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Effect of Sterically Hindered Ligands on the Solid-State Structures of Organosilanediols Containing Si−N Bonds[§]

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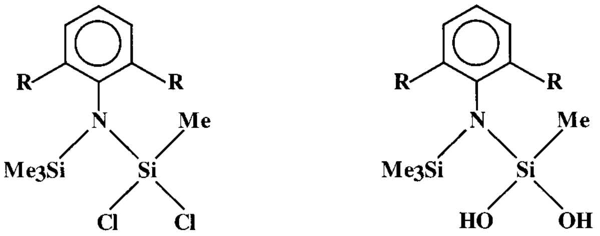
Organosilicon dichlorides containing Si−N bonds, $RN(SiMe_3)\{Si(Me)Cl_2\}$, R = 2,6-*i*-Pr_2−C_6H_3, **1a**, and R = 2,6-$Me_2C_6H_3$, **1b**, serve as excellent precursors for the corresponding silanediols, $RN(SiMe_3)\{Si(Me)(OH)_2\}$, R = 2,6-*i*-$Pr_2$−$C_6H_3$, **2a**, and R = 2,6-$Me_2C_6H_3$, **2b**. X-ray crystal structures of **1a**, **2a**, and **2b** have been carried out. The structure of **1a** represents the first example of an organosilicon dichloride containing Si−N bonds. The N-bonded silanediol **2a**, which contains the sterically encumbered isopropyl groups on the aromatic amino substituent on silicon, shows the formation of two different types of hexameric hydrogen-bonded clusters in the solid state. In contrast **2b** consists of cyclic hydrogen-bonded dimers linked by further intermolecular hydrogen bonding to afford an overall polymeric structure with a crinkled ribbon like arrangement.

Introduction

Silanols, compounds containing Si−OH groups, are attracting considerable interest in recent times because of several reasons.[1] Several types of silanols such as R_3SiOH,[2] $R_2Si(OH)_2$,[3] $RSi(OH)_3$,[4] $R_2Si(OH)OSi(OH)R_2$,[1a,5] $R_7Si_7O_9(OH)_3$,[1e] $RSi(OH)_2OSi(OH)_2R$,[6] and $[RSi(OH)O]_3$[6b] are known. These serve as excellent precursors for the preparation of a large variety of metallasiloxanes in acyclic, cyclic, or cage formulations, some of which have applications in material synthesis. Thus, utilizing the silanol $(t\text{-BuO})_3SiOH$, Tilley and co-workers have prepared a number of metallasiloxanes that serve as excellent low-temperature precursors for material synthesis because of the facile elimination of *i*-butene.[7] Apart from their synthetic applications, silanols such as silanediols $R_2Si(OH)_2$ have also been found to be potent protease inhibitors.[8] In addition, silanols

Chart 1



1a, R = *i*-Pr
1b, R = Me

2a, R = *i*-Pr
2b, R = Me

[§] Dedicated to Prof. T. Chivers on his 60th birthday.

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Table 1. Summary of Crystal and Structure Refinement Data for Compounds **1a**, **2a**, and **2b**

