

## DIPOLE MOMENTS OF PENTACOORDINATED SILICON DERIVATIVES

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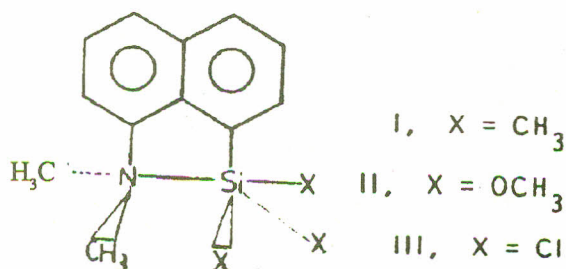
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Dipole moments of  $[(\text{CH}_3)_2\text{N}]\text{C}_{10}\text{H}_6\text{SiX}_3$  where  $\text{X}=\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{Cl}^-$  in different solvents and at different temperatures indicate that the intramolecular  $\text{N} \rightarrow \text{Si}$  coordinate bond is correlated with the strength of the  $\text{Si}-\text{X}$  bond.

**Key words:** Dipole moment, Silicon derivatives.

### Introduction

Many pentacoordinated compounds of silicon are known [1-5]. The recent [6] synthesis of rigid pentacoordinated compounds of tin surrounded by three carbon atoms led us to understand systematic study of dipole moments of corresponding silicon compounds. A recent publication [7] reports the synthesis and molecular structure of pentacoordinated silicon derivatives in which  $\text{C}_{10}\text{H}_7\text{N}(\text{CH}_3)_2$  is intramolecularly bonded to the silicon atom.



In the present work we report the dipole moments of pentacoordinated silicon atoms bonded to different groups such as methyl, methoxy and chloride, at different temperatures and a correlation has been established between the dipole moments and the nature of functional group bonded to the silicon atom.

### Experimental

Compounds I, II and III were prepared according to reference [6,7] and were characterized by nmr, mass spectra and elemental analysis before use. Di-electric constant of the solutions thermostated at desired temperature (error of  $\pm 1^\circ$ ) were measured on dipole meter Model DM01 of WTW. The dipole moment values were calculated using the usual Guggenheim-Debye equation [10].

Solvents used were purified as recommended for these measurements.

**Carbontetrachloride** (bp.  $76.8^\circ$ ). 150 ml. of carbontetrachloride (E. Merck Darmstadt) in 250 ml. separation funnel was shaken with conc.  $\text{H}_2\text{SO}_4$  (10 ml.), sulphuric acid layer was separated and  $\text{CCl}_4$  layer washed with

water and separated. Dried over  $\text{CaCl}_2$  for overnight and distilled. Thus obtained  $\text{CCl}_4$  was refluxed with  $\text{P}_2\text{O}_5$  for eighteen hrs. under dry nitrogen atmosphere and finely distilled at  $76.8^\circ$ .

**Toluene** (bp.  $110.8^\circ$ ). 500 ml of toluene was treated with 40 ml. of conc.  $\text{H}_2\text{SO}_4$  and mixture was vigorously stirred at room temperature for 30 mins. The dark coloured acid layer was separated off and the process was repeated until the acid layer was only faintly coloured. The toluene was then washed with  $\text{H}_2\text{O}$  dried over  $\text{CaCl}_2$  for 48 hr. and distilled. Thus obtained toluene was distilled over  $\text{CaH}_2$  under nitrogen and stored over sodium sand.

### Results and Discussion

The values of dipole moments of compound I, II and III in carbontetrachloride and in toluene has been determined from the data collected from dielectric constant and refractive indices of its solution at various temperatures and are given in Table 1.

TABLE 1. DIPOLE MOMENTS (D) FOR THE INVESTIGATED COMPOUNDS

Solvent	Temperature ( $^\circ\text{C}$ )	Dipole moments (D)		
		I	II	III
Carbontetrachloride	20	2.734	3.122	3.510
	30	2.814	3.212	3.610
	40	2.894	3.303	3.712
	50	2.975	3.396	3.860
Toluene	20	2.873	2.986	3.099
	30	2.951	3.068	3.185
	40	3.028	3.150	3.272
	50	3.107	3.234	3.361
	60	3.180	3.318	3.456
	70	3.268	3.404	3.540
	80	3.350	3.490	3.630

