Carbon-13 Chemical Shifts in Hexamethyldisilazane in Various Non-aromatic Solvents and Effect of van der Waals Interaction on these Shifts

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Introduction

A lot of work on solvent induced carbon-13 chemical shifts has been reported [1-3] but this work has been concerned with strong molecular interactions. The variation of chemical shift due to weak intermolecular interactions such as dispersion forces and van der waals interactions have been treated in detail by Tiffon and Doucet [4]. Medium or solvent effect on TMS carbon chemical shift has been studied in detail by Moreau-Descoings et al [5]. More recently ^{13}C chemical shift in various solvents have been measured on hexamethyldisiloxane in various solvents by kowalewski et al [6]. A correlation between ^{13}C chemical shifts in various solvents and refractive index has been proposed [4-7] to estimate the effect of van der waals forces. According to this correlation a plot is made between chemical shift values and g^2 factor of the solution, where

$$g^2 = [(n^2 - 1)/(2n^2 + 1)]^2 \quad (1)$$

and n is the refractive index of solution. Hexamethyldisilazane or hereafter referred as HDMSZ is a good compound to be used as a reference compound for H^1, ^{13}C ^{29}Si, ^{14}N and ^{15}N resonances [8]. This compound has been studied by NMR by various workers [9-17]. Evidence of solvent and temperature dependent multinuclear NMR chemical shift has been observed in various solvents by Khanzada *et al* [18] and Abid *et al* [19]. The concentration of HMDSZ used in above studied [18,19] was very hgih (82% to 55%). The present study is concerned with the low concentration (5% v/v) ^{13}C chemical shifts of HMDSZ in various solvents using TMS and cyclohexane (CYH) as external standard in a spherical cell. The solvents used are mostly aliphatic. For aromatic solvents a separate study is in progress.

Results and Discussion

Table 1 lists the solvents used, their refractive indices n, chemical shifts of HMDSZ with respect to TMS ($\delta_{HMDSZ/TMS}$) and cyclohexane ($\delta_{HMDSZ/CYC}$). The factor g^2 given by eqn (1) is also shown in Table 1. A plot of $g^2 \times 10^2$ versus

Table 1: Refractive indices, g^2 factor of the solutions and the ^{13}C-NMR chemical shifts of HMDSZ 5% v/v in different solvents, meausred with respect to TMS and CYH in spherical cell.

S. No.	Solvent	Refractive index n	$g^2 \times 10^2$[a]	δHMDSZ/TSM	δHMDSZ/CYH
#1	Dichloro methane	1.4092	3.9319	2.8712	-25.2431
2	Chloroform	1.4325	4.2485	3.3590	-24.5437
3	Carbontetra-chloride	1.4484	4.4648	3.5756	-24.3271
#4	Acetone	1.3541	3.1900	2.1668	-26.1691
5	n-Pentane	1.3525	3.1687	2.1127	-25.4015
6	n-Hexane	1.3709	3.4147	2.4922	-25.4438
7	n-Heptane	1.3811	3.5519	2.5463	-25.3565
8	Diethyl ether	1.3550	3.2020	2.2839	-25.3022
*#9	1-Propanol	1.3664	3.3544	1.8419	-26.1320
#10	2-Propanol	1.3789	3.5223	2.7629	-24.9232
11	Tertiary	1.3914	3.6909	2.8171	-25.0314
#12	1-Butanol	1.3925	3.7058	2.7088	-26.2237
*13	Cyclohexane	1.4008	3.8181	2.3839	-25.1098
*14	Tetrahydro furan	1.3991	3.7951	2.4922	-25.1398
15	1,4-Dioxane	1.3969	3.7653	2.7829	-25.0547
#16	Ethyl acetate	1.3609	3.2808	2.2690	-26.1841
*17	Dimethyl Formaamide	1.4219	4.1044	2.8171	-24.7066
18	2-Octanol	1.4175	4.0446	3.0337	-24.6521
19	1,2-Dichloro ethane	1.4394	4.3424	3.2507	-24.3671
*#20	Carbon disulphide	1.6016	6.5184	3.9010	-23.6227
*#21	Toluene	1.4831	4.9364	2.5463	-25.1398
*#22	Xylene	1.4839	4.9472	2.4922	-25.2481
*#23	Benzene	1.4862	4.9784	2.5463	-25.1398
*#	Diphenyl ether	1.5647	6.0327	3.0337	-24.5437
*#25	Dimethyl sulphaoxide	1.4726	4.7938	4.1717	-23.3529

* Points are not included in linear regression fit for δHMDSZ/TMS

\# Points are not included in linear regress ion fit for δHMDSZ/CYH

[a] $g^2 = [(n^2 - 1)/(2n^2 + 1)]^2$ ($g^2 = g^2$ of the solution; see text).