parameters	**1a**	**2a**	**2b**
empirical formula	$C_{16}H_{29}Cl_2NSi_2$	$C_{16}H_{31}NO_2Si_2$	$C_{12}H_{23}NO_2Si_2$
fw	362.48	325.60	269.49
temp, K	293(2)	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Cmcm*	*P*2/*c*	$P\bar{1}$
a, Å	12.351(2)	27.744(5)	10.496(2)
b, Å	12.086(2)	12.806(3)	11.4245(18)
c, Å	14.302(2)	14.302(2)	14.12(3)
α, deg	90	90	101.759(9)
β, deg	90	92.445(13)	101.022(14)
γ, deg	90	90	94.454(13)
vol, Å^3	2135.1(6)	12155(4)	1616.1(5)
Z	4	24	4
density (calcd), Mg/m^3	1.128	1.068	1.108
abs coeff, mm^{-1}	0.412	0. 179	0.212
F(000)	776	4272	584
cryst size, mm	0.60 × 0.80 × 0.76	0.40 × 0.99 × 0.40	0.20 × 0.80 × 0.40
θ range for data collection	2.36−27.50	2.10−25.00	2.10−25.00
limiting indices	$0 \leq h \leq 16, 0 \leq k \leq 15, -18 \leq l \leq 0$	$0 \leq h \leq 32, 0 \leq k \leq 15, -40 \leq l \leq 40$	$0 \leq h \leq 7, -13 \leq k \leq 13, -16 \leq l \leq 16$
reflns collected	1408	21 888	4594
independent reflns	1337 (R_{int} = 0.0649)	21 409 (R_{int} = 0.0524)	4254 (R_{int} = 0.0227)
abs correction	none	integration	none
refinement method on F^2	full-matrix least squares	full-matrix least squares	full-matrix least squares
data/restraints/params	1337/0/81	21409/0/1370	4254/8/405
goodness of fit on F^2	1.023	0.991	1.032
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0724, wR2 = 0.2081	R1 = 0.0866, wR2 = 0.1953	R1 = 0.0523, wR2 = 0.1165
R indices (all data)	R1 = 0.1192, wR2 = 0.2460	R1 = 0.1888, wR2 = 0.2486	R1 = 0.0836, wR2 = 0.1303
largest diff peak and hole, e Å^{-3}	0.406 and −0.190	0.435 and −0.443	0.202 and −0.168

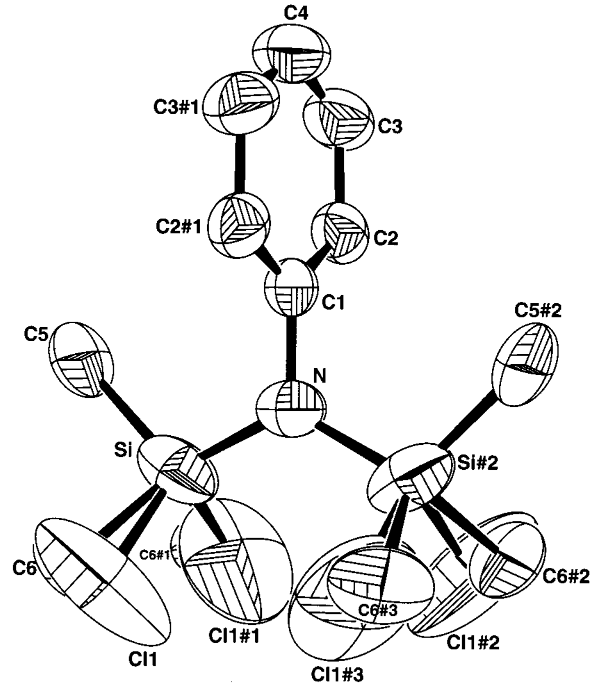

Figure 1. ORTEP diagram of **1a** shown at the 50% probability level.

have been viewed as simple models for understanding the nature of silica surfaces.[9]

Among the simplest and most useful of silanols are the silanediols $R_2Si(OH)_2$. Although many silanediols are known and are structurally characterized, there are only two examples of silanediols containing Si−N bonds that have been structurally characterized by X-ray crystallography.[3a,d] Apart from the obvious synthetic interest that these compounds possess, they are also interesting from a structural point of view, particularly in the solid state, in view of the diverse intra- and intermolecular hydrogen-bonding possibilities that exist. We report here the X-ray crystal structures of RN(SiMe$_3$){Si(Me)(OH)$_2$}, R = 2,6-*i*-Pr$_2$−C$_6$H$_3$, **2a**, and R = 2,6-Me$_2$C$_6$H$_3$, **2b**. The substituents present on the aromatic group in these two compounds exert a

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1a**[a]

