



Microwave, infrared, and Raman spectra, structural parameters, vibrational assignments and theoretical calculations of 1,3-disilacyclopentane



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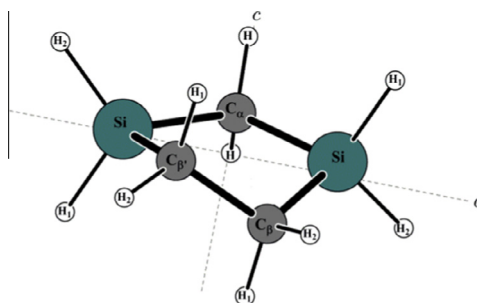
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HIGHLIGHTS

- Structural parameters have been determined for the stable twist conformer.
- Rotational constants for the five isotopologues for the twist conformer were determined from the microwave spectra.
- Vibrational assignments are given for the molecule.
- *Ab initio* and density functional theory calculations have been carried out for all possible conformers.

GRAPHICAL ABSTRACT



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ABSTRACT

The FT-microwave spectrum of 1,3-disilacyclopentane ($c\text{-C}_3\text{H}_6\text{Si}_2\text{H}_4$) has been recorded and 99 transitions for five isotopologues have been assigned for the twist form. The ground state rotational constants were determined from these assignments with following values for $A = 4417.6710(7)$, $B = 2887.0548(6)$, $C = 1938.2171(6)$. From the experimentally reported microwave rotational constants and *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters are reported for the most stable twist form distances (Å) $r_{\text{C}_\alpha\text{-Si}} = 1.886(2)$, $r_{\text{Si-C}_\beta\text{C}_\gamma} = 1.888(2)$, $r_{\text{C}_\beta\text{-C}_\gamma} = 1.552(2)$, and angles ($^\circ$) $\angle\text{SiC}_\alpha\text{Si} = 103.9(3)$, $\angle\text{C}_\alpha\text{SiC}_\beta = 102.2(3)$, $\angle\text{SiC}_\beta\text{C}_\gamma = 106.4(3)$, and $\tau_{\text{C}_\beta\text{SiC}_\alpha\text{Si}} = 11.5(3)$, $\tau_{\text{SiC}_\beta\text{C}_\gamma\text{Si}} = 45.6(3)$. The conformational stabilities have been predicted from theoretical calculations with basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been made for the observed bands for the twist conformer and the interpretation is utilized by *ab initio* calculations to predict harmonic force constants, vibrational wavenumbers, infrared intensities, Raman activities and depolarization ratios. The results are discussed and compared to the corresponding properties of some related molecules.

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1. Introduction

Considerable interest in the structure of cyclopentane resulted when it proposed that the two low frequency bending modes could have nearly equal frequencies which resulted in a vibration that was described as pseudorotation [1]. However the concept of this motion for cyclopentane was not readily accepted particularly

when the low frequency ring mode of this molecule appeared normal [2]. Also there was further reluctance to accept the pseudorotation motion of the puckering motion with the consequent indefiniteness of the mode [3,4]; however after two decades evidence was reported [5] from the CH₂ deformation of cyclopentane that the ring was undergoing pseudorotation which was nearly barrier free.

With the acceptance of pseudorotation there were a number of investigations on conformations of mono substituted cyclopentane molecules and the determination of the most stable structure. Some of the earliest conformational determinations were the halides, i.e. bromine, chlorine and fluorine. In the initial investigation [6,7] of these three molecules it was reported that all three had the envelope-equatorial conformer as the most stable forms in the fluid phases. A second conformer was also identified in the fluid phases as the envelope-axial form. However from later studies [8] it was demonstrated that there was only one conformer present in the fluid phases of fluorocyclopentane and it was the envelope-equatorial form. Much later it was shown that the one form was not the envelope conformer but the twisted form [9]. Also it should be noted that incorrect conformational structures for five membered rings with another species, such as nitrogen instead of CH₂ have been initially reported [10,11] as the envelope form. From a later vibrational infrared study [12] it was shown that the conformer was the twisted form. Thus it is not easy to predict what the conformational structure will be for many different types of five membered rings. The conformational and structural studies of five membered rings continue to be of scientific interest because of these uncertainties.

