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An Electron Spin Resonance Study of Silacyclopentyl and Related Radicals

Richard A. Jackson* and Antonios K. Zarkadis†
School of Chemistry and Molecular Sciences, University of Sussex, Brighton

Silacyclopentyl radicals, prepared by γ-irradiation of silacyclopentane in an adamantane matrix, exist at low temperatures in two equivalent twist conformations, which interconvert at higher temperatures. The temperature variation of the ESR spectrum gives the barrier to interconversion as 21.3 kJ mol^{-1}. Reversible hydrogen exchange with $[^2H]_{16}$adamantane takes place near room temperature but not at lower temperatures. 1-Methylsilacyclopentyl in solution or in adamantane appears to be similar, to silacyclopentyl at high temperatures, but there is some evidence that an envelope conformation may be preferred. 1-Deuteriosilacyclopentyl, 1-chlorosilacyclopentyl and 3,3-dichloro-3-silacyclopentyl radicals have also been studied.

In conformational studies of free radicals, 5-ring compounds have structures with considerable conformational restrictions, but relatively small ring strain. We report here[1] our results on silacyclopentyl and related free radicals in adamantane and $[^2H]_{16}$adamantane matrices.

Results and Discussion

Silacyclopentyl radicals were prepared at −196 °C by γ-irradiation of silacyclopentane in adamantane. The ESR spectrum at 15 °C (Figure 1) consisted of a doublet (23.4 G)‡ and three triplet splittings (7.4, 5.7 and 1.6 G) with a further possible triplet of *ca.* 0.3 G buried in the line width. Silicon satellites were observed, corresponding to $a(^{29}Si) = 181.1$ G. The spectrum is very temperature dependent: at −135 °C (spectrum very similar to that shown for −119 °C in Figure 1), we still observe a doublet coupling of 23.3 G, but the best analysis of the other couplings[2] is in terms of doublets of 11.2, 7.3, 4.5, 3.7 and 3.6 G, with further possible couplings of <1 G buried in the line shape. $a(^{29}Si)$ is slightly higher (182.1 G at −119 °C) than at room temperature.

The doublet pattern at low temperatures strongly indicates a twisted conformation for the radical (**1a**) or (**1b**), Figure 2, in agreement with the structure shown by electron diffraction and microwave spectroscopy for the parent silacyclopentane.[3] The alternative 'envelope' conformations (**2a, b**; R = H) would give triplet splittings at all temperatures for the pairs of equivalent C–H protons. At high temperatures, the twisted conformations (**1a**) and (**1b**) would interconvert, so that all the couplings attributable to β and γ protons would become triplets. The assignment of individual proton coupling constants shown takes account of the need for the couplings of interconverting protons to average to the high temperature triplet splittings, and is assisted by an UMINDO[4] calculation. Our previous studies[5] on silacyclobutyl showed that the fully optimized geometry of both the radical and the parent silane were too planar, so we constrained the geometry to the electron-diffraction values for the silane, allowing only the Si–H bond length and associated bond angles to vary. A similar approach here kept the bond lengths and bond angles fixed as in the parent silacyclopentane,[3] allowed the twist angles of the C–H protons to vary in pairs, fixed the twist angles 4,2,1,3 and 5,3,1,2 at 13.3°, and allowed the Si–H bond length and associated bond and twist angles to vary.

The largest and effectively invariant proton coupling of 23.3 G was assigned to the Si–H coupling. This is somewhat larger than the Si–H coupling observed for the dimethylsilyl radical[6] and is confirmed by analysis of the ESR spectrum of the corresponding α-deuteriated radical $\overline{\mathrm{CH_2[CH_2]_3Si}}\mathrm{D}\cdot$ which gave a low temperature spectrum analysable in terms of doublets of 11.5, 7.5, 4.7, 3.5 and 2.5 G, with a deuterium 1:1:1 triplet of 3.7 G. The a_H/a_D ratio of 6.3 agrees well with the calculated value of 6.514 based on the magnetogyric ratio[7] γ_H/γ_D, and the assignment is confirmed by comparison of the autocorrelograms of the protiated and deuteriated radicals; a technique[8] which allows establishment of the coupling of a particular proton without full analysis of the spectrum.