$\delta_{HMDSZ/TMS}$ is shown in Fig. 1 and that of $g^2 \times 10^2$ versus $\delta_{HMDSZ/CYC}$ is shown in Fig. 2. The minimum chemical shifts for carbon-13 is 1.8419 ppm in 1- propanol and maximum chemical shift is 4.1717 ppm in DMSO (with respect to TMS as external standard in spherical cell). Hence for 5% solution of HMDSZ in different solvents a difference of 4.1717 - 1.8419 = 2.3298 ppm with respect to TMS is observed. A similar difference of -23.3529 - (-26.2237) = 2.8708 is observed for the same 5% solutions in different solvents with respect to cyclohexane used as external standard in spherical tube. A linear regression program in BASIC language [20,21] was written for eqn (1) using some of data in Table 1. This program gives

$$\delta_{HMDSZ/TMS\ (Ext)} = [(1.004 \pm 0.057)\ g^2 \times 10^2] + (-0.980 \pm 0.214) \quad (2)$$

with a standard deviation around regression line σ = 0.92 and a correlation coefficient r = 0.984. The points marked by astrick (*) in Table 1 have not been included in this regression as these were too much away from straight line. A similar linear regression analysis for chemical shifts of HMDSZ using cyclohexane as an external standard gives

$$\delta_{HMDS/CYC(Ext)} = [(0.899 \pm 0.09)g^2 \times 10^2] + (-28.389 \pm 0.346) \quad (3)$$

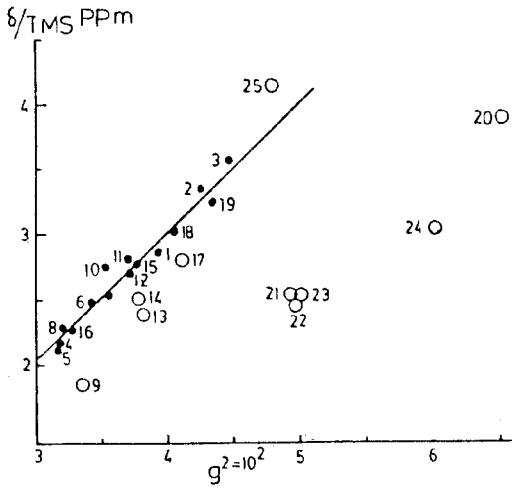

Fig.1: ^{13}C chemical shifts of hexamethyldisilazane in different solvents (5% v/v) with respect to external TMS in a spherical cell, as a function of factor of the solution. $g = (n^2-1)(2n^2+1)$ where n = refractive index of the solution. The data (O) were not included in the regression analysis. Numbers as in Table 1.

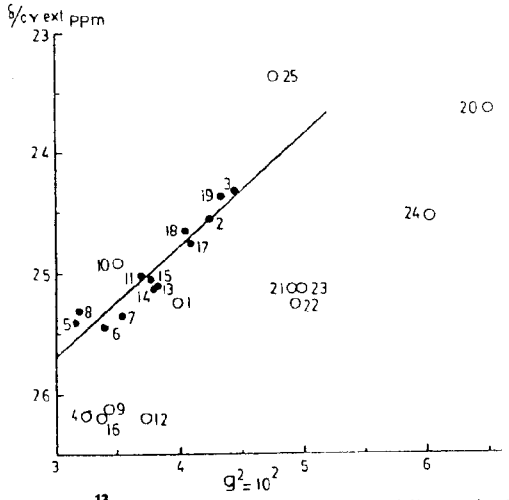

Fig.2: ^{13}C chemical shifts of hexamethyldisilazane in different solvents (5% v/v) with respect to external CYH in a sphercial cell, as a function of factor of the solution. $g=(n^2-1)/(2n^2+1)$ where n = refractive index of the solution. The data (O) were not included in the regression analysis. Numbers as in Table 1.

with standard deviation σ = 0.13 and correlation coefficient r = 0. 949. Data for marked by # were (see in Table 1) not included in this regression as these diverged too much from straight line.

