Conference paper

Michele Benedetti*, Federica De Castro, Antonella Ciccarese and
Francesco Paolo Fanizzi*

Is hydrogen electronegativity higher than Pauling's value? New clues from the ^{13}C and ^{29}Si NMR chemical shifts of [CHF$_3$] and [SiHF$_3$] molecules

Abstract: We previously demonstrated that the δ NMR chemical shift of central NMR active atoms (A), in simple halido [AX$_n$] (A = C, Si, Ge, Sn, Pb, Pt; X$_n$ = combination of n halides, n = 4 or 6) derivatives, could be directly related to X radii overall sum, $\Sigma(r_L)$. Further correlation have also been observed for tetrahedral [AX$_4$] (A = C, Si; X$_4$ = combination of four halides) compounds where the X Pauling electronegativities sum, $\Sigma(\chi_L^{Pau})$, exceeds a specific value (≈12.4). In this work, we focused on these latter systems considering the H vs. X substitution. The analysis of the literature reported δ(^{13}C) and δ(^{29}Si) NMR chemical shift for the mono hydrogenated derivatives and in particular for [CHF$_3$] and [SiHF$_3$], characterized by the lowest $\Sigma(r_L)$ and the highest $\Sigma(\chi_L^{Pau})$, suggests a revised value for the H electronegativity ranking with respect to Pauling's.

Keywords: Eurasia 2018; halo-methane derivatives; halo-silane derivatives; hydrogen electronegativity; NMR spectroscopy.

Introduction

The effect of mono-atomic L ligands, on the NMR chemical shift of the central A in [AL$_n$] (A = NMR active atom; L = generic monoatomic ligand) complexes, is of great interest [1–25]. At this regard, in the case of simple halido substituents Normal and Inverse Halogen Dependences (NHD and IHD, respectively), are generally observed. This corresponds in the NHD case, to a NMR chemical shift decrease of the central A, on increasing the steric hindrance of monoatomic ligands, vice-versa with IHD trends [3, 26–33]. Theoretical approaches provided a definitive explanation for both trends, at a fundamental level [18–21]. Nevertheless, in our previous work on halido derivatives of platinum and XIV group elements, we could relate both NHD and IHD trends, with the less fundamental but widely used chemico-physical parameters: r_L (ionic radius) and χ_L^{Pau} (Pauling's electronegativity) of the monoatomic L ligand [34–39]. We previously underlined, that this approach suggests the existence of electric ring currents, circulating around the L–A bonding axis, induced by applied magnetic fields. The advantage of this semi-empirical approach is that we can connect the NMR shielding ability of bonded monoatomic ligands to the basic properties of atoms generally used to describe molecular features [34–41]. In other words, the NMR chemical shift of a central atom can be directly related to the NMR shielding ability of single atom ligands. In this way, we could also underline that, as expected, the

---

---

*Corresponding authors: Michele Benedetti and Francesco Paolo Fanizzi, Department of Biological and Environmental Sciences and Technologies (DiSTeBA), University of Salento, Via Monteroni, I-73100 Lecce, Italy, Tel.: +39 0832299264, Fax: +39 0832 298626, E-mail: michele.benedetti@unisalento.it (M. Benedetti); Tel.: +39 0832299265, Fax: +39 0832 298626, E-mail: fp.fanizzi@unisalento.it (F. P. Fanizzi)
Federica De Castro and Antonella Ciccarese: Department of Biological and Environmental Sciences and Technologies (DiSTeBA), University of Salento, Via Monteroni, I-73100 Lecce, Italy
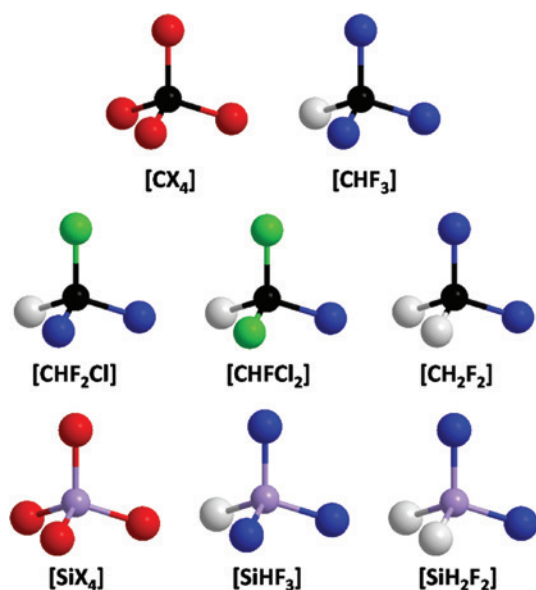
Fig. 1: General structures of the considered [AX$_4$] (A = C, Si; X$_4$ = combination of four halides) and [AH$_m$X$_n$] (A = C, Si; X$_n$ = combination of n Cl and/or F halides; m + n = 4) halomethane and halosilane derivatives, with atomic substituents and Pauling's electronegativities overall sum, $\Sigma(\chi_L^{Pau})$, ≥ 12.4. Generic halides, H, Cl, F, C and Si atoms are indicated in red, grey, green, blue, black and grey-blue, respectively.

electronegativity of single atom substituents plays a role in determining such a NMR shielding. Nevertheless, we interestingly found, in carbon and silicon tetrahalido derivatives, that this effect takes place only above a specific onset value (≈12.4) of the Pauling electronegativity overall sum of the single atom substituents, $\Sigma(\chi_L^{Pau})$ [34].

