

Crystal structure and Hirshfeld surface analysis of 1-[(benzyl dimethylsilyl)methyl]-1-ethylpiperidin-1-ium ethanesulfonate

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The title molecular salt, $C_{17}H_{30}NSi^+ \cdot C_2H_5O_4S^-$, belongs to the class of α -aminosilanes and was synthesized by the alkylation of 1-[(benzyl dimethylsilyl)methyl]piperidine using diethyl sulfate. This achiral salt crystallizes in the chiral space group $P2_1$. One of the Si—C bonds in the cation is unusually long [1.9075 (12) Å], which correlates with the adjacent quaternary N⁺ atom and was verified by quantum chemical calculations. In the crystal, the components are linked by weak C—H...O hydrogen bonds: a Hirshfeld surface analysis was performed to further investigate these intermolecular interactions and their effects on the crystal packing.

1. Chemical context

Selective bond transformations on silicon compounds for the cleavage of Si—C bonds are of high interest in silicon chemistry (Denmark *et al.*, 2007; Denmark & Liu, 2010). Compared to C—C bonds, analogous Si—C bonds can be cleaved heterolytically using strong nucleophiles (Tomooka *et al.*, 2000; Li & Hu, 2007). However, the selectivity of such reactions is limited to specific silanes. In particular, α -amino-functionalized silanes are well suited for these processes, as shown by our previous studies (Koller *et al.*, 2017). Our group has focused on using lithium organyls as strong nucleophiles to perform these Si—C transformations on highly substituted silanes (Bauer & Strohmann, 2014). In particular, derivatives of α -piperidinobenzylsilanes have been intensively studied by our group (Strohmann *et al.*, 2004; Otte *et al.*, 2017). When strong nucleophiles are used, deprotonation in the benzyl position competes with the selective Si—C bond cleavage of the benzyl group. For this purpose, the α -aminofunctionality seems to play a key role, which could be responsible for the activation of the subsequent Si—C bond cleavage. In addition, the positively charged ammonium group leads to an increased electronegativity, which enhances the electron-withdrawing effect of the substituted α -aminofunctionality. Consequently, the π -character of the Si—C bond is more pronounced, leading to an elongation of the bond. Thus, a selective cleavage of the amino functionality due to the elongated Si—C bond is also conceivable (Bent, 1960, 1961; Otte *et al.*, 2017).

Several derivatives of these α -piperidinobenzylsilanes have been synthesized by our research group: 1-[(benzyl dimethylsilyl)methyl]-1-ethylpiperidin-1-ium ethanesulfonate (**1**), the title compound, represents a compound that could lead to an extension of the aforementioned Si—C bond to the nitrogen

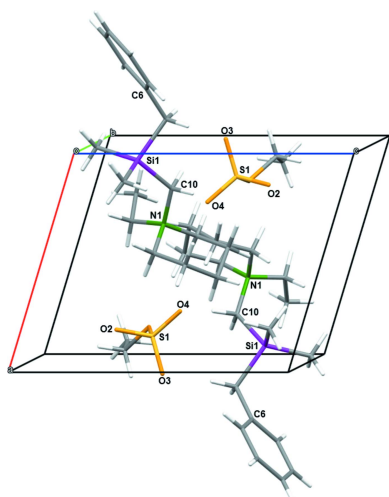
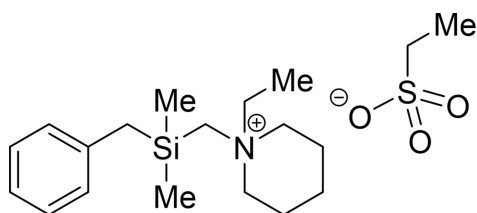


Table 1
Selected bond lengths (Å).

Si1—C7	1.8814 (11)	Si1—C9	1.8662 (18)
Si1—C8	1.862 (2)	Si1—C10	1.9075 (12)

atom *via* the quaternary ammonium cation. Structural studies concerning this type of compound should better elucidate the reactivity as well as selectivity of Si—C cleavages of the benzyl-substituted α -aminosilanes.



2. Structural commentary

Compound **1** crystallized from an *n*-pentane solution at 243 K in the form of colorless blocks with monoclinic ($P2_1$) symmetry. The chiral space group indicates that the achiral compound in the elementary cell is packed chirally; the Flack absolute structure parameter amounts to $-0.005(6)$ (Flack, 1983). The molecular structure of **1** is illustrated in Fig. 1. The Si—C bonds span the range 1.862 (2) to 1.908 (1) Å, as shown in Table 1. These values for the bond lengths are consistent with those in the literature, except for the long Si1—C10 bond

