

Cyclopentasilane Si₅H₁₀: First single crystal X-ray structure of an oligosilane Si_xH_y and thermal analysis with TG/MS



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ABSTRACT

Cyclopentasilane Si₅H₁₀ (CPS) – a liquid silicon precursor – was crystallized in situ at –100 °C which allowed determination of the single crystal X-ray structure, showing short intermolecular distances below the sum of the v.d.Waals radii of the corresponding atoms. Further characterization included a thermal analysis with mass spectrometry (TG/MS) of the segregated species hydrogen, mono- and disilane.

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Recently, attention has been paid to (liquid) oligosilanes Si_xH_y [1–7]. This renewed interest stems from the concept to prepare silicon films for transistors, solar cells and other devices via printing and deposition techniques, which are simpler and more cost efficient than traditional semiconductor processing [1–5]. Oligosilanes are convertible to a-Si:H at low temperatures (>250 °C). Suitable compounds are restricted to oxygen- and carbon-free liquid oligosilanes Si_xH_y, which was shown in a pioneering paper by Shimoda et al. [1]. The principal syntheses of CPS and other oligosilanes are long known since the early works of Stock [8] and Hengge [9]. However, several efforts have been undertaken in recent years to characterize the highly sensitive and pyrophoric CPS and to utilize it for “liquid silicon inks” [1–5]. Further interest arises from rocket technology, since oligosilanes might be very good combustion enhancing fuel additives [6], and useful for the synthesis of high capacity graphite–silicon composite anode materials for lithium-ion batteries [7]. Besides, oligosilanes are known to show the phenomenon of σ-delocalization, which refers to a σ-orbital interaction similar to the conjugation and delocalization of π-electrons in unsaturated carbon compounds [10]. There are few examples of crystal structure studies on hydrosilanes. These are restricted to powder-XRD of layered polysilane (Si₆H₆)_n [11], the crystal structure of a high-pressure phase of monosilane (SiH₄) [12], and the high-pressure v.d.Waals adduct SiH₄(H₂)₂ [13]. Thus, to the best of our knowledge no crystal structure analysis has been reported for any linear, cyclic or branched hydrosilane so far.

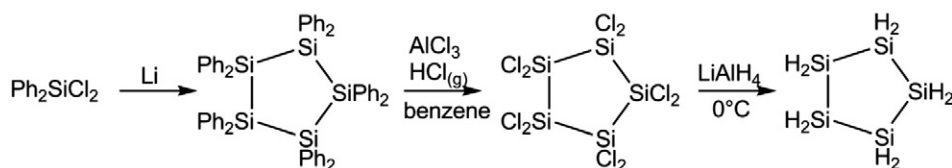
CPS was prepared according to known procedures with some modifications [9,14], according to Scheme 1. Formation of CPS was indicated

by ¹H and ²⁹Si NMR spectra in benzene solution, showing singlets at 3.5 ppm and -106.9 ppm, respectively. These values correspond well with the literature data. Similarly, Raman spectra obtained from samples in sealed capillaries correspond well with the data published by Hengge et al. [9].

For determination of a single crystal X-ray structure CPS was filled in a thin-walled glass capillary which was sealed and mounted on the goniometer head of the diffractometer. Freezing the liquid on the diffractometer gave polycrystalline material which was unsuitable for an X-ray structure analysis. Repeated melting and refreezing between 263 and 153 K under slow movement along the z-axis of the goniometer head, gave at last a monocrystalline block in the capillary which was suitable for a crystal structure determination. The data collection was performed at 173 K in order to reduce ice formation outside the glass capillary. CPS crystallizes in the monoclinic space group P 2₁/m (Fig. 1).

