

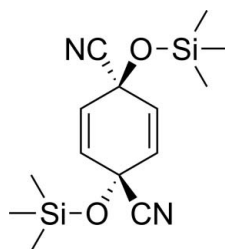
# Crystal structure of *trans*-1,4-bis[(trimethylsilyl)-oxy]cyclohexa-2,5-diene-1,4-dicarbonitrile

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The asymmetric unit of the title compound, C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>, contains one half of the molecule, which is completed by inversion symmetry. The cyclohexa-2,5-diene ring is exactly planar and reflects the bond-length distribution of a pair of located double bonds [1.3224 (14) Å] and two pairs of single bonds [1.5121 (13) and 1.5073 (14) Å]. The tetrahedral angle between the *sp*<sup>3</sup>-C atom and the two neighbouring *sp*<sup>2</sup>-C atoms in the cyclohexa-2,5-diene ring is enlarged by about 3°.

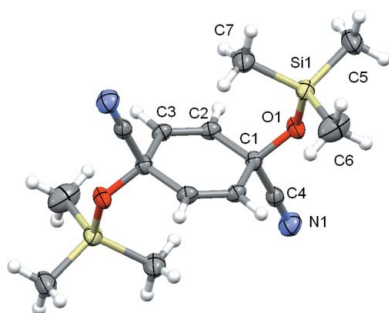
## 1. Chemical context

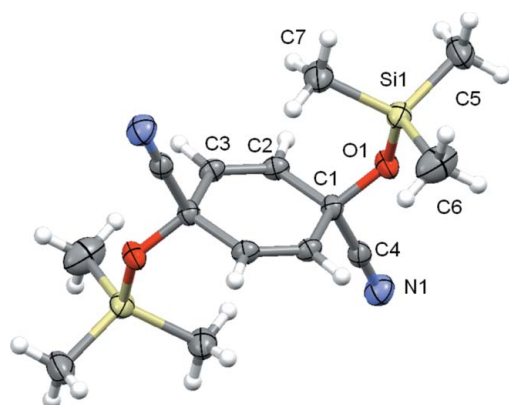
Cyanohydrins (Friedrich, 1983) are an important class of organic compounds. Silylated cyanohydrins are versatile precursor compounds in organic chemistry because the nitrile functional group can be modified by a variety of reactions such as hydrolysis, reduction or addition of organometallic reagents. The molecular and crystal structure of the title compound, a new silylated cyclohexa-2,5-diene with *trans* nitrile groups in the 1,4 positions, is reported herein.



## 2. Structural commentary

The molecular structure of the title compound is centrosymmetric, leading to a *trans*-1,4-configuration of the oxy(trimethylsilyl) and carbonitrile groups (Fig. 1). The cyclohexa-2,5-diene ring is exactly planar, but its angles differ from that of an ideal hexagon. Whereas the angle between the *sp*<sup>3</sup>-C atom (C1) and the neighbouring *sp*<sup>2</sup>-C atoms (C2, C3) is reduced to 112.58 (8)°, the other intra-ring angles are enlarged to 123.94 (9)° (C1–C2–C3) and 123.48 (9)° (C1<sup>i</sup>–C3–C2) [symmetry code: (i)  $-x + 1, -y + 1, -z$ ]. The tetrahedral angles around C1 are likewise distorted due to the ring strain. The angles involving the O atom of the oxy(trimethylsilyl) group and the ring C atoms are enlarged to 110.79 (8)° and 113.26 (8)° while the angle involving the O atom and the C atom of the carbonitrile group is reduced to 104.95 (8)°. The backbone of the 1,1-substituents is nearly perpendicular to the cyclohexa-2,5-diene ring, with a dihedral angle of 86.05 (7).