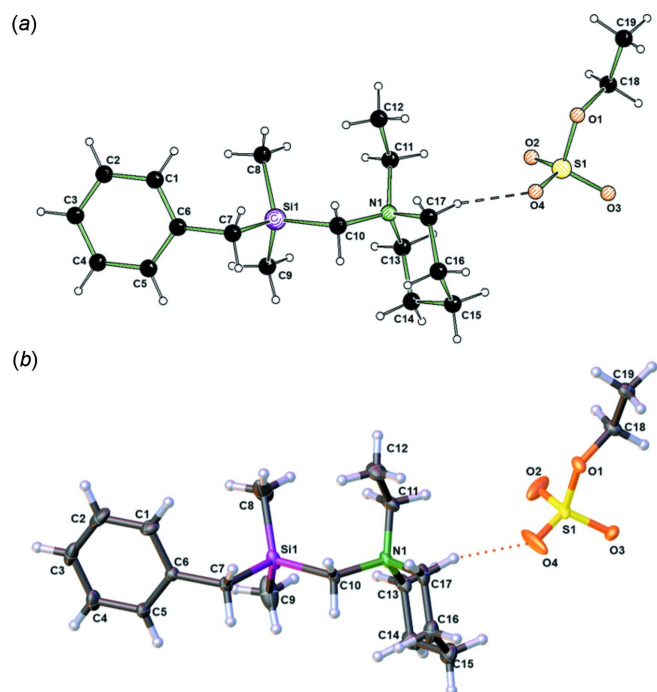


Figure 1
(a) The molecular structure of **1** illustrated using *SCHAKAL99* (Keller, 1999). (b) The molecular structure of **1** showing 50% displacement ellipsoids.

length, which is related to the α -aminosilane functionality (Allen *et al.*, 1987). This observed elongation of the bond can be explained by the very electropositive feature of carbon atom C10. In addition, the ethylated ammonium cation pushes even more electron density from C10 toward the amino functionality. There are only a few known species with such a long Si—C bond, which in turn may play a crucial role in the reactivity of α -amino-substituted silanes. Quantum chemical calculations at the M062X/6-31+G(d) level confirm the experimentally observed long Si—C bond. The calculated structure of compound **1** is shown in Fig. 2.

The silicon center in **1** features a tetrahedral geometry, which is significantly distorted, as shown by the smallest angle of $98.35(5)^\circ$ (C7—Si1—C10) and the largest angle of $114.32(7)^\circ$ (C8—Si1—C10). This geometric distortion has been observed in many complex substituted silicon compounds and depends on the substituents (Otte *et al.*, 2017). However, the distortion is large for compound **1** compared to most known silanes (Krupp *et al.*, 2020).

3. Supramolecular features

The crystal packing along the *b*-axis of compound **1** is illustrated in Fig. 3. Further studies of the packing in the solid state were aimed at finding hydrogen bonds of compound **1** as well as discussing the intensities of those hydrogen bonds. These studies were performed using Hirshfeld surface analysis. The Hirshfeld surface mapped over d_{norm} in the range from -0.072 to 1.201 arbitrary units as well as the related fingerprints plots generated by *CrystalExplorer2021* (Spackman *et al.*, 2021, Turner *et al.*, 2017) are illustrated in Fig. 4. With a share of 71.4%, most of the interactions relate to weak van der Waals H···H contacts, which should play a minor role for the packing of the crystal. In contrast, the role of O···H/H···O contacts should be predominant in the crystal arrangement in the unit cell, as shown by the significant red spots on the Hirshfeld surface. Numerous hydrogen bonds of the ethyl sulfate group to the ammonium cation are visible on the surface. The contribution of these contacts amounts to 16.6%. C···H/H···C contacts as well as H···H contacts do not

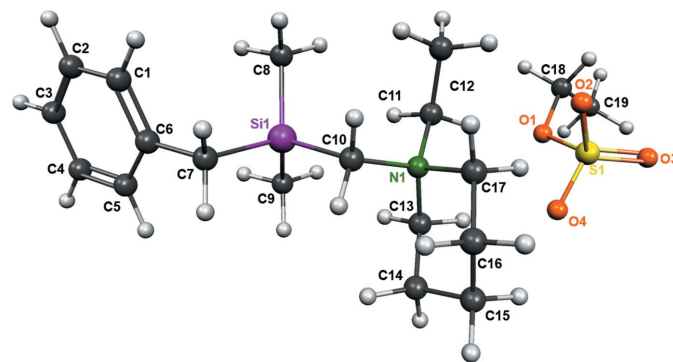


Figure 2
Visualization of the calculated structure of compound **1** with *Molekel 4.3* (Flükiger *et al.*, 2000) performed at the M062X/6-31+G(d) (Ditchfield *et al.*, 1970; Zhao & Truhlar, 2008) level.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O2^i$	0.93 (3)	2.39 (3)	3.2990 (17)	167 (2)
$C7-H7B\cdots O2^{ii}$	0.91 (3)	2.54 (3)	3.3881 (16)	156 (2)
$C17-H17A\cdots O4$	0.95 (2)	2.26 (2)	3.1815 (16)	162.8 (17)
$C17-H17B\cdots O3^{ii}$	0.93 (2)	2.47 (2)	3.3680 (15)	161.3 (19)

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z$; (ii) $x - 1, y, z$.

show as intense spots on the Hirshfeld surface and should not be considered as relevant as the $O\cdots H/H\cdots O$ contacts for the crystal packing. All hydrogen bonds up to a distance of 3.4 Å as well as an angle of at least 155° are listed in Table 2. According to Perlstein (2001), all hydrogen bonds listed in Table 2 have a weak to moderately strong character, which can be explained in particular by the non-linear angles of 156 (7)° ($C7-H7B\cdots O2^{ii}$) to 167 (2)° ($C3-H3\cdots O2^i$). The shortest hydrogen-bond length is 3.1815 (16) Å and is the strongest supramolecular interaction with an angle of 162.8 (17)° ($C17-H17A\cdots O4$). Analysis of the hydrogen-bonding network shows that all the hydrogen bonds shown in Table 2 can be assigned to one graph-set motif [$D_1^1(2)$; Etter *et al.*, 1990] and all of these bonds are linearly connected to two different atoms.

