3)_2Cl_2$	2373	154	137
$Sn(CH_3)Cl_3$	2454	73	21
$Sn(CH_3)_3Br$	2377	150	128
$Sn(CH_3)_2Br_2$	2318	209	70
$Sn(CH_3)Br_3$	2337	190	−165
$Sn(CH_3)_3I$	2388	139	38.6
$Sn(CH_3)_2I_2$	2297	230	−159
$Sn(CH_3)I_3$	2256	271	−699.5
$(CH_3)_3SnCH_2Cl$	2538	−11	4
$(CH_3)_3SnCHCl_2$	2521	6	33
$(CH_3)_3SnCCl_3$	2480	47	85
$(CH_3)_3SnCH_2Br$	2529	−2	6
$(CH_3)_3SnCHBr_2$	2503	24	42
$(CH_3)_3SnCBr_3$	2449	78	101
$(CH_3)_3SnEt$	2532	−5	4.2
$(CH_3)_3Sn(n\text{-}Pr)$	2537	−10	−2.3
$(CH_3)_3Sn(i\text{-}Pr)$	2534	−7	8.6
$(CH_3)_3Sn(n\text{-}Bu)$	2539	−12	−1
$(CH_3)_3Sn(s\text{-}Bu)$	2536	−9	3.3
$(CH_3)_3Sn(t\text{-}Bu)$	2528	−1	19.5
$Sn(CH_3)_3H$	2640	−113	−104.5
$Sn(CH_3)_2H_2$	2762	−235	−225
$Sn(CH_3)H_3$	2899	−372	−346
SnH_4	3039	−512	−500
$(CH_3)_3SnOH$	2429	98	118
$(CH_3)_3SnOCH_3$	2431	96	129
$(CH_3)_3SnO(i\text{-}Pr)$	2443	84	109
$(CH_3)_3SnO(t\text{-}Bu)$	2463	64	91
$(CH_3)_3SnOPh$	2420	107	134.3
$(CH_3)_3SnSCH_3$	2450	77	90
$(CH_3)_3SnSEt$	2458	69	78
$(CH_3)_3SnS(t\text{-}Bu)$	2479	48	55.5

angles and distances were used throughout this work using the standard structures given by Molden[53] (distances in Å involving Sn: Sn−H = 2.05, Sn−C = 2.51, Sn−Cl = 2.79, Sn−Br = 3.01, Sn−I = 3.19, Sn−O = 2.49, Sn−S = 2.82).

By calculating the energies of the radical (N electron system), the cation ($N - 1$ electron system), and the anion ($N + 1$ electron system) of the group G, all at the same geometry [cf. the requirement of constant external potential $\nu(r)$], one can determine the ionization energy and electron affinity of G and thus the group quantities via eqs 1−3. In the case of the compounds $SnMe_{4-n}H_n$, $SnMe_{4-n}X_n$, $SnMe_3R$, $Me_3SnCH_{3-n}X_n$, Me_3SnOR, and Me_3SnSR (with R = Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, and Ph, and X = F, Cl, Br, I) one of the methyl groups was systematically removed.

The calculations for the group electronegativities, hardness, and softness were carried out at the B3PW91 level[50,51] using a 6-311++G** basis set[54] for H, C, O, S, Cl, and Br and 3-21G[54] for Sn and I. The different basis set used when compared to the NMR part is justified, since the IGLO basis set requires extreme flexibility in the nuclear region, the description of the valence region being similar in the two cases.

All NMR and group properties calculations were performed using the Gaussian 98 program,[55] running on the Compaq-Digital Alphaserver GS140 of the Brussels Free Universities computer center.

3. Results and Discussion

3.1. Chemical Shift Calculation. The ^{119}Sn NMR chemical shifts of numerous tin compounds have been obtained experimentally.[15,16] They cover a range of approximately 6500 ppm, from 4000 to −2500 ppm. The experimental range of the chemical shifts investigated here amounts at 864 ppm. It is important to note that the experimental ^{119}Sn chemicals shifts for some compounds often depend on the nature of the solvent. In such cases, our comparison to experimental data corresponds to the values measured in CH_2Cl_2 or other noncoordinating solvents, because there is no coordination from such solvent molecules to the organotin moiety.

