

Synthesis and Characterization of New Organosilanediols with Si–N Bonds[#]

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Using 2,6- and 2,4,6-alkyl-substituted sterically hindered primary amines, N-bonded silicon dichlorides RN(SiMe₃)(Si(Me)Cl₂) (R = 2,6-Me₂C₆H₃ (**1a**), R = 2,6-*i*-Pr-C₆H₃ (**1b**) and R = 2,4,6-Me₃C₆H₂ (**1c**)) have been prepared. Controlled hydrolysis of these dichlorides afforded the N-bonded silanediols RN(SiMe₃)(Si(Me)(OH)₂) (R = 2,6-Me₂C₆H₃ (**2a**), R = 2,6-*i*-Pr-C₆H₃ (**2b**), and R = 2,4,6-Me₃C₆H₂ (**2c**)). The X-ray crystal structure of **2c** has been carried out. The structure of the diol consists of cyclic hydrogen-bonded dimers linked by further intermolecular hydrogen bonding into a polymeric ribbonlike arrangement.

Introduction

In recent years there has been considerable interest in the chemistry of compounds containing Si–OH functional group(s).^{1–8} Many such compounds react in a facile manner with a variety of metal substrates such as metal halides, metal hydrides, metal amides, or metal alkoxides and have proved to be excellent synthons for the assembly of metallasiloxanes in an open-chain, ring, or cage structural formulations. Some of these have also been proposed as model compounds to understand the nature of silica surfaces, particularly in the context of silica-supported transition metal catalysts.⁹ One of the simplest types of Si–OH containing compounds is a silanediol in which two hydroxyl groups are bound to the same silicon center. Several organosilanediols of the type RR'Si(OH)₂ and R₂Si(OH)₂ (where R and R' are alkyl or aryl substituents) have been synthesized^{2–3,10–13} and some of them structurally characterized.^{3,14–18} In addition to being precursors for metallasiloxanes,

silanediols have also recently been studied as a new class of potent protease inhibitors.¹⁹ Although many silanediols are known, most of the reactivity studies of these compounds have been carried out on diphenylsilanediol²⁰ and di-*tert*-butylsilanediol.^{21–24} Also there are very few examples of silanediols known in which silicon is bound to atoms other than carbon.^{3,25} Apart from academic interest, silanediols containing hydrolyzable Si–N bonds can lead to metallasiloxanes containing reactive functional groups. Recently two such examples containing Si–N bonds have been reported based either on an adventitious rearrangement of a silanetriol or on the modification of a silanetriol by the replacement of one of the OH groups with an OSiMe₃ group.²⁶ In this account we describe a *direct* synthesis of stable and soluble silanediols containing Si–N bonds by adapting a procedure developed by Roesky and co-workers for the preparation of N-bonded silanetriols.²⁷ These represent the first examples of silanediols containing a nitrogen and a carbon as substituents on silicon. We also report the X-ray crystal structure of (2,4,6-Me₃C₆H₂)N(SiMe₃)(Si(Me)(OH)₂), **2c**.

[#] Dedicated to Prof. H. W. Roesky on his 64th birthday and Prof. S. Krishnamurthy on his 60th birthday.

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Table 1. ^{29}Si NMR Chemical Shifts of N-Bonded Silicon Dichlorides and Diols and Related Silicon Trichlorides and Triols