Bond Distances			
Si−N	1.750(3)	Si#2−N	1.750(3)
Si−Cl(1)	1.962(8)	Si−Cl(1)#1	1.962(8)
Si−C(6)	2.023(14)	Si−C(6)#1	2.023(14)
Si−C(5)	1.936(6)	N−C(1)	1.440(7)
Bond Angles			
N−Si−C(5)	110.2	N−Si−Cl(1)#1	108.3(3)
C(5)−Si−Cl(1)#1	114.0(3)	Cl(1)#1−Si−Cl(1)	101.7(7)
N−Si−C(6)#1	115.8(7)	C(5)−Si−C(6)#1	101.1(5)
Cl(1)#1−Si−C(6)#1	13.0(8)	Cl(1)−Si−C(6)#1	107.6(4)
C(6)−Si−C(6)	110.9(13)	C(1)−N−Si	116.39(15)
C(1)−N−Si#2	116.39(15)	Si−N−Si#2	127.2(3)

[a] Symmetry transformations used to generate equivalent atoms. #1: $X, Y, -Z + {}^3/_2$. #2: $-X + 1, Y, -Z + {}^3/_2$. #3: $-X + 1, Y, Z$.

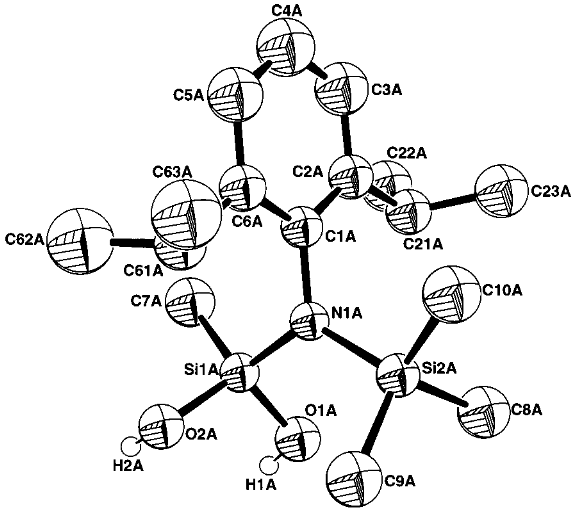

Figure 2. ORTEP diagram of **2a** shown at the 50% probability level. One of the six molecules present in the asymmetric unit are shown.

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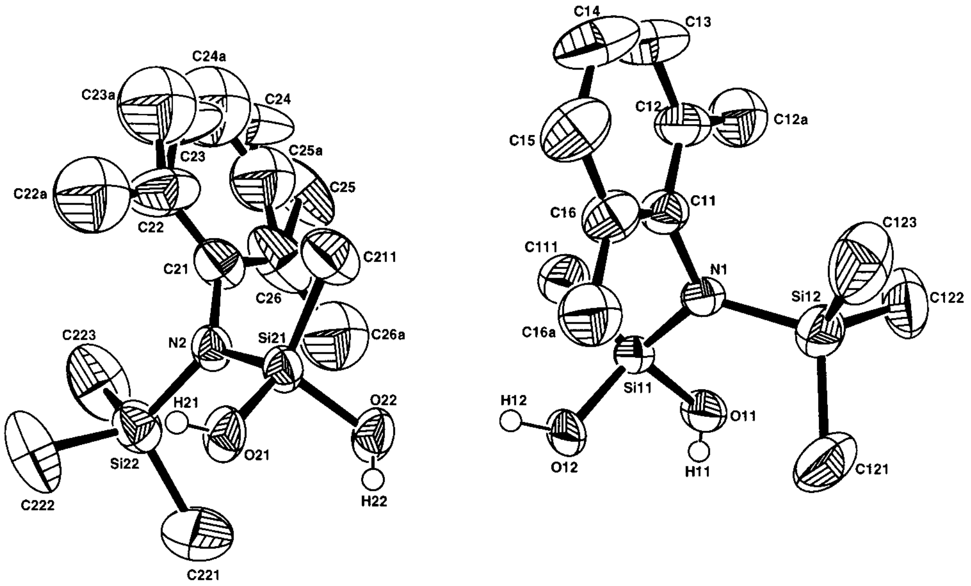