The structure is not isomorph with the X-ray structure of cyclopentane C₅H₁₀ which crystallizes in a hexagonal unit cell [15]. Silicon atom Si1 of CPS is situated on special position 2e, site symmetry *m*. Thereby Si2A and Si3A are generated by the crystallographic mirror plane. Thus, the CPS molecule has an envelope conformation with perfect C_s symmetry. Atom Si1 lies 0.54(1) Å outside the plane formed by the atoms Si2, Si3, Si3A, and Si2A. The angle between the plane formed by the atoms Si2, Si1, Si2A and the plane formed by the atoms Si2, Si3, Si3A and Si2A is 23.05(6)°. The Si–Si bond lengths are between 2.3353(1) and 2.3377(7) Å (Table S1). These bonds are shorter than in Si₅(CH₃)₁₀ [16] (2.349 Å), Si₅(C₆H₅)₁₀ [17] (2.396 Å) or Si₅Cl₁₀ [18] (2.347 and 2.363 Å). Also permethylated linear silanes have longer Si–Si bond lengths of 2.35 Å [19]. The structure of CPS was also investigated by gas-phase electron diffraction. Here

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Scheme 1. Synthesis pathway to obtain cyclopentasilane (CPS).

Si–Si bond lengths of 2.342(3) Å were found [20]. Quantum chemical calculations on different levels of theory estimated Si–Si bond lengths for CPS between 2.356 and 2.383 Å, dependent on the applied method/basis set combination [21].

The experimentally determined envelope conformation with C_s symmetry of CPS is in agreement with ab initio studies. In particular, Sagiya et al. investigated the planar (D_{5h}), envelope (C_s) and twist (C_2) conformation [22]. Their results show that the C_s and C_2 forms have very similar energies. The energy difference is approximately 1.01 to 1.02 meV. Whereby, the energy barrier for the structure transformation between these two geometries is low (<0.1 meV). The planar form (D_{5h}), on the other hand, is about 50 meV less stable than the C_s and C_2 forms. Similar results were found in [21]. A summary of all relevant atom distances and selected bond and dihedral angles is provided in Table S1.

Many of the properties of CPS (and other perhyrido-oligosilanes) are at least in part related to the comparatively long Si–Si distances and the small size of the hydrogen atoms (Fig. S1). This leaves the Si–Si bonds rather unprotected and allows a facile attack by oxygen (and other oxidative species) causing the pyrophoric behavior. The tendency of CPS to polymerize upon UV irradiation and the formation of α -Si:H upon thermolysis at low temperatures [1–5,22] are certainly also related to the structural features.

In the solvent-free crystals the CPS molecules are arranged in stacks along the crystallographic a axis (Fig. S2a). This is most likely due to the toroidal shape of the molecules (Figs. 1 and S1). In the stacking direction the hydrogen atoms H2 are situated above the center of the neighboring molecules forming short intermolecular contacts with Si2 and Si3 (H2...Si2 3.126 Å, H2...Si3 3.131 Å, Fig. 2). This is below the sum of the van der Waals radii of silicon and hydrogen with 3.3 Å [23]. The distance between two neighboring silicon atoms Si2...Si2' (symmetry operation: $1-x, 1-y, 1-z$) is 4.147 Å, i.e. also below the sum of v.d.Waals radii of two Si atoms with 4.2 Å [23]. The latter fact is probably more important than the recently discussed interaction of Si–H units in liquid CPS, which were studied by ab initio calculations [3].

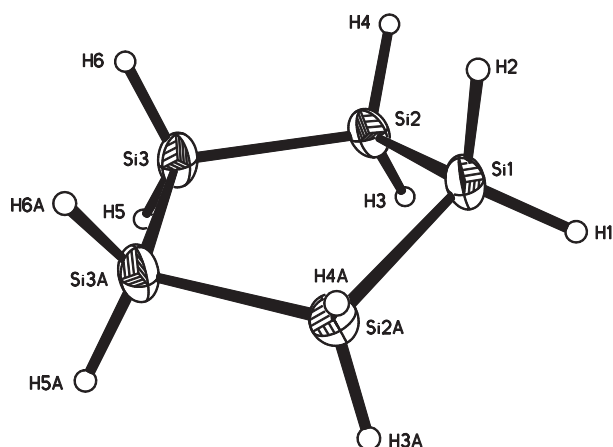


Fig. 1. Molecular structure of CPS (50% probability).