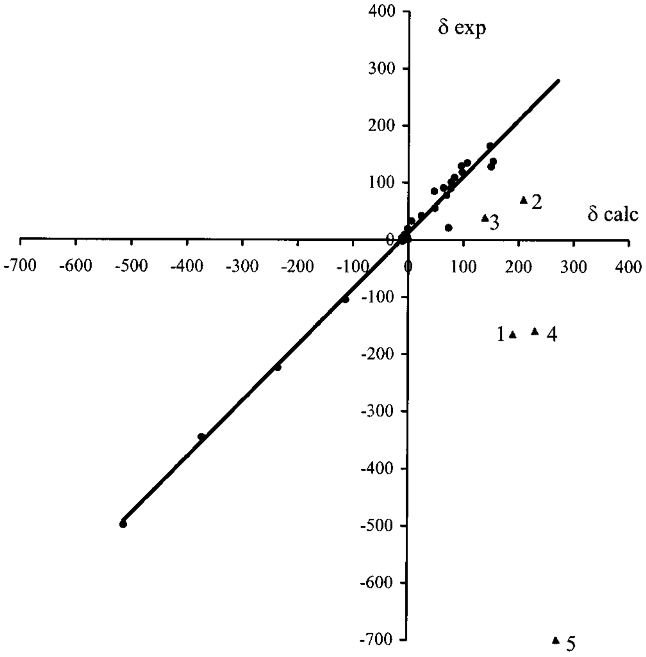

Figure 1. Experimental chemical shifts (ref 15) vs the calculated ones, for all compounds considered in Table 1. All values are in ppm. The regression line for all the compounds expect for $SnMe_2Br_2$ (1), $SnMeBr_3$ (2), $SnMe_3I$ (3), $SnMe_2I_2$ (4), and $SnMeI_3$ (5) is drawn.

The calculated chemical shifts are expressed as

$$\delta^{\mathrm{cal}}(\mathrm{sample}) = \sigma^{\mathrm{cal}}(\mathrm{SnMe_4}) - \sigma^{\mathrm{cal}}(\mathrm{sample}) \qquad (4)$$

where $\sigma^{\mathrm{cal}}(SnMe_4)$ and σ^{cal}(sample) are the isotropic NMR shieldings of the reference compound $SnMe_4$ and the sample in question, respectively.

The calculated ^{119}Sn chemical shifts for the total series, representing a wide range of organotin compounds, are given in Table 1, together with the experimental chemical shifts. As expected, the largest discrepancies between the theoretical and experimental values were obtained for $SnMe_2Br_2$, $SnMeBr_3$, $SnMe_3I$, $SnMe_2I_2$, and $SnMeI_3$ (five points indicated explicitly in the diagram), where the mean absolute deviation of the chemical shifts is 391 ppm (standard deviation 559 ppm) and the chemical shift range of these compounds is 770 ppm. The deviation is in line with our expectations on the noninclusion of relativistic effects in our calculations and is in accordance with the previously mentioned statement of Nakatsuji that the spin−orbit contribution to the chemical shielding is very important when heavy halogens are directly attached to the Sn atom.

On the other hand, the experimental chemical shifts of these products indicate that these compounds tend to associate in solution, meaning that the Sn atom is no longer tetravalent, as was assumed in the calculations. Leaving these problem cases out of the correlation analysis, Figure 1 shows that for the remaining series of compounds a correlation coefficient of 0.985 is found between the two sets of data: the regression line, shown

TABLE 2: Calculated Electronegativity (χ, in eV), Hardness (η, in eV), and Softness (S, 10^{-2} eV^{-1}) of Me$_3$SnCH$_n$X$_{3-n}$ Groups (n = 0, 1, 2) and Theoretical ^{119}Sn Chemical Shifts (δ, in ppm), for the Corresponding Compounds Me$_3$SnCH$_n$X$_{3-n}$

molecules	δ	χ	η	S
Me$_3$SnCH$_2$Cl	−11	4.64	2.94	16.98
Me$_3$SnCHCl$_2$	6	4.76	2.83	17.61
Me$_3$SnCCl$_3$	47	4.98	2.81	17.75
Me$_3$SnCH$_2$Br	−2	4.67	2.92	17.13
Me$_3$SnCHBr$_2$	24	4.77	2.76	18.09
Me$_3$SnCBr$_3$	78	4.97	2.72	18.35