Following our previous works on tetrahedral [AX$_4$] and [AH$_4$] (A = C, Si; X$_4$ = combination of four halides) tetrahalido and tetrahydrido compounds (Fig. 1, Tables S1, S2) [34, 35], in this work we decided to extend our studies to the literature reported ^{13}C and ^{29}Si NMR chemical shifts of partially hydrogenated [AH$_m$X$_n$] (A = C, Si; X$_n$ = combination of n Cl and/or F halides; m + n = 4; $\Sigma(\chi_L^{Pau})$ ≥ 12.4) compounds (Tables S3, S4) [32, 42]. Here we report new results offering interesting perspectives for the correlation of the NMR chemical shift of a central A atom, in [AH$_m$X$_n$] compounds, with both overall steric hindrance and electronegativity of the bonded atomic ligands. In analogy with a previous work by Robinson and Gillespie, we will continue to use the term ligand even for atoms bonded to a central carbon or silicon, notwithstanding their non-metallic character [43].

Results and discussion

^{13}C and ^{29}Si δ NMR chemical shifts as a function of the $\Sigma(r_L)$ values, in tetrahedral [AL$_4$] (A = C, Si) systems with $\Sigma(\chi_L^{Pau})$ ≥ 12.4: the case of [AH$_m$X$_n$] compounds (X$_n$ = combination of n halides; m + n = 4)

The δ(^{13}C) [32, 33, 44–47] and δ(^{29}Si) [42, 48–51] NMR chemical shifts for [AX$_4$] (A = C, Si; X$_4$ = combination of four Cl and/or F halides, Tables S1, S2) and [AH$_m$X$_n$] (X$_n$ = combination of n Cl and/or F halides; m + n = 4; $\Sigma(\chi_L^{Pau})$ ≥ 12.4; Tables S3, S4) compounds are reported in graph vs. the overall sum of ionic radii of A bonded atomic L ligands, $\Sigma(r_L)$, see Fig. 2a,b. The following ionic radii: r_{F-} = 133 [52]; r_{Cl-} = 181 [52]; r_{Br-} = 196 [52]; r_{I-} = 220 [52]; r_{H-} = 208 pm [53–55] were used. All the considered compounds are characterized by high overall Pauling electronegativity sum, $\Sigma(\chi_L^{Pau})$, for the A bonded atoms. Interestingly, these [AH$_m$X$_n$] hydrogenated compounds, with $\Sigma(\chi_L^{Pau})$ ≥ 12.4, show a specific behavior similar to that exhibited by the fully halogenated [AX$_4$] congeners, Fig. 2. The compounds characterized by high Pauling electronegativity overall sum of the C or Si bonded L atoms are generally located in the low $\Sigma(r_L)$ region and exhibit lower than expected NMR
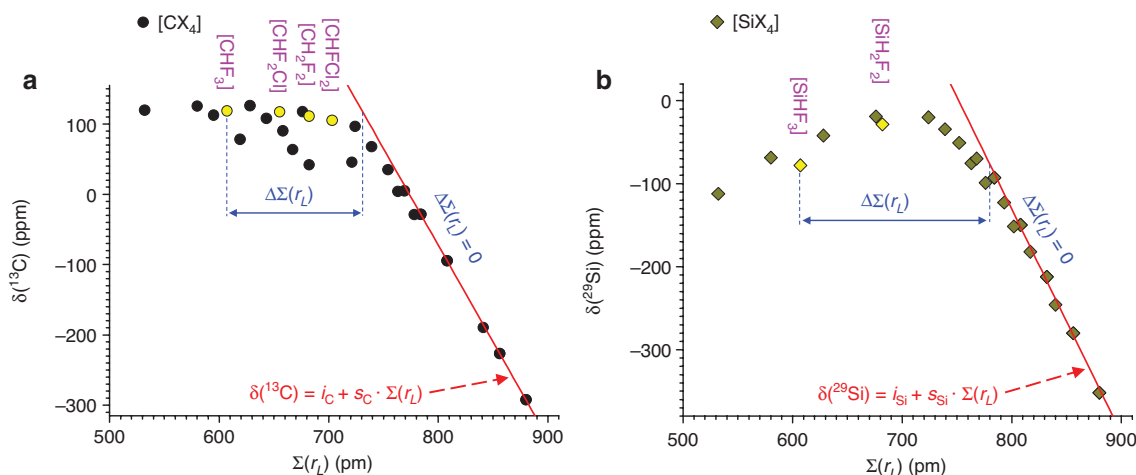
Fig. 2: (a, b) $\delta(^{13}C)$ and $\delta(^{29}Si)$ NMR chemical shifts vs. ionic radii overall sum of carbon and silicon bonded atomic ligands, $\Sigma(r_L)$, in tetrahedral $[AX_4]$ (A = C, Si; X_4 = combination of four halides) compounds. The partially hydrogenated $[AH_mX_n]$ (X_n = combination of n Cl and/or F halides; m + n = 4) compounds, with Pauling's electronegativities overall sum of the atomic substituents, $\Sigma(\chi_L^{Pau})$, ≥ 12.4 are indicated in yellow. The $\Delta\Sigma(r_L)$ differences are shown in the graphs by horizontal blue double arrows. The shown red lines, interpolating the data points of the sole $[ABr_mI_n]$ (m + n = 4) compounds with $\Sigma(\chi_L^{Pau}) \ll 12.4$, correspond to: $\Delta\Sigma(r_L) = 0$.