Figure 3. ORTEP diagram of **2b** shown at the 50% probability level. The two molecules present in the asymmetric unit are shown.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **2a**

bond distances		bond angles	
Molecule A			
Si(1A)−N(1A)	1.710(4)	O(1A)−Si(1A)−O(2A)	107.56(19)
Si(2A)−N(1A)	1.770(4)	Si(1A)−N(1A)−Si(2A)	123.4(2)
Si(1A)−O(1A)	1.634(3)	C(1A)−N(1A)−Si(1A)	118.9(3)
Si(1A)−O(2A)	1.651(3)	C(1A)−N(1A)−Si(2A)	117.8(3)
Molecule B			
Si(1B)−N(1B)	1.719(4)	O(1B)−Si(1B)−O(2B)	104.74(19)
Si(2B)−N(1B)	1.762(4)	Si(1B)−N(1B)−Si(2B)	123.7(2)
Si(1B)−O(1B)	1.646(4)	C(1B)−N(1B)−Si(1B)	118.5(3)
Si(1B)−O(2B)	1.647(3)	C(1B)−N(1B)−Si(2B)	117.8(3)
Molecule C			
Si(1C)−N(1C)	1.718(4)	O(1C)−Si(1C)−O(2C)	104.7(2)
Si(2C)−N(1C)	1.767(4)	Si(1C)−N(1C)−Si(2C)	121.5(2)
Si(1C)−O(1C)	1.608(4)	C(1C)−N(1C)−Si(1C)	120.1(3)
Si(1C)−O(2C)	1.659(4)	C(1C)−N(1C)−Si(2C)	118.4(3)
Molecule D			
Si(1D)−N(1D)	1.728(4)	O(1D)−Si(1D)−O(2D)	106.1(2)
Si(2D)−N(1D)	1.751(4)	Si(1D)−N(1D)−Si(2D)	124.5(2)
Si(1D)−O(1D)	1.650(4)	C(1D)−N(1D)−Si(1D)	116.0(3)
Si(1D)−O(2D)	1.628(3)	C(1D)−N(1D)−Si(2D)	119.4(3)
Molecule E			
Si(1E)−N(1E)	1.725(4)	O(1E)−Si(1E)−O(2E)	104.7(2)
Si(2E)−N(1E)	1.766(5)	Si(1E)−N(1E)−Si(2E)	122.8(3)
Si(1E)−O(1E)	1.635(4)	C(1E)−N(1E)−Si(1E)	119.3(4)
Si(1E)−O(2E)	1.638(4)	C(1E)−N(1E)−Si(2E)	117.9(4)
Molecule F			
Si(1F)−N(1F)	1.712(4)	O(1F)−Si(1F)−O(2F)	104.8(3)
Si(2F)−N(1F)	1.760(4)	Si(1F)−N(1F)−Si(2F)	121.1(2)
Si(1F)−O(1F)	1.624(4)	C(1F)−N(1F)−Si(1F)	120.6(3)
Si(1F)−O(2F)	1.636(4)	C(1F)−N(1F)−Si(2F)	118.3(3)

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for **2b**

Bond Distances			
molecule 1		molecule 2	
Si(11)−N(1)	1.717(3)	Si(21)−N(2)	1.717(3)
Si(12)−N(1)	1.754(3)	Si(22)−N(2)	1.756(3)
Si(11)−O(11)	1.632(3)	Si(21)−O(21)	1.630(3)
Si(11)−O(12)	1.643(3)	Si(21)−O(22)	1.642(3)
Bond Angles			
molecule 1		molecule 2	
Si(11)−N(1)−Si(12)	124.79(16)	Si(22)−N(2)−Si(21)	124.27(16)
C(11)−N(1)−Si(12)	116.9(2)	C(21)−N(2)−Si(21)	119.4(2)
C(11)−N(1)−Si(11)	118.3(2)	C(21)−N(2)−Si(22)	116.2(2)
O(12)−Si(11)−O(11)	104.65(16)	O(22)−Si(21)−O(21)	102.24(17)

subtle but important influence on the type of hydrogen-bonded structures that are formed in the solid state. Thus, the structure of **2a** is unprecedented for these classes of compounds showing two different types of cluster formations as a result of hydrogen-bonding association of six diol molecules. In contrast, **2b** is polymeric in the solid state with a crinkled ribbon type of structural architecture. We also report the first X-ray crystal structural characterization of an N-bonded silicon dichloride 2,6-i-Pr$_2$−C$_6$H$_3$N(SiMe$_3$){Si(Me)Cl$_2$}, **1a**, which shows an interesting positional disorder relating to the CH$_3$ and Cl groups.