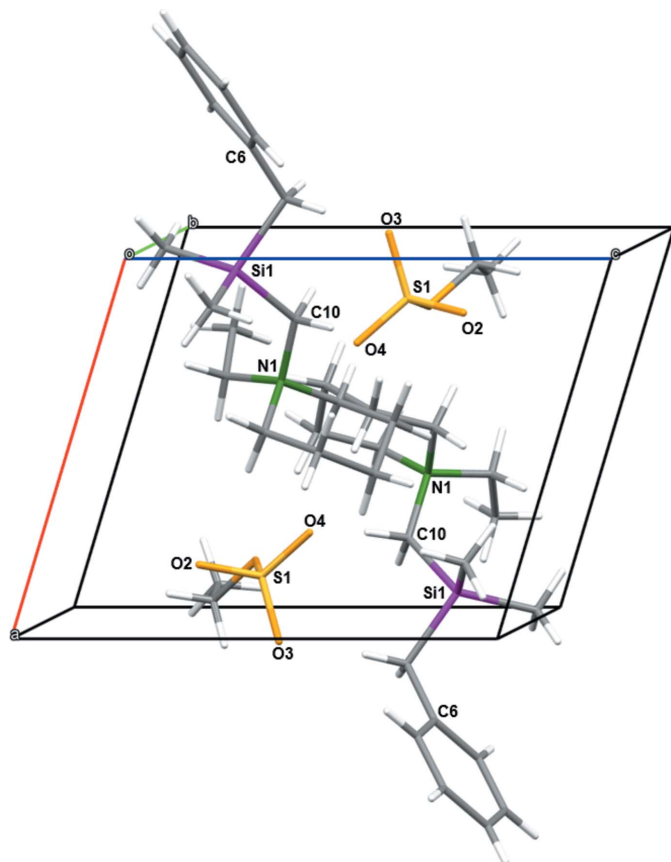


Figure 3
A view along the b -axis direction of the crystal packing of compound **1**.

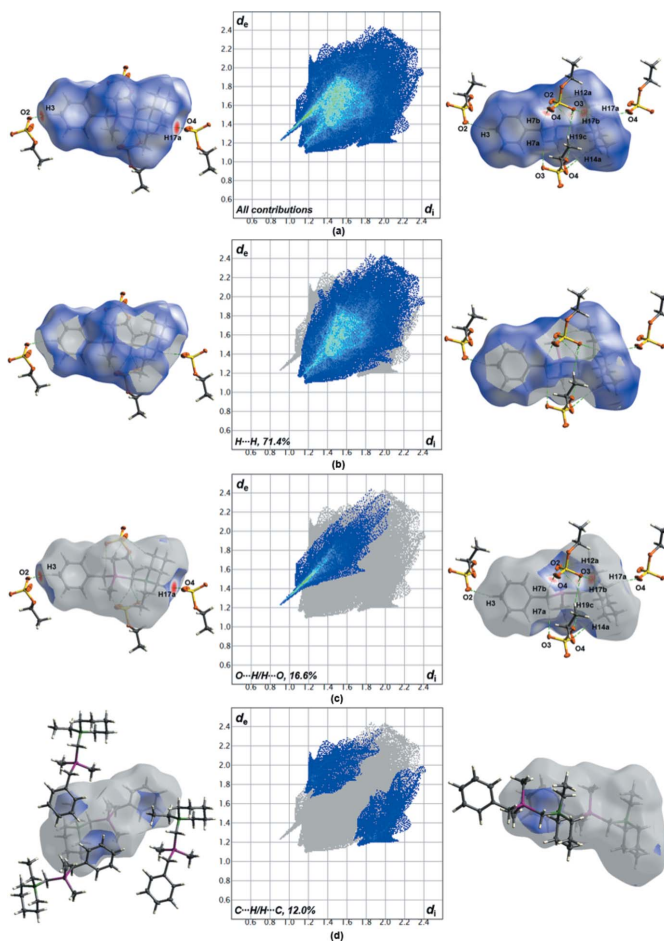


Figure 4
Hirshfeld surfaces and two-dimensional fingerprint plots of **1** showing close contacts for (a) all contributions in the crystal and (b) $H\cdots H$, (c) $O\cdots H/H\cdots O$ and (d) $C\cdots H/H\cdots C$ interactions. Symmetry code: $-x, \frac{1}{2} + y, -z$.

