Theoretical Calculations of Group Electro negativities and Hardness: Properties in Groups Containing Ge, Sn and Pb and Contrast with NMR Values

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Abstract – In this contribution DFT calculations were performed for a series of compounds of the type MPhxLy(CF3)zCF3, (where M= Pb, Sn, Ge; L= Cl, OAc; x+y+z= 3). The quantum chemical calculation of group electronegativities, hardness and softness of these compounds were carried out and these values compared with 19F NMR spectroscopy data. A good correlation between NMR spectroscopy data and group electronegativities and hardness was found. All the calculations were performed using the B3PW91 functional together with the LanL2DZ basis set.

Keywords: DFT Calculations, hardness, electronegativity, NMR

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I. INTRODUCTION

Electronegativity is a key concept in chemistry through this concept is explaining much aspect in chemistry. In the past the concepts of group quantities such as electronegativities, hardness and softness have been studied by Geerlings and co-workers [1]. These quantities are important as tools in structural and reactivity studies in organic and inorganic chemistry. It have been found, for example, that the use of the principle of hard and soft acids and bases requires taking into account the group electronegativities of the corresponding groups [2-4] and for this reason it is important to know in this case and others if the comparative group electronegativities of organometallic groups remain unchanged isostructural molecules.

Molecules such as $MPhxLy(CF_3)zCF_3$, (where M= Pb, Sn, Ge; L= Cl, OAc; x+y+z= 3) presents a good opportunity to expand our study of group electronegativities and hardness to other compounds of the 14 group and to make some comparisons between them [4]. The Pb atom gives some introductory results for the sixth row congeners of C. ¹⁹F NMR spectroscopical data, which is abundant and widely available for these compounds, provides an excellent opportunity for comparison with the experimental results. [5].

Theory and Computational Details

Quantum Chemical calculation of group electronegativities, hardness and softness have been carried out for a number of compounds such as $MPhn(CF_3)_{4-n}$, (where n run from 0 to 3,

M= Ge, Sn, Pb, L= Cl, OAc; x+y+z= 3), $PbPhLn(CF_3)_{3-n}$. A detailed discussion about the calculation of hardness, softness, and electronegativity can be found elsewhere [6-8], and only the relevant expressions used for the evaluation of these quantities are given below. The global hardness (η), and softness (S), electronegativity (χ), are calculated within DFT as follows:

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

Softness is the inverse of hardness:

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

The electronegativity is defined as:

$$\chi \approx \frac{IE + EA}{2} \quad (3)$$

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

We use the expressions 1-3 as working equations to calculate the group electronegativity, hardness, and softness.

All geometries were optimized in the ground state by using the Gaussian 98 suite of programs [9] using the B3PW91 [10, 11] functional together with the LanL2DZ [12-14] basis set. For a group G (e.g. the CH_3 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 CH_3 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 [15].

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

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of constant external potential $\upsilon(r)$), one can determine the ionization energy and electron affinity of G and thus the group quantities.

II. Results and Discussion

The electronegativities of MPhxLy$(CF_3)_z CF_3$ compounds are shown in Table 1. At this point we want to bring attention to the sub-series of compounds type PbPh$_n$(CF$_3$)$_{4-n}$ (the first 3 compounds in Table 1); in this series if the phenyl group is changed by CF$_3$, there is an increment in the electronegativity. To examine the influence of the central metal in the electronegativity of these compounds, the complexes GePh$_3$CF$_3$, SnPh$_3$CF$_3$ and PbPh$_3$CF$_3$ were chosen.

Comparison with experimental data.

Several experimental measure quantities have been postulated to correlate with substituent electronegativities [4, 16] a great deal arises from the NMR spectroscopy data for which many experimental values are available in literature [5].

Table 1. Calculated group electronegativity (χ, in eV), hardness (η, in eV) and softness (S, in 10^{-2} eV) for groups of the type MPh$_x$L$_y$(CF$_3$)$_z$CF$_3$ (x+y+z= 3), M= Pb, Sn, Ge together with experimental ^{19}F NMR shifts (δ ^{19}F, in ppm) and J(Pb-F) coupling constant (in Hz).

Fragments	δ^{19}F[5]	J(M-F)	χ	η	S
PbPh$_3$	37.8	324	4.63	2.40	20.92
PbPh$_2$CF$_3$	40.3	440	5.10	2.54	19.69
PbPh(CF$_3$)$_2$	41.2	560	5.60	2.72	18.32
PbPh$_2$Cl	40.2	301	5.58	2.53	19.76
PbPh$_2$(OAc)	40.6	321	5.62	2.43	20.49
PbPh(OAc)$_2$	40.5	349	6.25	2.55	19.61
PbPh(OAc)CF$_3$	39.4	503	6.07	2.54	19.69
SnPh$_3$	31.2	285	4.47	2.56	19.53
SnPh$_2$CF$_3$	30.1	427	4.92	2.70	18.59
GePh$_3$	28.2	--	4.29	2.75	18.18

For the compounds with phenyl and CF$_3$ groups acting as ligands (MPhn(CF$_3$)$_{4-n}$, with n running from 1 to 3 and M= Sn, Pb) a good agreement, with a linear correlation was found between J(M-F) and electronegativity (See Figure 1). The increase of the s character in the Pb-CF$_3$ bond as CF$_3$ groups are substituted for phenyl groups, has as consequence that 2J(M-^{19}F) increases from 323 to 557 Hz for the series PbPhn(CF$_3$)$_{4-n}$, SnPh$_3$(CF$_3$) and SnPh$_2$(CF3)2 [5]. The degree of this increase is followed by an increment in the electronegativity (χ) according to the following equation (4):

$$J(M-F)= 243.26\chi - 799.27; r^2= 0.997 \qquad (4)$$

For the MPh$_3$CF$_3$ compounds (M= Pb, Sn, Ge), ^{19}F chemical shifts become slightly more shielded as the central element becomes located more toward the top of the periodic table [3], and this is well correlated (see Figure 2), with the fact that ^{19}F chemical shifts increase when electronegativity (χ)

of the fragment increases according to the following Equation (5):

$$\Delta\delta= 28.24 \cdot - 93.52; r^2= 0.955 \qquad (5)$$

All these results suggest that a change in ^{19}F NMR Spectroscopy data in this kind of compounds qualitatively could reflect, with a large degree of certainty, the corresponding change in group electronegativities.