Experimental Section

X-ray Structure Determination of 1a, 2a, and 2b. The compounds **1a**, **1b**, **2a**, and **2b** (Chart 1) have been synthesized as described by us previously.[3a] X-ray quality crystals of **1a** were obtained from a solution of pentane/hexane mixture (1:1) at −30 °C. Crystals of **2a** and **2b** were grown from a solution of hexane at −20 °C. X-ray data were collected on a Siemens P4S diffractometer. The details pertaining to the data collection and refinement are given in Table 1. The structures were solved and refined using the SHELXTL Program.[10] Hydrogen atoms attached to oxygen atoms were located from the difference maps, and their positions were refined. The other hydrogen atoms were fixed at calculated positions.

Results and Discussion

X-ray Crystal Structure of 1a. The X-ray crystal structure of **1a** is very interesting from a crystallographic point of view. A positional disorder is found in the structure of **1a** with the Cl and CH$_3$ groups attached to silicon disordered over the same sites at 50% occupancy for each (Figure 1). This is manifested in the metric parameters found for this compound (Table 2) with the two Si−N bond distances being *exactly the same* with a value of 1.750(3) Å. This may be compared with the situation found for the silanediols (vide infra) where two different Si−N bond lengths were obtained with the shorter distance being associated with the silicon containing the more electronegative substituents.

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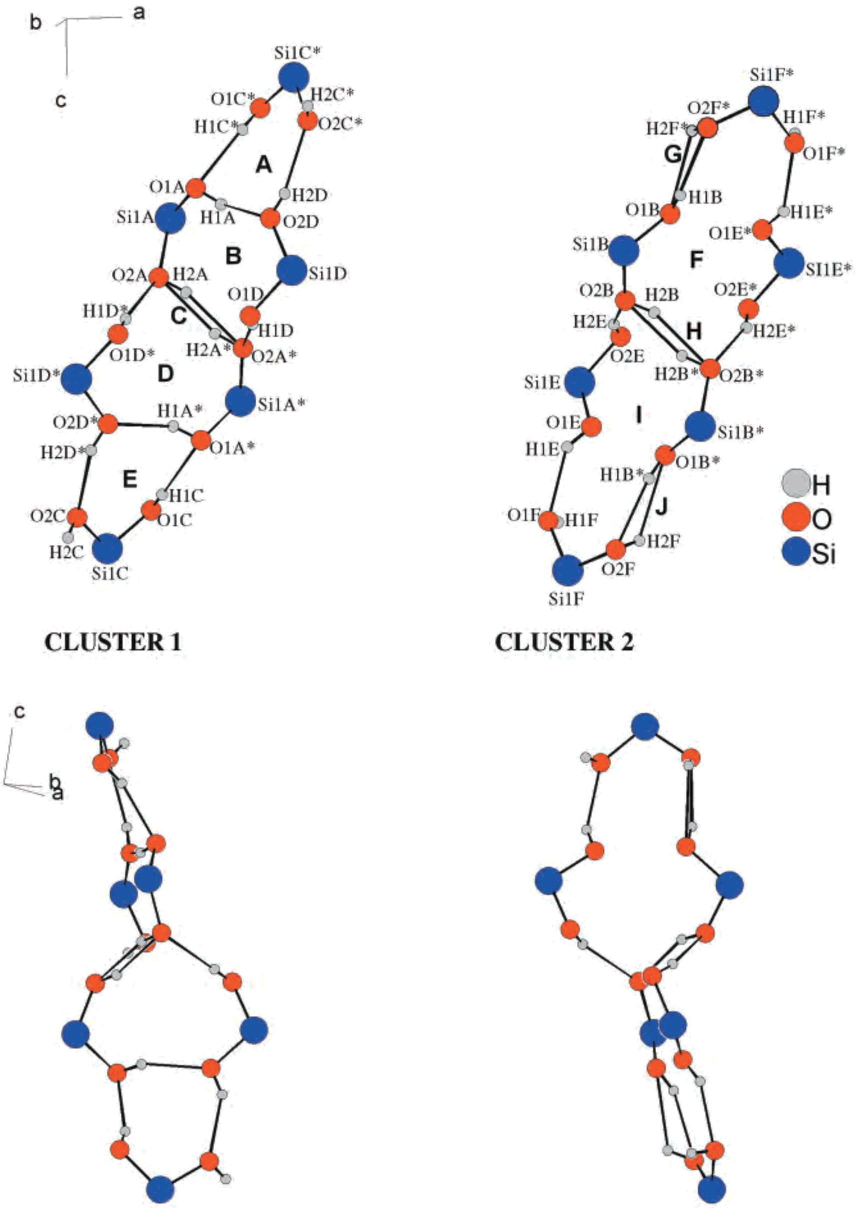
(10) Sheldrick, G. M. *SHELXTL*, verson 5.03; Siemens Analytical X-ray Division: Madison, WI 1994.