The large low-temperature doublet splitting of 11.2 G was assigned to H_6 in (**1a**) (Figure 2). The twisting motions which would convert a planar structure into (**1a**) would increase the β-proton/SOMO twist angle 6,2,1,15 from *ca.* −120 to −133° whilst the corresponding angle 9,3,1,15 would be reduced from *ca.* 120 to 107°. The movement towards 180° in the twist angles should increase the spin density on the proton as is shown by the UMINDO calculation. To give the correct average at high temperatures, the H_9 coupling was assigned as 3.7 or 3.6 G. H_7 was assigned to the larger coupling (7.3 G) of the 'nearly-eclipsed' β-protons. The calculated spin density is larger, and the twist angle 7,3,1,15 is smaller (−7°) than at the corresponding H_8 (twist angle −20°). Our results therefore accord with an angular dependence of β-proton coupling constants with a maximum value of the coupling constant that corresponds to a dihedral angle H–C–Si–• of 180°, with a smaller maximum at 0° and minimum values in the region of 60–90°; UMINDO and *ab initio* calculations on $CH_3SiH_2\cdot$ accord with this.[9]

The remaining low temperature doublet must be ascribed to just one of the γ-protons. The UMINDO calculations showed that the spin density on H_{13} is three times greater than on H_{12}, with negligible values at H_{10} and H_{11}. The dihedral angle 15,1,5,13 is −14°, not optimal for a long range interaction (W-arrangement), but better than the value of 32° for the corresponding twist angle to H_{10} (15,1,4,10). The observation that the high temperature triplet splitting of 1.6 G was less than half the 3.6 or 3.7 doublet splitting suggests that the small, hidden coupling to H_{10} is of opposite sign to the H_{13} coupling. Although the calculated UMINDO annihilated spin density at H_{10} is very small (−0.000 025) it is of opposite sign to that at H_{13} (0.004 972).

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† *Present address:* Department of Chemistry, University of Ioannina, Greece.

‡ 1 G = 10^{-4} T.

