

Configurations of silicon-centred radicals: the bis(trimethylsilyl)silyl radical

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Abstract

ESR data for the bis(trimethylsilyl)silyl radical are reported. Comparison of the hyperfine coupling constants of this radical with those for other silyl radicals indicates that the configuration is more pyramidal than expected.

The configurations of silicon-centred radicals have been the subject of many experimental and theoretical investigations. All experimental work on silyl itself shows it to be pyramidal [1–5], in contrast with methyl which is planar [3,4,6–12]. Chemical evidence for the non-planarity of silicon centred radicals is provided by the fact that Me-1-NpPhSi[•] radicals undergo a number of reactions with substantial retention of configuration [13–15]; a more recent paper [16] gives an estimate of the barrier to inversion for this radical of 5.6 kcal/mol on the basis of data of Sommer and Ulland [17] for the reaction of Me-1-NpPhSiH with varying concentrations of carbon tetrachloride. Silicon-centred radicals with an α -proton are of particular interest, since the α -(Si–H) coupling constant provides an additional probe for the geometry of the radical. We report here our results on the bis(trimethylsilyl)silyl radical.

Experimental

ESR spectrum of the [(CH₃)₃Si]₂SiH radical. The parent silane was photolysed with di-*t*-butyl peroxide in the cavity of the ESR spectrometer at –40 °C. The spectrum was recorded using a 200 G scan width, and the regions to the left and to the right of the main pattern were recorded at higher gain.

The central region of the spectrum was contaminated by an intense signal which we were unable to remove completely by our “chopping” technique [18] in which intermittent illumination is coupled with inversion of the spectrometer output and the spectrometer response is damped by the use of a relatively long time constant: this often eliminates signals due to persistent radicals.

Since this contaminating central peak interfered with an optimisation of the coupling constants of the radical of interest by use of the correlation technique MATCH [19], we adopted the procedure of manually checking the digital numbers of the spectrum to determine the range of points over which the contaminating peak was recorded. We then set the value of each of these points to zero; with the central peak removed in this way, we were now able to optimise the analysis of the desired radical, giving: 1(H) 11.07 G, and 18(H) 0.52 G. Because of the presence of the persistent radical and its prominent ^{29}Si satellites, we were unable to obtain unequivocally the positions of the $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{H}$ satellite lines by correlation techniques [19,20].

The persistent radical showed no resolvable proton hyperfine structure. Its centre was situated 1.53 G downfield of the $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{H}$ radical, corresponding to a g -value greater by 0.0010. The clearly visible ^{29}Si satellites give $a(^{29}\text{Si})$ 63.2 G. The tentative assignment of this radical as $[(\text{CH}_3)_3\text{Si}]_3\dot{\text{S}}\text{Si}[\text{Si}(\text{CH}_3)_3]$ is discussed below.

1,1,1,3,3,3-Hexamethyl-2,2-diphenyltrisilane. Dichlorodiphenylsilane (30 g, 0.12 mol) and trimethylchlorosilane (40 g, 0.37 mol) in cyclohexane (100 ml) were added during 30 minutes to molten potassium metal (18 g, 0.46 mol) in refluxing cyclohexane (300 ml), with stirring. The mixture was refluxed for a further 2 h, after which an intense blue precipitate was present. The mixture was filtered under nitrogen, and the cyclohexane evaporated from the filtrate. The residue was distilled under vacuum to give 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane (27 g, 69%), b.p. 109°C at 0.3 mmHg.

2,2-Dichloro-1,1,1,3,3,3-hexamethyltrisilane. 1,1,1,3,3,3-Hexamethyl-2,2-diphenyltrisilane (27 g, 0.082 mol) was added to ice-cold concentrated sulphuric acid (66 g), dropwise with vigorous stirring over 30 minutes. After a further 15 min stirring, ammonium chloride (13.2 g, 0.25 mol) was added in several portions. The organic layer was separated, and was then distilled under vacuum, to form 2,2-dichloro-1,1,1,3,3,3-hexamethyltrisilane (4.5 g, 22%), b.p. 42°C at 0.3 mmHg. $\delta(\text{CDCl}_3)$ 0.22(s) ppm.

1,1,1,3,3,3-Hexamethyltrisilane. 2,2-Dichloro-1,1,1,3,3,3-hexamethyltrisilane (4.5 g, 0.018 mol) was reduced with LiAlH_4 (1.0 g, 0.026 mol) in dry ether (50 ml) in the usual manner. The excess of the reagent was destroyed with water, and the ethereal layer was separated, dried, and distilled, to give 1,1,1,3,3,3-hexamethyltrisilane (3.1 g, 96%), b.p. 146°C , $\delta(\text{CDCl}_3)$ 0.19(9H, s, Me_3Si) and 2.54(2H, s, Si-H) ppm. $J(^{29}\text{Si}-\text{H})$ 166.8 Hz.

Results and discussion

The α -proton coupling in $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{H}$ is 11.1 G, and in connection with the radical geometry it is of interest to determine the sign of this coupling. Sharp and Symons [5] have noted that there is a broadening of the high field lines associated with the α -protons in the series of radicals: $(\text{CH}_3)_2\dot{\text{S}}\text{H}$, $\text{CH}_2\dot{\text{S}}\text{H}$, $\dot{\text{S}}\text{H}$, and, from their observation that $g_{\parallel} < g_{\perp}$, they infer that the α -proton couplings must be positive. We observe that the low field group of lines associated with the α -proton in the $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{H}$ radical are broadened, and therefore, since the signs of the various contributions to the linewidths [21] other than that due to the isotropic α -proton hyperfine coupling are likely to be the same in both this radical and in the

Table 1
Comparison of coupling constants for silicon centred radicals (G)