Table 5. Hydrogen Bonding Information for **2a** and **2b**

bond	distances (Å) O−H	O···O	H···O	angle (deg) O−H···O	symmetry
		2a, Cluster 1			
O1C*−H1C*···O1A	0.819(5)	2.751(15)	1.982(12)	156.0(30)	x, y, z
O2D−H2D···O2C*	0.820(6)	2.764(12)	2.045(7)	146.16(24)	$-x, -1 + y, 0.5 - z$
O1A−H1A···O2D	0.820(6)	2.713(9)	1.984(5)	147.57(26)	$-x, -1 + y, 0.5 - z$
O2A−H2A···O2A*	0.820(6)	2.872(20)	2.078(14)	162.79(22)	$-x, y, 0.5 - z$
O1D*−H1D*···O2A	0.821(4)	2.893(6)	2.086(5)	167.88(28)	$x, -1 + y, z$
		2a, Cluster 2			
O2F*−H2F*···O1B	0.819(5)	2.823(14)	2.347(9)	117.78(33)	$1-x, y, 0.5 - z$
O1B−H1B···O2F*	0.819(5)	2.823(14)	2.065(11)	153.78(28)	$1-x, y, 0.5 - z$
O1E*−H1E*···O1F*	0.820(6)	2.732(13)	2.026(7)	143.99(30)	x, y, z
O2E*−H2E*···O2B*	0.821(4)	2.929(6)	2.150(5)	158.46(29)	x, y, z
O2B−H2B···O2B*	0.821(5)	2.851(19)	2.080(14)	156.20(23)	$1-x, y, 0.5 - z$
		2b			
O11−H11···O12*	0.629(59)	2.761(9)	2.137(58)	171.31(642)	$-x, 1-y, -z$
O12−H12···O22	0.825(53)	2.807(13)	2.012(54)	161.54(503)	x, y, z
O21*−H21*···O11*	0.747(45)	2.821(7)	2.097(43)	163.33(441)	$-1 + x, y, z$
O22−H22···O21*	0.668(39)	2.843(17)	2.183(41)	169.93(456)	$-1 - x, 1 - y, -z$



CLUSTER 1 CLUSTER 2

Figure 4. Hexameric clusters of **2a** in two different views as generated by the program DIAMOND.

X-ray Crystal Structures of 2a and 2b. Molecular Structures. Some of the important metric parameters for these compounds are summarized in Tables 3 and 4. The ORTEP plots of **2a** and **2b** are shown in Figures 2 and 3, respectively. While the unit cell of **2a** contains six molecules in the asymmetric unit, that of **2b** contains two molecules.