chemical shifts, Fig. 2a,b [32, 42]. Indeed deviations from the linear correlation of δ vs. $\Sigma(r_L)$, Equations 1 in the Experimental, are observed for both $[AX_4]$ and $[AH_mX_n]$ species. These deviations, quantified as $\Delta\Sigma(r_L)$ differences by Equations 2 and reported in Fig. 3a,b, have been already analyzed and discussed in a previous work, for the sole $[AX_4]$ derivatives (Tables S1, S4) [34]. The $\Delta\Sigma(r_L)$ resulted linear dependent on the Pauling electronegativity overall sum for the single atomic substituents, $\Sigma(\chi_L^{Pau})$, as indicated by Equations 3 and were found to be triggered by the specific minimum onset $\Sigma(\chi_L^{Pau})$ value, equal to about 12.4, see Fig. 3a,b [34]. As discussed above, this effect can be expressed in term of electronegativity dependent apparent increase of the NMR effective atomic radii overall sum, $\Delta\Sigma(r_L)$, as shown by Equations 4. The Fig. 3a graph shows a trend of $\Delta\Sigma(r_L)$ vs. $\Sigma(\chi_L^{Pau})$ values already observed for the fully halogenated $[CX_4]$ and $[SiX_4]$ species. In fact, these exhibit for $\Delta\Sigma(r_L)$ values a region where it is about zero or strongly reduced (below or in proximity of the onset $\Sigma(\chi_L^{Pau})$ value, respectively) and a region where the $\Delta\Sigma(r_L)$ and $\Sigma(\chi_L^{Pau})$ values are linearly related [34]. The mono-hydrogenated compounds in Fig. 3a graph appear to line up following the expected trend already observed for the fully halogenated species. Interestingly these H containing compounds, characterized by $\Sigma(\chi_L^{Pau})$ higher than the onset value, appear linearly correlated with the $\Delta\Sigma(r_L)$ but shifted towards lower $\Sigma(\chi_L^{Pau})$ on a line nearly parallel to that previously described for the fully halogenated species [34]. The shift from this latter line appears to be nearly double for $[CH_2F_2]$ with respect to $[CHF_3]$, $[CHF_2Cl]$ and $[CHFCl_2]$, Fig. 3a. Although limited to the restricted available data set, similar shifts are also observed for the silicon $[SiHF_3]$ and $[SiH_2F_2]$ derivatives, Fig. 3b.

The observed positions of the data points for the considered carbon and silicon halo-hydrido derivatives reported in Fig. 3a,b, are characterized by the higher $\Sigma(\chi_L^{Pau})$ values (Fig. 3a,b), suggesting that differently from halides, the NMR data derived electronegativity of the C and Si bonded hydrogens should be higher than that reported in the L. Pauling's electronegativity scale [53, 54, 56].

Calculation of the NMR effective electronegativity value for the hydrogen atom, on the basis of the $[CHF_3]$ and $[SiHF_3]$ reference compounds

