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Crystal Structure of $((C_6H_{11})_2N)$ $(C_6H_{12}N)_2SiH$

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Abstract

The structure of the mixed tri(amino)silane has been determined by in the solid state. The compound crystallized in the monoclinic form. The crystallographic data of the compound is given in Table 1. A list of bond lengths and angles are Table 2. The refinement converged to a final R value of 0.0649 and wR= 00687 with weighting schemes based on counting statistics, where W = 0.00659. Fin: (shift/esd), maz =0.096. The molecular parameters obtained are Si1– N1 =1.712 Å (4) Si1 - N2=1.707 Å (4), Si-N3=1.717 Å (4), <N2 - Sil - N3=109.6(2), <N1 - Sil - N3=116.0(2), < N1 - Sil - N2= 107.0(2).

Keywords: Tri(amino)silane, ^{15}N NMR, ^{29}Si NMR, Dicyclohexylamine, Hexamethylene imine

Introduction:

Silicon - nitrogen compounds have gained a lot of importance. The Si-X bond is of particularly great importance in the chemistry of organosilicon compounds as almost all organosilicon compounds are ultimately obtained from elementary silicon through halides of silicon, $SiCl_4$, $SiHCl_3$. The Si-X bond is much more reactive than the C-X bond toward polar reagents [1,2]. There are only a few synthetic methods to prepare these compounds [3,4]. Single crystals of this compound were obtained by the slow crystallization of the liquid obtained after removal of the major portion of the solvent mixture at room temperature. This compound was found to be highly sensitive to moisture. Hence, the crystal was mounted in a lindemann capillary for data collection. The characterisation of this mixed tri(cyclo)silane has been done by using x-ray crystallography. Complete set of data was collected using Mo-Kα radiation.

Experiments:

The compound was prepared by transamination reaction [5] by taking tris(dicyclohexylamino)silane and hexamethyleneimine (1:2 ratio). 50 ml of 1:1 (v/v) benzene n- hexane solvent mixture was taken in a dry 250 ml side arm flask was flushed with dry, oxygen free nitrogen and stirred vigorously for 24 hours. As soon as the addition started a slight exothermic action took place. The solid products product formed was purified by repeated washing with n-hexane. A small portion of the sample were used for characterisation by ^{29}Si NMR [5],^{15}N NMR Fig.2 and FT-IR. The crystal was colourless and transparent. Crystallographic data of the compound is given in Table.1. Full lists of positional and thermal parameters, bond distances (Table 3) and bond angles are given (Table 4)

Table.1

Chemical Formula	$C_{24}H_{47}N_3Si$	Z	4
Formula weight	405.74	P*calcd*,g cm^{-3}	1.079
Crystal system	monoclinic		
Space Group	P21/n(No.1014)	μ(Mo-Kα), $cm^{-!}$	1.03
	10.490(1)	λ(Mo-Kα). Å	0.7107
a,Å	11.744(1)	T, °C	22
	20.310(2)		
b, Å	93.19(1)		
	2498(4)		
c, Å	16 ≤2 θ ≤24	Rα	0.0649
β,deg		Rw^b	0.0687
	4384	g	0.000827
V,^{0} $Å^3$		transm. coeff.	0.93-0.99
range of θ collected	|Fol ≥ 5σIFol		
Total no. of reflectn.			
No.of unique reflectn		Octants collected	0≤h<12
Criterion forbeing			0≤k≤13
observed			-24≤I≤24
		Total no. of reflectn	5079
		reflections observed	2037
Diffractometer used		Enraf Nonius CAD -4	
Computer Programs		SHELXS-86,	
used for structure		SHELX-76	
solution and			
refinement			
Source of scattering		International	
factor Tables		Tables	
Monochromator		graphite	
Criterion for being			
observed			Vol.4
weighting scheme			
Crystall			

Results and discussion:

Table 2

The ^{29}Si, ^{15}N chemical shift along with Si-H vibrational frequencies are given below

Characteristic Nuclear magnetic Resonance (∂ppm) and IR frequencies (cm^{-1}) of $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$ [6]				
^{1}H (ppm)	^{29}Si (ppm)	^{15}N (ppm)	νSi-H	νSi-N
4.34	-33.77	-313.7 -343.4	2122	669

