Theoretical study on the structural correlations between silyl radicals and their parent silanes

Maurizio Guerra
I.Co.C.E.A. Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129 Bologna, Italy

---

The geometries of $Y_n\dot{\mathrm{Si}}\mathrm{Me}_{3-n}$ radicals ($Y = \mathrm{Me_3Si}$, Cl; n = 0–3) and of their parent silanes have been determined by *ab initio* calculations at the UHF/TZP level. It is shown that the correlation between the Si–3s character in the singly occupied molecular orbital (SOMO) and in the σ(Si–H) bonding MO of the parent silanes does not lead to any structural information. The experimental ^{29}Si hyperfine splitting (hfs) constants are fairly well reproduced at the UMP2/DZP//TZP level. The large increments in $a(^{29}\mathrm{Si})$ observed experimentally when methyl groups are replaced successively by chlorine atoms are mainly due to the electronic influence of the substituent rather than to structural changes at the radical centre as previously suggested. This finding confirms that in localized radicals the relationship between the magnitude of the isotropic hfs constant for the central atom and the structure at the radical centre does not, in general, hold.

Silicon-centred radicals play an important role in organic synthesis. Knowledge of their structure is very useful for predicting their reactivity.[1] The structure of radicals in which the unpaired electron is localized at an atom X is usually determined from the s-character of the singly occupied molecular orbital (SOMO) estimated from the experimental X hyperfine splitting (hfs) constants.[2] Further information on the structure of localized radicals was obtained from the correlation between the values of a(X) and those of the J(X–H) coupling constant from the NMR spectra of the protic parents.[3–6] In fact, Dixon[3] pointed out that a good linear correlation between a(X) and J(X–H) would be expected when the homolysis of the X–H bond occurs without any significant variation in the angles between the remaining bonds since both constants depend mainly on the Fermi contact interaction, *i.e.* on the valence s-orbital population. In α-substituted silyl radicals structural information was obtained from the good linear correlation found between $a(^{29}\mathrm{Si})$ and $J(^{29}\mathrm{Si–H})$.[6,7] Small deviations from the straight line were observed in silyl radicals containing α-Si and -Cl substituents and were ascribed to delocalization of the unpaired electron onto α-substituents rather than to variations of hybridization at the central silicon caused by the homolysis of the Si–H bond.[6] By contrast, Chatgilialoglu *et al.*[1] pointed out that such a linear correlation has physical meaning only inside a family of substituents since in correlating $a(^{29}\mathrm{Si})$ for $Y_n\dot{\mathrm{Si}}\mathrm{Me}_{3-n}$ radicals ($Y = \mathrm{Me_3Si}$, Cl; n = 0–3) with $J(^{29}\mathrm{Si–H})$ for their parent silanes they found two good straight lines with a largely different slope, one for $Y = \mathrm{Me_3Si}$ and the other for Y = Cl. Besides, they found linear correlations between the Si–3s contribution to the SOMO and to the σ(Si–H) bonding MO of their parent silanes. Contrary to expectations, inspection of these relations reveals that a large rehybridization at silicon should occur on homolysis of the Si–H bond. Thus, *ab initio* calculations have been carried out to elucidate this point and to establish whether reliable structural information can be obtained from the correlation between $a(^{29}\mathrm{Si})$ and $J(^{29}\mathrm{Si–H})$ since we have recently shown that in symmetrically α-substituted silyl,[8] methyl[9] and phosphonyl radicals[10] there is not a strict relation between the s-character estimated from the experimental isotropic central-atom hfs constant and the structure at the radical site.

