Monatshefte für Chemie 130, 99–107 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

A Zwitterionic λ^5*Si*-Silicate with an Almost Ideal Square-Pyramidal Si Coordination Polyhedron: Synthesis and Crystal Structure Analysis

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Summary. The pentacoordinate silicon compound ((morpholinio)methyl)*bis*(3,4,5,6-tetrachlorobenzene-1,2-diolato(2−))silicate–acetonitrile (**4** · CH_3CN), a zwitterionic spirocyclic λ^5*Si*-silicate, has been synthesized and structurally characterized by single-crystal X-ray diffraction analysis. Compound **4** · CH_3CN was prepared by reaction of the silanes $(MeO)_3SiCH_2NR_2$, $Ph(MeO)_2SiCH_2NR$, or $Me(MeO)_2SiCH_2NR_2$ (NR_2 = morpholino) with two mol equivalents of 3,4,5,6-tetrachlorobenzene-1,2-diol in acetonitrile at room temperature. The Si coordination polyhedron of **4** · CH_3CN in the crystal is a nearly ideal square pyramid, the basal positions being occupied by the four oxygen atoms of the two diolato(2−) ligands. Significant differences between the isotropic ^{29}Si chemical shifts of **4** · CH_3CN in the crystal ($\delta = -85.1$) and in solution ($\delta = -131.9$, *DMSO*-d_6) indicate special structural features in solution.

Keywords. Pentacoordinate silicon; Zwitterionic λ^5*Si*-silicate; Crystal structure analysis; Solid-state ^{29}Si NMR; Solution-state ^{29}Si NMR.

Ein zwitterionisches λ^5*Si*-Silicat mit einem nahezu idealen quadratisch-planaren Si-Koordinationspolyeder: Synthese und Kristallstrukturanalyse

Zusammenfassung. Die pentakoordinierte Siliciumverbindung ((Morpholinio)methyl)*bis*(3,4,5,6-tetrachlorbenzol-1,2-diolato(2−))silicat–Acetonitril (**4** · CH_3CN), ein zwitterionisches spirocyclisches λ^5*Si*-Silicat, wurde synthetisiert und mittels Einkristallröntgenstrukturanalyse strukturell charakterisiert. Verbindung **4** · CH_3CN wurde durch Reaktion der Silane $(MeO)_3SiCH_2NR_2$, $Ph(MeO)_2SiCH_2NR_2$ oder $Me(MeO)_2SiCH_2NR_2$ (NR_2 = Morpholino) mit zwei Mol-Äquivalenten 3,4,5,6-Tetrachlorbenzol-1,2-diol in Acetonitril bei Raumtemperatur dargestellt. Das Si-Koordinationspolyeder von **4** · CH_3CN im Kristall ist eine nahezu ideale quadratische Pyramide, wobei die vier Sauerstoffatome der beiden Diolato(2−)-Liganden die basalen Positionen besetzen. Drastische Unterschiede in den isotropen ^{29}Si-chemischen Verschiebungen von **4** · CH_3CN im Kristall ($\delta = -85.1$) und in Lösung ($\delta = -131.9$, *DMSO*-d_6) weisen auf Besonderheiten der Struktur in Lösung hin.

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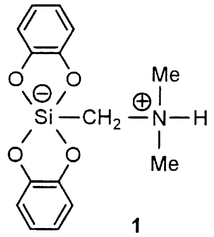
Introduction

In a series of recent papers, we have reported on the syntheses and crystal structures of some zwitterionic (ammoniomethyl)*bis*(benzene-1,2-diolato(2−))silicates [1], such as compounds **1** [1e,i] and **2** [1e,i]. Although most of the Si coordination polyhedra of pentacoordinate silicon compounds of this particular formula type have shown to be more or less distorted trigonal bipyramids, several intermediate structures between the ideal trigonal bipyramid and the ideal square pyramid have been observed [1].



