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

Jan-Lukas Kirchhoff, Stephan G. Koller, Kathrin Louven and Carsten Strohmann*

Technische Universität Dortmund, Fakultät Chemie und Chemische Biologie, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany. *Correspondence e-mail: carsten.strohmann@tu-dortmund.de

The title molecular salt, C_{17}H_{30}NSi^+\cdot C_{2}H_{5}O_{4}S^-, belongs to the class of α-aminosilanes and was synthesized by the alkylation of 1-[(benzyldimethylsilyl)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\cdots 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-aminofunctionalized 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-[(benzyldimethylsilyl)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
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 (P21) 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 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-aminosubstituted 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)° (C7—Si1—C10) and the largest angle of 114.32 (7)° (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 dnorm 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

### Table 1

| Bond | Length (Å) |
|------|------------|
| Si1—C7 | 1.8814 (11) |
| Si1—C8 | 1.9075 (12) |
| Si1—C9 | 1.8662 (18) |
show as intense spots on the Hirshfeld surface and should not be considered as relevant as the O···C1/C1/C1 H/H/C1/C1/C1 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···O2ii) to 167 (2)° (C3—H3/C1/O2i). 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···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 [D1(2); Etter et al., 1990] and all of these bonds are linearly connected to two different atoms.

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

| D···H | H···A | D···A | D···H | P     |
|------|------|------|------|------|
| C3—H3···O2i | 0.93 (3) | 2.39 (3) | 3.2990 (17) | 167 (2) |
| C7—H7B···O2ii | 0.91 (3) | 2.54 (3) | 3.3881 (16) | 156 (2) |
| C17—H17A···O4 | 0.95 (2) | 2.26 (2) | 3.1815 (16) | 162.8 (17) |
| C17—H17B···O3ii | 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.

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, C17H23GeNSiI (CSD refcode BOFLOY; Strohmann et al., 2008), (tri phenylsilypiperidinylcar bene)-tetracarbonyltungsten(0), C2H22NO4SiW (DIZWUE; Schubert et al., 1986), [bis(trimethylsilyl)methyl]bis[diphenyl(N-piperidinomethylsilyl)methyl]gallium n-pentane solvate, C45H20GaN5Si4.5(C5H12) (MASLUN; Uhl et al., 2000), 8-chloro-8,8-dimethyl-1-aza-7-oxa-8-silacyclo(4,3.0)non-6-ene, C6H16ClNOSi (FUSYIB; Macharashvili et al., 1987), 1-[[benzyl(methyl)phenylsilyl]methyl]piperidinium bromide, C20H25NSiBr (NUPMUI; Barth et al., 2015), N-(tri phenylsilylmethyl)-5,6-aza-C60fulleroid, C30H17NSi (YOXBOD; Hachiya et al., 2009).

![Figure 3](image-url) A view along the b-axis direction of the crystal packing of compound 1.

![Figure 4](image-url) Hirshfeld surfaces and two-dimensional fingerprint plots of 1 showing close contacts for (a) all contributions in the crystal and (b) H···H, (c) O···H···O and (d) C···H···C interactions. Symmetry code: -x, 1/2 + y, -z.
5. Synthesis and crystallization

The reaction scheme for the synthesis of 1 is illustrated in Fig. 5: 1-[(benzyldimethylsilyl)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, SiCH₂C₂H₅), 3.12 (s, 2H, SiCH₂N), 3.37–3.56 [br. m, 6H, NH (CH₂)₃], 4.12 (q, 2H, J₃-H-H = 7.1Hz, OCH₂CH₃), 4.12 (d, 2H, J₃-H-H = 7.0Hz, CH₂), 7.10–7.15 (m, 1H, CH₃), 7.24 (d, 2H, J₃-H-H = 7.6Hz, CH₂) 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 Uiso(H).

