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Evaluation of group electronegativities and hardness (softness) of group 14 elements and containing functional groups through density functional theory and correlation with NMR spectra data

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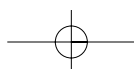
Abstract: Quantum Chemical calculations for group 14 elements of Periodic Table (C, Si, Ge, Sn, Pb) and their functional groups have been carried out using Density Functional Theory (DFT) based reactivity descriptors such as group electronegativities, hardness and softness. DFT calculations were performed for a large series of tetracoordinated Sn compounds of the $\text{CH}_3\text{SnRR}'\text{X}$ type, where X is a halogen and R and R' are alkyl, halogenated alkyl, alkoxy, or alkyl thio groups. The results were interpreted in terms of calculated electronegativity and hardness of the $\text{SnRR}'\text{X}$ groups, applying a methodology previously developed by Geerlings and coworkers (J. Phys. Chem. 1993, 97, 1826). These calculations allowed to see the regularities concerning the influence of the nature of organic groups RR' and inorganic group X on electronegativities and hardness of the $\text{SnRR}'\text{X}$ groups; in this case, it was found a very good correlation between the electronegativity of the fragment and experimental ^{119}Sn chemical shifts, a property that sensitively reflects the change in the valence electronic structure of molecules. This work was complemented with the study of some compounds of the EX and ER types, where $\text{E} = \text{C, Si, Ge, Sn}$ and $\text{R} = \text{CH}_3, \text{H}$, which was performed to study the influence that the central atom has on the electronegativity and hardness of molecules, or whether these properties are mainly affected for the type of ligand bound to the central atom. All these calculations were performed using the B3PW91 functional together with the 6-311++G** basis set level for H, C, Si, Ge, F, Cl and Br atoms and the 3-21G for Sn and I atoms.

Keywords: DFT Calculations; NMR; $\text{SnRR}'\text{X}$ groups; electronegativity; hardness; softness.

Introduction

Concepts such as group quantities, electronegativities, hardness and softness are important properties that have played a key role in the organization and rationalization of chemical facts and observations [1-3]. Whereas group elec-

tronegativity has already a longstanding history, the field of group hardness is considerably less developed [3]. The concept of group electronegativities is one of the oldest and most thoroughly investigated properties with a variety of scales [4]: due to the lack of a sharp definition of the electronegativity concept itself, there are scales



that were derived starting from experimental data such as bond vibrational data [5], inductive parameters [6], among others. An important advance which has helped to solve this situation is the definition of electronegativity by Iczkowski and Margave as the negative of derivative of the energy E of a system with respect to the number of electrons N [7], later identified with the negative of chemical potential by Parr and coworkers [8] within the context of Density Functional Theory (DFT) [9]. The last step offered the possibility of non empirical calculations of atomic, group and molecular electronegativities [1,10].

In the other hand, the concepts of hardness and softness were introduced by Pearson [11], but only after the identification by Parr and Pearson [12] 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 use of the principle of hard and soft acids and basis requires taking into account the group electronegativity of the corresponding groups [5,6] and for this reason, it is important to know if the comparative group electronegativities of organometallic groups remain invariant in isostructural molecules.

The methodology developed by Geerlings and coworkers [1-3] was applied in this case to a series that contains atoms of the 14 group of Periodic Table (C, Si, Ge, Sn, and Pb). Due to the large amount of experimental data on Sn NMR shifts that is available [13,14], this property can be an ideal probe to characterize charge distributions and the influence that different substituents have on it [15]. This methodology allows an evaluation of the discrepancies in electronegativity scales and associated properties at uniform level.

In spite of computational advances and the availability of large number of experimental data [13,14], no many theoretical studies have been reported for group electronegativities, hardness and softness on molecules that contain atoms of the fourth group [15-17]. Peregudov and his group have done studies on this kind of compounds [18-22], finding some good correlation between experimental and theoretical values of the electronegativity and experimental ^{19}F NMR spectroscopy data.

In this study, electronegativities, hardness and softness have been studied to several series of tin compounds of the $\text{SnRR}'\text{R}''\text{X}$ type, where the set of tin compounds in this study always contains a methyl group ($\text{R}'' = \text{CH}_3$) together with groups $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $\text{R} = \text{H}, \text{ph}, \text{OR}, \text{SR}, \text{Et}, \text{pr}, \text{Bu}$. These calculations will allow us to see the regularities concerning the influence of the nature of the organic groups RR' and the inorganic group X on electronegativities and hardness of the $\text{SnRR}'\text{X}$ fragments; in this case it was found a very good correlation between the electronegativity of fragments and ^{119}Sn Chemical shifts, a property which sensitively reflects the change in the valence electronic structure of molecules [15].