TABLE 3: Calculated Electronegativity (χ, in eV), Hardness (η, in eV), and Softness (S, in 10^{-2} eV^{-1}) of Me$_n$SnH$_{4-n}$ Groups (n = 1, 2, 3) and Theoretical ^{119}Sn Chemical Shifts (δ, in ppm), of the Corresponding Me$_{n+1}$SnH$_{4-n}$ Compounds

molecules	δ	χ	η	S
Me$_3$SnH	−113	4.63	3.12	16.04
Me$_2$SnH$_2$	−235	4.89	3.24	15.42
MeSnH$_3$	−372	5.19	3.39	14.76

TABLE 4: Calculated Electronegativity (χ, in eV), Hardness (η, in eV), and Softness (S, in 10^{-2} eV^{-1}) of Me$_2$SnOR and Me$_2$SnSR Groups and Theoretical ^{119}Sn Chemical Shifts (δ, in ppm), of the Corresponding Me$_3$SnOR and Me$_3$SnSR Compounds

molecules	δ	χ	η	S
Me$_3$SnOH	98	4.24	3.28	15.25
Me$_3$SnOCH$_3$	96	4.12	3.21	15.59
Me$_3$SnO(*i*-Pr)	84	4.06	3.10	16.14
Me$_3$SnOBu	64	4.08	3.06	16.35
Me$_3$SnOPh	107	4.31	3.07	16.30
Me$_3$SnSCH$_3$	77	4.02	3.04	16.46
Me$_3$SnSEt	69	3.97	3.01	16.63
Me$_3$SnSBu	48	3.88	2.93	17.05

in Figure 1, has the following equation:

$$\delta_{\text{exp}} = (0.984 \pm 0.023)\delta_{\text{calc}} + (12.05 \pm 3.3) \qquad (5)$$

As can be seen, the slope does not significantly differ from unity. Forcing the regression line through the origin yields a slope of 0.985 and a correlation coefficient of 0.978. The mean absolute deviation is 18.30 ppm on a total scale of 664 ppm. (standard deviation is 21.56 ppm). As a whole, these results indicate that the adopted nonrelativistic methodology yields excellent results for shifts, both in absolute and relative terms. This is due to the cancellation of relativistic and solvent effects when calculating the shifts as differences of shieldings. As already shown above, this was also witnessed by Ziegler et al. in their study on ^{125}Te chemical shifts, where it was noticed that relativity has a notable effect on the calculated absolute shieldings, but that part of these effects cancel when the chemical shifts are calculated.[17]

The whole of these results validates the nonrelativistic isolated molecule approach and meets the expectations of canceling of errors due to relativistic and (noncoordinating) solvent effects.

3.2. Group Electronegativity and Hardness Calculation. *Group Electronegativity.* The calculated group electronegativities of the tin-containing groups are shown in Tables 2−6. In Table 2 a series of groups of the type Me$_3$SnCH$_{3-n}$X$_n$ (X = Cl, Br) (n = 0, 1, 2) is shown. The substitution of a hydrogen atom in the methyl group by a more electronegative halogen atom (Cl, Br) results in the order of decreasing group electronegativity Me$_2$SnCCl$_3$ > Me$_2$SnCHCl$_2$ > Me$_2$SnCH$_2$Cl and Me$_2$SnCBr$_3$ > Me$_2$SnCHBr$_2$ > Me$_2$SnCH$_2$Br, nicely reflecting the increasing electronegativity when passing from H to Cl or Br. It can be noticed that for halogen-containing groups increasing the number of halogens has a larger influence than interchanging chlorine and bromine, the latter operation leading to similar electronegativities. Table 6 shows the same trends for the groups Me$_n$SnX$_{3-n}$ (X = Cl, Br, I) (n = 1, 2), indicating a similar trend as in our study on halogen-containing functional groups with C as the central atom.[28] Electronegativity variations on the substituents $\chi_F > \chi_{Cl} > \chi_{Br} > \chi_I$ are transmitted to the group as a whole when bound to a common atom. Note that for X = I the group electronegativity values are a bit smaller that for X = Br (n = 1 and 2). Again changes in the electronegativities are more sensitive to the number of halogen atoms than to the nature of the halogens.[56]