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![Figure 5](https://example.com/figure5.png)

Figure 5

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

Table 3

| Crystal data | Chemical formula | C₁₇H₃0NSi⁺·C₆H₄O₄S⁻⁺ |
|-------------|------------------|----------------------|
| Crystal system, space group | Monoclinic, P2₁ |
| Temperature (K) | 100 |
| a, b, c (Å) | 8.4627 (8), 12.8187 (11), 10.3926 (9) |
| β (°) | 107.033 (3) |
| V (Å³) | 1077.95 (17) |
| Z | 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 (SADABS: Bruker, 2021) |
| Tmin, Tmax | 0.699, 0.747 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 68418, 8122, 7987 |
| Rint | 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 |
| Δρmax, Δρmin (e Å⁻³) | 0.53, −0.59 |
| Absolute structure | Flack x determined using 3811 quotients [(Fₛ)−(Fₛ)]/[Fₛ+(Fₛ)] (Parsons et al., 2013) |
| Absolute structure parameter | ~0.005 (6) |

Computer programs: APEX4 and SAINT (Bruker, 2021); SHELXL (Sheldrick, 2008); SHELXL (Sheldrick, 2015); OLEX2 (Dolomanov et al., 2009); CrystalExplorer21 (Spackman et al., 2012; Turner et al., 2017); pubCIF (Westrip, 2010); Mercury (Macrae et al., 2020); GaussView 6.0.16 (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: SAINT (Bruker, 2021); data reduction: SAINT (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 6.0.16 (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, \( P2_1 \)
\[ a = 8.4627 (8) \text{ Å} \]
\[ b = 12.8187 (11) \text{ Å} \]
\[ c = 10.3926 (9) \text{ Å} \]
\[ \beta = 107.033 (3)^\circ \]
\[ V = 1077.95 (17) \text{ Å}^3 \]
\[ Z = 2 \]

\[ F(000) = 436 \]
\[ D_x = 1.237 \text{ Mg m}^{-3} \]
Mo Kα radiation, \( \lambda = 0.71073 \text{ Å} \)
Cell parameters from 9642 reflections
\[ \theta = 3.0–30.6^\circ \]
\[ \mu = 0.23 \text{ mm}^{-1} \]
\[ T = 100 \text{ K} \]
Block, colourless
\[ 0.82 \times 0.44 \times 0.38 \text{ mm} \]

Data collection
Bruker D8 VENTURE
diffractometer
Radiation source: microfocus sealed X-ray tube, Incoatec HELIOS
NEE 2815 mirror optics monochromator
Detector resolution: 10.4167 pixels mm\(^{-1}\)
\( \omega \) and \( \phi \) scans
Absorption correction: multi-scan (SADABS; Bruker, 2021)

\[ T_{\text{min}} = 0.699, \ T_{\text{max}} = 0.747 \]
68418 measured reflections
8122 independent reflections
7987 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.021 \)

\[ \theta_{\text{max}} = 33.0^\circ, \ \theta_{\text{min}} = 2.5^\circ \]
\[ h = -12 \rightarrow 12 \]
\[ k = -19 \rightarrow 19 \]
\[ l = -15 \rightarrow 15 \]

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
\[ w = \frac{1}{\sigma^2(F_o^2) + (0.039P)^2 + 0.1456P} \]

where \( P = \left( F_o^2 + 2F_c^2 \right)/3 \)

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

\( \Delta\rho_{\text{max}} = 0.53 \text{ e} \text{ Å}^{-3} \)

\( \Delta\rho_{\text{min}} = -0.59 \text{ e} \text{ Å}^{-3} \)

**Absolute structure:** Flack \( x \) determined using 3811 quotients \([|I^+|-|I^-|]/(|I^+|+|I^-|)\) (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 (Å²)**

|    | x   | y   | z   | \( U_{iso}^{*}/U_{eq} \) |
|----|-----|-----|-----|--------------------------|
| 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) | 0.03666 (15) |
| O1 | 0.85485 (10) | 0.74269 (6) | 0.37242 (10) | 0.01886 (15) |
| O4 | 0.77064 (16) | 0.60053 (10) | 0.4817 (2) | 0.01822 (15) |
| O2 | 0.85245 (18) | 0.56667 (8) | 0.27863 (13) | 0.01743 (15) |
| N1 | 0.35820 (12) | 0.43767 (7) | 0.34820 (11) | 0.01601 (18) |
| C10 | 0.19151 (13) | 0.39252 (8) | 0.33767 (12) | 0.01601 (18) |
| C14 | 0.53245 (16) | 0.29189 (10) | 0.48490 (16) | 0.01601 (18) |
| C17 | 0.41837 (15) | 0.50777 (10) | 0.47118 (15) | 0.01589 (17) |
| 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) | 0.01601 (18) |
| C15 | 0.59552 (18) | 0.36517 (13) | 0.60478 (17) | 0.01589 (17) |
| 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) | 0.034 (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 (Å²)

|   | U₁₁ | U₁₂ | U₁₃ | U₂₂ | U₂₃ | U₃₃ |
|---|-----|-----|-----|-----|-----|-----|
| S1 | 0.01109 (10) | 0.01196 (10) | 0.03141 (13) | 0.00019 (8) | 0.00167 (8) | 0.00310 (9) |
| S1 | 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) |