**Figure 1**

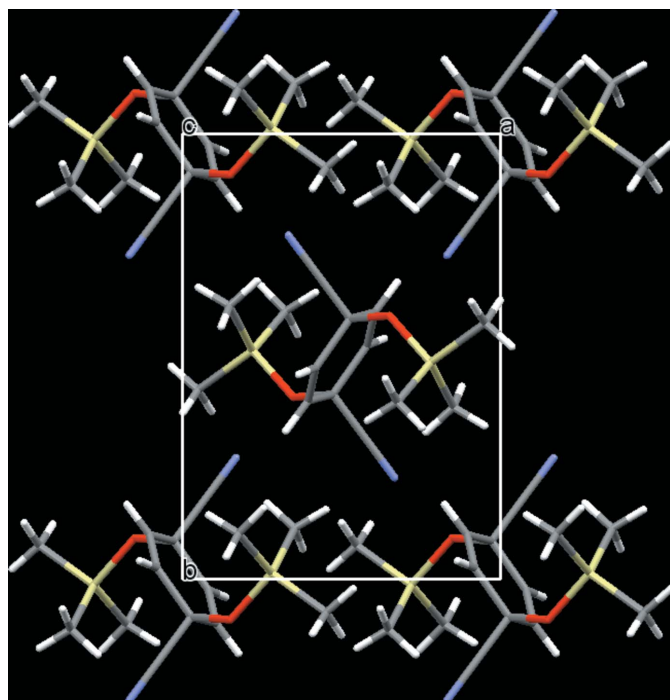
The molecular structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids drawn at the 80% probability level. Non-labelled atoms are generated by the symmetry code  $-x + 1, -y + 1, -z$ .

### 3. Supramolecular features

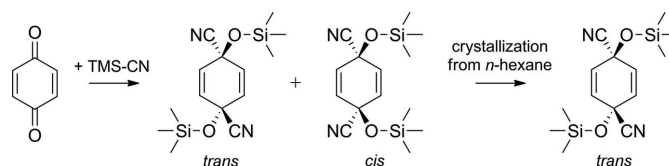
Notable features in terms of non-classical hydrogen bonding interactions are not observed in the crystal structure of the title compound. As a result of the bulky trimethylsilyl groups,  $\pi$ - $\pi$  stacking interactions between the rings are not possible. The packing of the molecules (Fig. 2) seems to be dominated mainly by van der Waals forces.

### 4. Database survey

In the current Cambridge Structural Database (Version 5.35, last update February 2014; Allen, 2002) only one example of a cyclohexa-2,5-diene with *trans* nitrile groups in the 1,4 posi-


**Figure 2**

A view of the crystal packing of the title compound along [001]. Colour code: O red, C grey, N light-blue, Si off-white, H white.


**Figure 3**

Reaction scheme to obtain the title compound.

tions is listed, namely 3,5-bis(4-(dimethylamino)phenyl)cyclohexa-2,5-diene-1,1,2,4,4-pentacarbonitrile (Jayamurugan *et al.*, 2011). The C–C bond lengths within the cyclohexa-2,5-diene are very similar to those of the title compound.

### 5. Synthesis and crystallization

1,4-Bis[(trimethylsilyl)oxy]cyclohexa-2,5-diene-1,4-dicarbonitrile was synthesized by a modified protocol reported by Onaka *et al.* (1989). The required heterogeneous catalyst Fe-montmorillonite (K10-FeAA) was prepared according to Pai *et al.* (2000) and activated at 393 K and 5 mbar for 2 h prior to use.

1,4-Benzoquinone (1.62 g, 15 mmol) was dissolved in 75 ml dichloromethane (0.2 M), purged with argon and cooled to 273 K. Trimethylsilyl cyanide (2.98 g, 30 mmol) and Fe-montmorillonite (0.75 g) were added sequentially and the mixture stirred for 1 h at 273 K under an argon atmosphere. The Fe-montmorillonite was filtered off (Por 4 glass filter) and the solvent was evaporated *in vacuo* to yield 4.23 g

**Table 1**

Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{22}N_2O_2Si_2$
$M_r$	306.5
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
$a, b, c$ (Å)	8.0770 (5), 11.2234 (6), 9.4377 (6)
$\beta$ (°)	97.7087 (19)
$V$ (Å <sup>3</sup> )	847.81 (9)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.21
Crystal size (mm)	0.65 × 0.26 × 0.12
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2013)
$T_{min}, T_{max}$	0.94, 0.98
No. of measured, independent and observed [ $I > 3\sigma(I)$ ] reflections	15160, 2487, 2123
$R_{int}$	0.024
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.705
Refinement	
$R[F^2 > 3\sigma(F^2)], wR(F^2), S$	0.030, 0.042, 2.38
No. of reflections	2487
No. of parameters	91
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.38, -0.20

Computer programs: APEX2 and SAINT-Plus (Bruker, 2013), SUPERFLIP (Palatinus & Chapuis, 2007), JANA2006 (Petříček, *et al.*, 2014), Mercury (Macrae *et al.*, 2008) and publCIF (Westrip, 2010).