TABLE 5: Calculated Electronegativity (χ, in eV), Hardness (η, in eV), and Softness (S, in 10^{-2} eV^{-1}) of Me$_2$SnR Groups and Theoretical ^{119}Sn Chemical Shifts (δ, in ppm), of the Corresponding Me$_3$SnR Compounds

molecules	δ	χ	η	S
Me$_4$Sn	0.0	3.91	3.19	15.63
Me$_3$SnEt	−5	3.94	3.14	15.92
Me$_3$Sn(*n*-Pr)	−10	3.97	3.13	16.03
Me$_3$Sn(*i*-Pr)	−7	4.01	3.02	16.45
Me$_3$Sn(*n*-Bu)	−12	3.96	3.13	16.03
Me$_3$Sn(*s*-Bu)	−9	4.00	3.06	16.34
Me$_3$Sn(*t*-Bu)	−1	3.93	3.03	16.50

TABLE 6: Calculated Electronegativity (χ, in eV), Hardness (η, in eV), and Softness (S, in 10^{-2} eV) of the Me$_n$SnX$_{3-n}$ Groups (n = 0, 1, 2) and Theoretical ^{119}Sn Chemical Shifts δ (in ppm), of the Corresponding Me$_{n+1}$SnX$_{3-n}$ Compounds

molecule	δ	χ	η	S
Me$_3$SnCl	148	4.56	3.27	15.26
Me$_2$SnCl$_2$	154	5.50	3.23	15.46
MeSnCl$_3$	73	6.72	3.12	15.99
Me$_3$SnBr	150	4.60	3.19	15.68
Me$_2$SnBr$_2$	209	5.51	3.03	16.49
MeSnBr$_3$	190	6.59	2.82	17.71
Me$_3$SnI	139	4.29	3.14	15.92
Me$_2$SnI$_2$	230	5.39	2.79	17.90

In Table 3, the evaluation of the electronegativity of the Me$_{n-1}$SnH$_{4-n}$ (n = 1, 2. 3) groups shows that electronegativity is increasing when the methyl group is systematically replaced in SnMe$_3$ by a more electronegative hydrogen atom (cf. absolute values:[27] H, 7.18 eV; CH$_3$, 4.96 eV).

In the series Me$_2$SnOR and Me$_2$SnSR′ (Table 4), with R = H, Me, *i*-Pr, *t*-Bu, and Ph and R′ = Me, Et, and *t*-Bu), replacing the Me group in SnMe$_3$ by a more electronegative OR group causes the electronegativity to become intermediate between those of Me$_2$SnCl and Me$_3$Sn, the values being systematically lower in the sulfur-containing groups, in accordance with the lower electronegativity of S as compared to O.

In Table 5 it is seen that for the series of Me$_2$SnR (R = H, Ph, Et, Pr, Bu) groups the effect of substituting a methyl by a larger alkyl group is very small as compared to substituting it by hydrogen atoms or halogens, preventing a meaningful correlation with the group properties.

Group Hardness. As can be seen in Table 2, replacing a methyl hydrogen in the SnMe$_3$ group by a softer halogen (Cl, Br) systematically decreases the hardness. Increasing the number of halogens continuously increases the group softness. The sequence for a given number of halogens shows higher hardness for the bromine than for the chlorine-containing groups, paralleling the higher softness of a bromine as compared to a chlorine atom. When in Table 6 a methyl group is replaced by a halogen (Cl, Br, I), the result is also a decreasing value of the hardness (except for the mono and dichloro cases), in agreement

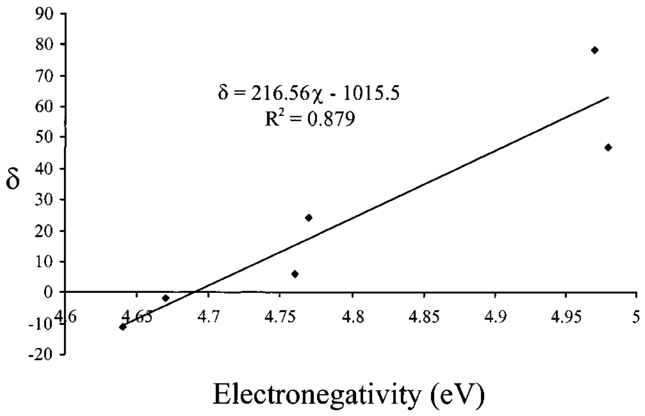

Figure 2. Correlation of the theoretical ^{119}Sn chemical shifts δ (in ppm) in $Me_3SnCH_nX_{3-n}$ compounds with the calculated electronegativity of the $Me_2SnCH_nX_{3-n}$ groups (in eV).

with the hardness sequence $CH_3 > Cl > Br$ (values from ref 27: 4.87 eV > 4.70 eV > 4.24 eV). The introduction of a harder hydrogen replacing a softer methyl group results in an increasing hardness (Table 3).