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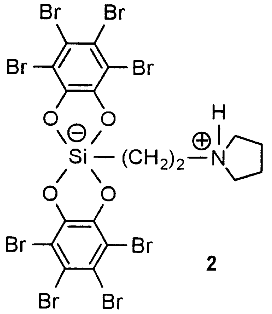

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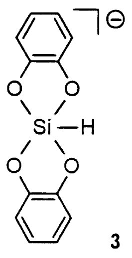

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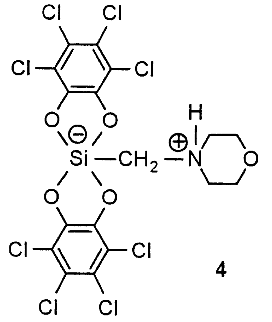

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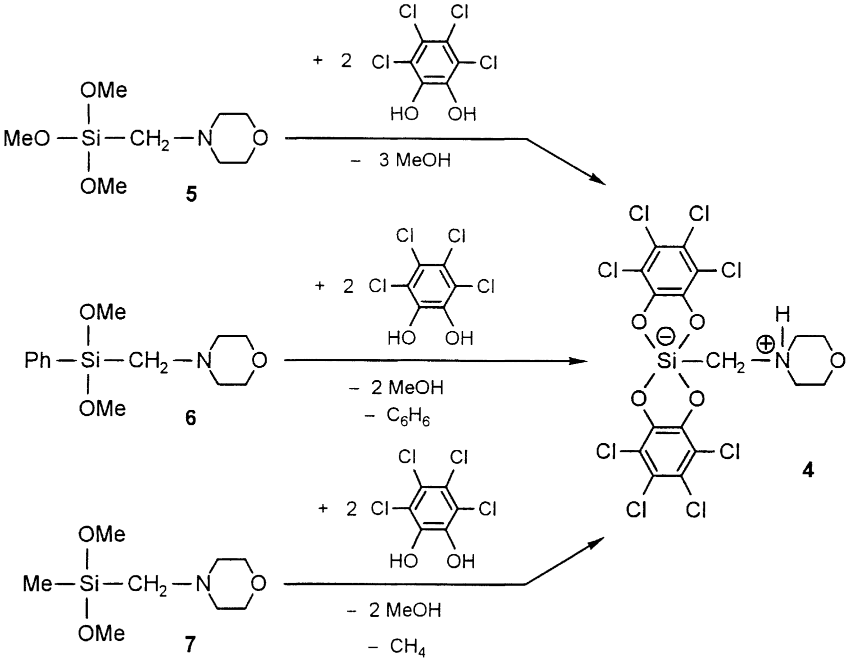
This is in good accordance with the results of *ab initio* studies with the anionic model species **3**. As shown by SCF/SVP geometry optimizations, the trigonal-bipyramidal structure of **3** (C_2 symmetry) is only 5.82 kJ mol^{-1} more stable than the alternative square-pyramidal structure (C_s symmetry) [2]. Thus, it is likely to assume that the geometries of the Si coordination polyhedra of the above-mentioned zwitterionic λ^5*Si*-silicates in the crystal are mainly governed by the crystal packing, including hydrogen bonds.

We have now succeeded in preparing a zwitterionic λ^5*Si*-silicate with an almost ideal square-pyramidal Si coordination polyhedron. We report here on the synthesis and crystal structure of ((morpholinio)methyl)*bis*(3,4,5,6-tetrachlorobenzene-1,2-diolato(2−))silicate–acetonitrile (**4** · CH_3CN). The studies presented here were carried out as a part of our systematic investigations on zwitterionic λ^5*Si*-silicates (in this context, see Ref. [3]; for reviews dealing with pentacoordinate silicon compounds, see Ref. [4]).

Results and Discussion

Syntheses

The zwitterionic λ^5Si-silicate **4** was synthesized by reaction of the silanes **5** [1h], **6** [1h], or **7** [5] with two mol equivalents of 3,4,5,6-tetrachlorobenzene-1,2-diol (Scheme 1). All syntheses were carried out in acetonitrile at room temperature. The first method (**5**→**4**) involves cleavage of three Si–O bonds (formation of three mol equivalents of methanol), whereas the second (**6**→**4**) and third method (**7**→**4**) are based on the cleavage of two Si–O bonds and one Si–C bond (formation of two mol equivalents of methanol and one mol equivalent of benzene and methane, respectively).