Table 3

Lists of bond lengths (Å) $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$

Sil - N1	1.712 4)	C26 - C27	1.411(14)
Sil - N2	1.707(4)	N3 - C31	1.480(6)
Sil - N3	1.717(4)	N3- C41	1.469(6)
N1 - C12	1.481(7)	C31 - C32	1.525(7)
N1 - C17	1.459(7)	C31 - C36	1.524(7)
C12 - C13	1.496(8)	C32 - C33	1.547(8)
C13 - C14	1.478(10)	C33 - C34	1.507(8)
C14 - C15	1.351(12)	C34 - C35	1.516(7)
C15 - C16	1.379(12)	C35 - C36	1.512(8)
C16 - C17	1.491(9)	C41 - C42	1.516(8)
N2 - C22	1.439(8)	C41 - C46	1.518(8)
N2- C27	1.458(8)	C42 - C43	1.523(9)
C22 - C23	1.566(11)	C43 - C44	1.490(10)
C23 - C24	1.471(13)	C44 - C45	1.528(10)
C24 - C25	1.563(16)	C45 - C46	1.524(7)
C25 - C26	1.372(16)		

Lists of bond angles(deg) $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$

Table 4

N2 - Sil - N3	109.6 (2)	N2 - C27 - C26	118.7 (7)
N1 - Sil - N3	116.0 (2)	Sil - N3 - C41	125.1 (3)
N1- Sil - N2	107.0 (2)	Sil - N3 - C31	116.6 (3)
Sil - N1 - C17	123.4 (3)	C31 - N3 - C41	116.3 (3)
Sil - N1 - C12	118.6 (4)	N3 - C31 - C36	114.3 (4)
C12- N1 - C17	113.0 (4)	N3 - C31 - C32	113.9 (4)
N1 - C12 - C13	115.1 (5)	C32- C31 - C36	110.0 (4)
C12- C13 - C14	114.5 (5)	C31 - C32 - C33	110.2 (4)
C13 - C14 - C15	124.9 (7)	C32 - C33 - C34	111.5 (5)
C14 - C15 - C16	135.0 (8)	C33- C34 - C35	111.8 (5)
C15- C16 - C17	123.4 (6)	C34 - C35 -C36	110.8 (4)

N1 - C17 - C16	117.5 (5)	C31 - C36 - C35	111.9 (4)
Sil - N2- C27	119.3 (4)	N3 - C41 - C46	113.9 (4)
Sil - N2- C22	124.8 (4)	N3 - C41 - C42	112.6 (4)
C22- N2 - C27	115.1 (5)	C42 - C41 - C46	110.2 (4)
N2 - C22- C23	111.7 (6)	C41 - C42 - C43	111.9 (4)
C22- C23 - C24	117.6 (7)	C42 - C43 - C44	112.2 (5)
C23 - C24 - C25	116.6 (8)	C43 - C44 - C45	110,2 (5)
C24 - C25 - C26	118.1 (10)	C44 - C45 - C46	109.6 (5)
C25- C26 - C27	120.6 (9)	C41 - C46 - C45	111.2 (5)

An **ORTEP** view of the full molecule is shown Fig.1.

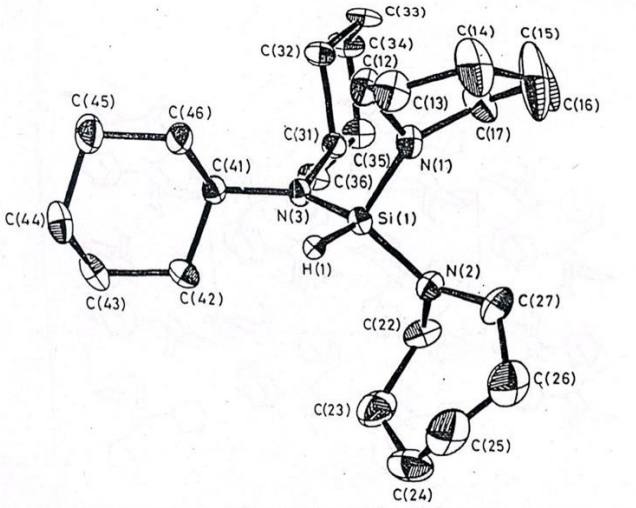

Fig.1.

