Silanediols Derived from Silanetriols. X-ray Crystal Structures of $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OSiMe_3)(OH)_2$ and $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OSiMe_2R)(OH)_2$ $[R = CH_2(2\text{-}NH_2\text{-}3,5\text{-}Me_2C_6H_2)]$

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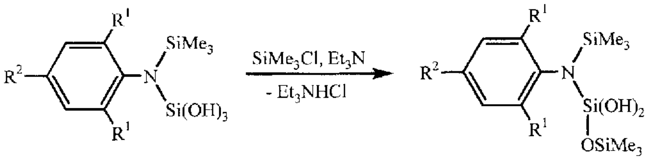
The silanediols $RN(SiMe_3)Si(OSiMe_3)(OH)_2$ (R = 2,4,6-$Me_3C_6H_2$ **4**, 2,6-$Me_2C_6H_3$ **5**, and 2,6-$i\text{Pr}_2C_6H_3$ **6**) were prepared by the reactions of the respective silanetriols $RN(SiMe_3)Si(OH)_3$ **1**–**3** with $SiMe_3Cl$ in THF/hexane. Silanetriol **1** in CH_2Cl_2/hexane solution converts over a period of 4 weeks into the silanediol $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OSiMe_2R)(OH)_2$ $[R = CH_2(2\text{-}NH_2\text{-}3,5\text{-}Me_2C_6H_2)]$ (**7**). Compounds **4**–**7** were characterized by means of mass, IR and NMR (^{1}H and ^{29}Si) spectroscopy. Additionally, the molecular structures of **4** and **7** were determined by single-crystal X-ray diffraction studies. Compound **4** forms O–H···O hydrogen-bonded tetramers in the solid state. A nine-membered ring formed by an intermolecular O–H···N hydrogen bond is found in the solid-state structure of **7**.

In recent years, there has been considerable interest in the synthesis of discrete silanols containing more than one hydroxy group in view of their use as building blocks for metallasiloxanes[1]. The interest in organosilanols is also due to their strong tendency to undergo self-association in the solid state by hydrogen bonds resulting in several interesting structural features[2]. Several methods are known for the preparation of silanediols starting from halo- or hydrosilanes[2]. The majority of the silanols contain alkyl or aryl groups attached to the central silicon atom. We were interested for some time in synthesizing silanols containing more than two hydroxy groups with hydrolyzable functionalities (such as Si–N bonds)[3] on the central silicon in order to use them for the preparation of metallasiloxanes[4–6]. To this end, we recently reported on the multistep synthesis of stable (silylamino)silanetriols of the type $RN(SiMe_3)Si(OH)_3$[3]. These silanetriols serve as useful starting materials for the preparation of a series of sterically hindered silanediols. During the course of this investigation, we also observed the conversion of one of the silanetriols into a silanediol containing an NH_2 group. These results, along with the crystal structure determinations of two silanediols, are described in this paper.

Results and Discussion

Starting from *ortho*-substituted anilines, we prepared *N*-bonded (silylamino)silanetriols **1**–**3** in high yields. The presence of a $SiMe_3$ group on the nitrogen atom is necessary to impart the desired stability and solubility properties in the silanetriols. These silanetriols are stable in the solid state for prolonged periods and also soluble in common organic solvents such as hexane, toluene, and THF. Silanetriols **1**–**3** react smoothly in THF/hexane with one equivalent of $SiMe_3Cl$ in the presence of Et_3N to yield the respective silanediols **4**–**6** (Scheme 1). Further substitution of the OH hydrogen atoms of the silanetriols is not observed under these conditions. Thus, even when the reaction of the silanetriols with $SiMe_3Cl$ were carried out in a 1:5 molar ratio of the reactants, only the silanediols **4**–**6** were isolated in nearly quantitative yields along with unreacted $SiMe_3Cl$ and Et_3N. However, it should be possible to effect further substitution by the use of stronger trimethylsilylating reagents such as $SiMe_3(CF_3SO_3)$[7].