From the ^{13}C and ^{29}Si NMR chemical shifts of $[CHF_3]$, $\delta(^{13}C) = +118.8$ ppm [32], and $[SiHF_3]$, $\delta(^{29}Si) = -77.8$ ppm [42], reference compounds, reported in the graphs of Fig. 2a,b vs. $\Sigma(r_L)$, it is possible to calculate the corresponding $\Delta\Sigma(r_L)$ values, see Experimental. As expected, these calculated values are the highest among
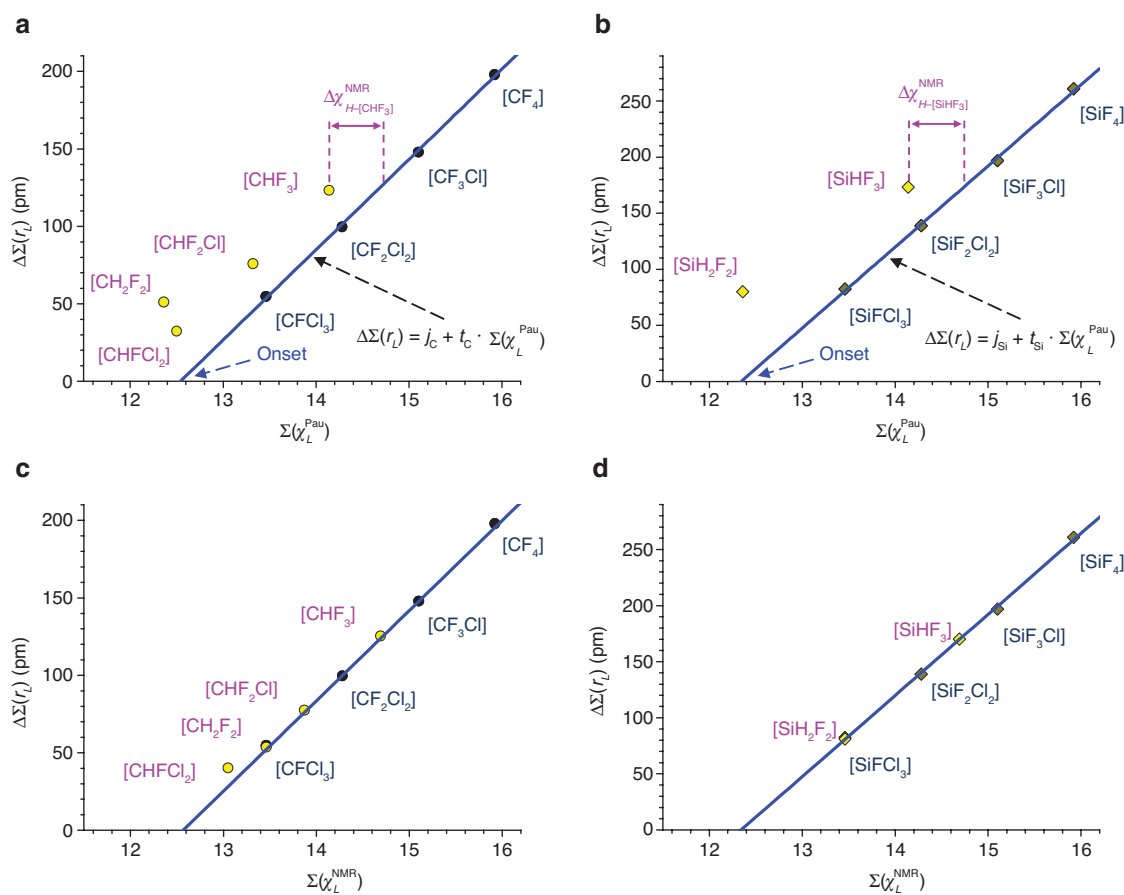
Fig. 3: (a, b) $\Delta\Sigma(r_L)$ differences vs. $\Sigma(\chi_L^{Pau})$ for [AX$_4$] (A = C, Si; X$_4$ = combination of four Cl and/or F halides) and partially hydrogenated [AH$_m$X$_n$] (X$_n$ = combination of n Cl and/or F halides; m + n = 4) compounds with $\Sigma(\chi_L^{Pau}) \geq 12.4$. In blue are indicated the straight lines interpolating the data points of the [AF$_4$], [AClF$_3$], [ACl$_2$F$_2$] and [ACl$_3$F] compounds. As indicated, the previously calculated onset $\Sigma(\chi_L^{Pau})$ value corresponds to the intersection between last interpolating lines and the zero line [34]. The necessary corrections to be operated to the hydrogen electronegativity, calculated for the reference [CHF$_3$] and [SiHF$_3$] compounds (i.e. $\Delta\chi_{H-[CHF_3]}^{NMR}$ and $\Delta\chi_{H-[SiHF_3]}^{NMR}$), are graphically shown by violet double arrows. By using, for the hydrogen atoms the corrected NMR effective electronegativity value ($\chi_H^{NMR} = 2.75$), we can calculate the $\Sigma(\chi_L^{NMR})$. The $\Delta\Sigma(r_L)$ vs. $\Sigma(\chi_L^{NMR})$ values are reported in (c, d). It can be observed that in this case the behavior of the shown partially hydrogenated [AH$_m$X$_n$] compounds is identical to that of the sole halogenated [AX$_4$] derivatives.

those obtained for the [CH$_m$X$_n$] and [SiH$_m$X$_n$] hydrogenated compounds, characterized by $\Sigma(\chi_L^{Pau}) \geq 12.4$, considered in this work (Tables S3, S4). This because the $\Delta\Sigma(r_L)$ are directly related to the $\Sigma(\chi_L^{Pau})$. The $\Delta\Sigma(r_L)$ values vs. $\Sigma(\chi_L^{Pau})$ for all considered [CH$_m$X$_n$] and [SiH$_m$X$_n$] compounds, including the fully halogenated are reported in the graphs of Fig. 3a,b. The data points of both [CHF$_3$] and [SiHF$_3$] reference compounds do not fall on the same straight lines interpolating the data points of the [CX$_4$] and [SiX$_4$] series of compounds (with $\Sigma(\chi_L^{Pau}) > 12.4$), respectively [34]. As described in the Experimental (Equations 5–7) we can easily calculate the corrections required for the Pauling's hydrogen electronegativity, $\Delta\chi_{H-[AHF_3]}^{NMR}$, required to shift the data points of the [CHF$_3$] and [SiHF$_3$] reference compounds on the respective straight line interpolating the [CX$_4$] and [SiX$_4$] (X$_4$ = combination of four F and/or Cl) derivatives with $\Sigma(\chi_L^{Pau}) > 12.4$, Fig. 3a,b. These corrections ($\Delta\chi_{H-[CHF_3]}^{NMR} = 0.52$ and $\Delta\chi_{H-[SiHF_3]}^{NMR} = 0.59$) for [CHF$_3$] and [SiHF$_3$] (Tables S3, S4), allow to calculate the following H electronegativity values: $\chi_{H-[CHF_3]}^{NMR} = 2.72$ and $\chi_{H-[SiHF_3]}^{NMR} = 2.79$ (Equations 6) required to align the data points of [CHF$_3$] and [SiHF$_3$] on the line interpolating the corresponding considered [CX$_4$] and [SiX$_4$] derivatives. Interestingly, it can be observed that the new obtained electronegativity values are very similar,