The results show that dipole moment values vary slightly at different temperature ranges i.e.  $20-50^\circ$  in carbontetrachloride and  $20-80^\circ$  in toluene and solvents has little effect on  $\mu$  values. From Fig. 1, it can be seen that dipole moment values of compounds (II) and (III) are higher in carbontetrachloride as compared to values in toluene, whereas for compound (I) the reverse is true. Generally, the

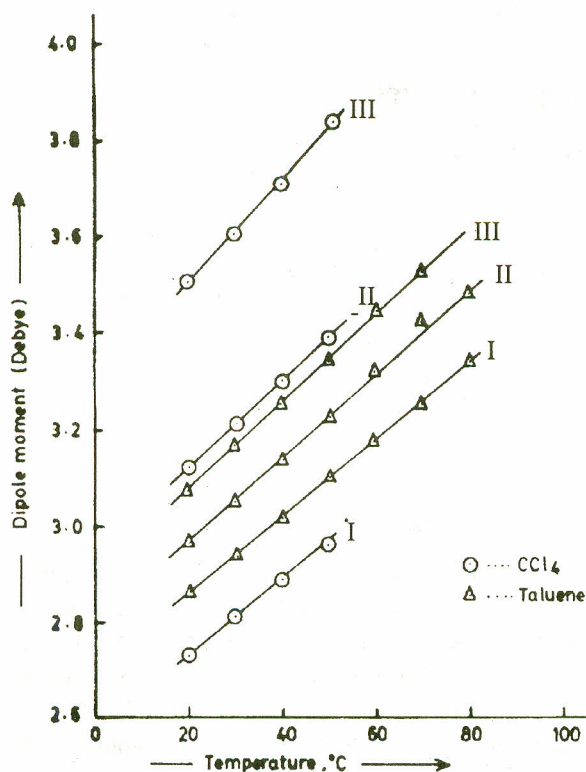


Fig 1. Plot of Dipolemoment Vs Temperature for Compounds I,II and III

dipole moment values of these compounds are low and fall in a range of 2.75 to 3.40 D. These low values indicate that i) intramolecular N - Si bond remains intact during course of measurements and ii) the charge from N,N-dimethyl-1-naphthylamine flows through nitrogen to the large apical ligand of the structurally rigid trigonal bipyramidal silicon

and most of the charge is retained by the empty d orbitals of silicon atoms. This could be the reason that by change of methyl group in (I) by more electron withdrawing methoxy and chloro groups in (II) and (III) respectively, has brought a small enhancement in the dipole moment values. This enhancement can be taken as evidence that the ease of transfer of electronic cloud from N  $\rightarrow$  Si follows the pattern  $\text{Cl} > \text{OCH}_3 > \text{CH}_3$  which is in accordance with the previous  $^1\text{H-nmr}$  studies on similar compounds [ 5,8,9].

#### References

1. C.L. Frye, J. Am. Chem. Soc., **86**, 3170 (1964) and **92**, 1205 (1970).
2. F.P. Boer, J. Flynn and J.W. Turley, J. Am. Chem. Soc., **90**, 6973 (1968).
3. M.G. Voronkov, Pure Appl. Chem., **13**, 35 (1966).
4. D. Kummer, H. Koster and M. Speck Angew. Chem., Int. Ed. Eng., **8**, 599 (1969).
5. R.J.P. Corriu, G. Royo and A.D. Saxce, J.C.S. Chem., Comm., 892 (1980).
6. J. Boyer, R.J.P. Corriu, M. Mazhar, and A. Kpton, J. Organomet. Chem., **301**, 131 (1986).
7. R.J.P. Corriu, M. Mazhar, M. Poirier and G. Royo, J. Organomet. Chem., **303**, (1986).
8. C. Breliere, F. Carre, R.J.P. Corriu, A.D. Saxce, M. Poirier and G. Royo, J. Organomet. Chem., **205**, C<sub>1</sub>-C<sub>3</sub> (1981).
9. R.J.P. Corriu, M. Poirier and G. Royo, J. Organomet. Chem., **233**, 165 (1982).
10. J.M. Wilson, R.J. New Comb, A.R. Denaro, R.M.W. Rickett, *Experiments in Physical Chemistry*, (Pergamon Press, London, 1968).