Of particular interest are heterocyclic five membered ring molecules many of which are important biomolecules. The five membered heterocyclic rings of silicon and carbon have not been significantly studied. Therefore, we recently began to investigate a number of mono-substituted 1-silacyclopentane compounds [13–15] of the form c-C₄H₈SiH-X where X has been several halogens. From these studies it was found that the twist conformer with no symmetry was the most stable form. However, only for the X = F molecule were the adjusted r_0 structural parameters determined. The 1,3-silacyclopentane compounds of the form c-C₃H₆(SiX₂)₂ where X = H and perhaps other halogens has largely not been studied due to difficulties in the synthesis of these compounds. The only previous publications of this compound are several synthesis studies [16–19] with only basic characterizations of these molecules. These compounds are of significant interest as the change from carbon to silicon significantly changes the physical and physiochemical properties of these molecules where the carbon analogue is normally stable in the equatorial and axial conformers. However, the single silicon heterocycle molecule is [16] the twist form with only one stable conformer, whereas the structure of the double silicon molecule has not previously been determined. Therefore, we have initiated microwave, infrared and Raman spectroscopy studies to determine the stable conformer or conformers, the structural parameters, and vibrational fundamental frequencies which we expect to compare to the corresponding carbon compound.

To support the experimental studies we have obtained harmonic force constants, infrared intensities, Raman activities, depolarization ratios, and frequencies of the vibration fundamentals from MP2(full)/6-31G(d) *ab initio* calculations. To obtain predictions on the conformational stabilities we have carried out MP2(full) *ab initio* and density functional theory (DFT) calculations by the B3LYP method by utilizing a variety of basis sets. The r_0 structural parameters have been obtained by combining the MP2(full)/6-311+G(d,p) *ab initio* predicted parameters with the determined rotational constants obtained from this study. The results of these spectroscopic, structural,

and theoretical studies of 1,3-disilacyclopentane (c-C₃H₆Si₂H₄) are reported herein.

2. Experimental and theoretical methods

The c-C₃H₆Si₂H₄ compound was prepared according to the method of Laane (personal communication) with modifications. The sample was first purified by trap-to-trap and was also further purified by a low-temperature, low-pressure fractionation column. The purity of the sample was checked by infrared and nuclear magnetic resonance spectroscopy.

The rotational spectrum of c-C₃H₆Si₂H₄ was obtained by using a CP-FTMW spectrometer developed at the University of Virginia, operating in the 6.5–18 GHz range. The chirped pulse methods used in this study have been described in detail previously [20], so only the brief details relevant to this experiment are necessary.

The microwave source was a 24 GS/s arbitrary waveform generator, producing a 12–0.5 GHz linear frequency sweep in 1 μs. The pulse was upconverted to 6.5–18 GHz by a 18.95 GHz phase-locked resonant dielectric oscillator (PDRO), and then amplified by a pulsed 300 W traveling wave tube amplifier. The amplified pulse is then transmitted through free space between two standard-gain microwave horns, where it interacts with a molecular beam generated by five pulsed nozzles (General Valve Series 9) operating perpendicular to the propagation direction of the microwave pulse. On the detection end, the receiver is protected from the high power pulse by a combination of a PIN diode limiter and single-pole microwave switch. The resulting molecular free induction decay (FID) was then amplified and digitized directly on a 100 GS/s oscilloscope with 33 GHz of hardware bandwidth, with a 20 μs detection time per FID. Due to the speed of this excitation and detection process, a sequence of 10 excitation/detection cycles is possible per gas pulse, and all ten detected FIDs are collected and averaged together before the next valve injection cycle begins. Phase stability of this experiment over the course of many valve injection cycles is enabled by locking all the frequency sources and the oscilloscope to a 10 MHz Rb-disciplined quartz oscillator. For this experiment, approximately 78,000 valve injection cycles of the sample gas were completed at 3.3 Hz to create a time-averaged spectrum of 780,000 molecular FIDs (approximately 6.5 h of averaging). Additionally, the time domain resolution afforded by a 20 μs FID generates an average Doppler broadened linewidth of approximately 130 kHz at FWHM.

The sample for spectral investigation was prepared by balancing c-C₃H₆Si₂H₄ vapor with approximately 3.4 atm of Ne gas (GTS Welco) for a total sample concentration of approximately 0.1%. This afforded a frequency-domain dynamic range of approximately 4000:1 at 780,000 averages, which enabled assignment of all common heavy atom single isotopologues (¹³C, ²⁹Si, ³⁰Si) in natural abundance as well as a double isotopologue (²⁹Si/³⁰Si). These assignments are listed in Tables 1–3 with an experimental uncertainty of approximately 20 kHz (line centers determined to ±10 kHz). The experimental analysis of c-C₃H₆Si₂H₄ was supplemented with *ab initio* electronic structure calculations for rotational constant and centrifugal distortion predictions (Table 4). These calculations were performed with the Gaussian 09 suite of programs [21].

The infrared spectrum of the gas (Fig. 1) was obtained from 4000 to 220 cm⁻¹ on a Perkin–Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectrum of the gas was obtained with a theoretical resolution of 0.5 cm⁻¹ with 128 interferograms added and truncated.

Raman spectrum (Fig. 2) of the liquid was collected in back-scattering geometry using the 514.532 nm line of an Argon ion

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