Scheme 1



$R^1 = R^2 = Me$	1	4
$R^1 = Me, R^2 = H$	2	5
$R^1 = i\text{Pr}, R^2 = H$	3	6

The new silanediols **4**–**6** were characterized by elemental analysis and as well as mass, IR and NMR (^{1}H and ^{29}Si) spectral data (Table 1). They are easily soluble in common organic solvents such as hexane, ether, THF, and CH_2Cl_2. All the compounds show molecular ion (M^+) peaks in their electron impact mass spectrum. The ^{1}H-NMR spectra of all the compounds exhibit two single resonances of equal intensity (between $\delta = 0.0$ and 0.2) due to the $OSiMe_3$ and $NSiMe_3$ protons. The ^{29}Si-NMR spectra of **4**–**6** are characterized by three resonances arising from the three non-

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equivalent silicon nuclei. The singlet observed around $\delta = -73$ is easily assigned to the silicon atom with the $NSiO_3$ coordination environment. The signals appearing around $\delta = 6$ and 10 are assigned to the silicon centers with $NSiMe_3$ and $OSiMe_3$ environments, respectively. This assignment is based on the chemical shifts of the parent silanetriols themselves[3].

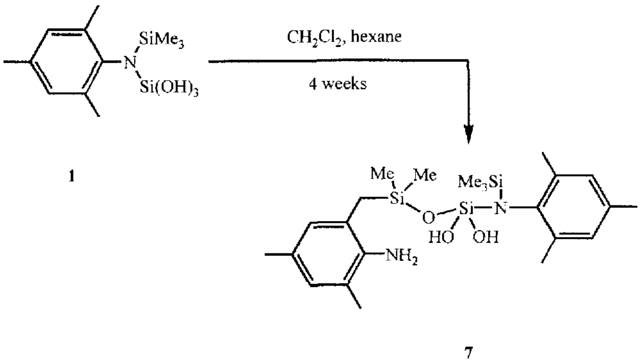
Table 1. Selected physical and spectroscopic data for silanediols

Compound	Yield	m.p.	[M$^+$], (%)[a]	IR,[b] ν (OH), cm^{-1}	^{1}H NMR,[c] δ, ppm	^{29}Si NMR δ, ppm
4	88	63	357 (20)	3660	0.03, 0.07	-72.9, 6.5, 10.3
5	75	98	343 (30)	3642	0.06, 0.18	-72.8, 6.3, 10.2
6	81	132	399 (98)	3658	0.09, 0.11	-72.9, 6.4, 10.3
7	30	145	476 (70)	3655	0.02, 0.08	-72.7, 5.2, 6.1

[a] EI conditions. – [b] Recorded as Nujol mulls. – [c] Only $NSiMe_3$ and $OSiMe_3$ resonances.

In an independent experiment, we observed that a dichloromethane/hexane (1:5) solution of the silanetriol **1** left in a screw-capped bottle converts into the aminosilanediol $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OSiMe_2R)(OH)_2$ [$R = CH_2(2\text{-}NH_2\text{-}3,5\text{-}Me_2C_6H_2)$] (**7**) (Scheme 2). Compound **7** was isolated in about 30% yield from this solution after 4 weeks as well-formed single crystals. In order to check whether this transformation takes place in other solvents, we left a solution of silanetriol **1** in toluene in a screw-capped bottle. After nearly 4 weeks compound **7** indeed had crystallized in about 20–25% yield. Compound **7** is a rare example of a silanediol containing an additional functional group (NH_2). However, the exact mechanism of the process leading to the formation of **7** is not clear as no intermediates or side products could be isolated and characterized.

Scheme 2



Compound **7** was characterized by elemental analysis as well as by its mass, IR, and NMR (^{1}H and ^{29}Si) spectral data (Table 1). The molecular ion (M^+) peak is observed at *m/z* 476 in its electron impact mass spectrum with 70% intensity. The ^{1}H resonances due to $NSiMe_3$ and $OSiMe_2$ groups appear at $\delta = 0.02$ and 0.08, respectively. A singlet of the CH_2 group is observed ($\delta = 1.91$). The resonances due to the four types of the aryl methyl groups appear at $\delta = 2.12$, 2.18, 2.19, and 2.20 in a ratio of 1:1:2:1. The three ^{29}Si resonances which are found at $\delta = -72.7$, 5.2, and 6.1 are assignable to SiO_3, $NSiMe_3$, $OSiMe_2R$ silicon centers, respectively.