An ORTEP view of the molecule is shown in Fig.1. The structure consists of one silicon atom in a tetracoordinate state bonded to three nitrogen atoms and one hydrogen atom. Two nitrogen atoms out of three, form a part of two cyclic seven membered ring and the other nitrogen atom is exocyclic with two cyclohexane rings. Here also the nitrogen atoms NI, N2 and N3 deviate from the plane by 0.201 Å (4), 0.082 Å (4) and 0.128 Å (3) respectively. These values indicate that in this molecule the nitrogen atoms are slightly more pyramidal than that reported earlier[9], where the substituents are less bulky, as reflected by the angles (total angles around the nitrogen atoms are N1 = 355.0°(11), N2 =359.2°(15) and N3 = 358(9) Table 4 . Various silicon-nitrogen bond lengths (Table3) indicate that one of the bond is marginally shorter (S1-N2) than the other two and also these bonds are slightly longer than that of the less sterically hindered amino group. This provides an evidence for the fact that in bulkier systems the silicon-nitrogen bond is slightly weaker [8,9]. The various C-C bond lengths are the range of 1.47 Å and do not exhibit much deviation as expected.

Newman projection diagram of $((C_6H_{11})_2N)$ $(C_6H_{12}N)_2SiH$ through Si-N bonds

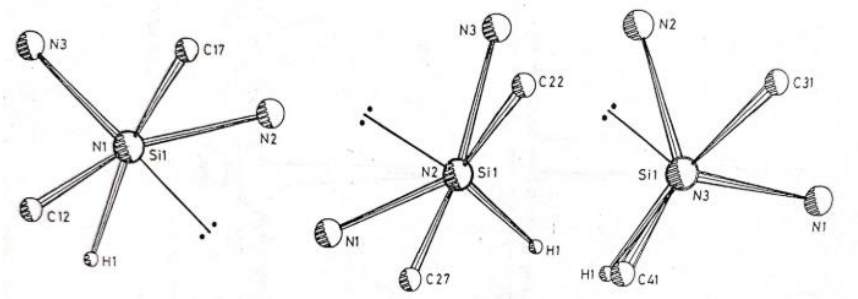

Fig:2

Fig.2**.** shows the Newman projection diagrams of compound and where the lone pair on N2 overlap with σ*Si-H. N1 and N3 lone pairs overlap with σ*Si-N3 and o* Si-NI respectively. As a result nitrogen atom N2 can be slightly deshielded when compared to the other two nitrogen atoms, which interact with each other as can be seen from the Fig.2. But in this compound, probably the interaction of the hydrogen attached to the silicon is slightly reduced, as can be seen from the Newman projection diagram and as a result only two signals are obtained for this compound in its ^{15}N NMR spectrum.

(Fig.3).15N NMR (40.56 MHz) spectrum of $(C_6H_{11})_2N)(C_6H_{12}N)_2SiH$ in paraffin.

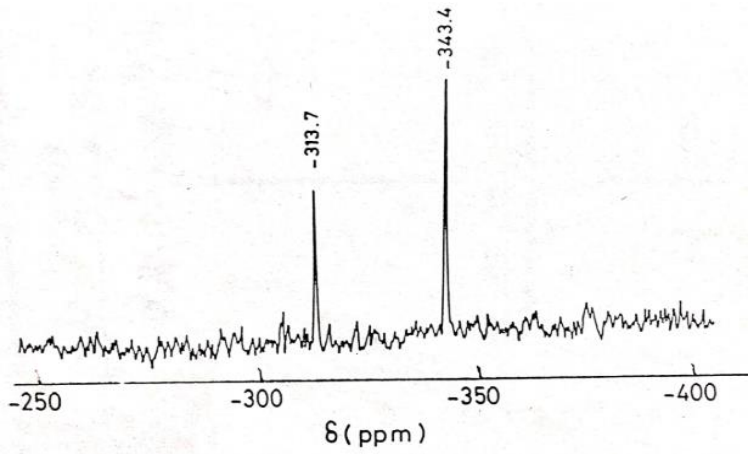

Fig.3 $\{^1H\}^{15}N$ NMR epectra of (a) hexamethyleneimine and (b) dicylohexylamine