Scheme 1

The zwitterionic λ^5Si-silicate **4** was isolated as the crystalline acetonitrile solvate **4** · CH_3CN (yield 77% (method 1), 33% (method 2), 60% (method 3)). Its identity was established by elemental analyses (C, H, N), solution-state (^1H, ^{13}C, ^{29}Si) and solid-state (^{29}Si CP/MAS) NMR experiments, and mass spectrometric studies. In addition, compound **4** · CH_3CN was structurally characterized by single-crystal X-ray diffraction.

Crystal structure analysis

Compound **4** · CH_3CN crystallizes in the space group $P\bar{1}$, the unit cell containing two zwitterions **4** and two acetonitrile molecules. The crystal data and experimental parameters used for this study are given in Table 1 (for further

Table 1. Crystal data and experimental parameters for the crystal structure analysis of **4** · CH_3CN

Empirical formula	$C_{19}H_{14}Cl_8N_2O_5Si$
Formula mass ($g \cdot mol^{-1}$)	662.01
Collection temperature (K)	133(2)
$\lambda(MoK_\alpha)$ (Å)	0.71073 Å
Crystal system	triclinic
Space group (no.)	$P\bar{1}(2)$
a (Å)	10.0594(1)
b (Å)	11.1881(1)
c (Å)	11.7878(1)
α (deg)	108.755(1)
β (deg)	95.931(1)
γ (deg)	96.621(1)
V (Å^3)	1233.86(2)
Z	2
D(calcd.) ($g \cdot cm^{-3}$)	1.782
μ (mm^{-1})	0.999
$F(000)$	664
Crystal dimensions (mm)	0.8×0.5×0.5
2θ range (deg)	3.70–56.62
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 15$
Reflections collected	18088
Independent reflections	5917
R_{int}	0.0210
Max/min transmission	0.6350/0.5021
Reflections used	5917
Parameters	322
S^a	1.048
Weight parameters a/b^b	0.0383/0.5661
$R1^c(I > 2\sigma(I))$	0.0267
$wR2^d$ (all data)	0.0716
Extinction coefficient	0.0082(8)
Max/min residual electron density ($e \cdot Å^{-3}$)	+0.462/−0.322

[a] $S = (\Sigma(w(F_o^2 - F_c^2)^2)/(n-p))^{0.5}$, n = no. of reflections, p = no. of parameters; [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$; [c] $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; [d] $wR2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{0.5}$

Table 2. Selected interatomic distances (Å) and angles (deg)

Si–O1	1.7513(10)	Si–O4	1.7421(10)
Si–O2	1.7309(10)	Si–C1	1.898(2)
Si–O3	1.7455(10)		
O1–Si–O2	88.93(5)	O2–Si–O4	152.54(5)
O1–Si–O3	157.76(5)	O2–Si–C1	105.43(5)
O1–Si–O4	86.43(5)	O3–Si–O4	89.27(5)
O1–Si–C1	105.49(6)	O3–Si–C1	96.75(6)
O2–Si–O3	84.88(5)	O4–Si–C1	101.89(5)

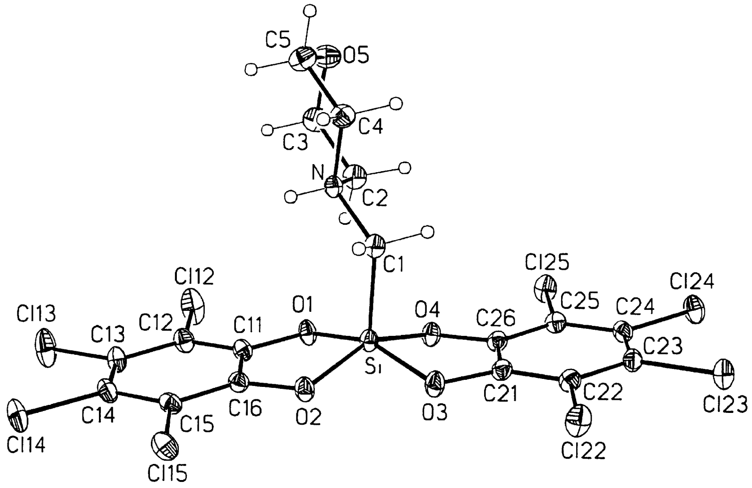


Fig. 1. Molecular structure of **4** in the crystal of **4**·CH_3CN (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme

details, see Experimental). The molecular structure of **4** in the crystal of the acetonitrile solvate **4**·CH_3CN is depicted in Fig. 1. Selected interatomic distances and angles are listed in Table 2.

