# Theoretical Study of the Effect of $\alpha$-Substituents on the $^{29}$Si hfs Constant in Silyl Radicals: An Electronic Rather than Structural Effect

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**Abstract:** The structural parameters of $\alpha$-substituted silyl radicals $(H_nX)_3Si^{\bullet}$ ($H_nX$ = H, $H_3C$, $H_2N$, HO, F, $H_3Si$, $H_2P$, HS, and Cl) have been determined by *ab initio* calculations at the UMP2/DZP level of theory. All radicals are found to be pyramidal at the radical center, the arrangement of atoms around silicon being essentially tetrahedral except for X = Si. The magnitude and the trend of the $^{29}$Si hyperfine splitting (hfs) constant from the ESR spectra are well reproduced by these calculations. There is no relation between the structure at the radical site and Si hybridization in the singly occupied molecular orbital (SOMO). The Si-3s character of the SOMO increases dramatically with the electronegativity of X. The large variations in the $^{29}$Si hfs constant observed experimentally upon $\alpha$-substitution are due to the electronic influence of $\alpha$-substituents rather than related to a change of geometry at the radical center as generally recognized.

## Introduction

ESR investigations on the magnitude and temperature dependence of the $^{13}$C hyperfine splitting (hfs) constant of $\alpha$-substituted alkyl radicals showed that the geometry at the carbon radical center depends on the electronegativity of the $\alpha$-substituents.[1] Unsubstituted alkyl radicals were found to be nearly planar, whereas the deviation from planarity was predicted to increase with the increasing electronegativity of the $\alpha$-substituents. By analogy, the large variations of the $^{29}$Si hfs constant in $\alpha$-substituted silyl radicals were related to substantial changes of geometry at the radical center.[2] In particular, Pedulli and coworkers determined the structure of silyl radicals simply from the percentage of Si-3s character in the singly occupied molecular orbital (SOMO) computed from experimental $^{29}$Si hfs constants with the assumption that both spin polarization and spin-density delocalization are negligible.[3] Also in this case, the degree of pyramidalization was found to increase with the electronegativity difference between the central atom and the $\alpha$-substituents.[3–5] The radical center was estimated to be slightly pyramidal when the electronegativity difference is small as in $(Me_3Si)_3Si^{\bullet}$ (4% 3s character, $\angle$SiSiSi = 118°)[3] and much more bent than tetrahedral (25% s character) with strongly electronegative $\alpha$-substituents as in $F_3Si^{\bullet}$ (30% 3s character).[4] This latter prediction is in contrast with the tetrahedral structure estimated from vibrational analysis.[6] It was hypothesized that either the spin-polarization effects contribute significantly to the s spin density or the Si–3s contribution to the SOMO increases as a result of the participation of the Si–3d orbitals in the Si–F bond.[4]

Recently, Hudson and co-workers found a linear relationship between the $^{29}$Si hfs constants of $\alpha$-substituted silyl radicals and the J($^{29}$SiH) coupling constants from the NMR spectra of the parent silanes.[7] This finding was used as a support to the hypothesis that the magnitude of the $^{29}$Si hfs constant is essentially related to the geometry at the radical center. The small deviations from the straight line were interpreted in terms of slight delocalization of the unpaired electron onto $\alpha$-substituents.[7,8] On the contrary, the existence of such a relation suggests to us that other effects than structural effects should be responsible for the large variations observed in the $^{29}$Si hfs constant because the geometry of silanes is not expected to depart sizably from the tetrahedral configuration upon $\alpha$-substitution.

In our view, the unexpectedly large Si-3s spin density in $F_3Si^{\bullet}$ could be caused by the great electronegativity difference between Si and F atoms, since in the pyramidal structure, the Si-3s character in the SOMO is predicted to increase as the $\alpha$-substituent becomes more electronegative.[9] This hypothesis, however, contrasts with the generally accepted view that in organic- and organometallic-localized radicals, the electron structure of $\alpha$- and $\beta$-substituents has little effect on spin distribution but can produce a sizable change in the equilibrium geometry. For example, an abnormal distortion at the $\beta$-carbon (asymmetric bridging) was hypothesized by ESR spectroscopy in order to explain the anomalously low values of the $\beta$-proton hfs constant measured in eclipsed $\beta$-substituted alkyl radicals when the $\beta$-substituent is more electronegative than hydrogen.[1] By contrast, we have recently shown by means of *ab initio* UMP2/DZP calculations that the observed trend depends essentially on the electronegativity of the $\beta$-substituents.[10]