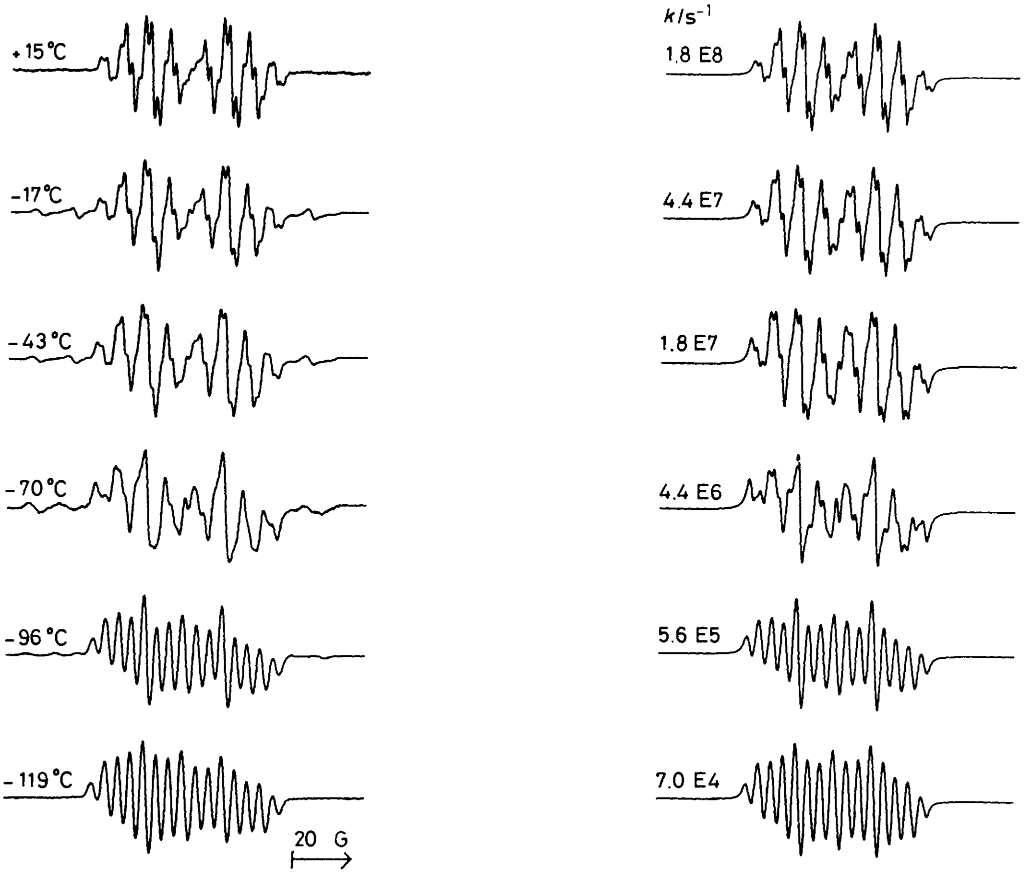


Figure 1. Temperature variation of the ESR spectrum of silacyclopentyl in adamantane.

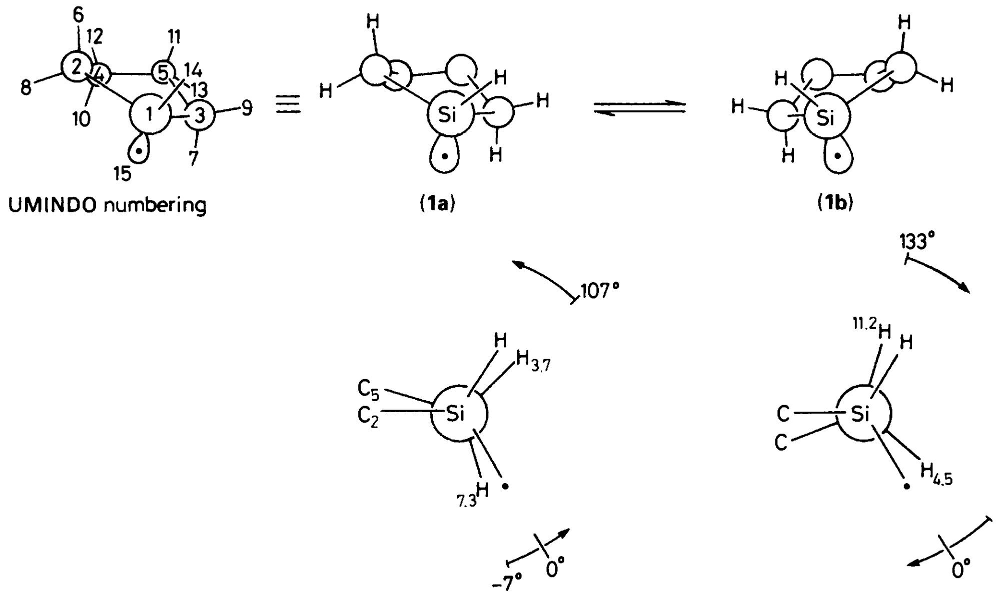


Figure 2. Conformational interchange in silacyclopentyl radicals. Numbering scheme is for UMINDO calculations on conformation (**1a**). Newman projections are down the Si–C_3 bond in (**1a**) and show the variation of coupling constants (*G*) with twist angle.