	δ NSiMe ₃	δ SiCl ₂	δ SiCl ₃	δ SiOH ₂	δ SiOH ₃	ref
(2,6-Me ₂ C ₆ H ₃)N(SiMe ₃)(MeSiCl ₂), 1a	10.3	-1.3				this work
(2,6- <i>i</i> -Pr ₂ -C ₆ H ₃)N(SiMe ₃)(MeSiCl ₂), 1b	10.4	-1.4				this work
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)(MeSiCl ₂), 1c	10.3	-1.2				this work
(2,6-Me ₂ C ₆ H ₃)N(SiMe ₃)(MeSi(OH) ₂), 2a	5.7			-29.4		this work
(2,6- <i>i</i> -Pr ₂ -C ₆ H ₃)N(SiMe ₃)(MeSi(OH) ₂), 2b	5.6			-29.9		this work
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)(MeSi(OH) ₂), 2c	5.8			-29.2		this work
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)Si(OSiMe ₃)(OH) ₂ , 3	6.5			-72.9		26
2,6-Me ₂ C ₆ H ₃ N(SiMe ₃)Si(OSiMe ₃)(OH) ₂ , 4	6.3			-72.8		26
2,6- <i>i</i> -Pr ₂ -C ₆ H ₃ N(SiMe ₃)Si(OSiMe ₃)(OH) ₂ , 5	6.4			-72.9		26
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)Si(OSiMe ₂ R)(OH) ₂ [R = CH ₂ (2-NH ₂ -3,5-Me ₂ C ₆ H ₂)], 6	5.2			-72.7		26
(2,6-Me ₂ C ₆ H ₃)N(SiMe ₃)(SiCl ₃), 7	12.5		-28.2			27
(2- <i>i</i> -Pr-6-MeC ₆ H ₃)N(SiMe ₃)(SiCl ₃), 8	12.2		-27.9			27
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)(SiCl ₃), 9	12.3		-28.3			27
(2,6-Me ₂ C ₆ H ₃)N(SiMe ₃)(SiOH ₃), 10	7.7				-66.2	27
(2- <i>i</i> -Pr-6-MeC ₆ H ₃)N(SiMe ₃)(SiOH ₃), 11	7.5				-65.3	27
(2,4,6-Me ₃ C ₆ H ₂)N(SiMe ₃)(SiOH ₃), 12	7.3				-65.8	27

Experimental Data

All the manipulations and reactions were performed under a dry nitrogen atmosphere by employing standard Schlenk techniques. Solvents were dried over sodium benzophenone ketyl and were collected from the still at the time of reaction. 2,6-Dimethylaniline, 2,4,6-trimethylaniline, and 2,6-diisopropylaniline (Fluka) were distilled under reduced pressure before use. Trimethylsilyl chloride, *n*-butyllithium (1.6 M solution in hexane), and methyltrichlorosilane (Fluka) were used as such without any further purification. Aniline (Spectrochem, India) was stored over CaH₂ and distilled before use. The instrumental methods employed have been described previously.²⁸

The N-bonded silicon dichlorides **1a**, **1b**, and **1c** and the corresponding diols **2a**, **2b**, and **2c** were synthesized by adopting the following procedure. The ^{29}Si NMR data for these compounds along with that of some related compounds are listed in Table 1.

Synthesis of the N-Bonded Silicon Dichlorides, [RN(SiMe₃)(Si(Me)Cl₂)]. *n*-BuLi (50 mmol) was added at a constant rate to a solution of RNH₂ (50 mmol) in diethyl ether (50 mL) at -78 °C. The reaction mixture was stirred at this temperature for 4 h and then brought to ambient temperature. It was then reacted with a solution of Me₃SiCl (50 mmol) in ether (25 mL) at -78 °C and allowed to come to room temperature. The LiCl precipitate was filtered, and the filtrate was reacted with *n*-BuLi (50 mmol) at room temperature. After heating under reflux for 4 h the solution was transferred to a pressure-equalizing dropping funnel and added slowly to a solution of MeSiCl₃ (50 mmol) in diethyl ether (25 mL) dropwise, stirred overnight, and then heated under reflux for 24 h. The precipitated LiCl was filtered, and the volatiles from the filtrate were removed in a vacuum to give a dark yellow viscous oily liquid. Subsequent vacuum distillation afforded the pure silicon dichlorides **1a** and **1c** as pale yellow oily liquids. **1b** was isolated as a solid.

(2,6-Me₂C₆H₃)N(SiMe₃)(Si(Me)Cl₂) (1a). Yield: 11.1 g (72.2%). Bp: 102 °C/0.08 mmHg. Anal. Calcd for C₁₂H₂₁NSi₂Cl₂: C, 47.04; H, 6.91; N, 4.57. Found: C, 46.95; H, 6.85; N, 4.63. Mass spectrum (EI, 70 eV): *m/e* 305 (M⁺, 17.4%, 2 Cl isotope pattern). ¹H NMR (200 MHz, CDCl₃): 6.95 (m, 3H, aromatic); 2.34 (s, 6H, Me); 0.50 (s, 3H, SiMeCl₂); 0.27 (s, 9H, SiMe₃).