4. Database survey

There are some other examples of crystallographically characterized α -aminosilane derivatives that are structurally based on compound **1** and its starting compound **2**. Examples of such α -piperidinosilanes found in the Cambridge Structural Database (WebCSD, November 2021; Groom *et al.*, 2016) are (*R*)-1-methyl-1-[[methyl(phenyl)(trimethylgermyl)silyl]methyl]piperidinium iodide, $C_{17}H_{32}GeNSiI$ (CSD refcode BOFLOY; Strohmam *et al.*, 2008), (triphenylsilylpiperidinylcarbene)tetracarbonyltungsten(0), $C_{28}H_{25}NO_4SiW$ (DIZWUE; Schubert *et al.*, 1986), [bis(trimethylsilyl)methyl]bis[diphenyl(*N*-piperidinomethylsilyl)methyl]gallium *n*-pentane solvate, $C_{45}H_{67}GaN_2Si_4\cdot 0.5(C_5H_{12})$ (MASLUN; Uhl *et al.*, 2000), 8-chloro-8,8-dimethyl-1-aza-7-oxa-8-silabicyclo(4.3.0)non-6-ene, $C_8H_{16}ClNOSi$ (FUSYIB; Macharashvili *et al.*, 1987), 1-[[benzyl(methyl)phenylsilyl]methyl]piperidinium bromide, $C_{20}H_{28}NSiBr$ (NUPMUI; Barth *et al.*, 2015), *N*-(triphenylsilylmethyl)-5,6-aza-C60fulleroid, $C_{79}H_{17}NSi$ (YOXBOD; Hachiya *et al.*, 2009).

5. Synthesis and crystallization

The reaction scheme for the synthesis of **1** is illustrated in Fig. 5: 1-[(benzyltrimethylsilyl)methyl]piperidine (**2**) (0.81 mmol) was dissolved in acetone (3 ml) and diethyl sulfate (0.81 mmol) was added dropwise to the solution. The reaction mixture was stirred and heated for 6 h at 329 K. Afterwards the reaction was quenched by the addition of a mixture of H₂O (2 ml) and NH₃ (2 ml). The aqueous phase was extracted three times with CH₂Cl₂ and the combined organic phases were dried over Na₂SO₄. After the removal of volatile compounds, the raw product was dissolved in *n*-pentane (1 ml) and stored at 243 K. The title salt (**1**) was isolated as colorless crystalline blocks.

¹H NMR (300.25 MHz, CDCl₃): δ = 0.30 [s, 6H, Si(CH₃)₂], 1.24–1.31 (*m*, 6H, OCH₂CH₃, NCH₂CH₃), 1.65–1.90 [*br. m*, 6H, N(CH₂CH₂)₂, NCH₂CH₂CH₂], 2.29 (*s*, 2H, SiCH₂C_{ar}), 3.12 (*s*, 2H, SiCH₂N), 3.37–3.56 [*br. m*, 6H, N(CH₂)₃], 4.12 (*q*, 2H, ³J_{H-H} = 7.1 Hz, OCH₂CH₃), 7.04 (*d*, 2H, ³J_{H-H} = 7.0 Hz, CH_{ar}), 7.10–7.15 (*m*, 1H, CH_{ar}), 7.24 (*d*, 2H, ³J_{H-H} = 7.6 Hz, CH_{ar}) ppm.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were refined freely using independent values for each *U*_{iso}(H).

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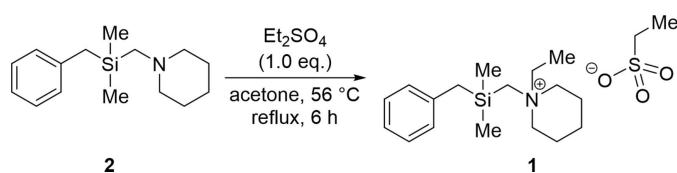


Figure 5
Reaction scheme of the alkylation of **2** with diethyl sulfate for the synthesis of **1**.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₇ H ₃₀ NSi ⁺ ·C ₂ H ₅ O ₄ S ⁻
<i>M_r</i>	401.63
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.4627 (8), 12.8187 (11), 10.3926 (9)
β (°)	107.033 (3)
<i>V</i> (Å ³)	1077.95 (17)
<i>Z</i>	2
Radiation type	Mo Kα
μ (mm ⁻¹)	0.23
Crystal size (mm)	0.82 × 0.44 × 0.38
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2021)
<i>T</i> _{min} , <i>T</i> _{max}	0.699, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	68418, 8122, 7987
<i>R</i> _{int}	0.021
(sin θ/λ) _{max} (Å ⁻¹)	0.766
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.065, 1.05
No. of reflections	8122
No. of parameters	375
No. of restraints	1
H-atom treatment	All H-atom parameters refined
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.53, -0.59
Absolute structure	Flack <i>x</i> determined using 3811 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.005 (6)

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *CrystalExplorer21* (Spackman *et al.*, 2021; Turner *et al.*, 2017), *pubCIF* (Westrip, 2010), *Mercury* (Macrae *et al.*, 2020), *GaussView 6.016* (Frisch *et al.*, 2016), *Gaussian 09 Revision A.02* (Frisch *et al.*, 2016), *SCHAKAL99* (Keller, 1999) and *Molekel 4.3* (Flükiger *et al.*, 2000).

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Computing details

Data collection: *APEX4* (Bruker, 2021); cell refinement: *SAINTE* (Bruker, 2021); data reduction: *SAINTE* (Bruker, 2021); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *CrystalExplorer21* (Spackman *et al.*, 2021; Turner *et al.*, 2017), *publCIF* (Westrip, 2010), *Mercury* (Macrae *et al.*, 2020), *GaussView 6.016* (Frisch *et al.*, 2016), *Gaussian 09 Revision A.02* (Frisch *et al.*, 2016), *SCHAKAL99* (Keller, 1999), *Molekel 4.3* (Flükiger *et al.*, 2000).