Silicon-centered radicals play an important role in organic synthesis.[11] Knowledge of their structure is very useful for predicting their selectivity. Therefore, it is important to assess the reliability of the structures determined simply from the magnitude of the $^{29}$Si hfs constants. UMP2/DZP calculations have been shown to predict both molecular structures[12] and hfs

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**Table I.** Optimized Structural Parameters[a] of α-Substituted Silyl Radicals $(H_nX)_3Si^\bullet$ at the UMP2/DZP Level

| $H_nX$ | r(Si–X) | ∠XSiX | r(X–H) | ∠SiXH | ω | γ | symmetry |
|---|---|---|---|---|---|---|---|
| H | 1.4766 | 111.15 | | | | 17.73 | $C_{3v}$ |
| $H_3C$ | 1.8967 | 110.24 | 1.0943 | 110.93 | 60.0 | 18.69 | $C_{3v}$ |
| $H_2N$ | 1.7582 | 107.34 | 1.0145 | 115.83 | 54.02 | 21.53 | $C_{3v}$ |
| HO | 1.6708 | 108.15 | 0.9651 | 115.77 | 62.59 | 20.76 | $C_3$ |
| F | 1.6177 | 108.14 | | | | 20.77 | $C_{3v}$ |
| $H_3Si$ | 2.3465 | 114.80 | 1.4798 | 110.22 | 60.0 | 13.40 | $C_{3v}$ |
| $H_2P$ | 2.2859 | 106.08 | 1.4175 | 97.06 | 47.06 | 22.68 | $C_{3v}$ |
| HS | 2.1532 | 108.41 | 1.3401 | 94.17 | 50.52 | 20.51 | $C_3$ |
| Cl | 2.0627 | 109.51 | | | | 19.43 | $C_{3v}$ |

[a] Bond lengths are given in angstroms and dihedral and bond angles in degrees; ω (dihedral angle between the Si-$3p_z$AO and the X–H bond) and γ (out-of-plane bending angle) are defined in Figure 1.

constants[13,14] reliably. Thus, in the present study, the structures and the $^{29}$Si hfs constants of symmetrically α-substituted silyl radicals have been determined using this computational approach for establishing whether electronic effects (i.e., spin polarization, spin-density delocalization, and mainly electronegativity difference) rather than structural effects are responsible for the large variations in the $^{29}$Si hfs constant observed upon α-substitution.

## Computational Details

*Ab initio* unrestricted Hartee–Fock (UHF) calculations have been performed on α-substituted silyl radicals $(H_nX)_3Si^\bullet$ ($H_nX$ = H, $H_3C$, $H_2N$, HO, F, $H_3Si$, $H_2P$, HS, and Cl) with the GAUSSIAN92 system of programs[15] running on a RISC-6000 IBM computer. Geometries have been optimized within the constraint of $C_3$ or $C_{3v}$ symmetry by means of an analytical gradient technique[16] employing a moderately sized basis set and estimating electron correlation energy with second-order Møller–Plesset perturbation theory (UMP2).[17] The planar and tetrahedral structures at the radical site have also been optimized. The basis set (DZP) consists of Dunning's full double-ζ (DZ) contraction of Huzinaga's primitives: (4s)/[2s] for hydrogen (9s5p)/[4s2p] for second- and 12(s8p)/[6s4p] for third-row atoms supplemented with polarization functions (*P*), p-functions on hydrogens, and d-functions on heavy atoms.[18] The UMP2 wave function correctly describes the doublet state since its contamination by higher spin multiplets is quite small, the $\langle S^2\rangle$ value being less than 0.76 for any radicals. $^{29}$Si hfs constants have been evaluated employing correlated spin densities obtained from the generalized density matrix corresponding to the second-order energy.[19,20] Values computed using uncorrelated spin densities (UHF/DZP//UMP2/DZP) are 15–20 G larger in absolute value. Preliminary configuration interaction (CI) calculations with single (S) and double (D) excitations (UCISD/DZP//UMP2/DZP) on halo derivatives (X = F and Cl) have shown that the values of the $^{29}$Si hfs constant change less than 1% using a different correlation method.