The coordination polyhedron around the silicon atom of **4** can be described as a nearly ideal square pyramid, the basal positions being occupied by the four oxygen atoms of the two 3,4,5,6-tetrachlorobenzene-1,2-diolato(2−) ligands. The two chelating ligands are almost coplanar, with the central silicon atom deviating from this plane by 0.38 Å.

As shown in Fig. 2 and 3, the zwitterions and acetonitrile molecules are connected by intermolecular N–H···N hydrogen bonds (N–H, 0.82(2) Å; H···N1A, 2.10(2) Å; N···N1A, 2.879(2) Å; N–H···N1A, 157(2)°). Obviously, the crystal packing of **4**·CH_3CN is mainly governed by intermolecular interactions between the almost coplanar aromatic 3,4,5,6-tetrachlorobenzene-1,2-diolato(2−) ligands of the zwitterions (mean distance between the two planes 3.37 Å, maximum deviation 0.04 Å), leading to a layer structure (Fig. 2). The acetonitrile molecules are also arranged almost coplanar to these layers. As can be seen from Fig. 3, the intermolecular interactions between the diolato(2−) ligands of two zwitterions leads to the formation of centrosymmetric dimeric building blocks in the crystal. It is likely to assume that this particular intermolecular interaction is mainly responsible for the existence of the energetically less favorable square-pyramidal Si coordination polyhedron of **4** in the crystal of **4**·CH_3CN.

NMR studies

The solution-state ^{1}H and ^{13}C NMR data of **4**·CH_3CN (solvent: *DMSO*-d_6) are compatible with the existence of the zwitterion **4** in solution. However, the results of the solid-state and solution-state ^{29}Si NMR studies are indicative of special structural features in solution. The isotropic ^{29}Si chemical shifts observed in the

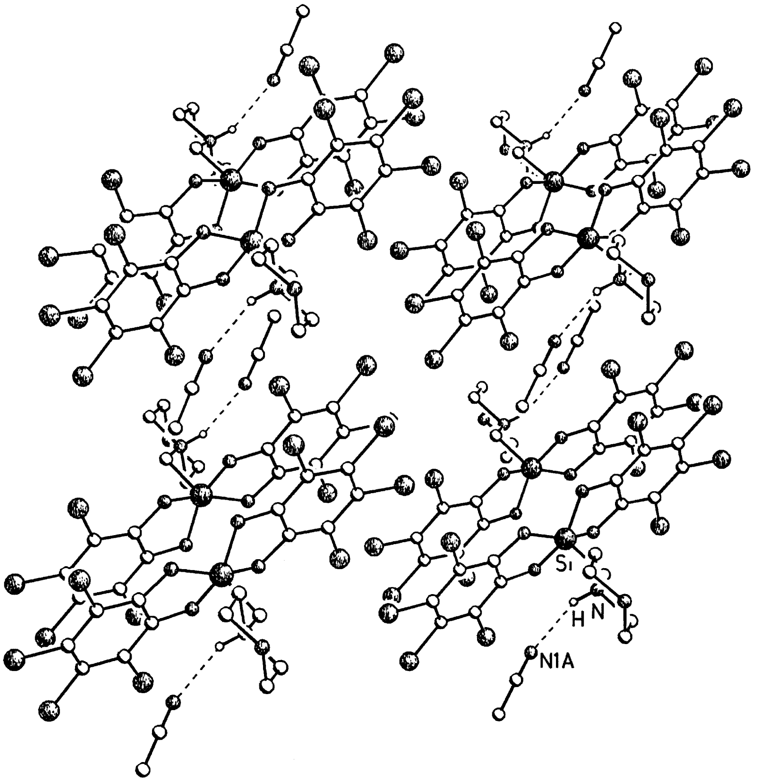


Fig. 2. Cell plot for **4** · CH_3CN in view along [001], showing the layer structure in the crystal lattice; hydrogen atoms (except NH) are omitted for clarity

