Short Communication

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EVIDENCE OF SOLVENT AND TEMPERATURE DEPENDENT MULTINUCLEAR NMR CHEMICAL SHIFTS IN 1,1,1,3,3,3-HEXAMETHYLDISILAZANE

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1,1,1,3,3,3-Hexamethyldisilazane or 1,1,1-Trimethyl-N- (Trimethylsilyl)- Silanamine or briefly HMDSZ has been used as silating agent, in complex catalysis and in chromatography [1,2]. This compound here after referred as HMDSZ has been studied by uv [3], ir [4], mass spectrometry [5] and by NMR [6-10] by various workers. NMR study has been made on proton [6,7], Carbon-13 chemical shifts [9], Silicon-29 chemical shifts [8,9], Nitrogen-14 [14] and Nitrogen-15 chemicals shifts [10,15]. In these studies either a pure compound is used or a solution in CD_2CL_2 or C_6D_6 is used. Silicon-29 chemicals shifts are heavily dependent on solvents and their concentrations [11] as well as that of nitrogen [12,13].

In a recent multinuclear NMR study by us on silicon compounds, we found that HMDSZ shows solvent and temperature dependent chemicals shifts. We were unable to study Nitrogen-15 resonance because of instrument limitations. These studies were conducted on JEOL FX90Q FT NMR equipped with a multinuclear and variable temperature facility. The spectra were run with 10 mm tunable probe. The 90° pulse width for proton, carbon-13, nitrogen-14 and silicon-29 were 30us, 25us, 47us, 15us respectively. The observations frequency for Nitrogen-14, Silicon-29, Carbon-13 and Proton were 6.43 MHz, 17.75 MHz, 22.49 MHz and 89.55 MHz respectively. Complete proton noise decoupling at a frequency of 1 kHz was used in case of Carbon-13, Silicon-29, and Nitrogen-14 resonances. Slight evidence of accoustic ringing was present in case of Nitrogen-14, but the peak was relatively sharp. Long delay time was used to avoid this. Temperature measurement were done by using JEOL NM-DSU digital set unit and NM-PVT variable temperature unit. The accuracy of temperature measurement was ±0.5°. The results of these preliminary investigations in two solvents are summarized in Table 1.

TABLE 1. CHEMICAL SHIFTS OF VARIOUS NUCLEI IN TWO VARIETY OF SOLVENTS [A], AT VARIABLE TEMPERATURES IN THIS WORK HEXAMETHYLDISILAZANE (HMDSZ).

Name of the nuclei with group	Temperature °C	50% HMDSZ in $CDC1_3$ [b]	50% HMDSZ in acetone [c]	50% HMDSZ in cyclohexane[c]	55% HMDSZ in Benzene[c]	Previous work
^1H of $-CH_3$group	35	0.053±0.001	0.045±0.002	0.048±0.001	0.051±0.000	0.05 [e]
	50	0.053±0.001	0.045±0.002	0.048±0.001	0.051±0.000	
^1H of>NH group	35	2.3-2.5[d]			3.645±0.011	
^{13}C of $-CH_3$ group	35	2.501±0.008	2.557±0.000	2.546±0.000	2.546±0.000	2.9 f]
	50	2.501±0.008	2.557±0.000	2.546±0.000	2.546±0.000	
Silicon - 29	35	2.464±0.038	1.974±0.008	2.400±0.015	2.331±0.006	2.2[g]
	50		2.066±0.012	2.468±0.010	2.400±0.007	2.22[f]
Nitrogen - 14	35	346.149±1.326	350.886±0.269	345.972±0.188	347.567±0.132	351[i]
	50		350.753±0.531	345.176±0.125[h]	346.769±0.050	
Nitrogen-15 [1]						

(a) Deuterected chloroform and acatone was used as polar and cyclohexane and benzene used as non-polar solvents, (b) Using interml deuterium lock, (c) Using external deuterium lock, (d) Broad peak depend on the concentration, solvent and temperature, (e) Ref. 6 cw work on 40 MHz, (f) Ref 9. The solvent is CD_2CL_2 not specified exactly, (g) Ref. 8 The solvent is not specified.(h) Temperature was 70°, (i) Ref. 14, (j) Ref. 10 Chemical shifts of neat compound relative to CH_3NO_2 as internal standard, (k) Ref. 13 50% solution of HMDSZ in acetone-d_6, (l) Not obtained, due to instrument limitation.
Note: Proton, Carbon-13 and Silicon-29 chemical shifts are relative to TMS as internal standard, while Nitrogen-14 chemical shifts are relative to CH_3NO_2 as internal standard.

It is seen from Table 1 that proton and carbon-13 chemical shifts are not temperature dependent. However, in different solvent these shifts shows solvent dependency. Proton chemical shifts is different in all solvents. However, carbon-13 chemical shifts remain same in cyclohexane and benzene. Silicon-29 chemical shifts are clearly dependent on solvent as well as on temperature. The d-orbitals of silicon are playing some role here. Nitrogen-14 chemical shifts are also solvent and temperature dependent. This may be due to some H-bonding effect of amino group with polar and non-polar solvents. The polar solvent increases H-bonding while non-polar reduces it.

A detailed study using various solvents, their concentration and at diferent temperatures is in progress.

Key words: NMR study, Hexamethyldisilazane, Chemical shifts.

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