Magnetic Non-equivalence in Organosilanes: Effects of Structure, Solvent, and Temperature

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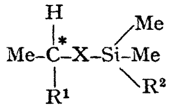
Summary The magnetic non-equivalence of *gem*-dimethyl groups for a series of asymmetric silanes and siloxy ethers is shown to be solvent and temperature dependent.

THE use of organosilicon substituted derivatives of organic and bio-organic molecules has extended the applications of g.c., m.s., and n.m.r. spectroscopy to the analysis and structural characterization of the often less tractible parent compounds.[1] That substitution of asymmetric molecules with suitable organosilicon groups could provide more detailed information about their structure and conformational behaviour was shown by recent studies of the magnetic non-equivalence of geminal groups in asymmetric carbon compounds.[2] Relatively few data exist for the corresponding systems containing hetero-atoms.[3,4] We report here the first systematic study of a series of asymmetric organosilicon compounds to determine which factors give rise to the observation of the magnetic non-equivalence of the *gem*-methyl groups in C*–$SiMe_2X$ molecules. We have also attempted to avoid the limitations of previous studies[2b] by considering a wide range of variables (temperature, solvent, concentration, and substituents.)

Magnetic non-equivalence of gem-*dimethyl groups*[a]



Compound	R^1	R^2	X	Δν ($SiMe_2$) (p.p.m.)
(1)	Et	Ph	CH_2	<0·008[b]
(2)	Ph	Ph	CH_2	0·049
(3)	Et	Ph	O	<0·008[b]
(4)	Ph	Ph	O	0·048
(5)	Ph	H	CH_2	<0·008[b,c]
(6)	Ph	H	O	0·089[c]
(7)	Ph	OMe	CH_2	<0·008[b]

[a] Spectra recorded on neat liquids at ambient temperature (60 MHz). [b] No separation observable at 60 or 100 MHz. [c] Resonances are doublets due to J(H–Si–Me) coupling.

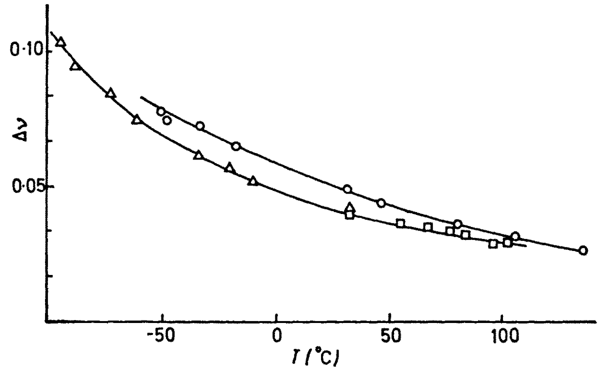


FIGURE. *Temperature dependence of the chemical shift non-equivalence of the* $SiMe_2$ *resonances of* Ph(Me)HC*CH_2SiMe_2Ph *in* CS_2 (△), CCl_4; (□), *and* [$^2H_8$]*toluene* (○) (*in* p.p.m.).

The choice of –$SiMe_2X$ substituents was based on two considerations (i) the non-equivalent methyl groups give rise to sharp singlet resonances (except when X = H), and (ii) the signals appear in a convenient and characteristic region of the spectrum.

The results (Table) show a marked dependence on the substituents on the asymmetric carbon, on the silicon, and on the intervening group. The presence of three substantially different groups at the asymmetric carbon enhances the observed non-equivalence under these conditions [compare (**1**) and (**3**) with (**2**) and (**4**)]. In all cases the trimethylsilyl analogues (R^2 = Me) gave a single sharp resonance line for all nine $SiMe_3$ protons.

The temperature and solvent dependence of the spectrum of (**2**) (Figure) demonstrate the importance of these factors in this system. No evidence for the appearance of separate rotamers could be detected at the lowest temperatures studied although some broadening of the signals at low temperatures did occur. The solvent effect is considerable at ambient temperature (*ca.* 16% greater for [$^2H_8$]toluene than for CS_2 or CCl_4), but the trends noted in the various solvents are similar. In particular, the values of $\Delta\nu$ converge at higher temperatures. This value of $\Delta\nu$, which is a measure of the intrinsic dissymmetry, is expected to be equal for the same compound in different solvents if specific solvent effects on the chemical shifts are minimal at the high temperature limit of equal conformer populations.

Raban[5] has indicated, however, that in the absence of the low temperature spectra of the individual rotamers, conclusions as to conformational preferences based on intrinsic dissymmetry may be fortuitous.

Inspection of resonances due to the intervening CH_2 group of (**2**) in [$^2H_8$]toluene solution reveals that the methylene protons are non-equivalent, giving rise to a strongly coupled AB pattern which is further split by the proton on the asymmetric carbon. The non-equivalence of the CH_2 protons, which is quite solvent dependent, increases with increasing temperature although the complexity of the resonances precludes a detailed analysis at present.

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