(13.8 mmol, 92%) of a *cis/trans* (3/1) isomeric mixture of 1,4-bis[(trimethylsilyl)oxy]cyclohexa-2,5-diene-1,4-dicarbonitrile (Fig. 3). Crystallization from *n*-hexane selectively yielded white crystals of the *trans*-isomer, which were suitable for single-crystal X-ray diffraction analysis.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 6.19$  (s, 4H), 0.23 (s, 18H) p.p.m.;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta = 238.3$  (s), 129.4 (d), 1.5 (q) p.p.m.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were included in calculated positions ( $\text{C}-\text{H} = 0.96 \text{ \AA}$ ) and treated as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Acknowledgements

The X-ray centre of the Vienna University of Technology is acknowledged for providing access to the single-crystal diffractometer.

## References

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## supporting information

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## Crystal structure of *trans*-1,4-bis[(trimethylsilyl)oxy]cyclohexa-2,5-diene-1,4-dicarbonitrile

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### Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE-Plus* (Bruker, 2013); data reduction: *SAINTE-Plus* (Bruker, 2013); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček, *et al.*, 2014); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### *trans*-1,4-Bis[(trimethylsilyl)oxy]cyclohexa-2,5-diene-1,4-dicarbonitrile

#### Crystal data

C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>

*M<sub>r</sub>* = 306.5

Monoclinic, *P2<sub>1</sub>/n*

Hall symbol: -*P* 2<sub>1</sub> *n*

*a* = 8.0770 (5) Å

*b* = 11.2234 (6) Å

*c* = 9.4377 (6) Å

β = 97.7087 (19)°

*V* = 847.81 (9) Å<sup>3</sup>

*Z* = 2

*F*(000) = 328

*D<sub>x</sub>* = 1.200 Mg m<sup>-3</sup>

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 7267 reflections

θ = 2.8–29.9°

μ = 0.21 mm<sup>-1</sup>

*T* = 100 K

Block, clear colourless

0.65 × 0.26 × 0.12 mm

#### Data collection

Bruker Kappa APEXII CCD  
diffractometer

Radiation source: X-ray tube

Graphite monochromator

ω and φ-scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2013)

*T<sub>min</sub>* = 0.94, *T<sub>max</sub>* = 0.98

15160 measured reflections

2487 independent reflections

2123 reflections with *I* > 3σ(*I*)

*R<sub>int</sub>* = 0.024

θ<sub>max</sub> = 30.1°, θ<sub>min</sub> = 2.8°

*h* = -11→11

*k* = -15→15

*l* = -13→13

#### Refinement

Refinement on *F*

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030

*wR*(*F*<sup>2</sup>) = 0.042

*S* = 2.38

2487 reflections

91 parameters

0 restraints

44 constraints

H-atom parameters constrained

Weighting scheme based on measured s.u.'s *w* =

1/(σ<sup>2</sup>(*F*) + 0.0001*F*<sup>2</sup>)

(Δ/σ)<sub>max</sub> = 0.023

Δρ<sub>max</sub> = 0.38 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.20 e Å<sup>-3</sup>