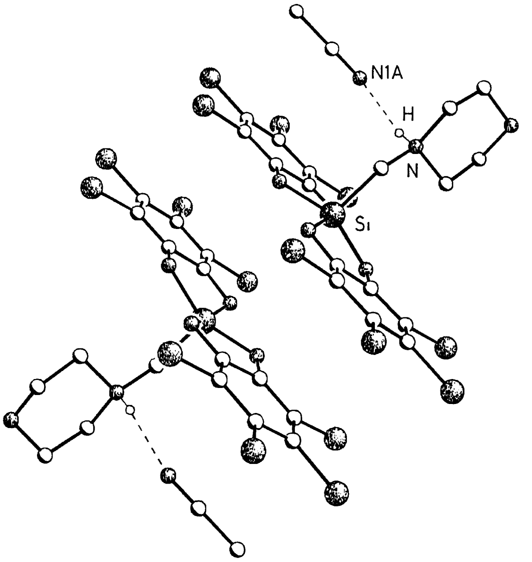


Fig. 3. Centrosymmetric dimeric building block in the crystal of **4** · CH_3CN; the mean distance between the two planes formed by the two almost coplanar diolato(2−) ligands of each zwitterion amounts to 3.37 Å

crystal ($\delta = -85.1$) and in solution ($\delta = -131.9$) differ significantly from each other, whereas the respective solid-state and solution-state ^{29}Si NMR data for compounds **1** and **2** are very similar. This remarkable discrepancy might be explained in terms of hexacoordination of the silicon atom of **4** in solution (*e.g.* intermolecular interactions of **4** with *DMSO*-d$_6$). However, further studies have to be performed to check this (rather speculative) hypothesis and to find an explanation for the quite different behavior of **1**/**2** and **4** in solution.

Experimental

Syntheses

All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Leitz Biomed microscope equipped with a heater (Leitz, Model M 350). The ^{1}H, ^{13}C, and ^{29}Si solution-state NMR spectra were recorded at room temperature on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz). *DMSO*-d$_6$ was used as solvent. Chemical shifts (ppm) were determined relative to internal *DMSO*-d$_5$ (^{1}H, $\delta = 2.49$), *DMSO*-d$_6$ (^{13}C, $\delta = 39.5$), and external *TMS* (^{29}Si, $\delta = 0$). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. The ^{29}Si CP/MAS NMR spectrum was recorded at room temperature on a Bruker DSX-500 NMR spectrometer with double air bearing rotors (ZrO$_2$, diameter 7 mm) containing *ca.* 200 mg of sample (99.4 MHz, *TMS* as external standard ($\delta = 0$), spinning rate 3980 Hz, contact time 7 ms, 90° ^{1}H transmitter pulse length 5.5 µs, repetition time 25 s). Mass spectra were obtained with a Finnigan MAT-8430 mass spectrometer (FAB MS, 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source).

((Morpholinio)methyl)bis(3,4,5,6-tetrachlorobenzene-1,2-diolato(2−))silicate–Acetonitrile (**4**·CH$_3$CN)

Method 1. Compound **5** (2.00 g, 9.04 mmol) was added dropwise at room temperature within 2 min to a solution of 3,4,5,6-tetrachlorobenzene-1,2-diol (4.48 g, 18.1 mmol) in acetonitrile (35 ml; formation of a precipitate after *ca.* 2 min). The reaction mixture was stirred for 2 min and then kept undisturbed at room temperature for 3 d. The precipitate was filtered off, washed with cold acetonitrile (2×10 ml), and then recrystallized from acetonitrile. The product was isolated by filtration and dried *in vacuo* (0.001 torr, 20°C, 5 h) to give 4.59 g of colorless crystals.