## Results and Discussion

The optimized structural parameters of α-substituted silyl radicals $(H_nX)_3Si^\bullet$ are listed in Table I. All radicals have been found to be pyramidal at the radical center, the arrangement of atoms around silicon being essentially tetrahedral except for X = Si. This theoretical finding is in contrast with structural information obtained simply from the magnitude of experimental $^{29}$Si hfs constants.[2-5,8] For example, the structures of the silyl radical $H_3Si^\bullet$ and of the α-alkyl derivatives $R_3Si^\bullet$ (R = Me, Et, and *t*-Bu) were predicted to depart sizably from the tetrahedral form (∠HSiH = 113° and ∠CSiC = 115°).[3] The degree of pyramidalization in $H_3Si^\bullet$ is estimated to further decrease (∠HSiH = 115°) using a more reliable value of the experimental $^{29}$Si hfs constant.[21]

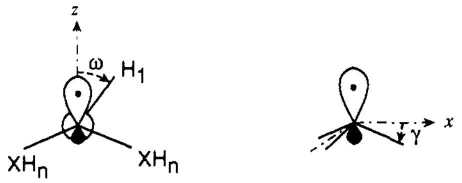

**Figure 1.**

**Table II.** Theoretical $^{29}$Si *hfs* Constants (G) of $(H_nX)_3Si^\bullet$ Radicals in Different Structures at the UMP2/DZP Level

| $H_nX$ | ground state[a] | tetrahedral | planar |
|---|---|---|---|
| H | –183.6 (189)[b] | –196.3 | –71.9 |
| $H_3C$ | –189.8 (183)[c] | –193.8 | –77.7 |
| $H_2N$ | –231.1 | –226.5 | –62.1 |
| HO | –336.8 (339)[d,e] | –335.6 | –60.0 |
| F | –501.9 (498)[f] | –500.7 | –83.5 |
| $H_3Si$ | –106.1 (65)[e,g] | –144.1 | –55.1 |
| $H_2P$ | –181.0 | –175.6 | –77.8 |
| HS | –275.8 | –274.2 | –103.5 |
| Cl | –416.1 (416)[h] | –416.1 | –92.2 |

[a] The *hfs* constant *a* computed at a nucleus other than α-silicon is also included when the experimental value, reported in parentheses, is available. [b] From ref 21; $a(^1H)$ = 2.90 G (7.84 G). [c] From ref 5; $a(^1H)$ = 5.48 G (6.34 G). [d] From ref 8. [e] Methylated β-atom. [f] From ref 4; $a(^{19}F)$ = 129.15 G (136.6 G). [g] From ref 22. [h] From ref 23; $a(^{35}Cl)$ = 11.31 G (12.4 G).

The $^{29}$Si hfs constants computed at the energy minimum (see Table II) are in excellent agreement[24] in absolute value with the available ESR data except for X = Si. In this case, the computed value is too large with respect to the experimental value measured for the fully methylated derivative. However, spin-density delocalization onto the Si–C β-bonds[25] and vibrational averaging over the inversion mode at the radical site[26] reduce sizably the $^{29}$Si hfs constant, bringing it close to the experimental value.[27] The $^{29}$Si hfs constants for the constrained planar and tetrahedral structures are also included in Table II for comparison. Interestingly, the hfs values do not vary significantly on going from the fully optimized to the constrained tetrahedral structure.

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(24) This confirms the reliability of the present method for hfs constant calculations. In addition, Table II shows that also the $^1$H, $^{19}$F, and $^{35}$Cl hfs constants are in excellent agreement with experiment except for the $^1$H hfs constant in $H_3Si^\bullet$. However, the difference between theory and experiment is not so large as it may seem. In fact, the calculations show that in this particular case, the small value of $a(^1H)$ is due to a partial cancellation of two large contribution (direct and spin polarization) which are similar and opposite in sign. This explains why the experimentally determined value is unusually small for an α-substituent, the spin density computed from the experimental value being only about 5% of that computed from the experimental halogen hfs constants.

(25) Preliminary calculations performed on the $SiH_3$–$SiH_2^\bullet$ and $SiMe_3$–$SiH_2^\bullet$ radicals at the UHF/DZP level of theory have shown that the theoretical $^{29}$Si hfs constant decreases in absolute value by about 15 G upon methylation. Similar calculations carried out on OH–$SiH_2^\bullet$ and OMe–$SiH_2^\bullet$ have shown that methyl substitution has a negligible effect in this case, probably because the O–C bond is nearly perpendicular to the SOMO.

