Crystal structure and Characterization of Tris (Morpholino) Silane: $(OC_4H_8N)_3SiH$

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Abstract:

The structure of tris(morpholino)silane has been determined in the solid state. The compound crystallised in monoclinic form. The refinement converged to a final R value of 0.0512 and wR = 0.0585 with weighing schemes based on counting statistics, where W = 0.001931 and final (shift/esd) max = 0.385. The molecular parameters obtained are Si—N1 = 1.692, Si-N2 = 1.699, Si-N3 = 1.695. The <N2-Si-N3 = 120, <N1-Si-N3 = 106, <N1-Si-N2 = 106. The ^{29}Si and ^{15}N NMR, FT-IR spectroscopy was used to characterize the compound. Since all nitrogen atoms were almost planar according to the bond angle obtained from crystallographic studies, it suggest a strong (p-d)π interactions and Si-N bonding.

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

Introduction

During the last few decades silicon - nitrogen compounds have gained a lot of importance [1]. These compounds have emerged as a precursor for many Si containing compounds. There are only a few synthetical methods to prepare these compounds [2]. The characterisation of tris(morpholino)silane has been done by using x-ray crystallography in the solid state under inert (nitrogen) atmosphere. A highly air sensitive compound was crystallized and characterised by spectroscopy. Further the single crystal was also characterised by X-ray crystallography. Complete set of data was collected using Mo-Kα radiation.

Experiments

The single crystals of this compound were obtained by keeping (at 5°C) a saturated solution of the compound prepared at 45°C in 2:1 (v/v) n-hexane-benzene solvent mixture. The crystals were found to be highly sensitive to moisture. So, the crystal was coated with an epoxy glue to prevent decomposition by moisture and a fast scanning method was employed for the data collection. Crystallographic data of the compound is given in Table.1. A small portion of the sample were used for characterisation by ^{29}Si NMR [3],^{15}N NMR Fig.1 and FT-IR [Table.2]. The crystals were colourless and transparent.

Table.1

Chemical Formula	$C_{12}H_{25}O_3N_3Si$	T, °C	22
Formula weight	287.43	Rα	0.0512
Crystal system	monoclinic	Rw^b	0.0585
Space Group	C2/c(No.15)	g	0.001931
a,Å	15.309(1)	transm. coeff.	0.88- 0.95
b, Å	9.036(1)	Range of 2θ for cell determination	16≤2 θ ≤20
c, Å	22.540(2)	using 25 reflections	

β,deg	100.09(1)	Octants collected	0≤h<16 0≤k≤9 -23≤I≤23
V,^{0} Å ^{3}	3070(5)		
Z	8	range of θ collected	1≤ θ ≤22
P*calcd*,g cm^{-3}	1.244	Total no. of reflectn.	1579
		No.of unique	1297
μ(Mo-Ka), cm -!	1.55	reflectn	920
λ(Mo-Ka). Å	0.7107	Reflections observed	
Criterion for being observed		|Fol ≥ 5σIFol	
weighting scheme		1.0/ σ^2| F| + gl F|^2	
Diffractometer used		Enraf Nonius CAD - 4	
Computer Programs used for structure solution and refinement		SHELXS-86, SHELX-76	
Source of scattering factor Tables		International Tables	Vol.4
Monochromator		graphite	

[a] R = ∑ ||F◦| - |Fc|| / ∑|F◦| .
[b] R = [∑w(|F◦|- |Fc|)^2 /∑w|F◦^{2}|]$^{1/2}$; w=k⁄[σ^2 (F◦)+g F◦^{2}]

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 $(OC_4H_8N)_3SiH$[4,5]				
1H	^{29}Si	^{15}N	vSi-H	vSi-N
4.21	-29	-342.21 -346.1	2107	694

Full lists of positional and thermal parameters, bond distances (Table 3) and bond angles are given (Table 4)

