Note

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Improved synthesis and crystal structure of the parent 1,3,5-trisilacyclohexane

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Abstract: The crystal structure and an improved synthesis of 1,3,5-trisilacyclohexane are reported. The solid state structure is compared with the reported structure determined in the gas phase by gas electron diffraction (GED). 1,3,5-Trisilacyclohexane adopts a chair conformation in the solid state. The Si–C bond lengths as well as all angles of 1,3,5-trisilacyclohexane in the solid state have similar dimensions compared to the structure in the gaseous phase.

Keywords: 1,3,5-trisilacyclohexane; crystallisation; in situ; silicon; structure of 1,3,5-trisilacyclohexane.

1 Introduction

Cyclohexane and its chair conformation are of fundamental interest to organic stereochemistry. Successive replacement of CH₂ units of cyclohexane by SiH₂ units allows comparing cyclohexane with its silicon analogues. For this reason some silacyclohexanes have been synthesised including 1-silacyclohexane [1], 1,2-disilacyclohexane [2], 1,3-disilacyclohexane [2], and 1,4-disilacyclohexane [2]. Symmetric exchange of CH₂ units leads to 1,3,5-trisilacyclohexane [3–5] and cyclohexane is one of the best investigated symmetric silacyclohexanes. For instance, studies by mass spectrometry [6, 7] and NMR spectroscopy [8] but also IR and Raman spectroscopy in gaseous and liquid phases have been performed to clarify the conformation of 1,3,5-trisilacyclohexane [9]. The structure of

Anorganische Chemie und Strukturchemie, Centrum für Molekulare Materialien CM₂, Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany, Fax: +(49) 521 106 6026, E-mail: mitzel@uni-bielefeld.de **Eugen Weisheim and Hans-Georg Stammler:** Lehrstuhl für 1,3,5-trisilycyclohexane in the gaseous phase has been determined twice: first by Dzhaparidze [10] and later by Arnason and Oberhammer [11]. However, until now no crystal structure of 1,3,5-trisilacyclohexane has been reported. Herein we present an improvement of the synthesis of 1,3,5-trisilacyclohexane and describe the single crystal structure, obtained by *in-situ* crystallisation and X-ray diffraction.

2 Results and discussion

The synthesis of 1,3,5-trisilacyclohexane (1) has been presented previously. Conversion of 1,1,3,3,5,5-hexamethoxy and 1,1,3,3,5,5-hexaethoxy-1,3,5-trisilacyclohexane has afforded 1 in moderate yields [11]. Better yields are achieved by reduction of the chlorine derivative (yield: 85%) [8], but its synthesis is demanding [5, 8]. An improvement of the workup procedure of 1 was now found to double the original yield of 1 [11]. Compound 1 was synthesised by conversion of 1,1,3,3,5,5-hexamethoxytrisilacyclohexane with LiAlH, in diethyl ether following the protocol of Arnason and co-workers [11]. After the reaction was finished, all volatiles and the product were condensed into a vessel held at -196 °C. This was then warmed to a temperature between -50 °C and -45 °C which led diethyl ether to condense off into another trap in static vacuum. The product remains as a colourless solid of high purity. In addition to the crystal structure determination, compound 1 was analysed by NMR, FT-IR spectroscopy and EI-MS spectrometry. The obtained data are in good agreement with the literature (NMR [8, 12–14] and FT-IR [9]).

2.1 Crystal structure

Compound **1** crystallises in the orthorhombic space group $Pmn2_1$ with two molecules per unit cell. It lies on a crystallographic mirror plane and adopts a chair conformation in the solid state (Fig. 1) as well as in the gaseous phase [11] (gas electron diffraction, GED). Table 1 reveals, that the

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Fig. 1: Molecular structure of 1,3,5-trisilacyclohexane (1) in the crystalline state. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Si(1)–C(1) 1.871(1), Si(2)–C(1) 1.873(1), Si(2)–C(2) 1.873(1), Si(1)–H(1A) 1.39(3), Si(1)–H(1B) 1.40(3), Si(2)–H(2A) 1.38(2), Si(2)–H(2B) 1.45(3); angles (deg): C(1)–Si(1)–C(1') 109.8(1), C(1)–Si(2)–C(2) 110.0(1), Si(1)–C(1)–Si(2) 113.5(1), Si(2)–C(2)–Si(2') 112.4(1), C(2)–Si(2)–C(1)–Si(1)–54.9(1). Symmetry code used for primed atoms: –*x*, *y*, *z*.

Table 1: Comparison of structural parameters of experimental XRD (mean values, individual values see caption to Fig. 1) and GED [11] data of 1,3,5-trisilacyclohexane (1). Distances, *r* in Å, angles in deg.

Parameters	XRD	GED [12]
r(Si–C)	1.872	1.872(1)
∠(Si–CH ₂ –Si)	112.9	113.0(4)
∠(C–SiH,–C)	109.9	110.7(14)
∠(H−Si−H)	107.5	107.4ª
$\varphi(CH_2 - Si - CH_2 - Si)$	54.9	53.7(4)

^aNot refined.

Si–C distances, in the solid state are as long as the in gas phase and an expansion of the C–Si–C angle compared to Si–C–Si angle has been observed in the crystal structure. The same relation between the angles has also been found in the gas phase structure.

