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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 chemical 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 observation 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.

It is seen from Table 1 that proton and carbon-13

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 in °C	50% HMDSZ in CDC1 [b]	50% HMDSZ in acetone [c]	50% HMDSZ in cyclohexane[c]	55% HMDSZ in benzene[c]	Previous work
^{1}H of -CH_3group	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	
^{1}H 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]						353.2[j] 354.2[k]

(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) 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 internal standard.

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. This 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, Hexamethyldisilazane.

References

1. *"Dictionary of Organic Compounds,"* J. Buckingham Exec. Editor, 3, 2929, H00759, 5th. ed., (Chapman and Hall, N.Y., USA., 1982).
2. C.A. Bruynes and T.K. Jurriens, J.Org. Chem., **47**, 3966 (1982).
3. C.G. Pitt and M.S. Fowler, J. Am. Chem. Soc., **89**, 6792 (1967).
4. J. Plazant, F. Metras, A. Marchand and J. Valade., Bull. Soc. Chim. Fr., 1920 (1967).

   Soc. Chim. Fr., 1920 (1967).
5. J. Talma's and P. Miklo's, Org. Mass Spectrum., **10**, 859 (1975).
6. E.A. Ebsworth and S.G. Frankiss, Trans. Faraday Soc., **63**, 1574 (1967).
7. H.C. Levy II, J.Inorg. Nuclear Chem., **29**, 1859 (1967).
8. H.C. Marsmann, Chem. Ztg., **96**, 288 (1972).
9. R.K. Harris and B.J. Kimber, J. Magn. Reson., **17**, 174 (1975).
10. J.P. Gouesnard and D. Dorie, Noveau J. Chim., **6**, 143 (1982).
11. H. Marsmann, *NMR, Basic Principles and Progress-Oxygen-17 and Silicon-29.* (Springer-Verlag, N.Y., 1981). Vol. 17, p. 65.
12. G.J. Martin, M.L. Martin and J.P. Gousenard, "NMR Basic Principle and Progress - Nitrogen-15 NMR Spectroscopy", **18**, 54 (1981).
13. M. Witanoski, L. Stefaniak and G.A. Webb, *Annual Reports on Spectroscopy - Nitrogen NMR Spectroscopy* (Academic Press, N.Y. 1986) Vol 18, p 81.
14. H. Noth, W. Tinhofand and B. Wrackmeyer, Chem., Ber., **107**, 518 (1974).
15. E. Kupce, E. Liepins, O. Pudova and E. Lukevics., J. Chem. Soc., Chem. Commun., 581 (1984).