Computational details

Ab initio unrestricted Hartree–Fock (UHF) calculations have been performed on $Y_n\dot{\mathrm{Si}}\mathrm{Me}_{3-n}$ radicals ($Y = \mathrm{Me_3Si}$, Cl; n = 0–3) and on their parent silanes with the GAUSSIAN 92 system of programs[11] running on a RISC-6000 IBM computer. Geometries have been optimized employing the 6-311G** triple-ζ basis set[12,13] (TZ) supplemented with polarization functions (*P*).[14] ^{29}Si hfs constants have been evaluated at the optimized geometries from correlated spin densities[15] corresponding to second order Møller–Plesset perturbation energy[16] employing the Dunning/Huzinaga full double-ζ basis set[17] (DZ) augmented with polarization functions. This level of theory (UMP2/DZP//TZP) provided hfs constants in excellent agreement with experiment in symmetrically α-substituted methyl[9] and phosphonyl[10] radicals where the contamination of the doublet state by higher spin multiplets was found to be quite small as in the present case, the expectation value of S^2 being approximately 0.76. It should be remarked that Carmichael[18] has shown that when the spin contamination is large the correlation contributions must be computed with the quadratic configuration interaction method[19] to obtain good results.

Results and discussion

Structural information on α-Si and -Cl substituted methylsilyl radicals and on their parent silanes were obtained by correlating EPR and NMR data.[1] In the first section, we examine the structural information obtained from this correlation. In the second one, this information is compared with that obtained in the present work by means of reliable *ab initio* calculations. Finally, further information on the radical species is obtained by comparing experimental and theoretical isotropic ^{29}Si hfs constants.

Structural information from correlations between EPR and NMR data

Structural information on $Y_n\dot{\mathrm{Si}}\mathrm{Me}_{3-n}$ radicals ($Y = \mathrm{Me_3Si}$, Cl; n = 0–3) were obtained relating the Si–3s character of the SOMO to that of the σ(Si–H) bonding MO of the parent silanes using eqn. (1), where m = 0.720 and 1.977, and C = 0.055 and

$$s(\mathrm{SOMO}) = ms[\sigma(\mathrm{Si–H})] - C \qquad (1)$$

0.377 for Y = Cl and $\mathrm{Me_3Si}$, respectively. This relationship was derived from the correlation found between experimental $a(^{29}\mathrm{Si})$ and $J(^{29}\mathrm{Si–H})$ constants. The Si–3s character in the SOMO was estimated by dividing the experimental $a(^{29}\mathrm{Si})$ constant by the value (A_0) computed for a unitary s-

Table 1 Si–3s population in the SOMO of $Y_n\dot{S}iMe_{3-n}$ radicals and in the σ(Si–H) bonding MO of their parent silanes estimated from the experimental $a(^{29}Si)$ constants reported in Table 3 using eqn. (1). Values estimated directly from experimental $J(^{29}Si–H)$ using eqn. (3) are reported in parentheses

Y	*n*	*s*(SOMO)	*s*[σ(Si–H)]
	0	0.112	0.231[a] (0.227)
Cl	3	0.254	0.429 (0.448)
	2	0.188	0.337 (0.345)
	1	0.140	0.270 (0.274)
Me_3Si	3	0.040	0.211 (0.191)
	2	0.055	0.219 (0.204)
	1	0.084	0.233 (0.216)

[a] From eqn. (1) using the linear correlation for Y = Cl, the value estimated from the correlation for Y = Me_3Si is 0.247.

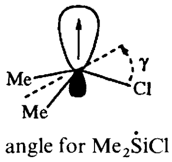

Fig. 1 Definition of the γ angle for $Me_2\dot{S}iCl$

Table 2 Optimized γ angles in $Y_n\dot{S}iMe_{3-n}$ radicals and in their parent silanes at the UHF/TZP level. For the symmetrically α-substituted derivatives the values determined from the s-population of Table 1 using eqn. (4) are reported in parentheses