Yield: 77%; m.p.: 278°C (dec); ^{1}H NMR: $\delta = 2.06$ (s, 3H, CH$_3$CN), 2.35 (d, $^3J_{HH} = 5.1$ Hz, 2H, SiCH$_2$N), 2.83–3.03, 3.41–3.58, 3.59–3.80, and 3.82–4.00 (m, 8H, CCH$_2$N, CCH$_2$O), 8.3 (br s, 1H, NH) ppm; ^{13}C NMR: $\delta = 1.2$ (*C*H$_3$CN), 54.4 (SiCH$_2$N), 54.9 (N*C*H$_2$C), 63.5 (C*C*H$_2$O), 113.0 (C-4/C-5, C$_6$Cl$_4$O$_2$), 118.1 (C-3/C-6, C$_6$Cl$_4$O$_2$), 147.5 (C-1/C-2, C$_6$Cl$_4$O$_2$) ppm, CH$_3$*C*N not localized; ^{29}Si NMR: $\delta = -131.9$ ppm; ^{29}Si CP/MAS NMR: $\delta = -85.1$ ppm; FAB MS (positive ions): $m/z = 622$ (12) $(\mathrm{M}({}^{12}\mathrm{C}_{17}{}^{1}\mathrm{H}_{11}{}^{35}\mathrm{Cl}_{6}{}^{37}\mathrm{Cl}_{2}{}^{14}\mathrm{N}^{16}\mathrm{O}_{5}{}^{28}\mathrm{Si})_{\mathrm{Zwitterion}}{+}\mathrm{H}^{+})$, 154 (100) (matrix); FAB MS (negative ions): $m/z = 620$ (12) $(\mathrm{M}({}^{12}\mathrm{C}_{17}{}^{1}\mathrm{H}_{11}{}^{35}\mathrm{Cl}_{6}{}^{37}\mathrm{Cl}_{2}{}^{14}\mathrm{N}^{16}\mathrm{O}_{5}{}^{28}\mathrm{Si})_{\mathrm{Zwitterion}}{-}\mathrm{H}^{+})$, 153 (100) (matrix); $C_{19}H_{14}Cl_8N_2O_5Si$ (662.0); calcd.: C 34.47, H 2.13, N 4.23; found: C 34.4, H 2.1, N 4.2.

Method 2. Compound **6** (1.00 g, 3.74 mmol) was added dropwise at room temperature within 3 min to a solution of 3,4,5,6-tetrachlorobenzene-1,2-diol (1.85 g, 7.46 mmol) in acetonitrile (15 ml; formation of a precipitate after *ca.* 20 min). The reaction mixture was stirred for 80 min and then kept undisturbed at room temperature for 8 d. The precipitate was filtered off and washed with cold acetonitrile (2×10 ml). The product was isolated by filtration and then dried *in vacuo* (0.001 torr, 20°C, 5 h) to give 815 mg (33%) of colorless crystals. M.p.: 278°C (dec); for analytical data, see above.

Method 3. Compounds **7** (1.00 g, 4.87 mmol) was added dropwise at room temperature within 3 min to a solution of 3,4,5,6-tetrachlorobenzene-1,2-diol (2.42 g, 9.76 mmol) in acetonitrile (35 ml; formation of a precipitate after *ca.* 1 d). The reaction mixture was stirred for 3 min and then kept undisturbed at room temperature for 5 d. The precipitate was filtered off, washed with cold acetonitrile (2×5 ml), and then recrystallized from acetonitrile. The product was isolated by filtration and then dried *in vacuo* (0.001 torr, 20°C, 5 h) to give 1.92 g (60%) of colorless crystals. M.p.: 278°C (dec); for analytical data, see above.

Trimethoxy((morpholino)methyl)silane (**5**): Synthesis according to Ref. [1h].

Dimethoxy((morpholino)methyl)phenylsilane (**6**): Synthesis according to Ref. [1h].

Dimethoxy(methyl)((morpholino)methyl)silane (**7**): Synthesis according to Ref. [5].

Crystal structure analysis

A suitable single crystal (obtained by recrystallization from acetonitrile at room temperature) was mounted in inert oil (Riedel-de Haën, RS 3000) on a glass fiber and then transferred to the cold gas stream of a Stoe-Huber-Siemens four-circle diffractometer fitted with a Siemens CCD detector (monochromated MoK_α radiation ($\lambda = 0.71073$ Å); for the low-temperature attachment, see Ref. [6]). A semiempirical absorption correction with all data was applied. The structure was solved by direct methods [7]. All non-hydrogen atoms were refined anisotropically [8]. A riding model was employed in the refinement of the CH hydrogen atom positions. The NH hydrogen atom was localized in difference *Fourier* syntheses and refined freely.

Additional material to the structure determination may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, referring to the deposition number CSD-408919, the names of the authors, and the citation of the present paper.

Acknowledgements

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. In addition, we thank Prof. *G. M. Sheldrick* (University of Göttingen) for providing diffractometer facilities for collecting the X-ray diffraction data.

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Received July 3, 1998. Accepted (revised) September 21, 1998