Crystal Structure of 4

The molecular structures of **4** and **7** were determined by single-crystal X-ray diffraction studies. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the asymmetric unit. A view of both the molecules with the atom numbering scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. These molecules differ with respect to each other in the relative orientation of the $OSiMe_3$ groups (see Figure 1) and in other bond parameters. For example, the Si(1)–N(1)–Si(2)–O(1) torsion angle in molecule A is 159.4(3)°, whereas the corresponding Si(4)–N(2)–Si(5)–O(4) torsion angle in molecule B is −43.2(3)°. The Si–O distances in both the molecules vary in the range of 1.593–1.638 Å with an average value of 1.614 Å. This value compares well with the Si–O distances found in many silanols. Among the two types of Si–N distances present, the shorter one is associated with the silicon atom attached to more electron-withdrawing atoms (SiO_3 unit). This observation is consistent with the multiple bonding effects observed for main group elements bound to more electron-withdrawing substituents such as oxygen and fluorine[8,9]. The siloxane Si–O–Si bond angles in the two molecules are 157.7(4) and 149.8(3)°, respectively, indicating the flexibility of the siloxane bridge[10]. The angles around all the silicon centers remain largely tetrahedral. In the solid state the molecules of silanediol **4** form tetramers by way of intermolecular hydrogen bonds (see Figure 2).

Crystal Structure of 7

The molecular structure of **7** along with the atom labeling scheme is shown in Figure 3. Selected structural parameters are listed in Table 3. The molecular structure of **7** has many similarities to that of **4**. The Si–O distances fall in the range 1.624–1.640 Å with an average value of 1.630 Å. This value is marginally longer than that observed for **4**. The two Si–N distances are 1.761(2) and 1.711(2) Å. The Si–O–Si angle of 146.05(13)° again points to the very flexible siloxane bridge[10]. In contrast to the case of **4**, there are no intermolecular hydrogen bonds in **7**. However, there exists an intramolecular O–H···N hydrogen bond, resulting in a nine-membered ring in the molecule (Figure 3).

In summary, we have presented a new synthetic route to soluble and hindered silanediols by starting from the (silylamino)silanetriols. In solution one of the silanetriols rearranges over a long period of time to an interesting silanediol which also contains an additional NH_2 group. These hindered silanediols would be useful precursors for stabilizing new metallasiloxanes with metals of low coordination numbers. We are currently investigating these possibilities.

Figure 1. Ball and stick views of the two crystallographically independent molecules of **4** (top: molecule A, bottom: molecule B)