1-[(Benzyldimethylsilyl)methyl]-1-ethylpiperidin-1-ium ethanesulfonate

Crystal data

$C_{17}H_{30}NSi^+ \cdot C_2H_5O_4S^-$
 $M_r = 401.63$
 Monoclinic, $P2_1$
 $a = 8.4627$ (8) Å
 $b = 12.8187$ (11) Å
 $c = 10.3926$ (9) Å
 $\beta = 107.033$ (3)°
 $V = 1077.95$ (17) Å³
 $Z = 2$

$F(000) = 436$
 $D_x = 1.237$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9642 reflections
 $\theta = 3.0$ – 30.6 °
 $\mu = 0.23$ mm⁻¹
 $T = 100$ K
 Block, colourless
 $0.82 \times 0.44 \times 0.38$ mm

Data collection

Bruker D8 VENTURE
 diffractometer
 Radiation source: microfocus sealed X-ray tube,
 Incoatec $I\mu$ s
 HELIOS mirror optics monochromator
 Detector resolution: 10.4167 pixels mm⁻¹
 ω and φ scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2021)

$T_{\min} = 0.699$, $T_{\max} = 0.747$
 68418 measured reflections
 8122 independent reflections
 7987 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 33.0$ °, $\theta_{\min} = 2.5$ °
 $h = -12 \rightarrow 12$
 $k = -19 \rightarrow 19$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.065$
 $S = 1.05$
 8122 reflections

375 parameters
 1 restraint
 Primary atom site location: iterative
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.1456P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
3811 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.005 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.88614 (3)	0.62026 (2)	0.40720 (3)	0.01913 (6)
Si1	0.05612 (4)	0.31084 (3)	0.20000 (3)	0.01987 (7)
O3	1.05747 (10)	0.61067 (7)	0.48491 (8)	0.01886 (15)
O1	0.85485 (10)	0.74269 (6)	0.37242 (10)	0.01822 (15)
O4	0.77064 (16)	0.60053 (10)	0.4817 (2)	0.0533 (5)
O2	0.85245 (18)	0.56667 (8)	0.27863 (13)	0.0439 (4)
N1	0.35820 (12)	0.43767 (7)	0.34820 (11)	0.01724 (16)
C10	0.19151 (13)	0.39252 (8)	0.34376 (12)	0.01601 (18)
C14	0.53245 (16)	0.29189 (10)	0.48490 (16)	0.0253 (2)
C17	0.41837 (15)	0.50777 (10)	0.47118 (15)	0.0230 (2)
C6	-0.27742 (13)	0.25033 (8)	0.16162 (10)	0.01469 (17)
C5	-0.31035 (14)	0.14496 (9)	0.17585 (11)	0.01782 (18)
C13	0.48527 (15)	0.35320 (9)	0.35398 (14)	0.0211 (2)
C7	-0.13320 (13)	0.30314 (9)	0.25953 (11)	0.01589 (17)
C1	-0.38217 (16)	0.30517 (11)	0.05336 (13)	0.0247 (2)
C15	0.59552 (18)	0.36517 (13)	0.60478 (17)	0.0298 (3)
C18	0.96437 (15)	0.78813 (9)	0.30464 (13)	0.0206 (2)
C4	-0.44312 (17)	0.09575 (11)	0.08387 (14)	0.0258 (2)
C3	-0.54609 (16)	0.15050 (14)	-0.02339 (13)	0.0295 (3)
C16	0.46575 (16)	0.44744 (12)	0.60249 (15)	0.0276 (3)
C11	0.35005 (16)	0.50178 (10)	0.22355 (15)	0.0245 (2)
C19	0.93127 (16)	0.90390 (9)	0.29232 (12)	0.0202 (2)
C12	0.23198 (19)	0.59372 (11)	0.19959 (18)	0.0306 (3)
C8	0.0020 (3)	0.3761 (2)	0.03268 (16)	0.0472 (5)
C2	-0.51474 (18)	0.25531 (15)	-0.03823 (14)	0.0316 (3)
C9	0.1422 (2)	0.17830 (15)	0.1885 (3)	0.0455 (5)
H13A	0.442 (2)	0.3078 (18)	0.274 (2)	0.024 (4)*
H3	-0.638 (3)	0.121 (2)	-0.085 (3)	0.043 (6)*
H13B	0.583 (3)	0.3899 (17)	0.346 (2)	0.025 (5)*
H5	-0.241 (2)	0.1076 (17)	0.250 (2)	0.024 (4)*
H11A	0.318 (2)	0.4547 (16)	0.1467 (19)	0.017 (4)*
H12A	0.122 (3)	0.5740 (19)	0.193 (2)	0.029 (5)*
H10A	0.128 (3)	0.4494 (18)	0.358 (2)	0.026 (5)*
H7A	-0.108 (3)	0.2671 (17)	0.343 (2)	0.023 (4)*