2,6-*i*-Pr-C₆H₃N(SiMe₃)(Si(Me)Cl₂) (1b). Yield: 10.2 g (57.9%). Mp: 160 °C. Anal. Calcd for C₁₆H₂₉NSi₂Cl₂: C, 53.02; H, 8.06; N, 3.86. Found: C, 52.94; H, 7.95; N, 3.80. Mass spectrum (EI, 70 eV): *m/e* 361 (M⁺, 29%, 2 Cl isotope pattern). ¹H NMR (200 MHz, CDCl₃): 7.10 (m, 3H, aromatic); 3.43 (m,

2H, CH), ³J(H–H), 6.8 Hz; 1.21 (d, 3H, Me), ³J(H–H), 6.8 Hz; 1.20 (d, 3H, Me), ³J(H–H), 6.8 Hz; 0.26 (s, 3H, SiMeCl₂); 0.10 (s, SiMe₃).

2,4,6-Me₃C₆H₂N(SiMe₃)(Si(Me)Cl₂) (1c). Yield: 10.5 g (65.5%). Bp: 120–124 °C/0.07 mmHg. Anal. Calcd for C₁₃H₂₃NSi₂Cl₂: C, 48.73; H, 7.24; N, 4.37. Found: C, 48.65; H, 7.21; N, 4.34. Mass spectrum (EI, 70 eV): *m/e* 319 (M⁺, 20%, 2 Cl isotope pattern). ¹H NMR (200 MHz, CDCl₃): 6.90 (s, 2H, aromatic); 2.34 (s, 6H, Me); 2.29 (s, 3H, Me); 0.50 (s, 3H, SiMeCl₂); 0.27 (s, 9H, SiMe₃).

Synthesis of N-Bonded Silanediods [RN(SiMe₃)(Si(Me)(OH)₂)]. A solution of the dichloride (18.5 mmol) in diethyl ether (50 mL) was added to a mixture of water (37 mmol) and aniline (37 mmol) in diethyl ether (400 mL) at 0 °C over a period of 1 h. It was then allowed to come to room temperature and stirred for 30 h. The precipitated aniline hydrochloride was filtered. The filtrate gave a pale yellow solid on removal of the solvent in a vacuum. Repeated recrystallization from hexane gave the pure silanediod as colorless needles.

[2,6-Me₂C₆H₃N(SiMe₃)(Si(Me)(OH)₂) (2a). Yield: 3.7 g (74.0%). Mp: 87–89 °C. Anal. Calcd for C₁₂H₂₃NSi₂O₂: C, 53.48; H, 8.60; N, 5.20. Found: C, 53.26; H, 8.75; N, 5.11. Mass spectrum (EI, 70 eV): *m/e* 269 (M⁺, 98%). ¹H NMR (200 MHz, CDCl₃): 6.95 (m, 3H, aromatic); 2.29 (s, 6H, Me); 0.10 (s, 12H, O₂SiMe and SiMe₃).

[2,6-*i*-Pr-C₆H₃N(SiMe₃)(Si(Me)(OH)₂) (2b). Yield: 3.3 g (54.8%). Mp: 108–110 °C. Anal. Calcd for C₁₆H₃₁NSi₂O₂: C, 59.02; H, 9.60; N, 4.30. Found: C, 58.92; H, 9.52; N, 4.21. Mass spectrum (EI, 70 eV): *m/e* 325 (M⁺, 65%). ¹H NMR (200 MHz, CDCl₃): 7.20 (m, 3H, aromatic); 3.54 (m, 2H, CH), ³J(H–H), 6.9 Hz; 1.23 (d, 3H, Me), ³J(H–H), 6.9 Hz; 1.21 (d, 3H, Me), ³J(H–H), 6.9 Hz; 0.17 (s, 3H, O₂SiMe); 0.15 (s, SiMe₃).