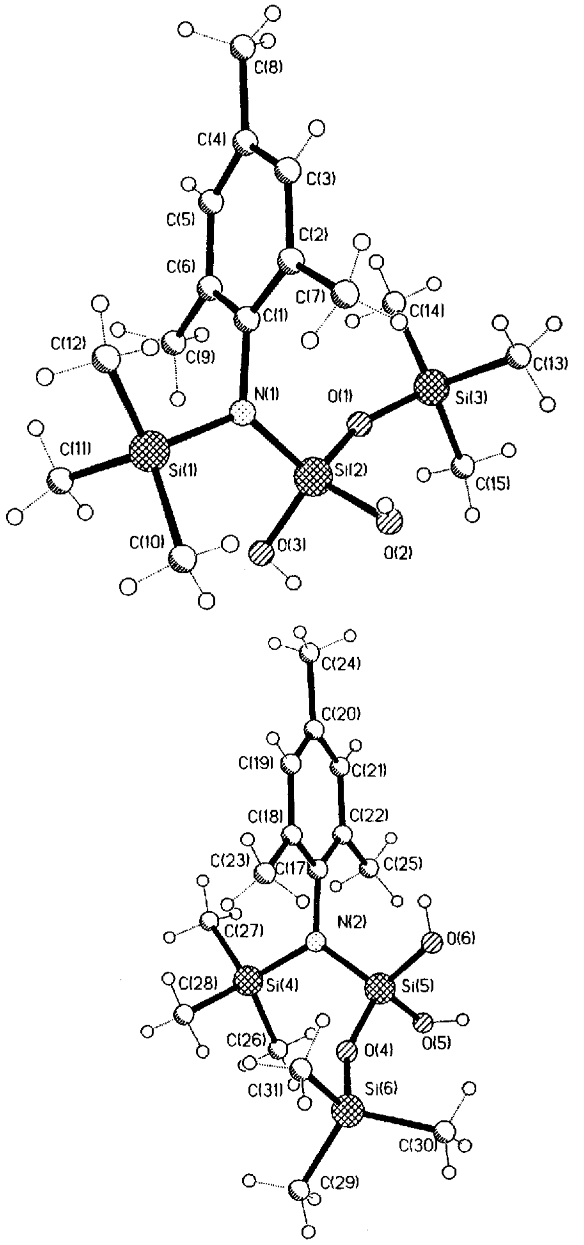


Figure 2. Schematic diagram of the hydrogen-bonding network in **4** leading to discrete tetrameric structures in the solid state

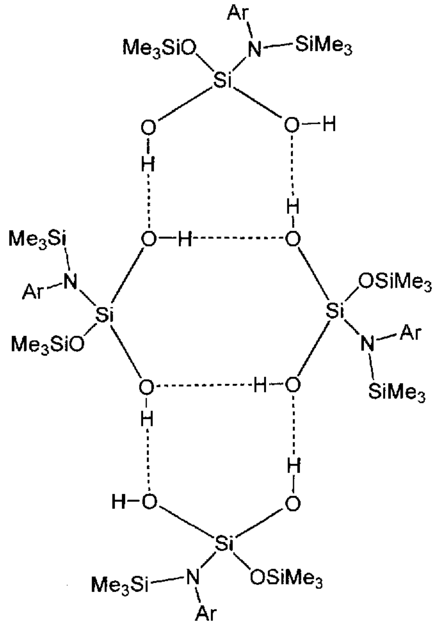


Table 2. Selected bond lengths [Å] and bond angles [°] in **4**

Si(1)-N(1)	1.747(5)	Si(2)-N(1)	1.702(4)
Si(2)-O(1)	1.598(5)	Si(2)-O(2)	1.628(4)
Si(2)-O(3)	1.598(4)	Si(3)-O(1)	1.613(5)
Si(4)-N(2)	1.763(4)	Si(5)-N(2)	1.710(4)
Si(5)-O(4)	1.593(4)	Si(5)-O(5)	1.622(4)
Si(5)-O(6)	1.624(4)	Si(6)-O(4)	1.637(4)
O(1)-Si(2)-O(3)	110.3(4)	O(1)-Si(2)-O(2)	106.6(3)
O(3)-Si(2)-O(2)	107.4(2)	Si(2)-O(1)-Si(3)	157.7(4)
O(4)-Si(5)-O(5)	105.4(2)	O(4)-Si(5)-O(6)	111.0(2)
O(5)-Si(5)-O(6)	107.4(2)	Si(5)-O(4)-Si(6)	149.8(3)

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Experimental

All reactions were carried out by using standard Schlenk procedures unless stated otherwise. Solvents were purified and dried according to standard methods. The silanetriols **1**–**3** were prepared as described previously[3]. – NMR: Bruker AM 200 or AS 400, δ values with reference to external $SiMe_4$. – IR: Bio-Rad Digilab FTS7 (only strong absorption values are given). – MS: Finnigan MAT System 8230 and Varian MAT CH5. – Melting points: HWS-SG 3000, uncorrected. – Elemental analyses: Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen.