For the mixed ligand species of this series (PbPh$_2$Cl, PbP$_2$(OAc), PbPh(OAc)$_2$ and PbPh(OAc)CF$_3$), the relation is not that simple. The best correlation found was a dual model including electronegativity and hardness (see Figure 3); the model suggest a good correlation between these quantities (χ,η) and $\Delta\delta$. Figure labels should be legible, at 8-point type.
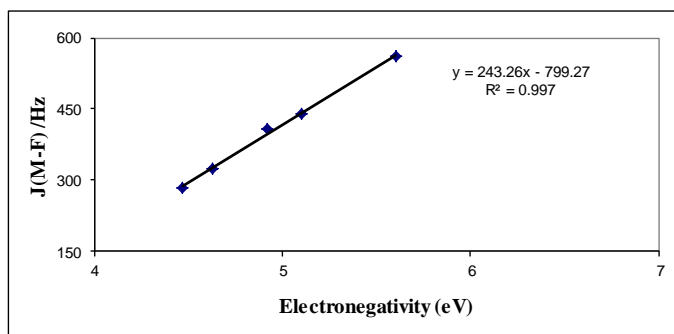
Figure 1. Experimental 2J(M-F) chemical Shifts vs. group electronegativity of $MPhn(CF_3)_{3-n}$ (M= Sn, Pb) compounds.
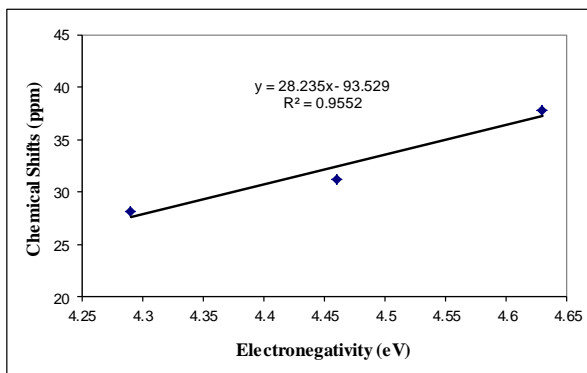

Figure 2. Experimental ^{19}F chemical shifts of $MPh_3(CF_3)$ (M= Ge, Sn, Pb) vs. group electronegativity values.
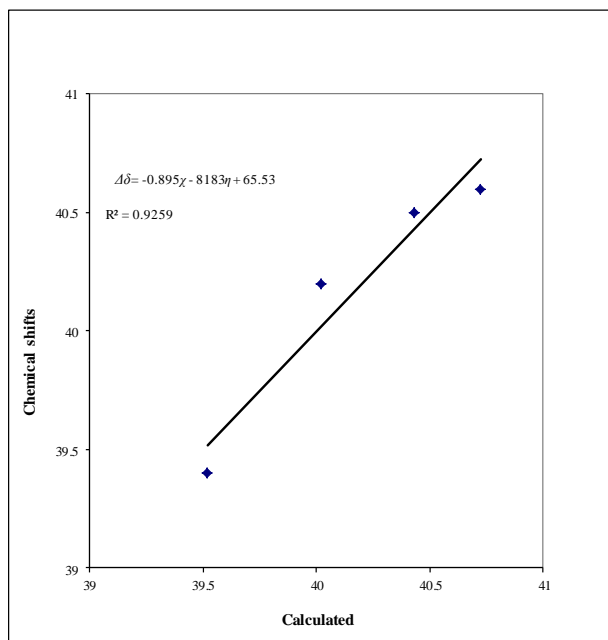

Figure 3. Experimental ^{19}F chemical shifts vs. values obtained via dual correlation between hardness and electronegativity for $PbPhLn(CF_3)_{3-n}$ and $PbPh_2L(CF_3)$ compounds

$$\Delta\delta= -0.895\chi - 8183\eta + 65.53; \; r^2= 0.926 \; (6)$$

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III. Conclusions

Quantum Chemical calculations of group electronegativities and hardness (softness) were carried out for some elements of Group 14 of the Periodic Table such as Ge, Sn, Pb and some of their Containing Functional Groups. These calculations allowed noticing the regularities concerning the influence exerted by of the nature of organic and inorganic groups on electronegativities. These data could also be used for interpretation of reactivity and how this is affected for the presence of different substituents and groups in a molecule.

The comparison between the group electronegativities and experimental chemicals shifts values are acceptable and all these results suggests that a change in ^{19}F NMR spectroscopy data in this kind of compounds qualitatively reflects a quite good degree of certainty the corresponding change in group electronegativities. For example, it was found that the group properties of molecules of the type $MPhxLy(CF_3)zCF_3$ are highlighted for the electronegativity and hardness of the substituent groups; in this way this kind of calculations is a valuable tool in order to interpret relevant structural information.

Acknowledgements

IV. References and Notes

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