H16A	0.368 (3)	0.4130 (18)	0.614 (2)	0.032 (5)*
H7B	-0.162 (3)	0.369 (2)	0.277 (3)	0.041 (6)*
H8A	-0.071 (4)	0.332 (3)	-0.020 (3)	0.056 (8)*
H18A	1.077 (3)	0.7716 (19)	0.355 (2)	0.037 (6)*
H17A	0.512 (3)	0.5403 (16)	0.456 (2)	0.023 (5)*
H16B	0.512 (3)	0.504 (2)	0.676 (3)	0.040 (6)*
H17B	0.331 (3)	0.5512 (18)	0.475 (2)	0.032 (5)*
H12B	0.233 (3)	0.630 (2)	0.106 (3)	0.043 (6)*
H2	-0.586 (3)	0.296 (2)	-0.110 (2)	0.041 (6)*
H11B	0.454 (3)	0.525 (2)	0.235 (2)	0.033 (6)*
H14A	0.439 (3)	0.2515 (19)	0.494 (2)	0.030 (5)*
H14B	0.617 (3)	0.2459 (19)	0.477 (2)	0.033 (6)*
H19A	0.825 (3)	0.916 (2)	0.235 (3)	0.040 (6)*
H19B	0.945 (3)	0.933 (2)	0.382 (2)	0.037 (6)*
H9A	0.058 (3)	0.133 (2)	0.123 (3)	0.048 (7)*
H19C	1.009 (3)	0.943 (2)	0.251 (2)	0.031 (5)*
H1	-0.362 (3)	0.379 (2)	0.045 (3)	0.041 (6)*
H10B	0.205 (3)	0.3469 (18)	0.418 (2)	0.027 (5)*
H9B	0.231 (5)	0.175 (4)	0.154 (4)	0.090 (13)*
H4	-0.477 (3)	0.018 (2)	0.093 (3)	0.037 (6)*
H8B	0.103 (6)	0.397 (4)	0.005 (4)	0.095 (14)*
H18B	0.945 (3)	0.751 (2)	0.216 (2)	0.037 (6)*
H15A	0.700 (4)	0.397 (2)	0.597 (3)	0.058 (8)*
H12C	0.274 (3)	0.647 (2)	0.270 (3)	0.046 (7)*
H15B	0.623 (4)	0.327 (2)	0.686 (3)	0.051 (7)*
H8C	-0.044 (5)	0.439 (4)	0.038 (4)	0.078 (11)*
H9C	0.167 (5)	0.140 (4)	0.293 (4)	0.092 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.01109 (10)	0.01196 (10)	0.03141 (13)	0.00019 (8)	0.00167 (8)	0.00310 (9)
Si1	0.01993 (14)	0.02043 (14)	0.02339 (14)	-0.00530 (11)	0.01279 (11)	-0.00846 (11)
O3	0.0134 (3)	0.0214 (4)	0.0193 (3)	0.0031 (3)	0.0009 (3)	0.0034 (3)
O1	0.0140 (3)	0.0118 (3)	0.0301 (4)	0.0013 (3)	0.0084 (3)	0.0021 (3)
O4	0.0297 (5)	0.0335 (7)	0.1128 (13)	0.0101 (5)	0.0458 (7)	0.0345 (7)
O2	0.0507 (7)	0.0172 (4)	0.0404 (6)	0.0058 (4)	-0.0234 (5)	-0.0085 (4)
N1	0.0133 (4)	0.0120 (4)	0.0294 (5)	-0.0001 (3)	0.0109 (3)	-0.0006 (3)
C10	0.0127 (4)	0.0146 (4)	0.0237 (5)	-0.0019 (3)	0.0099 (3)	-0.0023 (3)
C14	0.0194 (5)	0.0169 (5)	0.0405 (7)	0.0031 (4)	0.0104 (5)	0.0045 (4)
C17	0.0145 (4)	0.0161 (5)	0.0387 (6)	-0.0020 (4)	0.0082 (4)	-0.0083 (4)
C6	0.0134 (4)	0.0151 (4)	0.0158 (4)	0.0024 (3)	0.0045 (3)	-0.0004 (3)
C5	0.0185 (4)	0.0157 (4)	0.0178 (4)	-0.0026 (3)	0.0030 (3)	-0.0012 (3)
C13	0.0168 (4)	0.0148 (4)	0.0361 (6)	0.0035 (4)	0.0148 (4)	-0.0004 (4)
C7	0.0156 (4)	0.0146 (4)	0.0185 (4)	-0.0018 (3)	0.0066 (3)	-0.0030 (3)
C1	0.0215 (5)	0.0259 (5)	0.0243 (5)	0.0078 (4)	0.0032 (4)	0.0072 (5)
C15	0.0190 (5)	0.0313 (7)	0.0367 (7)	0.0027 (5)	0.0047 (5)	0.0017 (5)
C18	0.0222 (5)	0.0148 (4)	0.0282 (5)	0.0033 (4)	0.0129 (4)	0.0036 (4)