Preparation of **4**–**6**: The silanediols were prepared by following a similar procedure. To a THF/hexane (10 ml/20 ml) solution of the silanetriol (3 mmol, 0.86 g of **1**, 0.82 g of **2**, or 1.0 g of **3**) and triethylamine (3 mmol, 0.3 g), a solution of trimethylsilyl chloride (3 mmol, 0.33 g) in hexane (10 ml) was added dropwise at room temp. with continuous stirring. The reaction mixture was stirred for further 12 h and heated at reflux for 3 h. After cooling to room temp., the solvent was removed in vacuo, and the residue was extracted with hexane (40 ml) and the extract filtered. The solvent was removed from the filtrate to yield the respective silanediols. The crude products were recrystallized from a minimum amount of hexane at room temp.

4: Yield 0.94 g (88%), m.p. 63 °C. – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, $NSiMe_3$, 9 H), 0.07 (s, $OSiMe_3$, 9 H), 2.19 [s, Me (aryl), 3 H], 2.22 [s, Me (aryl), 6 H], 6.79 (s, aromatic, 2 H). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = −72.9 ($NSiO_3$), 6.5 ($NSiMe_3$), 10.3 ($OSiMe_3$). – MS (EI), *m/z* (%): 357 (20) [M^+]. – $C_{15}H_{31}NO_3Si_3$ (357.4): calcd. C 50.4, H 8.7, N 3.9; found C 50.3, H 8.7, N 4.0.

5: Yield 0.77 g (75%), m.p. 98 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, $NSiMe_3$, 9 H), 0.18 (s, $OSiMe_3$, 9 H), 2.33 [s, Me (aryl), 6 H], 6.87–7.00 (m, aromatic, 3 H). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = −72.8 ($NSiO_3$), 6.3 ($NSiMe_3$), 10.2 ($OSiMe_3$). – MS (EI), *m/z* (%): 343 (30) [M^+]. – $C_{14}H_{29}NO_3Si_3$ (343.4): calcd. C 48.9, H 8.5, N 4.1; found C 48.8, H 8.5, N 4.4.

Figure 3. A ball and stick view of **7**

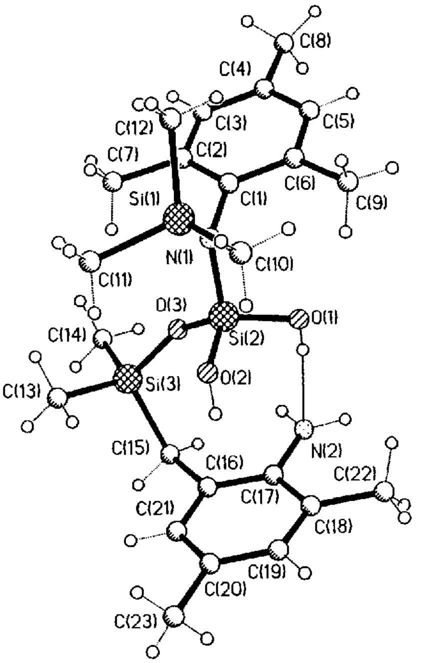

Table 3. Selected bond lengths [Å] and bond angles [°] in **7**

Si(1)-N(1)	1.761(2)	Si(2)-N(1)	1.711(2)
Si(2)-O(1)	1.624(2)	Si(2)-O(2)	1.629(2)
Si(2)-O(3)	1.628(2)	Si(3)-O(3)	1.640(2)
O(1)···N(2)	2.779(3)		
O(1)-Si(2)-O(3)	106.10(11)	O(1)-Si(2)-O(2)	113.64(12)
O(3)-Si(2)-O(2)	110.48(11)	O(2)-Si(2)-N(1)	105.49(11)
Si(2)-O(3)-Si(3)	146.05(13)	Si(1)-N(1)-Si(2)	126.48(14)

6: Yield 0.97 g (81%), m.p. 132°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.09 (s, $NSiMe_3$, 9H), 0.11 (s, $OSiMe_3$, 9H), 1.18 [d, $^3J_{HH}$ = 6.8 Hz, Me (*i*Pr), 6H], 1.20 [d, $^3J_{HH}$ = 6.8 Hz, Me (*i*Pr), 6H], 3.65 [sept, $^3J_{HH}$ = 6.8 Hz, CH (*i*Pr), 2H], 7.04 (m, aromatic, 3H). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = –72.9 ($NSiO_3$), 6.4 ($NSiMe_3$), 10.3 ($OSiMe_3$). – MS (EI), *m/z* (%): 399 (98) [M$^+$]. – $C_{18}H_{39}NO_3Si_3$ (399.5): calcd. C 54.1, H 9.3, N 3.5; found C 52.6, H 9.4, N 3.5.