This work was complemented with the study of some compounds of the EX and ER types, where $\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and $\text{R} = \text{CH}_3, \text{H}$ and a comparison between their electronegativity and hardness (softness) was done in order to study the influence that the central atom has on the electronegativity or hardness (softness), or whether these properties are mainly affected by the type of ligand bound to the central atom.

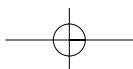
Theory and computational details

In DFT [9] the electronegativity χ was identified by Parr [8] as the negative of the partial derivative of the energy E of an atomic or molecular system with respect to the number of electrons N , for a constant external (i.e. due to the nuclei) potential $u(\mathbf{r})$ [7].

A detailed discussion about the calculation of hardness, softness, and electronegativity can be found elsewhere [2,9], and only the relevant expressions used for the evaluation of these quantities are given below. The electronegativity (χ), global hardness (h), and softness (S), are calculated within DFT as follows:

$$\chi = - \frac{\partial E}{\partial N}_{v(\mathbf{r})} \quad (1)$$

Assuming a quadratic relationship between the energy and the number of electrons, and using a finite difference approximation, one can obtain from (1), Mulliken's formula [23] for the electronegativity:



$$\chi \approx \frac{IE + EA}{2} \quad (2)$$

where IE and EA are the vertical ionisation energy and electron affinity of the system, respectively.

Moreover, theoretical justification was given from Sanderson's equalization principle [24], stating that when two atoms or fragments unite to form a molecule, their electronegativities will adjust to the same intermediate value [8].

The hardness of chemical species was defined by Parr and Pearson [12]:

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (3)$$

If only integer values are used for N, this expression can be rewritten as:

$$\eta \approx \frac{IE - EA}{2} \quad (4)$$

Finally, the global softness is defined as [25]:

$$S = \frac{1}{2\eta} \quad (5)$$

We can use the expressions (2), (4) and (5) as working equations to calculate the group electronegativity, group hardness and softness.

For a group G (e.g. the CH₃ group), 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 CH₃ radical, for example, is therefore considered in a pyramidal geometry and not in the planar geometry it adopts as an individual molecule. Within this option, standard bonds, angles and distances were used throughout this work using the standard structure given by Molden [26].

By calculating the radical (N electron system), the cation (N-1 electron system) and the anion (N+1 electron system) energies of the group G, all at the same geometry (c.f. the requirement of constant external potential $u(r)$), one can determine the ionization energy and electron affinity of G and thus the group quantities. In the case of SnRR'R''X the R''=CH₃ group was always removed.

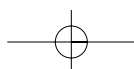
The calculations were carried out at B3PW91 functional [27, 28] together with the 6-311++G** basis set [29] for H, C, Si, Ge, F, Cl and Br and the 3-21G for Sn and I. All calculations were performed using the Gaussian 94 program [30].

Results and discussion

Group electronegativity

Among the most important trends found (see Table 1), we can highlight for the first series of compounds these ones: EF₃ > ECl₃ > EBr₃ > E(I)₃ and EH₃ > E(CH₃)₃. The first one shows how the electronegativity decreases as X progresses down from Cl to I, while the second one reflects the same behavior when H atoms are replaced by CH₃ fragments. These general trends of group electronegativities showed a good correlation with chemical intuition. However, it is also necessary to look at the trends that may exist between the different atoms with the different substituents to estimate the role the electronegativity of the central atom could have in these cases. It is known that the electronegativity of a group is primarily determined by the electronegativity of the central atom, but it is also known that the electronegativity of the atoms bound to the central atom has a clear effect on the electronegativity of the group [1].

The group electronegativities of the EX groups decreased monotonically in the series X₃Ge > X₃Sn > X₃Si > X₃C, but this trend changes when the halogen is changed by methyl or H: (CH₃)₃Ge > (CH₃)₃C > (CH₃)₃Sn > (CH₃)₃Si; H₃Si > H₃C > H₃Sn > H₃Ge, and the electronegativity values (eV) of the central atoms decrease in the series C (2.55) > Ge (2.01) > Sn (1.96) > Si (1.90) [31]. The absolute electronegativities of these atoms are (eV): 6.27 for C; 4.60 for Si; 4.3 for Ge and 3.90 for Sn [32] and they decrease in the order C > Si > Ge > Sn. On the other hand, the values of spectral electronegativities of these elements are C (2.54) > Ge (1.994) > Si (1.916) > Sn (1.884). From the obtained results and the above mentioned data of central atoms electronegativities, we can say that the electronegativity values of X₃E, (CH₃)₃E and H₃E groups show that there is no correlation with



the scale of absolute electronegativities or another of the earlier mentioned scales and, in this way, it is not possible to estimate group electronegativities based on the central atoms absolute electronegativities data for this kind of compounds.