FIG.1:15N NMR spectra [a)1H decoupled b)1H coupled] of $(OC_4H_8N)_3SiH$

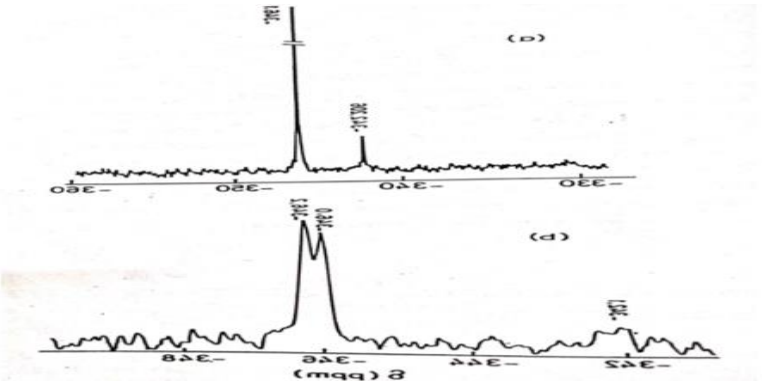


Table 3

Lists of bond lengths (Å) for $(OC_4H_8N)_3SiH$

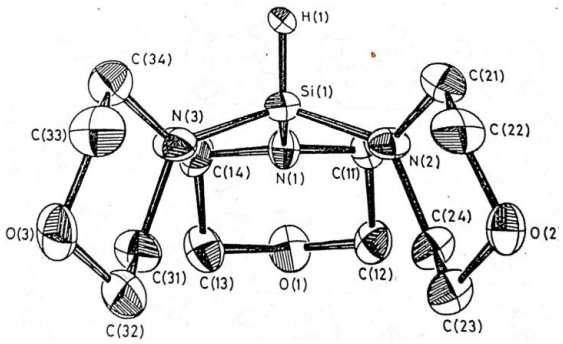
Sil - N1	1.692(6)	N2 - C21	1.478(9)
Sil - N2	1.699(5)	N3 - C31	1.471(8)
Sil - N3	1.695(5)	N3 - C34	1.468(10)
O1 - C13	1.417(9)	O3 - C32	1.409(10)
O1 - C12	1.427(8)	O3 - C33	1.410(9)
O2- C23	1.400(9)	C12 - C11	1.458(9)
O2- C22	1.413(9)	C24 - C23	1.480(13)
NI - C14	1.461(8)	C31 - C32	1.470(14)
N1 - C11	1.461(8)	C21 - C22	1.476(15)
C13- C14	1.467(9)	C34 - C33	1.481(16)
N2 - C24	1.460(9)		

Lists of bond angles (deg) for $(OC_4H_8N)_3SiH$

Table 4

N2 – Si1 - N3	120.0(3)	C31 - N3 - C34	109.9(5)
N1 – Si1 - N3	106.1(3)	C32 - O3 - C33	108.8(6)
N1 – Si1 - N2	106.5(3)	O1 - C12 - C11	111.7(5)
C13 - O1 - C12	108.2(5)	N1 - C14 - C13	110.6(5)
C23 - O2 - C22	109.5(5)	N1 - C11 - C12	111.1(5)
Si1 - N1 - C11	124.5(4)	N2 - C24 - C23	110.3(6)
Si1 - N1 - C14	125.0(4)	O2- C23 - C24	114.1(6)
C14 - N1 - C11	107.2(5)	N3 - C31 - C32	109.1(6)
O1 - C13 - C14	112.1(5)	N2 - C21 - C22	110.8(6)
Si1 - N2 - C21	124.7(4)	N3- C34 - C33	111.5(6)
Si1 - N2- C24	124.3(4)	O3- C32 - C31	113.8(6)
C24 - N2 - C21	110.5(5)	O3- C33- C34	110.7(7)
Si1 - N3 - C34	125.3(4)	O2- C22 - C21	111.8(6)
Si1 - N3 - C31	124.5(4)		

An ORTEP view of the full molecule is shown Fig.2.