producing an averaged $\overline{\chi}_{H-[AHF_3]}^{NMR} = 2.75$ value. It is noteworthy that the adoption of the $\overline{\chi}_{H-[AHF_3]}^{NMR}$ value in the calculation of the ligands' electronegativity overall sum results in a realignment of the data reported in Fig. 3a,b for both considered series of $[CH_mX_n]$ and $[SiH_mX_n]$ compounds, see Fig. 3c,d. Indeed, this occurs also in the case of the dihydrogenated $[CH_2X_2]$ and $[SiH_2X_2]$ compounds. Therefore, taking into account the required H electronegativity correction, the behavior of hydrogenated compounds becomes similar to that observed for fully halogenated congeners. This suggests that, the hydrogen's NMR effective electronegativity value could be simply indicated as: $\chi_H^{NMR} = 2.75$, without any reference to particular compounds.

Several electronegativity scales, calculated by using many physical parameters, have been proposed over the years after the original Pauling's concept definition [56]. Due to the importance of the Pauling's electronegativity scale [54], the others are routinely normalized to the former, obtaining an overall ranking range defined by single dimensionless numbers between 0.78 and 4.00. A slight variability of the electronegativity values ascribed to the same element in the different scales is generally observed. Hydrogen should be highlighted among the atoms having the wider range of attributed electronegativities, with values from 2.0 to 2.8 ($\chi_H^{Lang-Smith} = 2.00$; $\chi_H^{Allred-Rochov} \approx \chi_H^{Pauling} = 2.20$; $\chi_H^{Sanderson} = 2.31$; $\chi_H^{Mulliken} = 2.80$) [56]. Interestingly, our calculated χ_H^{NMR} value is higher than the hydrogen electronegativity reported in the Pauling's scale, but similar to the normalized value reported by Mulliken, which is the highest for H. It should be noted, that Pauling's and Mulliken's electronegativities of halides are both similarly NMR effective in the studied systems, but this does not occur for Hydrogen, where a correspondence is found only with the value reported by Mulliken. Noteworthy, it appears clear from the data of the present paper, that the H electronegativity should be better located above that of both C and Si (according to Mulliken [57] and the absolute electronegativity scale calculated with the Pearson–Parr approach [58, 59]) and not between them (according to Pauling). This buttresses our approximation of considering hydrogens as C and Si bonded hydrido ligands with respect to the considered central atoms. As stated by L. Pauling, the electronegativity can be defined as "*the power of an atom in a molecule to attract electrons to itself*" [53, 54]. This definition often loses the link to a molecule related property in the basic statement defining other scales (including Mulliken) [57]. It should be noted that the present approach allows a realignment of Hydrogen electronegativity to that of the Mulliken scale (based on atomic data) by using exclusively experimental NMR data of molecular compounds.

Conclusion

In this work, we have extended to the considered $[AH_mX_n]$ (A = C, Si; X_n = combination of n Cl and/or F halides; m + n = 4, with $\Sigma(\chi_L^{Pau}) \geq 12.4$) halo-hydrido derivatives the NMR chemical shifts analysis of the central atom (i.e. ^{13}C, ^{29}Si) as a function of the bonded ligands and their Pauling electronegativities (χ_L^{Pau}), already performed for simple halido $[AX_4]$ compounds [34]. The observed deviation in the NMR chemical shifts from the previously reported $\Sigma(\chi_L^{Pau})$ general dependence [34], suggests a correction for the H electronegativity to a value ($\chi_H^{NMR} = 2.75$) higher than that reported by L. Pauling ($\chi_H^{Pau} = 2.20$) [53, 54]. The calculated χ_H^{NMR} value falls at the higher extreme of the range (2–2.8) covered by the normalized H's electronegativity values in the most common scales and is almost perfectly corresponding to that reported by Mulliken ($\chi_H^{Mulliken} = 2.80$) [57]. Consistently, in a previous work, by analyzing the ^{13}C, ^{29}Si, ^{73}Ge, ^{119}Sn, and ^{207}Pb NMR chemical shifts of $[AH_4]$ (A = C, Si, Ge, Sn and Pb) compounds we found that the A bonded hydrogens show a very low radius variability ($\approx 1\%$) suggesting a constant oxidation state of the bonded hydrogen atoms along the series [39]. This indirectly confirms the present findings, suggesting that the hydrogen electronegativity should be considered higher than that of carbon. Interestingly, the present approach allows this specific electronegativity value realignment exclusively using molecules related experimental NMR data, rather than single atoms properties. Therefore in a way we were able to obtain H electronegativity value close to that obtained by Mulliken (based on atomic data) by using molecular compounds features (Pauling's like approach).

Experimental section

The here adopted ionic radii are: $r_{F^-} = 133$ [52]; $r_{Cl^-} = 181$ [52]; $r_{Br^-} = 196$ [52]; $r_{I^-} = 220$ [52] and $r_{H^-} = 208$ pm [53–55], instead the used Pauling's electronegativity values are: $\chi_F^{Pau} = 3.98$; $\chi_{Cl}^{Pau} = 3.16$; $\chi_{Br}^{Pau} = 2.96$; $\chi_I^{Pau} = 2.66$; $\chi_H^{Pau} = 2.20$.