[2,4,6-Me₃C₆H₂N(SiMe₃)(Si(Me)(OH)₂) (2c). Yield: 3.5 g (66.6%). Mp: 64–65 °C. Anal. Calcd for C₁₃H₂₅NSi₂O₂: C, 55.07; H, 8.89; N, 4.94. Found: C, 54.92; H, 8.75; N, 4.83. Mass spectrum (EI, 70 eV): *m/e* 283 (M⁺, 40%). ¹H NMR (200 MHz, CDCl₃): 6.79 (s, 2H, aromatic); 2.21 (s, 6H, Me); 2.18 (s, 3H, Me), 0.07 (s, 12H, O₂SiMe and SiMe₃).

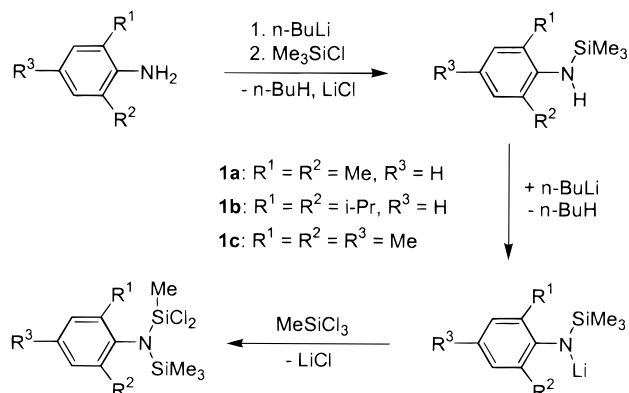
X-ray Structure Determination of 2c. Colorless crystals of **2c** were grown from a solution of hexane at -20 °C. A crystal of dimensions 0.14 × 0.14 × 0.8 mm was mounted on a Siemens SMART CCD diffractometer. The details pertaining to the data collection and refinement are given in Table 2. The structure was solved and refined using the SHELXTL program.²⁹ 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.

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Table 2. Crystal Data and Structure Refinement for 2c

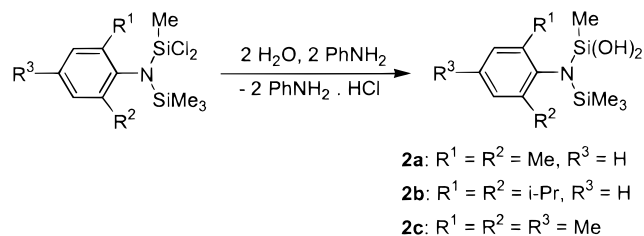
parameter	compound 2c
empirical formula	C ₁₃ H ₂₅ NO ₂ Si ₂
fw	283.52
temperature	166(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	C2/c
unit cell dimens	$a = 29.302(4)$, Å; $\alpha = 90^\circ$ $b = 10.4389(14)$, Å; $\beta = 104.987(2)^\circ$ $c = 23.561(3)$, Å; $\gamma = 90^\circ$
volume, Z	6961.1(17) Å ³ , 16
density (calcd)	1.074 Mg/m ³
abs coeff	0.200 mm ⁻¹
F(000)	2432
cryst size	0.14 × 0.14 × 0.8 mm
θ range for data collection	2.62–26.39°
limiting indices	$-36 \leq h \leq 35$, $-4 \leq k \leq 12$, $-27 \leq l \leq 29$
no. of reflns collected	20125
no. of indep reflns	6763 ($R_{\text{int}} = 0.0368$)
abs corr	none
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6763/4/403
goodness-of-fit on F^2	0.784
final R indices [$I > 2\sigma(I)$]	R1 = 0.0406, wR2 = 0.902
R indices (all data)	R1 = 0.0915, wR2 = 0.0958
extinction coeff	0.00049(7)
largest diff peak and hole	0.191 and -0.234 e Å ⁻³

Scheme 1. Synthesis of N-Bonded Silicon Dichlorides

Results and Discussion

Synthesis and Spectra. Sterically hindered aromatic primary amines were used as starting materials. The N-bonded silicon dichlorides **1a**, **1b**, and **1c** were prepared in good yields by a multistep synthetic strategy involving sequential deprotonation at nitrogen followed by reaction with silyl halides (Scheme 1). While **1a** and **1c** could be isolated as oils by vacuum distillation, **1b** was isolated as a solid. All the dichlorides were found to be stable and possess long shelf lives in the absence of moisture. However, in a controlled experiment when **1b** was left in the NMR tube for 2 days dissolved in CDCl₃, it was found to completely convert to the corresponding silanediol, suggesting that ambient moisture is sufficient to hydrolyze these compounds.