Other series of group electronegativities, in which the central atom is always tin, was also studied; in Table 2, a series of compounds of the $\text{Me}_3\text{SnCH}_{3-n}\text{X}_n$ ($\text{X} = \text{Cl}, \text{Br}$) type is depicted. Substitution of a hydrogen atom in the methyl group by a more electronegative halogen atom (Cl, Br) results in the following trends for group electronegativity: $\text{Me}_2\text{SnCCl}_3 > \text{Me}_2\text{SnCHCl}_2 > \text{Me}_2\text{SnCH}_2\text{Cl}$ and $\text{Me}_2\text{SnCBr}_3 > \text{Me}_2\text{SnCHBr}_2 > \text{Me}_2\text{SnCH}_2\text{Br}$, nicely reflecting the hydrogen substitution pattern. It can be noted in Table 2 that for a given number of halogen atoms, the bromine derivatives are more electronegative than the chlorine ones. Table 3 shows the same trends for the $\text{Me}_n\text{SnX}_{3-n}$ ($n = 1, 2, 3; \text{X} = \text{Cl}, \text{Br}$,

Table 1. Electronegativity (χ , in eV), hardness (η , in eV) and softness (S , in 10^{-2} eV^{-1}) of the EX_3 fragments calculated at B3PW91/6-311++G** level.

Fragment	Electronegativity	Hardness	Softness
CF_3	6.77	5.49	9.10
CCl_3	6.09	4.00	12.49
CBr_3	5.69	3.60	13.89
Cl_3	5.21	3.29	15.19
$\text{C}(\text{CH}_3)_3$	3.90	4.08	12.25
CH_3	5.56	5.34	9.37
SiF_3	7.60	4.42	11.31
SiCl_3	5.43	3.75	15.33
SiBr_3	5.89	3.26	15.34
SiI_3	5.17	3.03	16.49
$\text{Si}(\text{CH}_3)_3$	3.69	3.56	14.06
SiH_3	5.62	4.71	10.62
GeF_3	9.14	3.91	12.79
GeCl_3	7.05	3.23	15.49
GeBr_3	6.91	2.88	17.34
GeI_3	5.90	2.70	18.51
$\text{Ge}(\text{CH}_3)_3$	4.17	3.40	14.73
GeH_3	4.89	4.17	11.98
SnF_3	8.02	3.73	13.40
SnCl_3	6.17	3.26	15.35
SnBr_3	6.07	2.96	16.92
$^i\text{SnI}_3$	5.40	2.79	17.91
$\text{Sn}(\text{CH}_3)_3$	3.77	3.26	15.33
SnH_3	5.18	3.39	14.75

ⁱCalculated at B3PW91/3-21G level.

Table 2. Calculated electronegativity (χ , in eV), hardness (η , in eV) and softness (S , in 10^{-2} eV^{-1}) of $\text{Me}_3\text{SnCH}_{3-n}\text{X}_n$ groups ($n = 1, 2, 3$) and experimental ^{119}Sn chemical shifts (in ppm) [13-14].

Molecule	Chemical Shifts	χ	η	S
$\text{Me}_3\text{SnCH}_2\text{Cl}$	4	4.64	2.94	16.98
$\text{Me}_3\text{SnCHCl}_2$	33	4.76	2.83	17.61
$\text{Me}_3\text{SnCCl}_3$	85	4.98	2.81	17.75
$\text{Me}_3\text{SnCH}_2\text{Br}$	6	4.67	2.92	17.13
$\text{Me}_3\text{SnCHBr}_2$	42	4.77	2.76	18.09
$\text{Me}_3\text{SnCBr}_3$	101	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 $\text{Me}_{4-n}\text{SnX}_n$ groups ($n = 1, 2, 3$) and experimental ^{119}Sn chemical shifts (in ppm), [13-14].