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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, °)**

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| 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)   |          |           |

**Supporting Information**
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—C10 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)  C15—C16—H16A 111.58 (12)
C11—N1—C13 107.8 (13)  C17—C16—C15 110.9 (15)
C11—N1—C10 101.7 (14)  C17—C16—H16B 112.3 (19)
N1—C10—Si1 125.08 (8)  C17—C16—H16B 104.1 (15)
N1—C10—H10A 105.8 (14)  C15—C16—H16B 108.7 (14)
N1—C10—H10B 108.7 (13)  C17—C16—H16B 110.8 (15)
H10A—C10—H10B 106.6 (18)  H16A—C16—C15 112.3 (19)
C13—C14—C15 110.47 (11)  C15—C16—H16A 107.2 (12)
C13—C14—H14A 110.8 (14)  C17—C16—H16B 105.7 (15)
C13—C14—H14B 104.5 (14)  N1—C11—H11A 115.05 (11)
C15—C14—H14A 110.4 (14)  C12—C11—N1 109.7 (12)
C15—C14—H14B 111.0 (15)  C12—C11—H11A 110.9 (15)
H14A—C14—H14B 110 (2)  C12—C11—H11B 109.5 (16)
N1—C17—H17A 101.9 (12)  C18—C19—H19A 109.3 (15)
N1—C17—H17B 108.3 (14)  C18—C19—H19B 103.5 (14)
C16—C17—N1 112.92 (10)  C18—C19—H19C 113.5 (14)
C16—C17—H17A 111.3 (13)  H19A—C19—H19B 111 (2)
C16—C17—H17B 105.7 (14)  H19A—C19—H19C 106 (2)
H17A—C17—H17B 117 (2)  H19B—C19—H19C 107 (2)
C5—C6—C7 120.82 (10)  C11—C12—H12A 112.9 (14)
C5—C6—C1 118.15 (11)  C11—C12—H12B 107.8 (14)
C1—C6—C7 121.03 (10)  C11—C12—H12C 109.8 (16)
C6—C5—H5 118.5 (13)  C12—C11—H11B 108.6 (19)
C4—C5—C6 120.72 (11)  C12—C11—H11C 112 (2)
C4—C5—H5 120.8 (13)  H12A—C12—H12B 106 (2)
N1—C13—C14 113.73 (10)  Si1—C8—H8A 103 (2)
N1—C13—H13A 107.5 (12)  Si1—C8—H8B 113 (3)
N1—C13—H13B 105.1 (13)  Si1—C8—H8C 110 (2)
C14—C13—H13A 112.5 (13)  H8A—C8—H8B 118 (3)
C14—C13—H13B 108.6 (13)  H8A—C8—H8C 112 (3)
H13A—C13—H13B 109.1 (17)  H8B—C8—H8C 101 (3)
Si1—C7—H7A 109.8 (13)  C1—C2—H2 118.4 (17)
Si1—C7—H7B 108.6 (17)  C3—C2—C1 120.64 (13)
C6—C7—Si1 113.71 (7)  C3—C2—H2 121.0 (17)
C6—C7—Si1 113.71 (7)  Si1—C9—H9A 110.7 (16)
Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A | D···A  | D—H···A |
|----------|-------|-------|--------|---------|
| C3—H3···O2i | 0.93 (3) | 2.39 (3) | 3.2990 (17) | 167 (2) |
| C7—H7B···O2ii | 0.91 (3) | 2.54 (3) | 3.3881 (16) | 156 (2) |
| C17—H17A···O4 | 0.95 (2) | 2.26 (2) | 3.1815 (16) | 162.8 (17) |
| C17—H17B···O3ii | 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.