Controlled hydrolysis of the silicon dichlorides using an excess of diethyl ether as the solvent and aniline as the hydrogen chloride acceptor affords the N-bonded silanediols **2a**, **2b**, and **2c** as free flowing white powders with long shelf lives (Scheme 2). These compounds are

Scheme 2. Synthesis of N-Bonded Silanediols

extremely lipophilic and are soluble in a large range of organic solvents including hexane. This favorable solubility property, which undoubtedly is the result of the SiMe₃ substituent on nitrogen and the alkyl substituents on the aromatic group, would be of considerable synthetic value in the use of these silanediols for further reactions.

All the new N-bonded silicon dichlorides and silanediols have been characterized by mass spectroscopy, elemental analysis, infrared spectroscopy, and NMR. Prominent parent ions are seen in the electron impact mass spectra for all the compounds. The ²⁹Si NMR data are summarized in Table 1 along with those of some related compounds. The ²⁹Si resonances move upfield upon hydrolysis. This is accentuated for the chemical shift of the SiCl₂. In comparison to the other N-bonded silanediols known in the literature where the silicon is attached to *three* oxygens, the corresponding silicons in **2a**, **2b**, and **2c** are attached to only two oxygens, and consequently the chemical shifts in the latter are downfield. It is interesting to note that the chemical shifts of SiCl₃ in N-bonded silicon trichlorides are very similar to the chemical shifts of Si(OH)₂ in **2a**, **2b**, and **2c**. In comparison the chemical shifts of Si(OH)₃ in related compounds are upfield.

The infrared spectra of silanediols **2a**, **2b**, and **2c** in the solid state recorded as KBr pellets or in Nujol mull are characterized by the presence of a strong and broad absorption centered around 3350 cm⁻¹. In solution (dichloromethane or carbon tetrachloride) a new sharp peak at 3620 cm⁻¹ begins to predominate at the expense of the broad absorption, with the final disappearance of the latter upon dilution. These observations are reminiscent of the situation found for organic alcoholic compounds³⁰ as well as for other organosilanediols.^{3,31} Therefore, it may be possible to assign the absorption at 3620 cm⁻¹ to the *free* hydroxyl groups of the silane diols in the present instance.

X-ray Crystal Structure of 2c. The molecule crystallizes in the monoclinic space group C2/c with Z = 16. There are two independent molecules in the asymmetric unit. The molecular structure of **2c** is depicted in Figure 1. Some of the important structural parameters are summarized in Table 3.

The structure of **2c** shows that there are two different kinds of Si–N bonds (Si(11)–N(1), 1.7140(18) Å, and Si(21)–N(2), 1.7586(18) Å). The shorter bond length is associated with the silicon atom that is attached to two oxygen atoms and a carbon atom, while the longer bond length corresponds to the silicon atom attached to three

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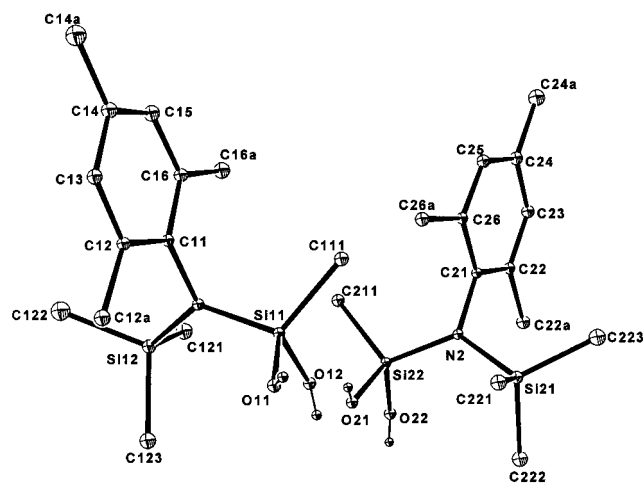


Figure 1. Molecular structure of the two crystallographically independent molecules of **2c**.