A comprehensive understanding of the decomposition and photopolymerization of CPS is a matter of current experimental and theoretical investigations. Silyl radicals, different silylenes and other species may be involved. The thermal decomposition properties are crucial for the application of CPS as a precursor for liquid deposition of silicon mentioned above. A recent TG study of Masuda et al. [4b] on CPS-derived polydihydrosilane indicates that the decomposition starts at 100 °C, followed by a mass loss of 58% between 100 and 360 °C, where the major weight losses take place at 100, 200 and 300 °C. The maximum of the DTA curve was found at 360 °C. For an analysis of the evolved species during thermal conversion into α -Si:H we performed TG–MS measurements of the CPS (Fig. 3).

A weak exothermic heat flow signal below 80 °C was assigned to polymerization of CPS. A second more pronounced exothermic effect at 178 °C may be due to a cross-linking as indicated by the MS spectra (see below). The third exothermic peak around 300 °C was small and weaker in comparison to the results reported by Masuda et al. [4b]. The major weight loss of our samples takes place in two steps. First, evolution of molecular hydrogen was detected at ~84 °C. Interestingly, not only hydrogen is evolved, but also monosilane SiH₄. Later during the second decomposition step at ~178 °C we detected disilane, monosilane and hydrogen (Fig. 4). The weight loss was 17% and 33% during the first and second step, respectively.

A detailed analysis of the thermal (and photochemical) polymerization and decomposition processes are a matter of current work in our group and will be published in the future.

In 2006 [1] it was shown that semiconductor devices are obtainable from CPS, which can be p- and n-doped by addition of e.g. P₄ or B₁₀H₁₄ [24], by printing techniques followed by annealing at >250 °C. We characterized CPS by single crystal X-ray structure analysis. This first crystal structure of an oligosilane shows the expected envelope conformation.

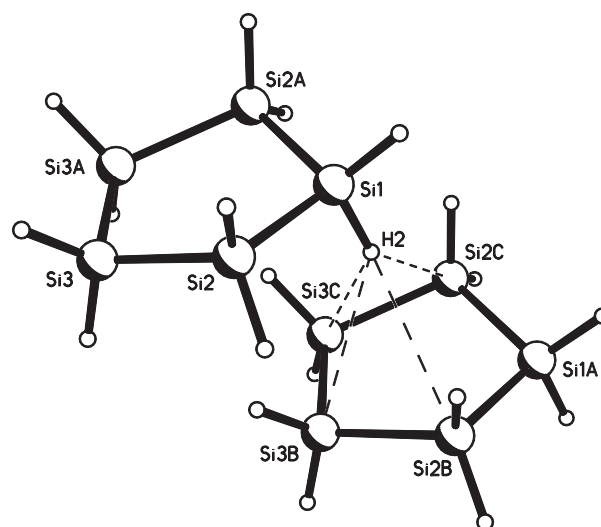


Fig. 2. Intermolecular contacts between H2 and Si2 and Si3 from neighboring molecule (H2...Si2 3.126 Å, H2...Si3 3.131 Å).