In Table 4, it can be seen that replacing O by the softer S increases its global group softness, the influence of the alkyl group being similar to that shown in Table 5.

3.3. Correlation of Chemical Shifts with Group Properties. On the basis of the literature data,[15,16] the quantity considered as the first and possibly mostly rewarding for correlation with ^{119}Sn shifts is the electronegativity of the SnRR′R″ group.

It can be seen from Table 2 that the ^{119}Sn shielding increases when going from Me_3SnCH_2Cl to $Me_3SnCHCl_3$, thus reflecting a group electronegativity increase from Me_3SnCH_2Cl to Me_3SnCCl_3. The same tendency is observed for the case of Me_3SnCH_2Br, $Me_3SnCHBr_2$, and Me_3SnCBr_3, both for the ^{119}Sn shielding and for the group electronegativities [remember that the theoretical chemical shifts values of these compounds match very well the experimental ones (see Figure 1)], probably because the halogen is not directly bonded to the metal atom. Introducing a single halogen atom in one of the methyl groups slightly increases the shielding of the tin atom, but when two or three halogens are introduced, the tin atom again becomes more deshielded.

A good correlation between ^{119}Sn shielding and group electronegativities was obtained (see Figure 2) for these six cases,

$$\delta^{119}\mathrm{Sn} = 216.56\chi - 1015.5 \quad (r^2 = 0.879) \qquad (6)$$

indicating that increasing group electronegativity leads to increasing Sn chemical shift.

In the case of the series of compounds Me_nSnH_{4-n} ($n = 1$, 2, 3), Table 3 shows that the ^{119}Sn shielding decreases in going from Me_3SnH to $MeSnH_3$; at the same time, however, the electronegativity increases, yielding the following correlation:

$$\delta^{119}\mathrm{Sn} = -462.35\chi - 2027.1 \quad (r^2 = 0.999) \qquad (7)$$

Here an inverse sign of the δ vs χ correlation is observed as compared to the previous equation, which can be traced back to the fact that in this case it appears that the chemical shift does not follow the trend in electronegativity; one would expect that upon substitution of the electrodonating methyl group by a more electronegativite hydrogen, the chemical shifts would increase.

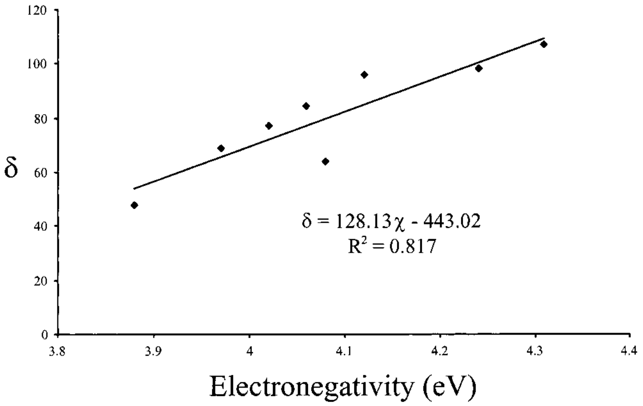

Figure 3. Correlation of the theoretical ^{119}Sn chemical shifts δ (in ppm) in Me_3SnOR and Me_3SnSR compounds with the calculated electronegativity of the Me_2SnOR and Me_2SnSR groups (in eV).

For the compounds of the type Me_3SnOR and Me_3SnSR (Table 4 and Figure 3), a good correlation has been found between the corresponding values of ^{119}Sn chemical shifts and group electronegativities,

$$\delta^{119}\mathrm{Sn} = 128.13\chi - 443.02 \quad (r^2 = 0.817) \qquad (8)$$

indicating again that increasing the group electronegativities yields increasing chemical shifts. As can be seen in Table 4, replacing the Me by a more electronegative OR group increases the chemical shift. The replacement of Me by a SR′ group also increases the chemical shift, but to a lesser degree than the OR compounds, in accordance with the lower electronegativity of S vs O, as reflected also in the group electronegativity values.