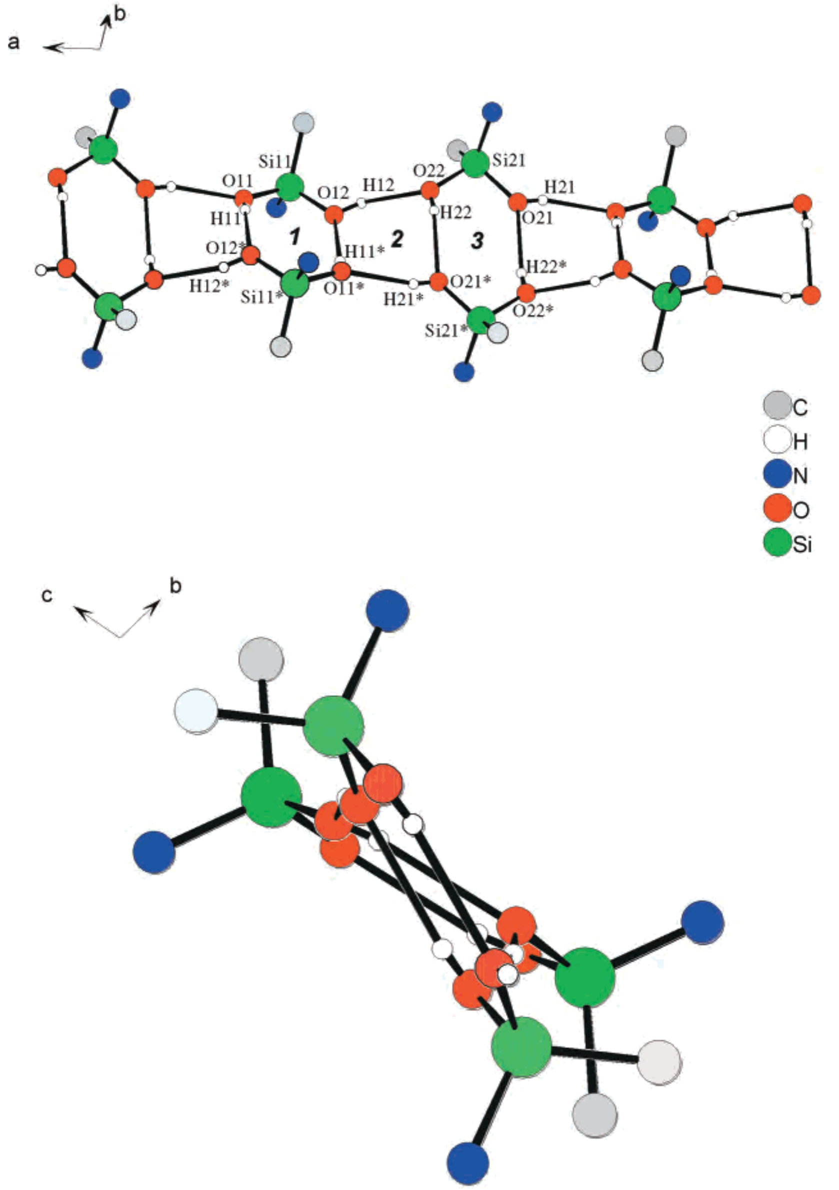


Figure 5. Polymeric ribbon of **2b** in two different views as generated by the program DIAMOND.

Both **2a** and **2b** contain two different kinds of Si−N bonds, with the shorter bond length in **2a** averaging to 1.718 (3) Å, while in **2b** the average value for this bond length is 1.717(3) Å. This short Si−N bond length is associated with the silicon attached to two electronegative oxygen atoms. Also, the geometry of nitrogen in both **2a** and **2b** is perfectly planar. These observations are consistent with the multiple bonding effects found for heavier group 14 elements.[11] The average Si−O bond length for **2a** and **2b** is 1.638(4) Å, while the average O−Si−O bond angle observed for **2a** and **2b** are 105.4(4)° and 103.45(16)°, respectively. The latter is reminiscent of the situation in silanediols containing sterically hindered substituents.[3a,g]

Hydrogen Bonding in 2a and 2b. The silanediols **2a** and **2b** show extensive intermolecular hydrogen bonding to afford discrete clusters or a polymeric network. The hydrogen-bonding parameters for these compounds are summarized in Table 5.