C4	0.0235 (5)	0.0286 (6)	0.0240 (5)	-0.0094 (4)	0.0052 (4)	-0.0081 (4)
C3	0.0162 (5)	0.0506 (8)	0.0197 (5)	-0.0043 (5)	0.0022 (4)	-0.0102 (5)
C16	0.0177 (5)	0.0326 (6)	0.0321 (6)	-0.0019 (5)	0.0064 (4)	-0.0093 (5)
C11	0.0217 (5)	0.0200 (5)	0.0367 (6)	0.0007 (4)	0.0163 (5)	0.0072 (5)
C19	0.0250 (5)	0.0131 (4)	0.0230 (5)	-0.0009 (4)	0.0081 (4)	-0.0012 (4)
C12	0.0283 (6)	0.0195 (5)	0.0444 (8)	0.0042 (4)	0.0115 (6)	0.0082 (5)
C8	0.0582 (11)	0.0667 (13)	0.0200 (6)	-0.0352 (11)	0.0163 (7)	-0.0063 (7)
C2	0.0201 (5)	0.0496 (9)	0.0211 (5)	0.0105 (6)	-0.0004 (4)	0.0041 (5)
C9	0.0296 (7)	0.0320 (7)	0.0824 (14)	-0.0062 (6)	0.0279 (9)	-0.0332 (9)

Geometric parameters (Å, °)

S1—O3	1.4435 (8)	C1—C2	1.396 (2)
S1—O1	1.6149 (9)	C1—H1	0.98 (3)
S1—O4	1.4364 (12)	C15—C16	1.518 (2)
S1—O2	1.4545 (13)	C15—H15A	1.00 (3)
Si1—C7	1.8814 (11)	C15—H15B	0.95 (3)
Si1—C8	1.862 (2)	C18—C19	1.5086 (16)
Si1—C9	1.8662 (18)	C18—H18A	0.97 (3)
Si1—C10	1.9075 (12)	C18—H18B	1.00 (3)
O1—C18	1.4412 (14)	C4—C3	1.388 (2)
N1—C10	1.5130 (14)	C4—H4	1.05 (3)
N1—C17	1.5227 (17)	C3—C2	1.387 (3)
N1—C13	1.5148 (15)	C3—H3	0.93 (3)
N1—C11	1.5186 (17)	C16—H16A	0.98 (2)
C10—H10A	0.94 (2)	C16—H16B	1.04 (3)
C10—H10B	0.95 (2)	C11—C12	1.5177 (19)
C14—C13	1.5199 (19)	C11—H11A	0.97 (2)
C14—C15	1.526 (2)	C11—H11B	0.91 (2)
C14—H14A	0.97 (2)	C19—H19A	0.94 (3)
C14—H14B	0.95 (2)	C19—H19B	0.99 (2)
C17—C16	1.517 (2)	C19—H19C	1.01 (2)
C17—H17A	0.95 (2)	C12—H12A	0.94 (2)
C17—H17B	0.93 (2)	C12—H12B	1.08 (3)
C6—C5	1.3957 (15)	C12—H12C	0.99 (3)
C6—C7	1.5019 (15)	C8—H8A	0.89 (3)
C6—C1	1.4005 (16)	C8—H8B	1.01 (5)
C5—C4	1.3946 (16)	C8—H8C	0.91 (4)
C5—H5	0.95 (2)	C2—H2	0.96 (3)
C13—H13A	0.99 (2)	C9—H9A	1.01 (3)
C13—H13B	0.97 (2)	C9—H9B	0.92 (4)
C7—H7A	0.95 (2)	C9—H9C	1.15 (4)
C7—H7B	0.91 (3)		
O3—S1—O1	106.26 (5)	C14—C15—H15A	106.7 (18)
O3—S1—O2	111.61 (7)	C14—C15—H15B	110.4 (18)
O4—S1—O3	114.45 (8)	C16—C15—C14	109.66 (11)
O4—S1—O1	101.47 (6)	C16—C15—H15A	111.9 (18)