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] for **2c**

		Bond Distances			
		molecule 1	molecule 2		
Si(11)–N(1)	1.7140(18)	Si(21)–N(2)	1.7586(18)		
Si(12)–N(1)	1.7510(18)	Si(22)–N(2)	1.7125(18)		
Si(11)–O(11)	1.6379(18)	Si(22)–O(21)	1.6373(18)		
Si(11)–O(12)	1.6336(18)	Si(22)–O(22)	1.636(2)		
		Bond Angles			
		molecule 1	molecule 2		
Si(11)–N(1)–Si(12)	125.48(10)	Si(22)–N(2)–Si(21)	124.64(10)		
C(11)–N(1)–Si(11)	116.30(13)	C(21)–N(2)–Si(21)	116.28(14)		
C(11)–N(1)–Si(12)	118.01(14)	C(21)–N(2)–Si(22)	119.02(13)		
O(12)–Si(11)–O(11)	104.42(10)	O(22)–Si(21)–O(21)	102.01(11)		
		Hydrogen Bonding			
H-bond	O–H	O···O	H···O	O–H···O	symmetry
O11A–H11D···O22B	0.642	2.810	2.176	169.6	<i>x</i> , 1+ <i>y</i> , <i>z</i>
O12–H12···O11A	0.650	2.769	2.124	172.0	– <i>x</i> , 1– <i>y</i> , 1– <i>z</i>
O21–H21···O12	0.638	2.782	2.208	150.6	<i>x</i> , <i>y</i> , <i>z</i>
O22–H22···O21B	0.645	2.801	2.198	156.3	– <i>x</i> , – <i>y</i> , 1– <i>z</i>

carbon atoms. This trend is also seen for the N-bonded silanetriol **12**. Also the corresponding Si–N bond length in **12** of 1.710(12) Å is shorter than that observed in the present instance. These observations are consistent with multiple bonding effects found in group 14 and 15 elements that are bound to electronegative substituents.³² The Si–O bond distances in **2c** average to 1.6358(18) Å. This value is comparable to that found in many silanols.³ The bond angles around nitrogen add up to nearly 360°. This feature is consistent with that observed for **12**.²⁷ The observed O–Si–O bond angles in the two molecules are 104.42(10)° and 102.01(11)°. These values are closer to those observed for silanediols bearing sterically hindered substituents, (C₆H₁₁)₂Si(OH)₂ (106.00(7)°),¹⁷ *t*-Bu₂Si(OH)₂ (106.0(5)°)¹⁴ and Cp*₂Si(OH)₂ (106(1)°)¹⁸ than to those that have sterically unencumbered substituents, Et₂Si(OH)₂ (109.8(2)°).³³

The silanediol **2c** is involved in extensive intermolecular hydrogen bonding. Two molecules are involved

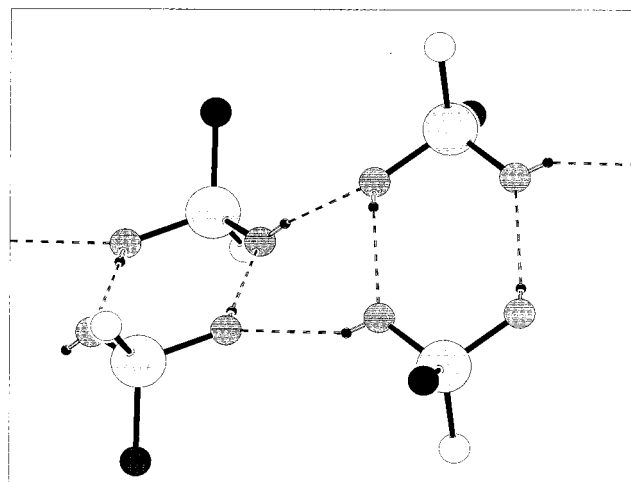


Figure 2. PLATON and line diagrams of two interconnected dimeric units of **2c** showing the twisted ribbon arrangement.