Radical	$a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(^{29}\text{Si})$
$[(\text{CH}_3)_3\text{Si}]_3\text{Si}$	–	–	65 ^a
$[(\text{CH}_3)_3\text{Si}]_2\text{SiCH}_3$	–	9.36 ^a	71 ^a
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2$	–	8.21 ^a	137 ^a
$(\text{CH}_3)_3\text{SiSiHCH}_3$	16.30 ^c	8.15 ^c	
$[(\text{CH}_3)_3\text{Si}]_2\text{SiH}$	11.1 ^b	–	
$[(\text{CH}_3)_3\text{C}]_3\text{Si}$	–	–	163 ^e
$(\text{C}_2\text{H}_5)_3\text{Si}$	–	5.69 ^d	170 ⁱ
$(\text{CH}_3)_3\text{CSi}(\text{CH}_3)_2$	–	6.4 ^f	175 ^f
SiH_3	7.84 ^c	–	190 ^g
	7.96 ^d		
CH_3SiH_2	12.11 ^c	8.21 ^c	181 ^d
	11.82 ^d	7.98 ^d	
$(\text{CH}_3)_2\text{SiH}$	17.29 ^c	7.30 ^c	183 ^d
	16.99 ^d	7.19 ^d	
$(\text{CH}_3)_3\text{Si}$	–	6.28 ^d	181 ^d
	–	6.34 ^c	183 ^c
$(\text{CH}_3)_2\text{SiCl}$	–	5.2 ^h	229 ^h

^a From ref. 22. ^b This work. ^c Ref. 1. ^d Ref. 2. ^e Ref. 23. ^f Ref. 20. ^g Ref. 4. ^h Ref. 24. ⁱ Ref. 19.

above silyl radicals, we must assign a negative sign to this α -proton coupling in order to fit the linewidth asymmetry.

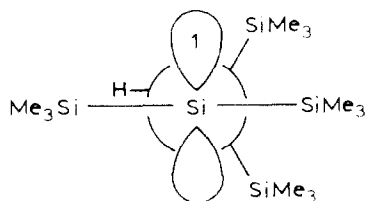
It is of interest to consider why this coupling should be smaller than the 16.3 G α -proton coupling in the $(\text{CH}_3)_3\text{SiSiHCH}_3$ radical, to which a negative sign must also be ascribed by the following comparison with the data for the other radicals in Table 1.

Silicon substituents are believed to cause an increase in the planarity of the radical centre, as evidenced by the fall in the ^{29}Si couplings as alkyl or hydrogen substituents are replaced by $(\text{CH}_3)_3\text{Si}$ groups [23]; this is mirrored by the increase in the methyl proton couplings through the series: $(\text{CH}_3)_3\text{Si}$, $(\text{CH}_3)_2\text{SiH}$, $(\text{CH}_3)_3\text{SiSiHCH}_3$, $[(\text{CH}_3)_3\text{Si}]_2\text{SiCH}_3$. Therefore, the $(\text{CH}_3)_3\text{SiSiHCH}_3$ radical must be more planar than the methyl-substituted silyl radicals, for which the positive α -proton couplings fall in absolute magnitude while their β -proton couplings increase as the radicals become more planar. We must therefore accommodate the 16.3 G α -proton coupling in $(\text{CH}_3)_3\text{SiSiHCH}_3$ by giving it a negative sign.

From the coupling constants collated in the Table, we conclude that the $(\text{CH}_3)_3\text{Si}$ substituted silyl radicals increase in planarity in the following order: $[(\text{CH}_3)_3\text{Si}]_2\text{SiH} > (\text{CH}_3)_3\text{SiSiHCH}_3 > (\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2 > [(\text{CH}_3)_3\text{Si}]_2\text{SiCH}_3 > [(\text{CH}_3)_3\text{Si}]_3\text{Si}$. The order of the first two radicals is incompatible with a balance between CH_3 substituents, which cause slight bending, and $(\text{CH}_3)_3\text{Si}$ substituents, which should increase the planarity of the radical centre on electronegativity grounds, and, additionally, reduce the ^{29}Si coupling by spin delocalisation. (This is likely to lead to a further increase in the planarity of the radical centre since partial Si=Si double bond character is introduced.) It therefore seems likely that there is a greater steric interaction between the Si- CH_3 group and the Si-Si $(\text{CH}_3)_3$ group than between two Si-Si $(\text{CH}_3)_3$ groups in spite of the smaller size of the methyl group,

because of the shorter C–Si bond. This effect will be enhanced in the $(\text{CH}_3)_3\text{Si}\dot{\text{S}}\text{i}(\text{CH}_3)_2$ radical, in which there are two such interactions.

Structure of the persistent radical We tentatively identify the persistent radical formed during the photolysis of a mixture of $[(\text{CH}_3)_3\text{Si}]_2\text{SiH}_2$ and t-butyl peroxide as $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{i}-\text{SiH}[\dot{\text{S}}\text{i}(\text{CH}_3)_3]_2$, formed by dimerization of the $[(\text{CH}_3)_3\text{Si}]_2\dot{\text{S}}\text{iH}$ radical followed by hydrogen abstraction. For a near-planar configuration at the silicon radical centre (cf. ref 23), the conformation shown should be favoured: the near 90° dihedral angle between the β -proton and the singly occupied orbital on silicon would account for the absence of an observable proton coupling. The ^{29}Si coupling constant is slightly smaller than that for $[(\text{CH}_3)_3\text{Si}]_3\dot{\text{S}}\text{i}$, in accord with the near-planarity expected for both radicals, and the g -shift is also in line with a silicon-centred radical with three silicon substituents. Steric crowding will make bimolecular self-reactions of this radical difficult, and account for its persistence.



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