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A STUDY OF ELECTRON SPIN RESONANCE SPECTRA OF THE 1,1,2,2-TETRAMETHYLDISILANYL RADICAL(1)

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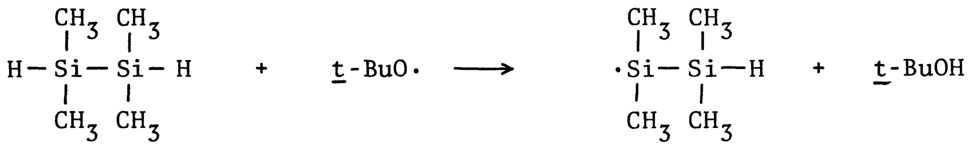
The title radical, $(CH_3)_2\dot{S}iSi(CH_3)_2H$, was generated by hydrogen abstraction from $H(CH_3)_2SiSi(CH_3)_2H$. The most stable conformation of the radical at low temperature deduced from the ESR spectrum is the one in which the β-Si-H bond eclipses the p orbital on the silyl radical site.

During a study on silyl radicals,(2) especially in an effort to evaluate β-SiH hyperfine coupling constants (hfcc) of silyl radicals, we found an interesting example of a radical with a preferred conformation in which the β-SiH bond occupies an eclipsed position relative to the half-filled silicon p orbital.

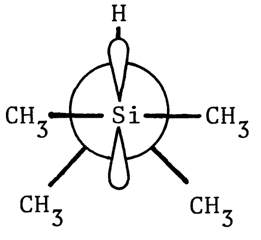
Irradiation of a mixture of 1,1,2,2-tetramethyldisilane(3) and di-t-butyl peroxide (with cyclopropane as a solvent at temperature lower than -50°C) in an esr cavity gave a well-resolved esr spectrum of the 1,1,2,2-tetramethyldisilanyl radical



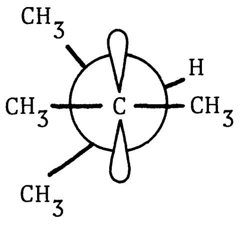
$$H(CH_3)_2Si-Si(CH_3)_2H + \underline{t}\text{-BuO}\cdot \longrightarrow \cdot Si(CH_3)_2-Si(CH_3)_2H + \underline{t}\text{-BuOH}$$

Its esr spectrum at -70°C consists of an octet of septet (7.79 and 0.25 G) with a g factor of 2.00375, and the septet can be assigned to the six protons of the β-$SiCH_3$ groups. The octet should be ascribed to six α-$SiCH_3$ protons and one SiH proton with equal hfcc.(4) This fact appears very interesting, since in spite of the Si-Si bond length longer than Si-C, spin delocalization from the half-filled orbital of the silicon atom onto the β-SiH group is comparable to that onto the β-CH group. However, the hfcc of the β-SiH showed a marked temperature dependence, while almost constant hfcc values were observed for both β-CH and γ-CH in the temperature range studied (Table I). Thus, values of the hfcc for β-SiH increase as the temperature is lowered. Figure 1 shows the temperature dependence of $a_{\beta\text{-SiH}}$ and $a_{\beta\text{-CH}}$ carefully determined by computer simulation.

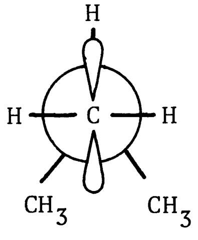
The temperature-dependent behavior of the hyperfine splitting pattern shows that the most stable conformation of this radical is the one in which the β-silicon-hydrogen bond essentially eclipses the p orbital on the silyl radical-site as shown in (I), while the CH_3 groups are rotating freely in this temperature range. Incidentally, disilanyl radicals are considered to be planar or quasi-planar from esr$^{5,6)}$ and chemical$^{7,8)}$ evidences. Absence of any selective line broadening in this radical is also consistent with (I), since in a symmetrical equilibrium conformation such as (I), α-CH_3 protons are magnetically equivalent.



(I)



(II)



(III)

It is interesting to compare the present findings with those for the 1,1,2-trimethylpropyl radical, $(CH_3)_2\dot{C}C(CH_3)_2H$,$^{9)}$ and the isobutyl radical, $H_2\dot{C}C(CH_3)_2H$.$^{10)}$ From the relative magnitudes of the β-coupling constants, the equilibrium conformations (II) and (III), respectively, were inferred for these radicals.