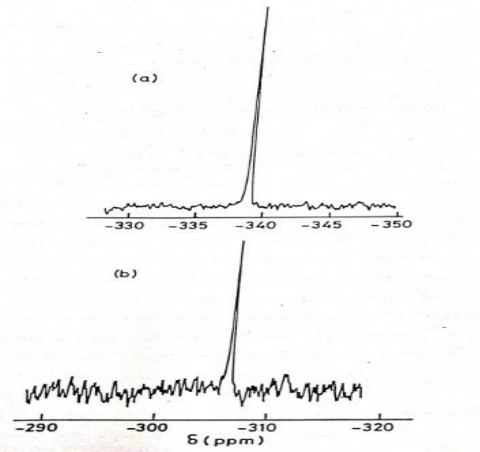

Fig.4(a) and (b)

Fig.4(a) and (b) shows the$\{^1H\}^{15}N$ of the hexamethyleneimine and dicyclohexylamine which resonates at -338.9 and -306.5 ppm respectively [6]. But in the present study, nitrogen atoms show resonances at -343.4 and 313.7ppm. These peaks can be assigned due to the fact that one of the nitrogen N2, which is a

part of the seven membered ring, (is having conjugation with σ* Si-H bond) is deshielded when compared to the parent amine (-338.9 ppm). Whereas, the other two nitrogen atoms are having mutual interactions and as a result they resonate at -343.4 ppm. In the present study when the nitrogen becomes slightly non-planar, the (p-d)π interaction will be slightly decreased. This is evident from the comparatively longer bond length in this compound. Crystallographic data as well as spectroscopic studies (data given in Table 3,4) provide evidence for this observation.

Conclusion

In this study there is a small increment in Si-N bond length (1.71 Å), deshielding of the Si-H hydrogen (∂= 4.34 ppm) and small increase in Si-H stretching frequency (νSi-H 2122 cm^{-1}). From the Newman projection it is clear that the orientation of the lone pair on N2 with σ* Si-H bond is slightly less than 180^0. Even though the shift is not a significant one. Thereby showing a small decrease in conjugation of lone pair on N2 with σ* Si-H bond. This may be the reason for the marginal increment of Si-H frequency along with mild desheilding of the Si-H protons.

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References:

1. (a) B. Kanner, C.L. Schilling and S..P. Hopper, U.S. Pat. C.A: 99, No. 176052 (1983). (b) B. Kanner, J.M. Quirk, A.P. De Monte and K.R. Mehta, U.S. Pat. 4558146 (1985); C.A: 104, No. 207443 (1986).
2. Synthesis of organosilicon Monomers by A. D. Petrov, B. F, Mironov, V.A. Ponomarenko, and E. A. Chernyshev, Consultant Bureau, New York 1964.
3. K.N. Radhamani and D.K. Padma – High Yield room temperature synthesis of mixed tri(amino)silanes by trans amination of tris(dicyclohexylamino)silane and its characteristion :Phosphorous, Sulfur, Silicon and related elements -vol79,65-68 (1993).
4. K.N. Radhamani: A convenient method of preparation of tri(amino)silanes using transamination, Biochemical Science, Vol.4 ISSN 2230-8474,pp.21-23 issue 1.22 Dec 2013.
5. K.N. Radhamani and D.K. Padma – High Yield room temperature synthesis of mixed tri(amino)silanes by transamination of tris(dicyclohexylamino)silane and their characterisation Phosphorous, Sulfur, Silicon and related elements -vol79, pp-65-78, 1993.
6. K.N. Radhamani, Ph.D thesis, Indian Institute of Science., May 1993.
7. K.N.Radhamani :Crystal structure and Characterisation of Tris(Morpholino)silane: International Journal of Innovative Research and creative technology, Vol 10, Issue 2 (March-April 2024) (E-ISSN:2454-5988)
8. K.N.Radhamani :A study on Infrared Spectroscopic Frequencies of H-Si bonds in tri(amino) Silanes : $(R_2N)_3SiH$: Research Arena Vol4, ISSUE 8,Nov:2016 ISSN2320-6263 9. G. Gundersen, R.A. Mayo and D.W.H. Rankin, J. Acta. Chem. Scand., 138A, 579 (1984).