Influence of steric hindrance and electronegativity of atomic substituents on the ^{13}C and ^{29}Si NMR chemical shifts of $[AH_mX_n]$ (A = C, Si; X_n = combination of n Cl and/or F halides; m + n = 4) compounds

The ^{13}C and ^{29}Si NMR chemical-shift of $[AX_4]$ (X_4 = combination of four halides) compounds are reported in Tables S1, S2 together with the overall sum of halides ionic radii, $\Sigma(r_L)$. Instead in Tables S3, S4 are reported the ^{13}C and ^{29}Si NMR chemical shifts of the considered $[AH_mX_n]$ compounds whose $\Sigma(\chi_L^{Pau}) \geq 12.4$, together with the $\Sigma(r_L)$ values. Last NMR data are plotted in the graphs of Fig. 2a,b vs. $\Sigma(r_L)$. In these graphs the red straight lines of Fig. 2a,b are obtained by interpolation of the data points of the subgroup of $[ABr_mI_n]$ (A = C, Si; m + n = 4) compounds, characterized by a $\Sigma(\chi_L^{Pau}) \ll 12.4$, as previously shown [34]. These straight lines correspond to the following Equations:

$$\delta(^{13}C) = i_C + s_C \cdot \Sigma(r_L) \tag{1A}$$

where $i_C = 2126.5$ ppm; $s_C = -2.7488$ ppm/pm.

$$\delta(^{29}Si) = i_{Si} + s_{Si} \cdot \Sigma(r_L) \tag{1B}$$

where $i_{Si} = 2031$ ppm; $s_{Si} = -2.703$ ppm/pm.

We can calculate the horizontal distance, indicated as $\Delta\Sigma(r_L)$ in the graphs of Fig. 2a,b (blue double arrows), between a given data point and the corresponding straight line, as follows:

$$\Delta\Sigma(r_L) = \frac{\delta(^{13}C) - i_C}{s_C} - \Sigma(r_L) \tag{2A}$$

$$\Delta\Sigma(r_L) = \frac{\delta(^{29}Si) - i_{Si}}{s_{Si}} - \Sigma(r_L) \tag{2B}$$

We previously shown that when $\Sigma(\chi_L^{Pau}) > 12.4$, for the two groups of cabon ($[CF_4]$, $[CF_3Cl]$, $[CF_2Cl_2]$, $[CFCl_3]$) and silicon ($[SiF_4]$, $[SiF_3Cl]$, $[SiF_2Cl_2]$, $[SiFCl_3]$) tetrahalido coordination compounds there exist linear correlations ($R^2 \approx 0.999$) between $\Delta\Sigma(r_L)$ and $\Sigma(\chi_L^{Pau})$ as described by following equations [34]:

$$\Delta\Sigma(r_L) = j_C + t_C \cdot \Sigma(\chi_L^{Pau}) \tag{3A}$$

where $j_C = -731$ pm; $t_C = +58.3$ pm.

$$\Delta\Sigma(r_L) = j_{Si} + t_{Si} \cdot \Sigma(\chi_L^{Pau}) \tag{3B}$$

where $j_{Si} = -892$ pm; $t_{Si} = +72.3$ pm.

Last straight lines are represented in the graphs of Fig. 3a,b, by blue skew lines crossing the zero line in proximity of the averaged onset electronegativity value corresponding to: $\Sigma(\chi_L^{Pau}) \approx 12.4$ [34].

Following Equations deriving from Equations 1 directly relate the $\delta(^{13}C)$ and $\delta(^{29}Si)$ NMR chemical shifts to the $\Sigma(r_L)$ and $\Delta\Sigma(r_L)$ values in the $\Sigma(\chi_L^{Pau}) > 12.4$ range, given that when $\Sigma(\chi_L^{Pau}) < 12.4$ it results $\Delta\Sigma(r_L) \approx 0$ [34]:

$$\delta(^{13}C) = i_C + s_C \cdot [\Sigma(r_L) + \Delta\Sigma(r_L)] \tag{4A}$$

$$\delta(^{29}\text{Si}) = i_{\text{Si}} + s_{\text{Si}} \cdot [\Sigma(r_L) + \Delta\Sigma(r_L)] \tag{4B}$$

It is noteworthy that none of the considered hydrogenated $[AH_mX_n]$ derivatives, showing a $\Sigma(\chi_L^{\text{Pau}}) \geq 12.4$, falls on the straight lines calculated by Equations 3, evidenced in blue, in Fig. 3a,b.