The intermolecular hydrogen bonding in **2a** leads to the formation of a hitherto unknown structural type in silanediols. Two different types of clusters are formed as a result of intricate hydrogen bonding between six organosilanediol molecules (Figure 4). Previously known discrete cluster structures include tetrameric structures formed by $(C_5Me_5)_2Si(OH)_2$[3f] and 2,4,6-$Me_3C_6H_2N(SiMe_3)Si(OSiMe_3)(OH)_2$.[3d] The hexameric cluster 1 is formed from two symmetrically related trimers (Si1C, Si1A*, Si1D* and Si1C*, Si1A, Si1D). These are attached to each other by the two Si−OH units, leading to the formation of a central symmetric four-membered ring C (O2A*, H2A*, O2A, H2A). The other ring formations in this cluster are the rings A and B (and the symmetrically related rings D and E). The trimeric units consisting of rings A and B or D and E are nearly perpendicular to each other (Figure 4). All the ring structures formed in this intricate cluster are nonplanar. Cluster 2, although also hexameric, is slightly differently formed. Two 14-membered ring structures can be identified (F and I). These are connected to each other by a four-membered ring H comprised of two OH units (O2B and O2B*). Further, within the ring I, a dimeric fragment (Si1E and Si1F) is attached to a third silicon (Si 1B*), leading to another four-membered ring formation (J). The formation of such four-membered rings by

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[11] Murugavel, R.; Krishnamurthy, S. S.; Chandrsekhar, J.; Nethaji, M. *Inorg. Chem.* **1993**, *32*, 5447.

the interaction of two intermolecular Si(OH) fragments is quite rare among silanols.[1d,4a]

The silanediol **2b** is also involved in an extensive intermolecular hydrogen bonding. However, in this case the hydrogen bonding leads to a different but more commonly found structural arrangement. Two molecules are involved in the formation of an eight-membered ring (**1**). The eight-membered rings are connected to each other by further hydrogen bonding to afford a one-dimensional polymeric structure (Figure 5). On the basis of the classification given by Whitesides,[12] the observed polymeric structure for **2b** is termed a polymeric *ribbon.* It is noted readily that the ribbon structure is highly crinkled because alternate eight-membered rings are arranged in a criss-cross manner with respect to each other. Figure 5 shows a clear illustration of this arrangement. The dihedral angle between the planes defined by two neighboring eight-membered rings (planes 1 and 2, Figure 5) is 20.808(23)°. The eight-membered ring formed as a result of hydrogen bonding between two silanediol units in **2b** (plane 1, Figure 5) is *perfectly planar*. The ring system formed as a result of the interconnection of two dimeric units (plane 2, Figure 5) is, however, nonplanar. The differences in the solid-state structural arrangement of **2a** and **2b** may be related to the substituents on the aromatic amino moiety attached to silicon. While a remote extra methyl group present in 2,4,6-$Me_3-C_6H_2N(SiMe_3)\{SiMe(OH)_2\}$[3a] leads to an exactly similar structure as found for **2b**, bulkier isopropyl substituents attached in the ortho positions of the aromatic moiety seem to inhibit the formation of polymeric structures. This feature is also found in the structures of the corresponding silanetriols. Thus, while the structure of 2,4,6-$Me_3-C_6H_2N(SiMe_3)\{Si(OH)_3\}$ consists of linear polymeric columns,[4c] upon incorporation of the greater sterically hindered isopropyl substituents in 2,6-i-$Pr_2-C_6H_3N$-$(SiMe_2$*i*-Pr$)\{Si(OH)_3\}$, a discrete tetrameric cluster is obtained.[4a] Thus, it seems possible to be able to modulate the type of solid-state structures formed by silanols by changing the substituents on silicon.

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Supporting Information Available: Tables giving atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **1a**, **2a**, **2b** and least-squares plane information for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev*. **1994**, *94*, 2383.