The formal substitution of silicon by germanium atoms leads to the known isostructurally crystallising compound 1,3,5-trigermacyclohexane [15]. The structure 1,3,5-trigermacyclohexane in the solid state has – like **1** – a chair conformation and, expectedly, larger bond lengths (Ge–C, mean: 1.951 Å). The angle Ge–C–Ge (mean: 112.0°) and the angle C–Ge–C (mean: 109.8°) are comparable with those of compound **1** (Table 1).

3 Experimental section

All manipulations were performed under dried argon or nitrogen using *Schlenk* and *Stock* techniques. Tetrahydrofuran was dried with potassium, hexane and diethyl ether with LiAlH₄. The solvents were distilled prior to use. C_6D_6 was dried with Na/K alloy and condensed. NMR measurements were performed on Bruker Avance III 500 and Bruker DRX 500 instruments. NMR spectra were referenced to the residual signal of used protonated solvents (¹H, ¹³C) or external standards (²⁹Si: TMS). GC/EI-MS analyses were done using a Shimadzu GC-2010/GCMS-QP 2010S instrument (capillary column: Rtx®-200, Crossbond, trifluoropropylmethylpolysiloxane, 30 m, 25 mm, 0.25 μ m). FT-IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer.

3.1 Synthesis of 1,1,3,3,5,5-Trisilacyclohexane (1)

1,1,3,3,5,5-Hexamethoxy-1,3,5-trisilacyclohexane (8.56 g, 27.4 mmol), dissolved in diethyl ether (10 mL), was dropped to a suspension of LiAlH₄ (3.26 g, 85.9 mmol) in diethyl ether (80 mL) in a Young-tap ampoule. Afterwards the ampoule was cooled to -196 °C, evacuated, sealed and heated at 45 °C for 4.5 d. Workup: All volatile constituents of the reaction were condensed into another ampoule. This was cooled to a temperature between -50 °C and -45 °C and the diethyl ether was condensed off in dynamic vacuum. The product remained as colourless, acicular solid, with a melting point of 10 °C [lit. [8]: 10 °C]. Yield: 2.97 g (22.5 mmol, 82%). –¹H NMR (500 MHz, C₆D₆, 298 K): $\delta = 4.18$ (quint, ${}^{3}J_{H,H} = 3.6$ Hz, 6H, $-CH_{2}SiH_{2}CH_{2}$, ${}^{1}J_{Si,H} = 196$ Hz), -0.35 (quint, ${}^{3}J_{H,H} = 3.6$ Hz, 6H, $-SiH_{2}CH_{2}SiH_{2}-$, ${}^{2}J_{Si,H} =$ 117 Hz). – ¹³C{¹H} NMR (126 MHz, $C_6 D_6$, 298 K): $\delta = -10.3$ (s, $-\text{Si}C\text{H}_2\text{Si}-$, ${}^{1}J_{\text{Si}C} = 43$ Hz). $-{}^{29}\text{Si}\{{}^{1}\text{H}\}$ NMR (99 MHz, C_6D_6 , 298 K): $\delta = -34.3$ (s, $-CH_2SiCH_2$ -). -GC/EI-MS: m/z (%) = 130 (100) [M–H₂]⁺, 101 [M–SiH₂]⁺, retention time: 2.6 min. - FT-IR (gas phase) ν (cm⁻¹) = 2153 (Si-H, s), 2143 (Si-H, s).

3.2 X-Ray diffraction experiments

Single crystals of compound **1** suitable for X-ray diffraction measurement were obtained by *in situ* crystallisation in a glass capillary on the goniometer of the diffractometer. This was achieved by first establishing a solid-liquid equilibrium at 288.2 K close to the melting point, then melting all solid but a tiny crystal seed (using a thin copper wire as external heat source) followed by chilling very slowly with 3 K h⁻¹ until the whole capillary was filled with a single crystalline specimen at 285 K, then chilling with 10 K h⁻¹ to 265 K and 25 K h⁻¹ to the temperature of measurement at 100 K. The measurement was carried out
 Table 2:
 Crystallographic data for 1,3,5-trisilacyclohexane (1).

	1
Formula	C ₃ H ₁₂ Si ₃
<i>M</i> _r	132.40
Cryst. form	cylinder
Cryst. size, mm	$\emptyset = 0.1, l = 0.3$
Crystal system	orthorhombic
Space group	Pmn2 ₁
a, Å	8.553(1)
<i>b</i> , Å	7.643(2)
<i>c</i> , Å	6.029(1)
<i>V</i> , Å ³	394.06(9)
Ζ	2
$D_{\rm calcd}$, g cm ⁻³	1.116
μ (MoK α), cm ⁻¹	0.493
F(000), e	144
θ_{\max} , deg	30.0
Completeness to θ max.,%	99.6
hkl range	$\pm 12, \pm 10, \pm 8$
Refl. measured/unique	6718/1172
R _{int}	0.0220
Refl. with $l > 2 \sigma(l)$	1155
Parameters refined	59
$R(F)/wR(F^2)$ ($I > 2 \sigma(I)$)	0.0149/0.0373
$R(F)/wR(F^2)$ (all refl.)	0.0154/0.0375
<i>x</i> (Flack)	0.30(17)
GoF (<i>F</i> ²)	1.113
$\Delta \! ho_{fin}$ (max/min), e Å-3	0.18/-0.14

with MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods and refined by full-matrix least-squares cycles (programs: SHELXS/L-97) [16]. Further details of data collection and refinements are listed in Table 2.

CCDC 1419824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Graphical synopsis

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