The 29-silicon coupling constant (182.1 G at −119 °C) is in the normal range for silicon-centred radicals. We have shown that there is a linear relationship between $a(^{29}Si)$ for the radical and $J(^{29}Si–H)$ for the corresponding silane.[10] $J(^{29}Si–H)$ for silacyclopentane is 190.8 Hz, which gives 186.1 G as the predicted value for $a(^{29}Si)$ in the radical. We have argued that if the observed value is smaller than the calculated value, this is an indication that delocalization is important in the radical, and we have observed such differences in chlorine and silicon substituted radicals[10] and in silacyclobutyl.[5] The difference here is more modest, but may be connected with the small coupling to one of the γ-protons, resulting in a slight reduction in spin density at silicon.

Temperature Dependence of the ESR Spectra.—Silacyclopentyl. Figure 1 shows the ESR spectra of the silacyclopentyl radical at six temperatures between −119 and +15°, along with modified Bloch equation[11] simulations based on the low temperature (−135 °C) coupling constants, and a single kinetic process for interconverting pairs of protons. A straight line Arrhenius plot was obtained, giving $\log_{10}(A/s^{-1}) = 12.1 \pm 0.1$ and $E = 21.3 \pm 0.4$ kJ mol^{-1}. The A factor is within the range found for the temperature dependence of a number of 1-substituted cyclopentyl radicals.[12] The activation energy for the silacyclopentyl interconversion is significantly higher than for cyclopentyl[12] (5.4 kJ mol^{-1}) but only slightly higher than the value of the 16.9 kJ mol^{-1} found by microwave studies of silacyclopentane itself,[13] in line with our supposition of similar geometries for the radical and the parent molecule.

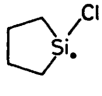
1-*Methylsilacyclopentyl.* Methylsilacyclopentane was the only compound in this series from which we were able to observe the ESR spectrum of the radical by photolysis of the silane with t-butyl peroxide. At −42 °C, the spectrum showed the methyl quartet (6.3 G) along with triplet splittings of 6.1, 4.7 and 1.5 G. At −100°, the lines became broader, but the low temperature 'frozen' conformation was not achieved. In an adamantane matrix at −47 °C, similar splittings were observed: a quartet of 6.1 G and triplets of 6.3, 4.1, and 1.5 G [*n.b.* in these spectra, the quartet and the largest of the triplet assignments could be reversed], with silicon satellites corresponding to $a(^{29}\mathrm{Si}) = 179.9$ G.

The failure of the spectrum to change at low temperatures to one based on doublets from individual protons, as is the case for silacyclopentyl itself, may indicate a preference for the 'envelope' conformation. In an adamantane matrix, this conformation (**2a**: R = CH_3) should fit the near-spherical adamantane cavity better than the twist conformation analogous to (**1a**) or (**1b**). The ^{29}Si coupling constant is slightly lower than in silacyclopentyl, which may indicate a marginal increase in delocalization in the 1-methylsilacyclopentyl radical.

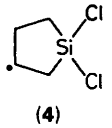
1-*Chlorosilacyclopentyl* (**3**). This radical was prepared by irradiation of 1-chlorosilacyclopentane in adamantane at −47 °C. The spectrum consists of a 1 : 1 : 1 : 1 quartet of relatively broad lines, which corresponds to $a(^{35}\mathrm{Cl}) = 8.3$ G. No proton coupling was observed, though small couplings could have been hidden in the line shape. The radical was established as a silicon-centred radical by the clearly visible ^{29}Si satellites which give $a(^{29}\mathrm{Si}) = 226.1$ G. The increase in this splitting compared with values in the region of 180 G for organosilyl radicals was expected as electronegative substituents make the radicals more pyramidal and increase the s character of the SOMO. $a(^{29}\mathrm{Si})$ values of 215 G or 229 G have been reported in matrix studies[14] of $Me_2\dot{Si}Cl$ at −88 °C.