(26) The $^{29}$Si hfs constant in the excited vibrational states is smaller since its value diminishes in the constrained planar structure (see Table II). For X = Si, some excited vibrational levels are thermally populated because the double minimum potential for the inversion mode is predicted to be extremely shallow, the optimized planar structure lying only 1.14 kcal mol$^{-1}$ above the bent structure. The vibrational effect is expected to be negligible for all other radicals since the barrier to inversion is estimated to be much higher. For example, the $^{29}$Si hfs constant in $H_3Si^\bullet$, for which we estimate an inversion barrier of 6.1 kcal mol$^{-1}$, was found to decrease by only 3.1 G at the UHF/DZP level of theory.[14]

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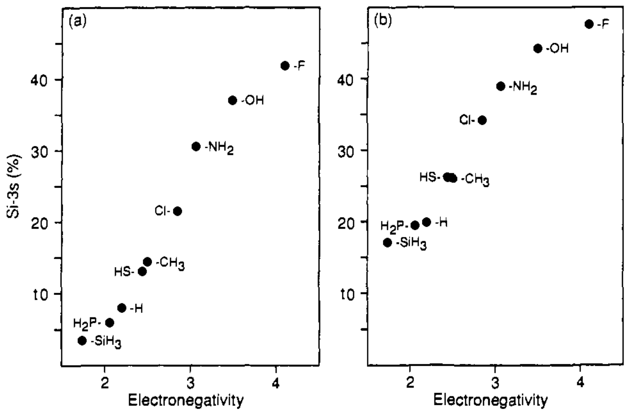

**Figure 2.** (a) Si-3s population (%) in the SOMO and (b) Si-3s total spin density (%) in the constrained tetrahedral structure of $(H_nX)_3Si^•$ radicals versus the Allred–Rochow electronegativity of X.

Thus, theoretical information about the structural and magnetic properties of $\alpha$-substituted silyl radicals clearly indicates that the large variations observed experimentally in the $^{29}$Si hfs constant can not be interpreted as due essentially to structural effects. Indeed, the $^{29}$Si hfs constant in $H_3Si^•$ computed as a function of the out-of-plane bending angle $\gamma$ varies to a much lesser extent than expected. Its variation in the absence of the electronic influence of the $\alpha$-substituent is small in the range of the optimized out-of-plane angle $\gamma$ (17.5°–22.5°) going from −181.6 to −217.2 G, whereas the experimental values of the $\alpha$-substituted silyl radicals range from 183 to 500 G excluding the moderately pyramidal $\alpha$-trialkylsilyl derivative. It should be noted that the magnitude of the $^{29}$Si hfs constant measured in $F_3Si^•$ is reproduced with an out-of-plane angle of 52.5° which has no chemical significance. The Si-3s spin density appears to increase with $\alpha$-substitution. This suggests that either the spin-polarization effects are not negligible or the percentage of Si-3s character in the SOMO is strongly influenced by the electronegativity of the $\alpha$-substituents. Conversely, spin-density delocalization is expected to decrease the Si-3s spin density. In order to establish which electronic factor is more important, the electron distribution in the SOMO has been computed for the constrained tetrahedral structure.

Figure 2 shows that the Si–3s population increases sizably with the increasing electronegativity[28] of X. In particular, its value for X = Si (s% = 3.4) and for X = F (s% = 41.8) differs dramatically from the expected for $sp^3$ hybridization (s% = 25). This finding indicates that the Si-3s character in the SOMO is not related to the geometry at the radical center as previously hypothesized but depends strongly on the electronic nature of $\alpha$-substituents. The computed trend can be rationalized on the basis of one-electron perturbation molecular orbital (PMO) theory.[29] In the pyramidal structure, the Si-3s character in the SOMO depends on the mixing of the Si-$3p_z$ AO with the lowest symmetric Si–X antibonding MO ($\sigma^*_{Si-X}$) that has a large Si-3s character. According to PMO theory, the extent of their mixing is inversely proportional to their energy difference ($\Delta E$) in the planar form. The $\Delta E$ value is expected to decrease with increasing electronegativity of the $\alpha$-substituent;[9] consequently, the Si-3s character in the SOMO increases as X becomes more electronegative.

Comparison in Figure 2 of the 3s population in the SOMO with the 3s total spin density, which takes into account both direct and spin-polarization contributions, indicates that the spin-polarization contribution is sizable but not very dependent on the electronic structure of the $\alpha$-substituents, being only slightly larger for the $\alpha$-substituents bearing third-row elements.