Y	*n*	Silyl radicals γ/degrees	Silanes γ/degrees
	0	52.03 (38.58)	52.47 (52.97)
Cl	3	54.87 (55.07)	54.66 (67.66)
	2	55.00	54.45
	1	56.17	55.71
Me_3Si	3	31.03 (23.74)	43.15 (51.00)
	2	42.93	50.10
	1	47.31	50.61

population[20] and the Si–3s character in the σ(Si–H) MO using

$$s(\text{SOMO}) = a(^{29}\text{Si})/A_0 \qquad (2)$$

the relationship previously found for α-methyl substituted silanes.[21]

$$s[\sigma(\text{Si–H})] = J(^{29}\text{Si–H})/810 \qquad (3)$$

The slope *m* of the straight line described by eqn. (1) was related to the capability of a substituent to induce a change of geometry at the silicon radical centre. It was concluded that the replacement of a methyl group by a chlorine atom largely increases the pyramidality at the radical centre, the effect being cumulative. Successive substitution of a methyl group with a trimethylsilyl group produces a much larger effect in the opposite direction. It is immediately apparent that this conclusion is not in complete accord with the trend of the Si–3s population in the SOMO (Table 1) estimated from the experimental $a(^{29}Si)$ constants using eqn. (2). In fact, the Si–3s population varies more rapidly when methyl groups are replaced successively by chlorine atoms than by trimethylsilyl groups so that smaller changes in radical geometries are expected in the latter series of radicals assuming that the nuclear coordinates follow the interorbital angles (complete orbital following)[22] as it is generally supposed by EPR spectroscopists in determining local radical geometries from experimental hfs constants.[2]

A simple way by which to establish the reliability of the structural information obtained from this correlation is to examine the trend in hybridization at the central silicon predicted for the parent silanes. In fact, in this case the geometry at the central silicon is expected to be approximately tetrahedral (25% s-character) in all the silanes. The Si–3s populations (Table 1) estimated for trimethylsilane and for the trimethylsilyl derivatives are in accord with this expectation. On the contrary, the use of eqn. (1) provides 'structural' information which has no chemical meaning for the chlorosilanes since the σ(Si–H) bond is predicted to be sp^2 hybridized (33% s-character) in $Cl_2Si(H)Me$ and even nearly sp hybridized (50% s-character) in Cl_3SiH. Obviously, the type of hybridization of the σ(Si–H) bond in silanes depends on the use of eqn. (3) as shown in Table 1 by the Si–3s population evaluated directly from this equation. This indicates that either the use of this equation is incorrect for substituted silanes since it was derived without taking into account the effect of the electronic nature of the substituents Y or that there is not a strict relation between hybridization of the σ(Si–H) bonding MO and geometry at the central silicon as previously found for the SOMO in symmetrically α-substituted silyl radicals.[8]

Comparison with structures from *ab initio* calculations

Inspection of eqn. (1) has shown that the structural information previously obtained from this relation should be unreliable. Thus, it is of interest to make a comparison between this structural information and that obtained by means of reliable *ab initio* calculations (UHF/TZP). The 6-311G** triple-ζ basis set has been used in these calculations since it is known that this basis set is especially suited to determining geometries and, in particular, it generally gives bond angles which are in excellent agreement with the experimental ones.[23] In $Y_n\dot{S}iMe_{3-n}$ radicals the degree of pyramidalization at the radical centre can be represented from the angle γ (Fig. 1) between the plane defined by the silicon atom and two equivalent α-substituents and the third bond.[24] The optimized values of γ are reported in Table 2. All the radicals have been found to be pyramidal at the radical centre, the arrangement of atoms around silicon being essentially tetrahedral ($\gamma_{\text{tetr}} = 54.8°$) for Y = Cl and slightly less pyramidal for Y = Si. In this case the mono-, di- and tri-substituted silyl derivatives are about 87.4%, 79.7% and 56.6% pyramidalized to a perfectly tetrahedral structure, respectively; the percentage of pyramidalization being defined as equal to the $\gamma:\gamma_{\text{tetr}}$ ratio.[24] These results are in contrast to the structural information obtained from the Si–3s character in the SOMO predicting a strong increase in the degree of pyramidalization at the central silicon atom when methyl groups are replaced successively by chlorine atoms. For radicals with C_{3v} symmetry the value of γ can be evaluated directly from the Si–3s character in the SOMO assuming complete orbital following. The value of γ is related to the Si–3s character by eqn. (4) that has been

$$\gamma = \arccos\{(1 - s)/[0.5(2s + 1)(s + 2)]^{\frac{1}{2}}\} \qquad (4)$$

obtained from the equation derived by Coulson[25] in terms of the ∠YSiY angle. Table 2 shows that also for α-Me and -$SiMe_3$ substituents there is no accord between the structural information obtained from EPR data and from *ab initio* calculations since for $Me_3\dot{S}i$ and $(SiMe_3)_3\dot{S}i$ the value of γ estimated from the Si–3s character in the SOMO is much smaller than that determined at the UHF/TZP level. These findings confirm that the structural information obtained from eqn. (1) is unreliable and indicate that this is due to a major breakdown in orbital following.

