

HEXAMETHYLDISILANE — A CONVENIENT SOLVENT AND SECONDARY ^1H -NMR REFERENCE

J. SCHRAML

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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Hexamethyldisilane (HMDSS) can be used as a solvent and at the same time it can serve as a convenient substitute for tetramethylsilane, the volatile standard NMR reference compound. The proton chemical shift of HMDSS is given in several solvents. The shift, though internally referenced, depends on the magnetic susceptibility of the solvent.

The standard NMR reference compound, tetramethylsilane (TMS), has several advantages over other reference materials. The advantages were listed by Tiers¹ when proposing this reference in 1958. In the following years the advantages have been tested (for a review see²) and TMS has gained the universal acceptance though other, secondary, reference compounds were suggested for special purposes (measurements in aqueous solutions, high-temperature work *etc.*²). It is especially the low boiling point of TMS, an advantage in removing it from samples in analytical applications, which coupled with its low specific gravity and surface tension makes its use in a quantitative work difficult and necessitates the use of ternary systems (solute, solvent, reference). As hexamethyldisiloxane (HMDSO) is much easier to handle it is frequently used instead of TMS. It is, however, much less inert than TMS and it is a recognized proton acceptor. These properties prohibit the use of HMDSO as a reference in solvent effect studies and in cases when association with the reference might affect the observed chemical shifts.

Following Cartledge and Riedel³ we found⁴ that ^{13}C — ^1H coupling constants exhibited reasonable Hammett-type correlation in silyl- and germyl-substituted toluenes only if hexamethyldisilane (HMDSS) was used as a solvent. Since then, HMDSS has been used frequently as a solvent and/or reference in ^1H -NMR work (both in routine analytical applications and nuclear Overhauser effect studies^{5,6}) in this laboratory. HMDSS retains some of the advantages of TMS (solubility, low reactivity, non-associative, and sharp NMR line at high field) while having considerably higher boiling point (b.p. 113°C). It is easy to prepare^{4,7} and is available commercially⁸. For these reasons HMDSS can be recommended as a secondary reference in proton NMR work.

High resolution NMR spectra of hexamethyldisilane (HMDSS) have been studied on several occasions; the most recent references include proton⁹⁻¹¹, carbon-13¹², and silicon-29^{12,13} NMR studies, references to earlier work can be found in a compilation^{7,14}. Here we report the chemical shifts for this reference measured in several solvents.

EXPERIMENTAL

The chemical shifts summarized in Table I were obtained on a modified Tesla BS 477 spectrometer operating at 60 MHz. The spectra were measured at $27.5 \pm 1^\circ\text{C}$. In the case of aprotic solvent the line of trifluoroacetic acid in a sealed capillary served as locking signal, in other cases the line of the solvent was used for the lock. Audio frequencies of both HMDSS and TMS lines were determined by an electronic frequency counter BM 445 in 50 Hz sweep-width spectra and the chemical shift calculated as the difference of the two frequencies. The indicated errors are root-mean-square deviations calculated from at least six measurements.

The solutions were prepared from Uvasol quality tetrachloromethane, chloroform, TMS, and cyclohexane (Merck), from pure acetonitrile (Lachema) and nitromethane (Xenon), and analytically pure benzene, dioxane and acetone (Lachema). HMDSS was obtained from PCR, Inc.

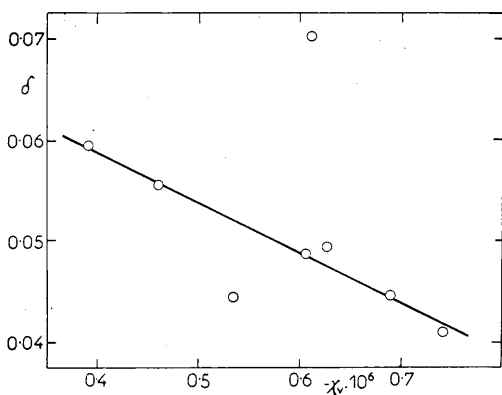


FIG. 1
The Dependence of Hexamethyldisilane Chemical Shift on the Volume Magnetic Susceptibility of the Solvent (susceptibility values taken from ref.¹⁵)

TABLE I
¹H-NMR Chemical Shift of Hexamethyldisilane in Several Solvents

Solvent	Mixture, mol. $\cdot 10^3$			δ^a
	HMDSS	TMS	solvent	
Cyclohexane	0.32	1.07	9.88	0.0495 ± 0.0013
Chloroform	0.55	1.12	11.09	0.0408 ± 0.0012
Benzene	0.53	1.26	10.0	0.0703 ± 0.0013
Dioxane	0.45	1.10	0.87	0.0488 ± 0.0020
Acetonitrile ^b	0.49	1.21	9.38	0.0445 ± 0.0015
Nitromethane	0.38	1.00	10.49	0.0595 ± 0.0020
Acetone	0.37	1.20	11.97	0.0555 ± 0.0017
Tetrachloromethane	0.34	0.87	10.24	0.0423 ± 0.0022

^a Chemical shift in p.p.m. units downfield from TMS line; ^b components of the measured mixture are not fully miscible.

At the beginning the solutions were (the exact composition is indicated in Table I) mixtures of approximately 0.01 mol of the solvent, 0.0003 mol of HMDSS and 0.01 mol of TMS. After the first measurement the solutions were kept open to let the solution evaporate and the variation of the chemical shifts was followed as the ratio of integrals of TMS and HMDSS lines decreased.

RESULTS AND DISCUSSION

The chemical shifts determined in the solutions the concentrations of which were precisely known are summarized in Table I. It is clear from these data that for a routine analytical use the chemical shift of HMDSS can be taken $\delta = 0.045$ in all the studied solvents except for benzene.

In solvent effect studies a care should be taken since the chemical shift of HMDSS exhibits a linear dependence on the volume magnetic susceptibility of the solvent. This dependence is illustrated on Fig. 1, the two points falling off the least-square line are those corresponding to benzene and acetonitrile solutions. Benzene is well known to be magnetically anisotropic and acetonitrile does not mix properly with HMDSS.

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