O4—S1—O2	115.54 (11)	C16—C15—H15B	111.2 (18)
O2—S1—O1	106.15 (6)	H15A—C15—H15B	107 (3)
C7—Si1—C10	98.35 (5)	O1—C18—C19	108.00 (9)
C8—Si1—C10	114.32 (7)	O1—C18—H18A	108.5 (14)
C8—Si1—C7	109.31 (9)	O1—C18—H18B	107.5 (15)
C8—Si1—C9	110.06 (12)	C19—C18—H18A	112.9 (15)
C9—Si1—C10	113.19 (8)	C19—C18—H18B	114.0 (15)
C9—Si1—C7	111.06 (7)	H18A—C18—H18B	106 (2)
C18—O1—S1	114.55 (7)	C5—C4—H4	123.5 (14)
C10—N1—C17	109.32 (9)	C3—C4—C5	120.81 (13)
C10—N1—C13	111.87 (9)	C3—C4—H4	115.5 (14)
C10—N1—C11	111.84 (9)	C4—C3—H3	123.5 (18)
C13—N1—C17	109.24 (10)	C2—C3—C4	118.93 (12)
C13—N1—C11	105.96 (9)	C2—C3—H3	117.5 (18)
C11—N1—C17	108.49 (10)	C17—C16—C15	111.58 (12)
Si1—C10—H10A	107.8 (13)	C17—C16—H16A	109.3 (13)
Si1—C10—H10B	101.7 (14)	C17—C16—H16B	104.1 (15)
N1—C10—Si1	125.08 (8)	C15—C16—H16A	108.7 (14)
N1—C10—H10A	105.8 (14)	C15—C16—H16B	110.8 (15)
N1—C10—H10B	108.7 (13)	H16A—C16—H16B	112.3 (19)
H10A—C10—H10B	106.6 (18)	N1—C11—H11A	107.2 (12)
C13—C14—C15	110.47 (11)	N1—C11—H11B	105.7 (15)
C13—C14—H14A	110.8 (14)	C12—C11—N1	115.05 (11)
C13—C14—H14B	104.5 (14)	C12—C11—H11A	109.7 (12)
C15—C14—H14A	110.4 (14)	C12—C11—H11B	109.4 (16)
C15—C14—H14B	111.0 (15)	H11A—C11—H11B	109.7 (19)
H14A—C14—H14B	110 (2)	C18—C19—H19A	109.5 (16)
N1—C17—H17A	101.9 (12)	C18—C19—H19B	109.3 (15)
N1—C17—H17B	108.3 (14)	C18—C19—H19C	113.5 (14)
C16—C17—N1	112.92 (10)	H19A—C19—H19B	111 (2)
C16—C17—H17A	111.3 (13)	H19A—C19—H19C	106 (2)
C16—C17—H17B	105.7 (14)	H19B—C19—H19C	107 (2)
H17A—C17—H17B	117 (2)	C11—C12—H12A	112.9 (14)
C5—C6—C7	120.82 (10)	C11—C12—H12B	107.8 (14)
C5—C6—C1	118.15 (11)	C11—C12—H12C	109.8 (16)
C1—C6—C7	121.03 (10)	H12A—C12—H12B	108.6 (19)
C6—C5—H5	118.5 (13)	H12A—C12—H12C	112 (2)
C4—C5—C6	120.72 (11)	H12B—C12—H12C	106 (2)
C4—C5—H5	120.8 (13)	Si1—C8—H8A	103 (2)
N1—C13—C14	113.73 (10)	Si1—C8—H8B	113 (3)
N1—C13—H13A	107.5 (12)	Si1—C8—H8C	110 (2)
N1—C13—H13B	105.1 (13)	H8A—C8—H8B	118 (3)
C14—C13—H13A	112.5 (13)	H8A—C8—H8C	112 (3)
C14—C13—H13B	108.6 (13)	H8B—C8—H8C	101 (3)
H13A—C13—H13B	109.1 (17)	C1—C2—H2	118.4 (17)
Si1—C7—H7A	109.8 (13)	C3—C2—C1	120.64 (13)
Si1—C7—H7B	108.6 (17)	C3—C2—H2	121.0 (17)
C6—C7—Si1	113.71 (7)	Si1—C9—H9A	110.7 (16)

C6—C7—H7A	108.8 (13)	Si1—C9—H9B	116 (3)
C6—C7—H7B	109.9 (17)	Si1—C9—H9C	107 (2)
H7A—C7—H7B	106 (2)	H9A—C9—H9B	102 (3)
C6—C1—H1	118.4 (16)	H9A—C9—H9C	107 (3)
C2—C1—C6	120.75 (13)	H9B—C9—H9C	114 (3)
C2—C1—H1	120.8 (16)		
S1—O1—C18—C19	-174.27 (8)	C5—C4—C3—C2	0.2 (2)
O3—S1—O1—C18	55.64 (10)	C13—N1—C10—Si1	-65.17 (13)
O4—S1—O1—C18	175.59 (11)	C13—N1—C17—C16	-52.78 (12)
O2—S1—O1—C18	-63.30 (11)	C13—N1—C11—C12	-178.50 (12)
N1—C17—C16—C15	56.11 (14)	C13—C14—C15—C16	56.25 (15)
C10—Si1—C7—C6	174.81 (8)	C7—C6—C5—C4	-179.20 (11)
C10—N1—C17—C16	69.94 (12)	C7—C6—C1—C2	179.19 (11)
C10—N1—C13—C14	-67.70 (13)	C1—C6—C5—C4	0.58 (17)
C10—N1—C11—C12	59.35 (15)	C1—C6—C7—Si1	-82.81 (12)
C14—C15—C16—C17	-56.65 (16)	C15—C14—C13—N1	-56.46 (14)
C17—N1—C10—Si1	173.69 (8)	C4—C3—C2—C1	-0.2 (2)
C17—N1—C13—C14	53.48 (13)	C11—N1—C10—Si1	53.52 (12)
C17—N1—C11—C12	-61.30 (14)	C11—N1—C17—C16	-167.85 (10)
C6—C5—C4—C3	-0.40 (19)	C11—N1—C13—C14	170.17 (10)
C6—C1—C2—C3	0.4 (2)	C8—Si1—C7—C6	55.31 (11)
C5—C6—C7—Si1	96.96 (11)	C9—Si1—C7—C6	-66.31 (12)
C5—C6—C1—C2	-0.59 (19)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C3—H3 \cdots O2 ⁱ	0.93 (3)	2.39 (3)	3.2990 (17)	167 (2)
C7—H7B \cdots O2 ⁱⁱ	0.91 (3)	2.54 (3)	3.3881 (16)	156 (2)
C17—H17A \cdots O4	0.95 (2)	2.26 (2)	3.1815 (16)	162.8 (17)
C17—H17B \cdots O3 ⁱⁱ	0.93 (2)	2.47 (2)	3.3680 (15)	161.3 (19)

Symmetry codes: (i) $-x, y-1/2, -z$; (ii) $x-1, y, z$.