As expected, the optimized UHF/TZP values of γ in the parent silanes indicate that in all the chlorosilanes the arrangement of atoms about silicon is essentially tetrahedral. This result is in contrast to the large variations in hybridization in the σ(Si–H) bonding MO with successive chlorine

Table 3 Theoretical (UMP2/DZP//TZP) and experimental ^{29}Si hfs constants (G) of $\mathrm{Y}_n\dot{\mathrm{S}}\mathrm{iMe}_{3-n}$ radicals

		$a(^{29}\mathrm{Si})$/G	
Y	n	Theory	Experiment
	0	−187.5	183[a]
Cl	3	−412.3	416[b]
	2	−301.9	308[b]
	1	−232.3	229[b]
$\mathrm{Me_3Si}$	3	−73.2	65[c]
	2	−107.8	90.3[d]
	1	−147.9	137[a]

[a] From ref. 27. [b] From ref. 28. [c] From ref. 29. [d] From ref. 1.

substitution estimated from eqn. (1) (Table 1). Indeed, Table 2 shows that the value of γ estimated for $\mathrm{Cl_3SiH}$ from eqn. (4) using the s-population of the σ(Si–H) bonding MO from eqn. (1) is much larger than that obtained with the *ab initio* calculation and does not correspond to a reasonable chemical structure since the chlorine atoms are predicted to be very close to each other, being anomalously shifted towards the C_{3v} axis. This confirms also that the structural information on silanes obtained from eqn. (1) is unreliable.

The present calculations suggest also that the smaller values of $a(^{29}\mathrm{Si})$ observed with α-trimethylsilyl substituents with respect to those expected from the linear correlation found between $a(^{29}\mathrm{Si})$ and $J(^{29}\mathrm{Si–H})$[6] are due at least in part to the decrease in the degree of pyramidalization at the radical centre caused by such a strong electron-releasing group.[26] In this connection, note that the present calculations and those performed on symmetrically α-substituted silyl radicals[8] show that all the other investigated α-substituted silyl radicals are essentially tetrahedral at the radical centre like the parent silanes. This is in line with the hypothesis that a good linear correlation between a and J should exist only when no significant structural changes occur on homolysis of the X–H bond.[3]

Theoretical hyperfine splitting constants

Isotropic ^{29}Si hfs constants have been computed at the optimized geometries at the UMP2/DZP level (UMP2/DZP//TZP). The computed values reported in Table 3 are in good agreement in absolute value with those obtained from the EPR spectra. In particular, the trend is very well reproduced. Interestingly, the experimental value for the tris(trimethylsilyl)silyl radical is well reproduced by the present calculations. Note that in previous work the experimental hfs constant was found to be significantly lower with respect to the theoretical value computed for the non-methylated derivative.[8] It was argued that the spin density delocalization onto the Si–C bonds as well as vibrational contributions from flatter geometries should reduce the hfs constant at the radical centre making it closer to the experimental value. The present calculations confirm this hypothesis and show that the reduction of the hfs constant is mainly due to the spin delocalization, the vibrational contribution estimated for the inversion motion about the radical centre being small (3.2 G) as found in the α-tris(trimethylsilyl)methyl radical.[9] The vibrational contribution has been estimated by averaging the computed hfs constants over the vibrational states of a double well potential using the procedure described in ref. 9. The following values have been employed for the parameters: $E_{\mathrm{inv}} = 1.53$ kcal mol^{-1}, $k_{\mathrm{m}} = 0.244$ au rad^{-2}, $\mu = 31.463$ au, $T = 203$ K.