In the case of $[CHF_3]$ and $[SiHF_3]$ compounds, the following Equations give the NMR effective electronegativity sum, $\Sigma(\chi_{H-[AHF_3]}^{\text{NMR}})$, of C and Si bonded atoms:

$$\Sigma(\chi_{H-[CHF_3]}^{\text{NMR}}) = \frac{[\Delta\Sigma(r_L) - j_C]}{t_C} = 14.655 \tag{5A}$$

$$\Sigma(\chi_{H-[SiHF_3]}^{\text{NMR}}) = \frac{[\Delta\Sigma(r_L) - j_{Si}]}{t_{Si}} = 14.733 \tag{5B}$$

By subtracting the contribution of the Pauling's fluorine atoms electronegativity ($\chi_F^{\text{Pau}} = 3.98$) from the last calculated sums we can obtain the NMR effective electronegativity of the single bonded hydrogen atom in the considered $[CHF_3]$ and $[SiHF_3]$ compounds:

$$\chi_{H-[CHF_3]}^{\text{NMR}} = \Sigma(\chi_{L-[CHF_3]}^{\text{NMR}}) - 3\chi_F^{\text{Pau}} = 2.715 \tag{6A}$$

$$\chi_{H-[SiHF_3]}^{\text{NMR}} = \Sigma(\chi_{L-[SiHF_3]}^{\text{NMR}}) - 3\chi_F^{\text{Pau}} = 2.793 \tag{6B}$$

The differences between the NMR effective and the Pauling's electronegativities overall sums are as follows:

$$\Delta\chi_{H-[CHF_3]}^{\text{NMR}} = \Sigma(\chi_{L-[CHF_3]}^{\text{NMR}}) - \Sigma(\chi_{L-[CHF_3]}^{\text{Pau}}) = 0.52 \tag{7A}$$

$$\Delta\chi_{H-[SiHF_3]}^{\text{NMR}} = \Sigma(\chi_{L-[SiHF_3]}^{\text{NMR}}) - \Sigma(\chi_{L-[SiHF_3]}^{\text{Pau}}) = 0.59 \tag{7B}$$

These are graphically shown by horizontal violet double arrows in the graphs of Fig. 3a,b, for both reference $[CHF_3]$ and $[SiHF_3]$ compounds. Because the hydrogen electronegativity value is expected to be constant and independent from molecular environment, we can indicate the averaged NMR effective electronegativity of hydrogen ($\overline{\chi}_{H-[AHF_3]}^{\text{NMR}} = 2.75$) simply as: χ_H^{NMR} and use this value as NMR effective electronegativity of the bonded hydrogen atom.

Authors Contribution: M.B. and F.P.F. designed research; M.B., A.C. and F.D.C performed research; M.B. performed calculations; M.B. and F.P.F. analyzed data; M.B. and F.P.F. wrote the paper; M.B. and F.P.F. active discussion and paper revision.

References

[1]   H. Genther. *NMR Spectroscopy*, 2nd ed., Wiley, New York (1995).
[2]   H. Marsmann. *29Si NMR Spectroscopic Results, Oxygen-17 and Silicon-29-NMR Basic Principles and Progress*, pp. 65–235, Springer, Berlin, Heidelberg **17**, (1981).
[3]   P. S. Pregosin. *Transition Metal Magnetic Resonance*, Elsevier, Amsterdam (1991).
[4]   M. R. Burger, J. Kramer, H. Chermette, K. R. Koch. *Magn. Reson. Chem.* **48**, S38 (2010).