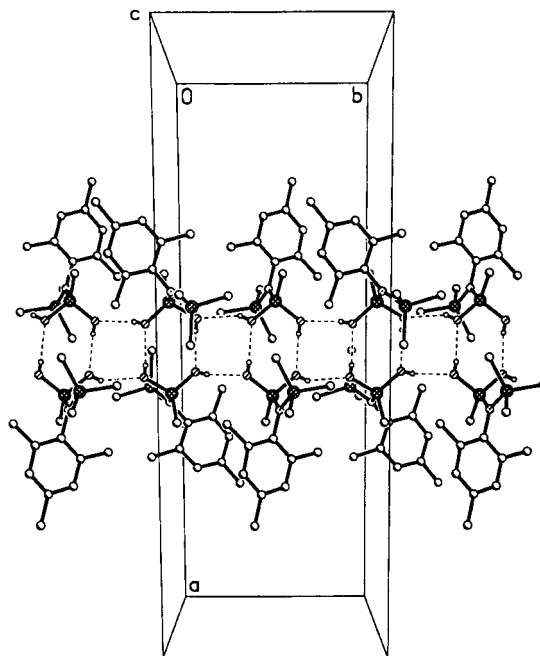


Figure 3. Packing diagram of **2c** showing the proliferation of the ribbon structural motif in the *ab*-plane.

in the formation of an eight-membered ring. The eight-membered rings are connected to each other by further hydrogen bonding to afford ribbonlike structures (Figure 2). Although these structures could be also termed as tapes, recently Whitesides has come out with a systematic classification of polymeric sheetlike structures that occur as a result of hydrogen bonding in amides, and the tapes have been distinguished from the ribbons by the fact that in the former each molecule is hydrogen

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Table 4. Least-Squares Plane Information for 2c^a

plane A		plane B	
atom	deviation (Å)	atom	deviation (Å)
Si22	-0.0210	O12	-0.4106
O21	0.0469	H12	-0.1979
O22	-0.0830	O21	0.3521
H22	0.1285	H21	0.2535
Si2D	0.0210	O22B	-0.2647
O21B	-0.0469	H2Z	-0.3148
O22B	0.0830	O11A	0.3820
H2Z	-0.1285	H11D	0.2003
mean deviation from plane	0.0698	mean deviation from plane	0.2970

^a Angle between planes A and B is 23.6°; between A and C, 30.146(017)°; and between B and C, 22.365(023)°.

bonded to *two* neighboring molecules, whereas a ribbon motif is generated when each molecule is hydrogen bonded to *three or more* molecules.³⁴ Applying Whitesides' classification, **2c** is called a ribbon. The ribbon runs in the *ab*-plane parallel to *b*, being centered at $a = 0$, $a = 0.5$, $a = 1$, $a = 1.5$, etc (Figure 3). The hydrogen-bonding parameters are summarized in Table 3. The eight-membered ring formed as a result of hydrogen bonding between two silanediol units is perfectly symmetric with respect to the bond lengths and angles involved. Also the ring is very nearly planar, although the two silicons involved in the dimer formation deviate from the mean plane in opposite directions (~ 0.02 Å). The hydrogens involved, viz., H22 and H2Z, also deviate in a similar manner albeit with a slightly larger magnitude (~ 0.13 Å) (Table 4). However, the overall deviations from the mean plane defined by the atoms involved in the formation of the eight-membered ring, Si22, O21, O22, H22, Si2D, O21B, O22B, and H2Z, are very small, with the mean deviation from the plane being about 0.07 Å. This feature is in contrast to other such dimeric structures, which have been found to be in a clear chair conformation.¹⁴ The angle between two adjacent eight-membered rings is nearly 30°. The ring

system formed as a result of the interconnection of two dimeric units is completely nonplanar, with an overall mean deviation from this plane being about 0.30 Å (Table 4). The overall result of this type of arrangement is the formation of a twisted ribbon running in the *ab*-plane (Figures 2 and 3). It is interesting to compare the structure of **2c** with the N-bonded silanetriol **12**. In the latter, the presence of an additional OH on silicon allows the molecules to arrange themselves in a tubular structure constructed from four one-dimensional linear columns. The absence of the third hydroxyl substituent in **2c** favors the dimer formation between two diol molecules.²⁷ This arrangement limits additional hydrogen-bonding possibilities and directs the formation of the observed twisted ribbon structure.

Conclusions

We have synthesized and characterized the first examples of silanediols that contain a nitrogen and a carbon as substituents on silicon. These compounds are air stable and are soluble in a wide range of organic solvents from hexane to methanol, making them excellent starting reagents for further reactions with various transition metal and main-group substrates. These studies are in progress.

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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 **2c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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