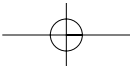
Molecule	Chemical Shifts	χ	η	S
Me_3SnCl	164.2	4.56	3.27	15.26
Me_2SnCl_2	137.0	5.50	3.23	15.46
MeSnCl_3	21.0	6.72	3.12	15.99
Me_3SnBr	128.0	4.60	3.19	15.68
Me_2SnBr_2	70.0	5.51	3.03	16.49
MeSnBr_3	-165.0	6.59	2.82	17.71
Me_3SnI	38.6	4.29	3.14	15.92
Me_2SnI_2	-159.0	5.39	2.79	17.90

I) groups, where the halogen exerts direct influence on the tin atom.

In Table 4, evaluation of the electronegativity of $\text{Me}_{3-n}\text{SnH}_n$ compounds shows that this property increases when systematically replacing the methyl group in SnMe_3 by a more electronegative hydrogen atom, which confirms again the great influence that the substituents have on the electronegativity of the molecule.

Table 4. Calculated electronegativity (χ , in eV), hardness (η , in eV) and softness (S , in 10^{-2} eV^{-1}) of $\text{Me}_{4-n}\text{SnH}_n$ groups ($n = 1, 2, 3$) and experimental ^{119}Sn chemical shifts (in ppm), [13-14].

Molecule	Chemical Shifts	χ	η	S
Me_3SnH	-104.5	4.63	3.12	16.04
Me_2SnH_2	-225.0	4.89	3.24	15.42
MeSnH_3	-346.0	5.19	3.39	14.76



The series Me_3SnOR and $\text{Me}_3\text{SnSR}'$ (with $\text{R} = \text{H, Me, ipr, tBut and Ph}$ and $\text{R}' = \text{Me, Et and tBut}$) as can be seen in Table 5, resulted from replacing the Me by more electronegative OR and SR groups, shows that an increment in the electronegativity of the ligands brings as a consequence an increase of electronegativity with respect to the series of Me_3SnR molecules (see Table 6).

In Table 6, the evolution of the calculated electronegativity of Me_3SnR compounds is shown. As it can be seen, the effect of substituting a methyl by other alkyl group appears to be small compared to substituting it by hydrogen atoms or halogens, due to the lower difference among the electronegativity values of the alkyl substituents. However, a small trend can be found for these molecules: in general terms, as the substituents become bigger (in atom number and volume), the electronegativity values become greater. This is only a general trend and

Table 5. Calculated electronegativity (χ , in eV), hardness (η , in eV) and softness (S , in 10^{-2} eV^{-1}) of Me_3SnOR and Me_3SnSR groups and experimental ^{119}Sn chemical shifts (in ppm), [13-14].

Molecule	Chemical Shifts	χ	η	S
Me_3SnOH	118.0	4.24	3.28	15.25
$\text{Me}_3\text{SnOCH}_3$	129.0	4.12	3.21	15.59
Me_3SnOPri	109.0	4.06	3.10	16.14
Me_3SnOBu	91.0	4.08	3.06	16.35
Me_3SnOPh	134.3	4.31	3.07	16.30
$\text{Me}_3\text{SnSCH}_3$	90.0	4.02	3.04	16.46
Me_3SnSEt	78.0	3.97	3.01	16.63
Me_3SnSBu	55.5	3.88	2.93	17.05

Table 6. Calculated electronegativity (χ , in eV), hardness (η , in eV) and softness (S , in 10^{-2} eV^{-1}) of Me_3SnR groups and experimental ^{119}Sn chemical shifts (in ppm), [13-14].

Molecule	Chemical Shifts	χ	η	S
Me_4Sn	0.0	3.91	3.19	15.63
Me_3SnEt	4.2	3.94	3.14	15.92
Me_3SnPrn	-2.3	3.97	3.13	16.03
Me_3SnPri	8.6	4.01	3.02	16.45
Me_3SnBun	-1.0	3.96	3.13	16.03
Me_3SnBus	3.3	4.00	3.06	16.34
Me_3SnBut	19.5	3.93	3.03	16.50

exceptions can be found in the cases of Me_3SnBu^n , Me_3SnBu^s and Me_3SnBu^l . Of course, the small difference between the values makes more difficult to affirm or refuse this trend.

In general, as depicted in Tables 2-6, the trends obtained from the electronegativity values with the different groups and with different kind of substitutions on tin atom show an increment when increasing the electron-withdrawing properties of substituents.

Comparison with experimental data

Several experimental measurable quantities have been postulated to correlate with substituent electronegativities. A great prospect arises from the chemical shifts for which many experimental values are available in literature [13-14]. The results of calculations of group electronegativities, hardness and softness of $\text{SnRR}'\text{R}''\text{X}$ ^{119}Sn chemical shifts for the corresponding compounds are given in the Tables 2-6.