3,3-*Dichloro*-3-*silacyclopentyl* (**4**). Irradiation of 1,1-dichlorosilacyclopentane in $[^2H]_{16}$ adamantane at −82 °C showed that hydrogen abstraction to give (**4**) rather than chlorine abstraction to give (**3**) had taken place, in contrast to the chlorine abstraction observed[14] for $(CH_3)_{4-n}SiCl_n$. Coupling constants were $a(\alpha\text{-H}) = 21.9$ G (doublet) and two triplets of 30.4 and 31.6 G which correspond to the two pairs of β-protons made non-equivalent by the 3-silicon substituent. For comparison, the cyclopentyl radical shows $a(\alpha\text{-H}) = 20.25$ G, $a(\beta\text{-H}) = 31.6$ G [quintet][12] in adamantane at −58 °C. The alternative radical formed by hydrogen abstraction from the C–H bonds adjacent to the silicon atom was not observed.

(**2a**) (**2b**)



(**3**)



(**4**)

1-*Phenyl- and* 1-*t-butyl-silacyclopentyl radicals.* These were not identified when the parent silanes were irradiated in adamantane matrices. Broad unresolved spectra were obtained: these bulky substituents probably prevent the radicals from tumbling freely.

Exchange of Hydrogen with the Matrix.—When irradiated samples of silacyclopentane in $[^2H]_{16}$adamantane were allowed to warm to room temperature, the ESR spectrum changed from silacyclopentyl to 1-deuteriosilacyclopentyl. Similarly, for a sample of 1,1-dideuteriosilacyclopentane in $[^1H]_{16}$adamantane, the 1-deuteriosilacyclopentyl spectrum changed to that of the protiated radical on warming. On cooling, the normal temperature variation of the new radical was observed: there was no reversion to the original radical.

We interpret these changes as due to reversible hydrogen or deuterium exchange reactions between adamantane matrix molecules and the silicon radical centre according to equation (1). Si–H bonds are weaker than C–H bonds, so that abstraction of hydrogen by a silicon-centred radical from an adamantane molecule will be endothermic, have a substantial activation energy, and therefore only take place at higher temperatures. The reverse reaction will always be more favourable, leading to deuterium (or hydrogen) incorporation at the silicon centre.

$$\mathrm{C_4H_8\dot{S}iH + C_{10}D_{16} \rightleftharpoons C_4H_8SiHD + C_{10}\dot{D}_{15} \rightleftharpoons C_4H_8\dot{S}iD + C_{10}D_{15}H} \quad (1)$$

These reactions appear to be localised and do not appear to lead to extensive exchange of hydrogen or deuterium atoms in organosilicon hydride molecules away from the original radical centre: when a sample of $\overline{\mathrm{CH_2[CH_2]_3Si}}\mathrm{D_2}$ in adamantane was irradiated at −196 °C, warmed to room temperature to convert the deuteriated into the protiated silacyclopentyl radical, further heated to destroy the radical, then cooled and re-irradiated, the deuteriated radical was seen once again. Thus there is no extensive migration of radical centres in the matrix by a sequence involving alternately rotation of the adamantyl radical and hydrogen abstraction from a new adamantane molecule.

In principle, the procedure of irradiation of an organosilicon hydride in $[^2H]_{16}$ adamantane followed by warming can be used as a general method of making deuteriated silyl radicals without the need to synthesize deuteriated precursors. In practice, not all organosilyl radicals undergo exchange as completely as does silacyclopentyl: small differences in bond energies and conformations in the matrix cavities can have a strong influence on the rates of the exchange reactions.

Experimental

1,1-Dichlorosilacyclopentane, 1-methylsilacyclopentane and silacyclopentane were prepared by West's method;[15] the other silacyclopentane compounds were prepared analogously. All compounds had purity >99% by GC. Silacyclopentane had δ($CDCl_3$) 0.67 (4 H, m), 1.46 (4 H, m), and 3.62 [2 H, apparent quintet, SiH_2, $J(^{29}Si\text{–}H) = 190.8$ Hz].