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	0.21973 (4)	0.48658 (3)	0.25729 (3)	0.01515 (9)
O1	0.34897 (9)	0.59176 (6)	0.20989 (8)	0.0151 (2)
N1	0.66734 (12)	0.77227 (8)	0.18067 (10)	0.0203 (3)
C1	0.47262 (12)	0.58514 (9)	0.11702 (10)	0.0118 (3)
C2	0.39530 (12)	0.59953 (9)	−0.03704 (10)	0.0130 (3)
C3	0.41937 (12)	0.52449 (9)	−0.14034 (11)	0.0125 (3)
C4	0.58275 (13)	0.69117 (9)	0.15441 (10)	0.0136 (3)
C5	0.04800 (15)	0.57505 (11)	0.31580 (13)	0.0244 (4)
C6	0.32433 (16)	0.39773 (11)	0.40911 (13)	0.0303 (4)
C7	0.14743 (14)	0.38628 (10)	0.10522 (12)	0.0208 (3)
H1c2	0.324479	0.667221	−0.061301	0.0155*
H1c3	0.365173	0.540694	−0.235238	0.015*
H1c5	−0.036613	0.522349	0.341718	0.0293*
H2c5	0.09082	0.622785	0.396915	0.0293*
H3c5	0.000656	0.625942	0.239152	0.0293*
H1c6	0.246714	0.341141	0.438738	0.0363*
H2c6	0.417964	0.356223	0.379805	0.0363*
H3c6	0.362472	0.449816	0.487404	0.0363*
H1c7	0.049234	0.344384	0.124438	0.0249*
H2c7	0.121741	0.432548	0.019545	0.0249*
H3c7	0.233911	0.330007	0.093019	0.0249*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Si1	0.01621 (16)	0.01632 (17)	0.01325 (15)	−0.00379 (11)	0.00316 (11)	−0.00069 (11)
O1	0.0166 (4)	0.0138 (4)	0.0161 (4)	−0.0014 (3)	0.0071 (3)	−0.0023 (3)
N1	0.0220 (5)	0.0178 (5)	0.0210 (5)	−0.0034 (4)	0.0026 (4)	−0.0036 (4)
C1	0.0132 (4)	0.0106 (5)	0.0118 (4)	−0.0006 (3)	0.0026 (3)	−0.0006 (3)
C2	0.0126 (4)	0.0112 (5)	0.0147 (5)	0.0009 (4)	0.0001 (4)	0.0016 (4)
C3	0.0126 (5)	0.0121 (5)	0.0122 (4)	0.0000 (4)	−0.0005 (4)	0.0017 (4)
C4	0.0151 (5)	0.0143 (5)	0.0115 (4)	0.0018 (4)	0.0021 (3)	−0.0004 (4)
C5	0.0226 (6)	0.0291 (7)	0.0236 (6)	−0.0046 (5)	0.0102 (5)	−0.0070 (5)
C6	0.0327 (7)	0.0314 (7)	0.0249 (6)	−0.0108 (5)	−0.0029 (5)	0.0105 (5)
C7	0.0215 (6)	0.0219 (6)	0.0198 (5)	−0.0064 (4)	0.0058 (4)	−0.0038 (4)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Si1—C5	1.8495 (13)	C3—H1c3	0.96
Si1—C6	1.8537 (13)	C5—H1c5	0.96
Si1—C7	1.8555 (11)	C5—H2c5	0.96
O1—C1	1.4163 (13)	C5—H3c5	0.96
N1—C4	1.1451 (14)	C6—H1c6	0.96
C1—C2	1.5121 (13)	C6—H2c6	0.96
C1—C3 <sup>i</sup>	1.5073 (14)	C6—H3c6	0.96

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C1—C4	1.4993 (14)	C7—H1c7	0.96
C2—C3	1.3224 (14)	C7—H2c7	0.96
C2—H1c2	0.96	C7—H3c7	0.96
C5—Si1—C6	109.89 (6)	Si1—C5—H2c5	109.47
C5—Si1—C7	112.70 (5)	Si1—C5—H3c5	109.47
C6—Si1—C7	109.57 (5)	H1c5—C5—H2c5	109.47
O1—C1—C2	110.79 (8)	H1c5—C5—H3c5	109.47
O1—C1—C3 <sup>i</sup>	113.26 (8)	H2c5—C5—H3c5	109.47
O1—C1—C4	104.95 (8)	Si1—C6—H1c6	109.47
C2—C1—C3 <sup>i</sup>	112.58 (8)	Si1—C6—H2c6	109.47
C2—C1—C4	107.28 (8)	Si1—C6—H3c6	109.47
C3 <sup>i</sup> —C1—C4	107.46 (8)	H1c6—C6—H2c6	109.47
C1—C2—C3	123.94 (9)	H1c6—C6—H3c6	109.47
C1—C2—H1c2	118.03	H2c6—C6—H3c6	109.47
C3—C2—H1c2	118.03	Si1—C7—H1c7	109.47
C1 <sup>i</sup> —C3—C2	123.48 (9)	Si1—C7—H2c7	109.47
C1 <sup>i</sup> —C3—H1c3	118.26	Si1—C7—H3c7	109.47
C2—C3—H1c3	118.26	H1c7—C7—H2c7	109.47
N1—C4—C1	178.87 (11)	H1c7—C7—H3c7	109.47
Si1—C5—H1c5	109.47	H2c7—C7—H3c7	109.47

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Symmetry code: (i)  $-x+1, -y+1, -z$ .