No reliable relationship for the groups Me_3SnR (involving a replacement of an alkyl group by another one) could be obtained, because of the short range of chemical shifts, 15 ppm, as compared with others sequences. Also when a halogen is directly bonded to the Sn atom, the electronegativity correlation fails and the relationship obviously involves some interplay between electronegativity and hardness.

Let us now introduce hardness into the picture. Coming back to the results in Table 3, we are reminded that the correlation between chemical shift and electronegativity showed an unexpected sign. Indeed, upon replacing more methyl groups by hydrogens, the substituents on Sn increase in electronegativity, which would yield a less shielded Sn and more positive δ values. The sequence of χ values for the groups reflects this effect; the δ values do not. If we, however, consider the hardness of the methyl group as compared to the hydrogen, it is observed that replacing methyl by the harder hydrogen atom decreases the charge capacity in the Sn neighborhood, leading to a more shielded Sn atom and more negative δ values.

Hardness also seems to play a decisive role in the results of Table 6, where halogen atoms directly bonded to Sn are varied across the periodic table. It turns out that the correlation with group electronegativity, the values of which seemed reasonable in Table 1, does not work at all. However, Figure 4 indicates that, except for $MeSnCl_3$, a fair correlation is obtained between δ and η, with the same sign of the Me_nSnH_{4-n} compounds (discussed previously in eq 7). Introducing harder halogens on the Sn atom (increasing the hardness of the Me_nSnX_{3-n} functional group) decreases the charge capacity in the Sn neighborhood, leading to a more shielded Sn atom, lowering the δ value.

In general, the following rule appears to emerge: if in a system Sn−A−B the atom A is replaced by an atom of the same

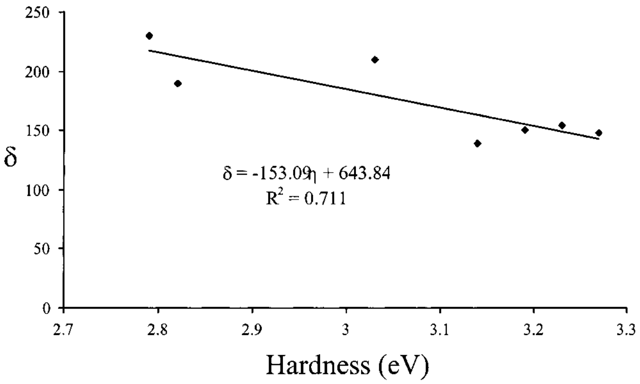

Figure 4. Correlation of the theoretical ^{119}Sn chemical shifts δ (in ppm) in $Me_{n+1}SnX_{3-n}$ compounds with the calculated hardness of the Me_nSnX_{3-n} groups (in eV) ($MeSnCl_3$ left out).

column but with higher atomic number, the increase in softness appears to be the dominant factor in the evolution of the Sn chemical shifts. If, however, B is replaced in this way, A being constant, electronegativity effects dominate.

4. Conclusions

Density functional calculations were presented for a series of tetracoordinated Sn compounds, using a large IGLO basis set and the GIAO method neglecting relativistic and solvent effects. As such, this paper presents the first large scale systematic study of the ^{119}Sn chemical shifts for a large series of Sn compounds. In general, it can be concluded that the experimental chemical shifts can be reproduced to a very good accuracy, due to the cancellation of relativistic and solvent effects, except for the expected cases where a heavy halogen atom is directly bonded to the Sn atom. An overall correlation coefficient of 0.978 is obtained for 29 compounds with a slope value differing from 1.00 by only 0.015 The accuracy of these calculated ^{119}Sn chemical shifts is promising for the study of large Sn-containing molecules and tin chemistry as a whole.

The interpretation of these data via the first ab initio calculated Sn-containing group properties (electronegativity, hardness, and softness) is highly satisfactory. The preliminary analyses of the group properties of SnRR′R″ highlights the influence of the R, R′, R″ electronegativity and hardness on the corresponding values of the global group, joining the results of the previously reported carbon analogues.

The correlation with the calculated chemical shifts points out that group electronegativity is dominant when replacing groups in the β position, and group hardness is dominant for substituents in the α position, especially when also a change in the row of the periodic table is involved.

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