Thus, the agreement between theory and experiment lends confidence to the local radical geometries determined at the UHF/TZP level and confirms that the large increments in $a(^{29}\mathrm{Si})$ observed experimentally when methyl groups are replaced successively by chlorine atoms are not due to a change of geometry at the radical site. This conclusion is in contrast with the tenet that in silyl radicals the magnitude of $a(^{29}\mathrm{Si})$ is strictly related to the geometry at the silicon radical centre.[1,6,27,30,31]

Conclusion

UMP2/DZP//TZP calculations reproduce very well the isotropic ^{29}Si hfs constant in α-Si and -Cl substituted methylsilyl radicals as previously found for other localized radicals. The large variations observed experimentally when methyl groups are replaced successively by chlorine atoms are due to the electronic influence of the α-substituent rather than to a structural change at the radical centre which remains essentially tetrahedral. On the other hand, the strongly electron-releasing trimethylsilyl group decreases slightly the pyramidality at the radical centre. It has also been shown that the linear relations previously found between the Si–3s contribution to the SOMO and to the σ(Si–H) bonding MO of the parent silanes [eqn. (1)] provide unreliable structural information both on silyl radicals and on their parent silanes.

References

1 C. Chatgilialoglu, A. Guerrini and M. Lucarini, *J. Org. Chem.*, 1992, **57**, 3405.

2 H. Fischer, in *Free Radicals*, ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 19; M. C. R. Symons, *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, Van Nostrand Reinhold Co., Melbourne, 1978.

3 W. T. Dixon, *Theor. Chem. Acta*, 1966, **6**, 359.

4 A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. A*, 1971, 124.

5 A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold and B. P. Roberts, *Mol. Phys.*, 1973, **25**, 989.

6 A. Hudson, R. A. Jackson, C. J. Rhodes and A. L. Del Vecchio, *J. Organomet. Chem.*, 1985, **280**, 173.

7 B. P. Roberts and K. M. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1111.

8 M. Guerra, *J. Am. Chem. Soc.*, 1993, **115**, 11 926.

9 M. Guerra, *J. Phys. Chem.*, 1995, **99**, 81.

10 M. Guerra, *Chem. Phys. Lett.*, 1995, **237**, 61.

11 M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, GAUSSIAN 92, Revision C, Gaussian, Inc., Pittsburgh PA, 1992.

12 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

13 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.

14 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265, 3269.

15 K. B. Wiberg, C. M. Hadad, T. J. Le Page, C. R. Breneman and M. J. Frisch, *J. Phys. Chem.*, 1992, **96**, 671.

16 R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 4244.

17 T. H. Dunning and J. P. Hay, in *Methods of Electronic Structure Theory*, ed. H. F. Schaefer III, Plenum Press, New York, 1976, ch. 1.

18 I. Carmichael, *J. Phys. Chem.*, 1994, **98**, 5044.

19 J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.*, 1987, **87**, 5968.

20 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

21 A. Rastelli and S. A. Pozzoli, *J. Mol. Struct.*, 1973, **18**, 463.

22 D. M. Schrader and M. Karplus, *J. Chem. Phys.*, 1964, **40**, 1593.

23 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

24 M. N. Paddon-Row and K. N. Houk, *J. Am. Chem. Soc.*, 1981, **103**, 5046.

25 C. A. Coulson, *Volume Commemoratif Victor Henry, Contribution a l'Etude de la Structure Moleculaire*, Desoer, Liege, 1948, p. 15.

26 L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.
27 S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson and K. D. J. Root, *J. Chem. Soc. A*, 1970, 348.
28 C. Hesse, N. Leray and J. Roncin, *J. Chem. Phys.*, 1972, **57**, 749.
29 J. Cooper, A. Hudson and R. A. Jackson, *Mol. Phys.*, 1972, **23**, 209.
30 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938.
31 A. Alberti and G. F. Pedulli, *Rev. Chem. Intermediates*, 1987, **8**, 207.

Paper 5/00854I
Received 13*th February* 1995
Accepted 1*st May* 1995