**Table III.** $\alpha$-Silicon Electron Distribution in the SOMO of $(H_nX)_3Si^•$ Radicals in the Constrained Tetrahedral Structure Along with the Corresponding Electron Transfer to $\alpha$-Substituents

| | electron distribution (%) | | | |
|---|---|---|---|---|
| $H_nX$ | 3s | 3p | 3d | electron transfer (%) |
| H | 7.9 | 79.3 | 1.3 | 11.5 |
| $H_3C$ | 14.3 | 64.6 | 2.1 | 19.0 |
| $H_2N$ | 30.5 | 31.4 | 5.0 | 33.1 |
| HO | 37.0 | 34.0 | 6.6 | 22.4 |
| F | 41.8 | 36.2 | 6.4 | 15.6 |
| $H_3Si$ | 3.4 | 77.6 | 0.4 | 18.6 |
| $H_2P$ | 5.9 | 43.5 | 1.1 | 49.5 |
| HS | 13.0 | 30.5 | 2.2 | 54.3 |
| Cl | 21.5 | 32.6 | 3.2 | 42.7 |

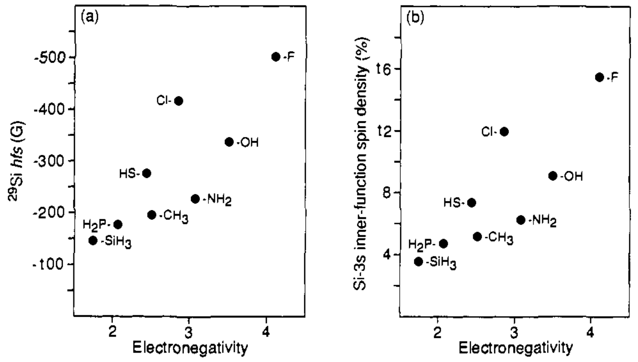

**Figure 3.** (a) $^{29}$Si hfs constant at the UMP2/DZP level and (b) Si-3s inner function spin density (%) in the constrained tetrahedral structure of $(H_nX)_3Si^•$ radicals versus the Allred–Rochow electronegativity of X.

Table III shows that in the SOMO, there is a sizable delocalization of the unpaired electron onto the $\alpha$-substituents containing third-row elements, while the electron transfer to second-row $\alpha$-substituents is significantly lower. However, a correlation between the $^{29}$Si hfs constant and the electron charge transfer does not exist, probably because the electron transfer in the SOMO derives essentially from the Si-$3p_z$ AO. The participation of polarization Si-3d orbitals in the SOMO is small. Their population increases as the electronegativity of X increases in accord with their charge-polarization property.

Thus, the electronegativity difference is the main factor governing the large variations observed in the $^{29}$Si hfs constant upon $\alpha$-substitution. It should, however, be noted that the experimental value of the $^{29}$Si hfs constant does not strictly depend on the electronegativity of the $\alpha$-substituent being larger for the chlorine than for the methoxy substituents. This is confirmed in the present calculations, the $^{29}$Si hfs constant being computed to be larger for X = Cl than for X = O and N. This apparently anomalous trend could be due to a markedly different polarization of the Si-s AOs between their inner and outer components in full double-$\zeta$ calculations, since Fermi-contact integrals are much greater for the former. Indeed, Figure 3 shows that in the constrained tetrahedral structure, the theoretical $^{29}$Si hfs constant and the Si-3s inner function spin density follow the same trend as a function of electronegativity. In particular, two trends, one for each of the isoelectronic series, can be identified in both plots, the Si-3s inner function spin density being much greater for X from third than from second row with respect to the trend expected on the electronegativity basis. This contraction of the Si-3s AO toward the nucleus could be a consequence of the large electron transfer occurring from the Si-$3p_z$ AO to the third-row $\alpha$-substituents.

## Conclusion

It has been shown that the structures of $\alpha$-substituted silyl radicals can not be discussed on the basis of the s spin density derived from experimental $^{29}$Si hfs constants since Si hybridization

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can not be directly related to the geometry at the radical center. The large variations in the $^{29}$Si hfs constant observed upon $\alpha$-substitution are essentially due to the electronic influence of the $\alpha$-substituents, the Si-3s character of the SOMO depending mainly on their electronegativity. However, the Si-3s AO is more contracted toward the nucleus for X from third than from second row. This explains why the experimental $^{29}$Si hfs constant in silyl radicals bearing third-row substituents is larger than that expected on a simple electronegativity basis. In contrast to what is generally assumed,[3,7,8] spin polarization as well as spin-density delocalization onto $\alpha$-substituents is sizable. However, they both do not appear to influence significantly the trends of the $\alpha$-silicon hfs constant in a direct way.

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