Moreau-Descolings et al [5] have studied the effect of solvent on chemical shift of TMS at 35°C using cyclohexane as an external standard. These authors obtained

$$\delta_{TMS/CYC(Ext)} = [(0.78 \pm 0.04)\ g^2 \times 10^2] + (-30.4 \pm 0.2) \quad (4)$$

From eqn (3) and (4) one can get by difference

$$(\delta_{HMDSZi} - \delta_{TMSi})_{ext} = [(0.119 \pm 0.098)\ g^2 \times 10^2] + (2.0 \pm 0.39) \quad (5)$$

The line representing eqn (3) and (4) are shown in Fig. 3. We can derive a relation for δ_{Ci} of carbon atom of any solvent folliwing g^2 relationship of eqn (3) using eqn (5) and this relation is

$$\delta_{Ci/TMSi} = \delta_{Ci/HMDSZi} + (\delta_{HMDSZi} - \delta_{TMSi})_{ext} \quad (6)$$

Here $\delta_{Ci/TMSi}$ chemical shift of carbon i with respect to TMS and $\delta_{Ci/HMDSZi}$ is chemical shift of carbon i of compound under study with respect to HMDSZi used as a reference.

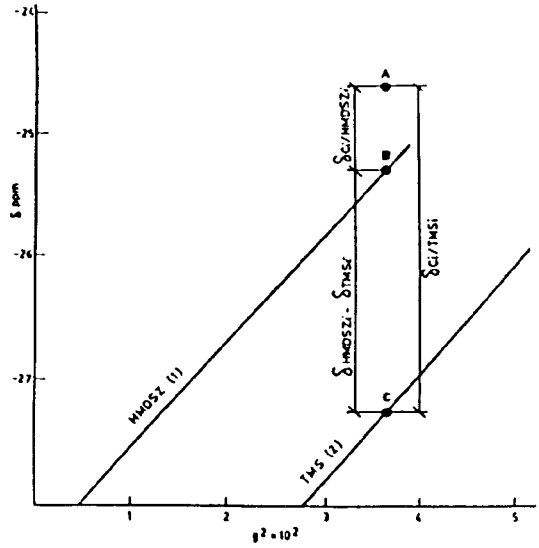

Fig.3: Plot the chemical shifts $d_{HMDSZ/CYH\ ex}$ (line 1) and $\delta_{TMS/CYH\ ex}$ (line 2) with respect to g^2 for different solutions. The distance AB represent the measured chemical shift of a carbon, Ci, $d_{Ci/HMDSZ}$; BC is the difference between the two reference for the same value of g^2; AC represent $\delta_{Ci/TMSi}$.

Van-der Waals effect is clearly seen by plot of δ versus g^2 solvent factor. The deviation from this correlation is observed for certain solvents and aromatic solvent clearly do not fall in this correlation region because of ASIS effect [22].

Experimental

All the spectra were recorded using JEOL FX-90Q FT NMR spectrometer operating in the Fourier transform (FT) mode with 10 mm tunable probe equipped with a multinuclear unit. The temperature of measurement was 35°C and was maintained and measured by JEOL NM-DSU digital set unit and JEOL NM PVT variable temperature unit with an accuracy of ± 0.5°C. The 90° pulse width for carbon-13 measurement was 25 ms and spectra were recorded in completely p;roton noise decoupling mode at a noise decoupling frequency of 1 kHz. TMS and cyclohexane were used as an external references in a spherical cell in all set of experiments.

All the solvents used were of commercial origin and were of analytical grade. These were used as such. Hexamethyldisilazane was obtained from Fluka and had purity greater than 99% GC. It was used as such 5% v/v solutions of HMDSZ in various solvents were used. External deuteruim lock was used in all experiments.

The following recording condition were used for natural abundance carbon-13 magnetic resonances. Pulse delay 200 μs; acquestion time 0.81925 s; three scan with 8K data point; spectral width 5000Hz; digital resolution was 0.2440.

Refractive indices were measured by Bausch and Lomb Abbe's Refractometer. The temperature of measurement was 35°C and it was controlled by a Julabo V thermostat with an accuracy of ± 0.1°C.

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