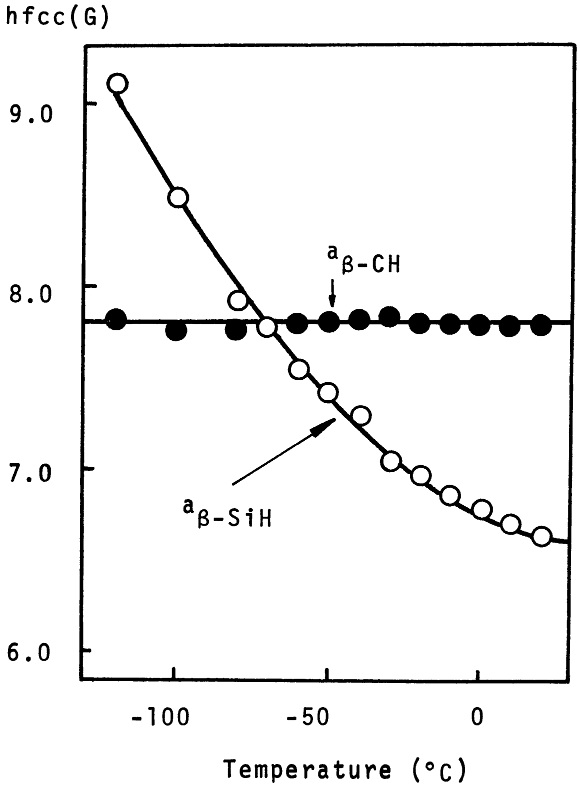
One of the most important factor to sustain the conformation (I) in this radical is apparently the long Si-Si bond length (2.34 Å) compared to the C-C bond (1.54 Å). Lesser nonbonded interactions between α and β methyl groups allow the $(CH_3)_2\dot{S}iSi(CH_3)_2H$ radical to take the eclipsed conformation without serious steric hindrance. However, this factor alone is not sufficient for favoring the conformation (I). Since both (p-p)$^{11)}$ and (p-d)$^{12)}$ homoconjugations observed for heteroatom-substituted ethyl radicals are impossible, the equilibrium conformation of the radical should be caused by hyperconjugation between the β-SiH bond and the p orbital on silicon.

Table I. Temperature Dependence of Hyperfine Coupling Constants of the 1,1,2,2-Tetramethyldisilanyl Radical

Temp. °C	Hyperfine Coupling Constants, G $a_{\beta\text{-CH}}$	$a_{\beta\text{-SiH}}$	$a_{\beta\text{-SiMe}}$
20	7.79	6.63	0.30
10	7.80	6.71	0.30
0	7.80	6.78	0.30
-10	7.82	6.87	0.30
-20	7.81	6.97	0.30
-30	7.85	7.05^{5}	0.30
-40	7.83	7.30	0.30
-50	7.83	7.43	0.29
-60	7.80	7.55^{5}	0.29
-70	7.79	7.79	0.25^{5}
-80	7.77	7.93	0.26^{5}
-100	7.77	8.50^{5}	0.23^{5}
-120	7.83	9.14	——

Figure 1.

Temperature dependence of $a_{\beta\text{-CH}}$ and $a_{\beta\text{-SiH}}$ of the $\dot{S}i(CH_3)_2Si(CH_3)_2H$ radical.



The ability of the β-SiH group to sustain the eclipsed conformation is not restricted to the silyl radical under consideration. A similar conformation analogous to the isobutyl radical (III) was also found for $\dot{\mathrm{C}}\mathrm{H_2Si(CH_3)_2H}$ radical,[13] in which hfcc of the β-SiH increased from 13.78G at +20°C to 15.24G at -120°C.

Acknowledgment

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4) For $\mathrm{Me_3Si\dot{S}iMe_2}$[5] $a_{\alpha\text{-}\mathrm{SiCH_3}}$=8.21G, $a_{\beta\text{-}\mathrm{SiCH_3}}$=0.47G, g=2.0037, and for $\mathrm{Me_3Si\dot{S}iMeH}$[6] $a_{\alpha\text{-}\mathrm{SiCH_3}}$=8.15G, $a_{\beta\text{-}\mathrm{SiCH_3}}$=0.30, g=2.0037.

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