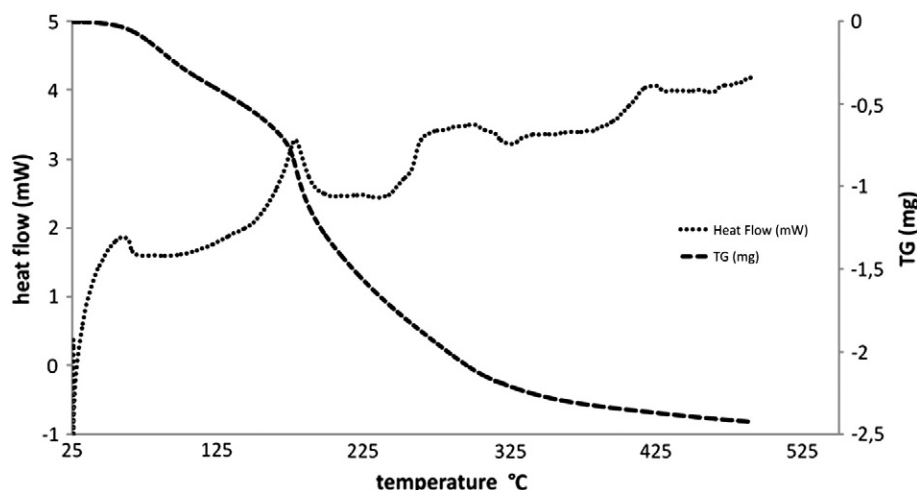


Fig. 3. Thermal gravimetric analysis (TG) and heat flow (DTA) of cyclopentasilane in the temperature range up to 500 °C. In an Al₂O₃ crucible, 4.5 mg of CPS were heated from 25 to 500 °C (heating rate: 5 K/min).

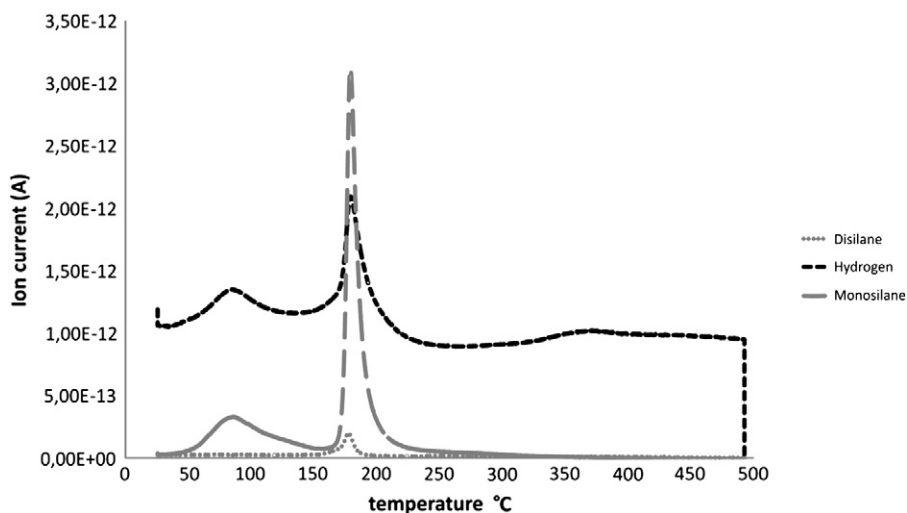


Fig. 4. Selected TG-MS analysis data of CPS: Ion current curves for H₂⁺, SiH₄⁺ and Si₂H₆⁺.

Close contacts are found between Si–H units and Si₅-rings of neighboring CPS molecules as well as short intermolecular Si–Si distances, which are both below the sum of the v.d.Waals radii of the corresponding atoms. TG/DTA-MS indicates exothermal H₂ and SiH₄ formation at 84 °C followed by a second exothermal step at 180 °C with additional Si₂H₆ evolution. Both, the XRD and the TG/MS data provide a basis for mechanistic studies and optimization of the CPS processing and a-Si:H formation. Further motivation to study the structures and properties of (cyclo)oligosilanes including CPS in more detail stems from the continued discussion of σ -delocalization [10] and σ -aromaticity [25], several potential applications of oligosilanes [1,6,7] as well as recently reported partial chlorination of CPS and related pentasilanes [26].

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Appendix A. Supplementary material

The electronic supplementary information can be found at <http://dx.doi.org/10.1016/j.inoche.2013.05.023>. It contains synthesis and crystal data for CPS; Table S1: Bond lengths & angles; Fig. S1: Space-filling molecular plot; Fig. S2: Views along the crystallographic *a*- and *c*-axes. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-425931.

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