The structure consists of one silicon atom bonded to three nitrogen atoms and one hydrogen atom. These are a part of a six membered heterocyclic ring which also have an oxygen atom. It is worthy to note that the nitrogen atoms N1, N2 and N3 are deviating from the planarity by $0.162A^0(5)$, $0.065Á^0(6)$ and $0.0484A^0(6)$

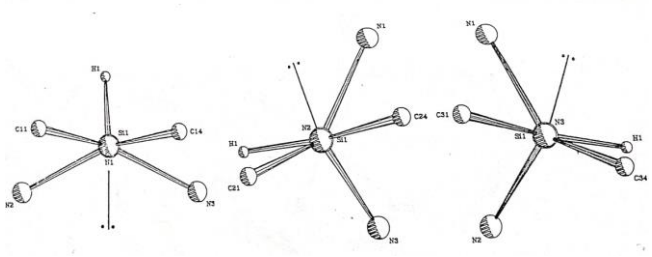
respectively. Table 5 shows a comparison of the various Si-N bond lengths reported for alkylaminosilanes both by electron diffraction and crystallography.

Table 5

A comparison of Si-N bond lengths and total angle around nitrogen in amino silanes[7,8]			
Serial no	Compound	Si-N bond length Å	Total angle around Nitrogen(deg)
1	$(CH_3)_2SiHN(CH_3)_2$	1.719(5)	352.4(18)
2	$((CH_3)_3Si)N(CH_3)_2$	1.710(5)	360.0
3	$CH_3SiH_2N(CH_3)_2$	1.715(6)	355.6(15)
4	$SiH_3N(CH_3)_2$	1.713(5)	354.6(7)
5	$(OC_4H_8N)_3Si\text{-}H$	1.692(6) Si1-N1 1.699(5) Si1-N2 1.695(5) Si1-N3	356.7(13) (N1) 359.5(13) (N2) 359.7(13) N3

Various C-C and C-O bond distances are in the expected range of 1.44Å. The total angle around various nitrogen atoms N1, N2 and N3 are 356.7°(13), 359.5°(13) and 359.7°(13) respectively, which shows that one of the nitrogen atoms is slightly more pyramidal than the other two, even though the difference is not very significant.

Fig.3 Newman projection diagrams of $(OC_4H_8N)_3Si\text{-}H$



Newman projection diagrams of compound (Fig.3) show that, lone pair orbitals on N2 and N3 nitrogen atoms overlap with σ*Si-N3 and σ*Si-N2 respectively, while the one pair orbital on N1 overlaps only with σ*Si-H. This predicts that the nitrogen N1 can be slightly electron deficient when compared with other two nitrogen atoms, where these two are having mutual interactions. This is clear from the ^{15}N NMR spectrum of this compound Fig1. The splitting of one of the nitrogen signal is due to the coupling of hydrogen attached to silicon. In this compound chemical shift in Si-H proton is ∂ 4.21 ppm and the Si-H stretching frequency (2107 cm^{-1}).

Conclusion

It clearly shows that the Si-N bond distance in this compound (1.69 Å) is shorter than those reported (Table.5), thus indicating the existence of a strong silicon-nitrogen bonding. These results indicate that may be the conjugation of the nitrogen lone pair on NI with σ* Si-H bond is maximum, the lone pair is oriented exactly anti-periplanar with Si-H bond, as can be seen from the T**.**

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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. K.N. Radhamani, Anil.J. Elias and D.K. Padma – High Yield room temperature synthesis and spectral studies of tri(amino)silanes: $(R_2N)_3SiH$ -Phosphorous, Sulfur, Silicon and related elements -vol66,297 1992.
3. A comparative Study on the ^{29}Si chemical shifts in tri(amino) silanes with the basicity of pure amines, Indian Science congress, 3-7th Jan 2015, Mumbai.
4. K.N. Radhamani, Ph.D thesis, Indian Institute of Science., May 1993.
5. 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
6. 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
7. G. Gundersen, R.A. Mayo and D.W.H. Rankin, J. Acta. Chem. Scand., 138A, 579 (1984).
8. A.J. Blake, E.A.V. Ebsworth, D.W.H. Rankin, H.E. Robertson, D. Ewan smith and A.J. Welch, J. Chem. Soc., Dalt. Trans., 91, (1986).