It is pleasing to notice that good linear relationships are observed between ^{119}Sn chemical shifts and the corresponding values of electronega-

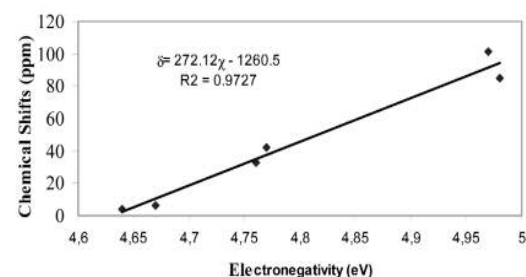


Figure 1. Experimental $\delta(^{119}\text{Sn})$ vs Electronegativity of $\text{Me}_2\text{SnCH}_n\text{X}_{3-n}$ groups ($\text{X} = \text{Cl, Br}$) (see Table 2).

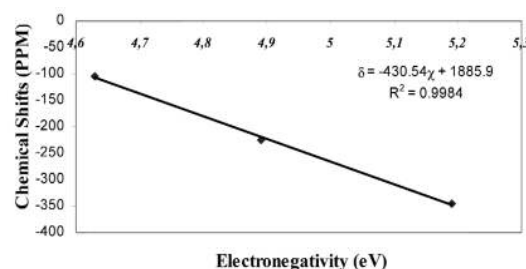


Figure 2. Experimental $\delta(^{119}\text{Sn})$ vs Electronegativity of $\text{Me}_{n+1}\text{SnH}_{3-n}$ compounds (see Table 4).

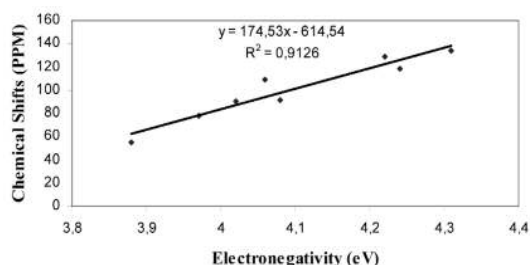


Figure 3. Experimental ^{119}Sn chemical shifts vs Electronegativity of Me_2SnOR and Me_2SnSR groups (see Table 5).

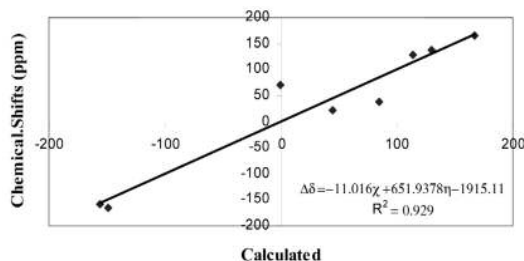


Figure 5. Experimental ^{119}Sn Chemical shifts vs values obtained via the dual correlation between hardness and Electronegativity of $\text{Me}_{4-n}\text{SnX}_n$ compounds (Table 3).

tivities (see Figures 1-3), all these relationships characterized by large correlation coefficients.

There are two groups (Me_3SnR and $\text{Me}_{3-n}\text{SnX}_n$) in which the relation is not so simple, but it was also found a dependency with the hardness; the relationships suggest a good correlation with these quantities. A simple correlation with the electronegativity fails, but when including the hardness in a dual correlation, it yields in both cases a fair result as seen in Figures 4 and 5. These two series will be discussed in more detail when the hardness of these types of molecules will be analyzed.

^{119}Sn CS = $-172.086\chi - 146.67\eta + 1140.75$ (Me_3SnR); $r = 0.968$.

All these results suggest that a change in ^{119}Sn chemical shifts data in this kind of compounds qualitatively could reflect, with a large degree of certainty, the corresponding change in group electronegativities.

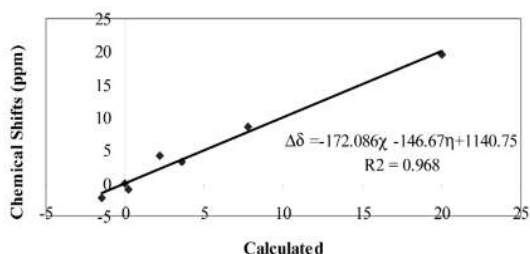


Figure 4. Experimental ^{119}Sn Chemical shifts vs values obtained via the dual correlation between hardness and electronegativity of Me_3SnR compounds (Table 6).