1,1-Dideuteriosilacyclopentane was prepared by reduction of 1,1-dichlorosilacyclopentane (5.6 g, 36.3 mmol) with $LiAlD_4$ (1.5 g, 35.7 mmol), (1.7 g, 53%), b.p. 73–74 °C, δ(CCl_4) 0.78 (4 H, m, CH_2-SiD_2) and 1.58 (4 H, m, CH_2-CH_2).

1-Chlorosilacyclopentane was made from $Br(CH_2)_4Br$ (69.5 g, 0.32 mol), Mg (16.8 g, 0.69 mol) and $HSiCl_3$ (41.3 g, 0.30 mol), (12.1 g, 33%), b.p. 63–65 °C (130 mmHg), δ(CCl_4) 0.98 (4 H, m, CH_2Si), 1.63 (4 H, m, CH_2CH_2), and 5.00 (1 H, m, SiH).

1-Chloro-1-phenylsilacyclopentane was made from $Br(CH_2)_4Br$ (20.0 g, 92.6 mmol), magnesium (5.0 g, 0.21 mol) and $PhSiCl_3$ (18.1 g, 85.6 mmol), (7.6 g, 42%), b.p. 109–111 °C (1 mm Hg), δ(CCl_4) 1.15 (4 H, m, CH_2Si), 1.79 (4 H, m, CH_2-CH_2), and 7.50 (5 H, m, Ph).

1-Phenylsilacyclopentane was made by reduction of 1-chloro-1-phenylsilacyclopentane (5.2 g, 26.4 mmol) with $LiAlH_4$ (0.4 g, 10.5 mmol) in dry THF, b.p. 57 °C (0.6 mmHg) (2.9 g 68%), (Found: C, 73.7; H, 9.0. $C_{10}H_{14}Si$ requires C, 74.00; H, 8.69%); δ(CCl_4) 0.89 (4 H, m, CH_2Si), 1.64 (4 H, m, CH_2CH_2), 4.40 (1 H, apparent quintet, SiH), and 7.16 (5 H, m, Ph).

1-t-Butylsilacyclopentane was prepared as follows. 1,1-Dichlorosilacyclopentane (15.0 g, 96.7 mmol) was allowed to react with t-butyl-lithium (100.7 mmol, 53 cm^3 of a 1.9 mol dm^{-3} solution in pentane), followed without isolation of 1-chloro-1-t-butyl-silacyclopentane[16] by reduction with $LiAlH_4$ (1.7 g, 44.8 mmol). Yield (5.3 g, 38%), b.p. 91 °C 120 mmHg) (Found: C, 67.2; H, 12.9. $C_8H_{18}Si$ requires C, 67.52; H, 12.75%); δ(CCl_4) 0.64 (4 H, m, CH_2Si), 0.92 [9 H, s, $C(CH_3)_3$], 1.54 (4 H, m, CH_2CH_2), and 3.78 (1 H, apparent quintet, Si–H).

Matrix samples of the above compounds in purified adamantane or perdeuterioadamantane were prepared[5,17] and γ-irradiated[5] to give the corresponding radicals. ESR measurements and computations were carried out as described previously.[10,18] UMINDO anihilated s spin densities/10^{-3} (numbering scheme as in Figure 1) were 1, 128; 2, 4; 3, 3; 4, 1; 5, 6; 6, 33; 7, 11; 8, 7; 9, 15; 10, −0.025; 11, −0.021; 12, 1; 13, 5; 14, 4. The temperature variation of the ESR of silacyclopentyl (Figure 1) was simulated using an invariant SiH coupling of 23.26 G and the following pairs of couplings/G: 11.21, 3.73; 7.28, 4.47; 3.62, −0.32; 0.96, −0.21, with the rate constants shown.

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