Preparation of **7**: A CH_2Cl_2/hexane solution (10 ml/50 ml) of the silanetriol **1** (2 mmol, 0.57 g) in a 100-ml screw-capped bottle, not rigorously excluding air and moisture, was left for 4 weeks during which period colorless rectangular crystals of **7** deposited. The crystals were filtered off from the mother liquor and dried in vacuo. Yield 0.14 g (30%), m.p. 145°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, $NSiMe_3$, 9H), 0.08 (s, $OSiMe_2$, 9H), 1.91 (s, CH_2, 2H), 2.12, 2.18, 2.19, 2.20 [all s, Me (aryl), 15H], 6.64 (AB pattern, aromatic, 2H), 6.77 (s, aromatic, 2H), 3.50 (s, br, OH/NH_2). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = –72.7 ($NSiO_3$), 5.2 ($NSiMe_3$), 6.1 ($OSiMe_2R$). – MS (EI), *m/z* (%): 476 (70) [M$^+$]. – $C_{23}H_{40}N_2O_3Si_3$ (476.8): calcd. C 57.9, H 8.5, N 5.9; found C 57.9, H 8.5, N 6.2.

Crystal Structure Determination Details of **4** *and* **7**: Colorless crystals of **4** suitable for X-ray diffraction were grown from a concentrated solution of hexane at room temp.; rectangular colorless crystals of **7** were obtained from a CH_2Cl_2/hexane solution at room temperature (see above). A suitable crystal of each compound was mounted on a Siemens Stoe AED2 four-circle diffractometer for unit cell determination and intensity data collection. The unit cell constants were derived and refined from randomly selected well-centered reflections in the 2Θ range 20–25°. The structures were solved by direct methods[11] and refined by using SHELXL-93[12]. The hydrogen atoms were geometrically positioned and subsequently refined by using a riding model. All the nonhydrogen atoms were refined with anisotropic thermal parameters. Other details pertaining to data collection, structure solution and refinement are listed in Table 4[13].

Tablc 4. Crystal data and structure refinement for **4** and **7**

	4	**7**
Empirical formula	$C_{15}H_{31}NO_3Si_3$	$C_{23}H_{40}N_2O_3Si_3$
Formula weight	357.7	476.8
Temperature, K	210(2)	153(2)
Wavelength, Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	14.725(3)	11.161(1)
b, Å	11.358(2)	11.138(1)
c, Å	25.754(5)	22.466(3)
β, °	99.59(3)	103.09(1)
V, Å^3	4247(1)	2720.2(5)
Z	8	4
D_{calcd}, g.cm^{-3}	1.11976	1.164
μ, mm^{-1}	0.233	0.199
F(000)	1552	1032
Crystal size, mm	0.5 × 0.4 × 0.2	0.9 × 0.4 × 0.3
2θ range, °	3.5 to 22.6	3.5 to 22.5
Index range	$-15 \le h \le 15$	$-11 \le h \le 11$
	$-11 \le k \le 12$	$-4 \le k \le 11$
	$-27 \le l \le 27$	$-17 \le l \le 24$
Total reflections	7642	3588
Independent reflections	5542	3504
Refinement method	Full-matrix least	squares on F^2
Data	5530	3491
Restraints	2	0
Parameters	419	297
$R1$, $R2$ (I>2σ(I))	0.075, 0.188	0.047, 0.121
$R1$, $R2$ (all data)	0.1072, 0.233	0.053, 0.137
S	1.048	1.069
Largest difference peak e.Å^{-3}	0.410	0.395
Largest difference hole e.Å^{-3}	-0.466	–0.410

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