Group hardness and softness

In this part, only the main trends for the groups' hardness will be considered. The results for the groups' softness are completely analogous, since softness is simply the inverse of the group hardness divided by two. The evolution of the group hardness when going from up to down in the IV group in periodic table is: $\text{CX}_3 > \text{SiX}_3 > \text{GeX}_3 > \text{SnX}_3$ and $\text{CR}_3 > \text{SiR}_3 > \text{GeR}_3 > \text{SnR}_3$ ($\text{R} = \text{H}, \text{CH}_3, \text{ph}$), and the values of absolute hardness of the atoms are: 5.00, 3.38, 3.35, and 3.05 for C, Si, Ge and Sn respectively [9] and they decrease in the order $\text{C} > \text{Si} > \text{Ge} > \text{Sn}$. It can be seen that this last trend is the same as the ones found for their corresponding groups when they act as central atoms. This could mean that the group hardness and softness are largely determined by the hardness (or softness) of the central atoms.

As it can be seen in Table 2, replacing a hydrogen atom of the methyl in the SnMe_3 group by a softer halogen (Cl, Br), systematically decreases the hardness, which means that increasing the number of halogens for these molecules continuously increases the group softness. The sequence for a given number of halogens shows higher softness for the bromine than for the chlorine-containing groups in agreement with the higher softness of bromine compared to a with the 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 hardness (except for the mono and dichloro cases), in accord with the hardness sequence (eV): CH_3 (4.87) $>$ Cl (4.70) $>$ Br (4.24) [9]. On the other hand, the introduction of a harder hydrogen atom

replacing a softer methyl group results in an increment of hardness (Table 3). A similar case can be found in Table 5, when the replacement of S by a harder O, makes the global group softness decreases. Also for this last set of molecules, it is shown that the hardness is affected by the nature of the alkyl group in both cases.

Figure 6 shows that there is a good correlation between hardness (in addition with electronegativity) and the NMR chemical shifts of the $\text{Me}_n\text{SnX}_{4-n}$ series; this good agreement can be due to the fact that the change of a methyl group by an halogen is more accentuated than when the change is made for an alkyl group. In fact, the difference in hardness values between the whole $\text{Me}_n\text{SnX}_{4-n}$ series is 0.48, while the difference in the values of the Me_3SnR series is only 0.16. When a softer substituting group (e.g. methyl) is replaced by a harder one (halogen), this causes the ^{119}Sn resonance to shift to lower values. In Table 3, two facts can be observed: first, as the halide becomes heavier and thus softer ($\text{Cl} < \text{Br} < \text{I}$), $\delta(^{119}\text{Sn})$ values become lower. Second, as the number of X ($n = 1, 2, 3$) increases, the molecule becomes softer and again, chemical shifts change to lower values (even negative ones). Exactly the contrary tendency is observed in the $\text{SnMe}_{4-n}\text{H}_n$ set.

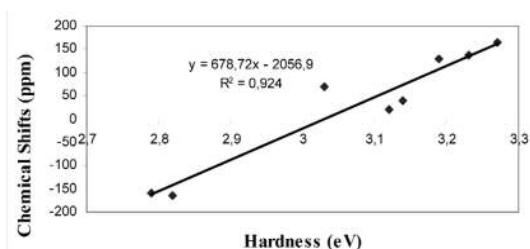


Figure 6. Experimental $\delta(^{119}\text{Sn})$ of compounds vs Hardness of $\text{Me}_2\text{SnCH}_n\text{X}_{3-n}$ group ($\text{X} = \text{Cl}, \text{Br}$) (see Table 2).

Conclusions

Quantum Chemical calculation of group electronegativities and hardness (softness) were carried out for Group 14 of the Periodic Table (C, Si, Ge, Sn, Pb) and their Containing Functional Groups; these calculations allow seeing the regu-

larities concerning the influence of the nature of organic and inorganic groups on electronegativities. These data also could be used for interpretation of reactivity and how this reactivity is affected by the presence of different substituents and groups in a molecule.

The comparison between the group electronegativities and experimental chemical shift values is satisfactory and all these results suggests that a change in ^{119}Sn chemical shifts data in this kind of compounds qualitatively reflects with a large degree of certainty the corresponding change in group electronegativities.

The inclusion of the 6-311++G** basis set has a greater influence on the values for the group electronegativities, hardness and softness for the Si, Ge, and Sn compounds than for the C ones, which could be due to the fact that a greater base set describes better the correlation effect, which is important when the size of the atoms enlarges; additionally, a diffuse function gives better description of the anionic system.

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