[5]   B. M. Still, P. G. Anil Kumar, J. R. Aldrich-Wright, W. S. Price. *Chem. Soc. Rev.* **36**, 665 (2007).
[6]   S. Fukawa, M. Hada, R. Fukuda, S. Tanaka, H. Nakatsuji. *J. Comput. Chem.* **22**, 528 (2001).
[7]   C. Corminboeuf, T. Heine, J. Weber. *Chem. Phys. Lett.* **357**, 1 (2002).
[8]   C. S. Weinert. *ISRN Spectroscopy* **2012**, 1 (2012).
[9]   J. C. Davis, M. Bühl, K. R. Koch. *J. Chem. Theory Comput.* **8**, 1344 (2012).
[10] B. E. G. Lucier, K. E. Johnston, W. Xu, J. C. Hanson, S. D. Senanayake, S. M. Yao, W. Bourassa, M. Srebro, J. Autschbach, R. W. Schurko. *J. Am. Chem. Soc.* **136**, 1333 (2014).
[11] A. F. Maldonado, C. A. Gimenez, G. A. Aucar. *Chem. Phys.* **395**, 75 (2012).
[12] A. F. Maldonado, G. A. Aucar. *J. Phys. Chem. A* **118**, 7863 (2014).
[13] Y. Takeuchi, K. Tanaka, T. Harazono, S. Yoshimura. *Bull. Chem. Soc. Jpn.* **63**, 708 (1990).
[14] R. Vivas-Reyes, F. D. Proft, M. Biesemans, R. Willem, P. Geerlings. *J. Phys. Chem. A* **106**, 2753 (2002).
[15] P. Avalle, R. K. Harris, P. B. Karadakov, P. J. Wilson. *Phys. Chem. Chem. Phys.* **4**, 5925 (2002).
[16] A. Bagno, G. Casella, G. Saielli. *J. Chem. Theory Comput.* **2**, 37 (2006).
[17] E. Malkin, S. Komorovsky, M. Repisky, T. B. Demissie, K. Ruud. *J. Phys. Chem. Lett.* **4**, 459 (2013).
[18] J. Autschbach, T. Ziegler. *Relativistic Computation of NMR Shielding and Spin-Spin Constants-Encyclopedia of Nuclear Magnetic Resonance*, pp. 306, Wiley, Chichester, (2002).
[19] H. Nakatsuji, H. Takashima, M. Hada. *Chem. Phys. Lett.* **233**, 95 (1995).
[20] H. Nakatsuji, T. Nakajima, M. Hada, H. Takashima, S. Tanaka. *Chem. Phys. Lett.* **247**, 418 (1995).
[21] H. Kaneko, M. Hada, T. Nakajima, H. Nakatsuji. *Chem. Phys. Lett.* **261**, 1 (1996).
[22] T. N. Mitchell. *J. Organomet. Chem*. **255**, 279 (1983).
[23] P. J. Watkinson, K. M. Mackay. *J. Organomet. Chem.* **275**, 39 (1984).
[24] J. D. Kennedy, W. Mcfarlane, G. S. Pyne. *J. Chem. Soc.*, *Dalton Trans.* **23**, 2332 (1977).
[25] J. A. Tossell. *Nuclear Magnetic Shieldings and Molecular Structure*, Kluwer Academic Publishers, Dordrecht (1993).
[26] R. G. Kidd. *Annu. Rep. NMR Spectrosc.* **10A**, 1 (1980).
[27] R. G. Kidd. *Annu. Rep. NMR Spectrosc.* **23**, 85 (1991).
[28] M. Benedetti, P. Papadia, C. R. Girelli, F. De Castro, F. Capitelli, F. P. Fanizzi. *Inorg. Chim. Acta* **428**, 8 (2015).
[29] H. O. Kalinowski, S. Berger, S. Braun. *¹³C-NMR-Spektroskopie*, Thieme, Stuttgart (1984).
[30] M. Kaupp, O. L. Malkina, V. G. Malkin, P. Pyykkö. *Chem. Eur. J.* **4**, 118 (1998).
[31] A. A. Cheremisin, P. V. Schastnev. *J. Magn. Res.* **40**, 459 (1980).
[32] R. Gollakota, J. Somayajulu, R. Kennedy, T. M. Vickrey, B. J. Zwolinski. *J. Magn. Reson.* **33**, 559 (1969).
[33] R. A. De Marco, W. B. Fox, W. B. Moniz, S. A. Sojka. *J. Magn. Reson.* **18**, 522 (1975).
[34] M. Benedetti, F. De Castro, F. P. Fanizzi. *Chem. Eur. J.* **23**, 16877 (2017).
[35] M. Benedetti, F. De Castro, A. Ciccarese, F. P. Fanizzi. *Dalton Trans.* **46**, 14094 (2017).
[36] M. Benedetti, F. De Castro, E. Lamacchia, C. Pacifico, G. Natile, F. P. Fanizzi. *Dalton Trans.* **46**, 15819 (2017).
[37] M. Benedetti, F. De Castro, D. Antonucci, P. Papadia, F. P. Fanizzi. *Dalton Trans.* **44**, 15377 (2015).
[38] M. Benedetti, F. De Castro, F. P. Fanizzi. *Eur. J. Inorg. Chem.* **2016**, 3957 (2016).
[39] M. Benedetti, F. De Castro, F. P. Fanizzi. *Dalton Trans.* **46**, 2855 (2017).
[40] M. Benedetti, C. R. Girelli, D. Antonucci, F. P. Fanizzi. *J. Organomet. Chem.* **771**, 40 (2014).
[41] M. Benedetti, D. Antonucci, C. R. Girelli, F. P. Fanizzi. *Eur. J. Inorg. Chem.* **2015**, 2308 (2015).
[42] U. Niemann, H. C. Marsmann. *Z. Naturforsch.* **30b**, 202 (1975).
[43] E. A. Robinson, R. J. Gillespie. *Inorg. Chem.* **43**, 2318 (2004).
[44] W. M. Litchman, D. M. Grant. *J. Am. Chem. Soc.* **90**, 1400 (1968).
[45] P. C. Lauterbur. *Ann. NY Acad. Sci.* **70**, 841 (1958).
[46] O. W. Howarth, R. J. Lynch. *Mol. Phys.* **15**, 431 (1968).
[47] G. R. Fulmer. *Organometallics* **29**, 2176 (2010).
[48] R. B. Johannesen, F. E. Brinkman, T. D. Coyle. *J. Phys. Chem*. **72**, 660 (1968).
[49] F. Klanberg, E. L. Muetterties. *Inorg. Chem.* **7**, 155 (1968).
[50] T. Heine. *J. Phys. Chem. A.* **105**, 620 (2001).
[51] G. A. Olah', L. D. Field. *Organometallics* **1**, 1485 (1982).
[52] R. D. Shannon. *Acta Crystallogr. Sect.* **A32**, 751 (1976).
[53] L. Pauling. *J. Am. Chem. Soc.* **54**, 3570 (1932).
[54] L. Pauling. *The Nature of the Chemical Bond* 3ʳᵈ, 13ᵗʰ Printing 1995 ed., Cornell University Press, Ithaca, New York (1960).
[55] D. F. C. Morris, G. L. Reed. *J. Inorg. Nucl. Chem.* **27**, 1715 (1965).
[56] M. R. Leach. *Found. Chem.* **15**, 13 (2013).
[57] R. S. Mulliken. *J. Chem. Phys.* **2**, 782 (1934).
[58] R. G. Parr, R. G. Pearson. *JACS* **105**, 7512 (1983).
[59] R. G. Pearson. *Inorg. Chem.* **27**, 734 (1988).