

# Theoretical calculations, far-infrared spectra and the potential energy surfaces of four cyclic silanes



Hye Jin Chun, Lloyd F. Colegrove, Jaan Laane\*

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, United States

## ARTICLE INFO

### Article history:

Received 22 November 2013  
In final form 24 December 2013  
Available online 8 January 2014

### Keywords:

Potential energy surfaces  
Cyclic silanes  
Theoretical calculations  
Far-infrared spectra  
Hindered pseudorotation

## ABSTRACT

Theoretical computations have been carried out to calculate the potential energy functions for the out-of-plane vibrations of four cyclic silanes, and the results were compared to experimental functions determined from far-infrared data. The experimental and computed ring-puckering potential functions for 1-silacyclopent-3-ene, which are in excellent agreement, are quartic in nature with tiny barriers to planarity. Similarly, the calculated and experimental potential functions for 1,3-disilacyclopent-3-ene are nearly identical. For silacyclopentane and 1,3-disilacyclopentane the calculations predict ring-twisting barriers of  $2493\text{ cm}^{-1}$  (vs.  $2110\text{ cm}^{-1}$  observed) and  $1395\text{ cm}^{-1}$ , respectively. The conformational energies for the bent forms were calculated to be  $1467\text{ cm}^{-1}$  (vs.  $1509\text{ cm}^{-1}$  observed) for the former and  $878\text{ cm}^{-1}$  for the latter relative to the energy of the twist minima. One-dimensional hindered pseudorotational potential energy functions were found to work well for predicting the observed far-infrared spectra for the bending (pseudorotational) vibration.

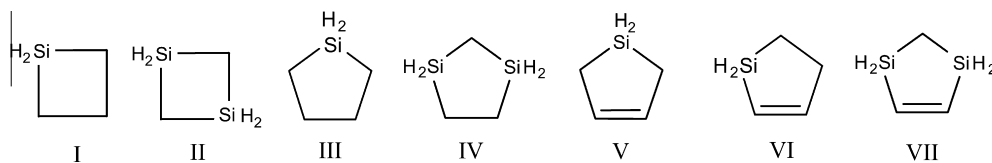
© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

We have for many years been investigating the low-frequency vibrations and potential energy surfaces of small ring compounds [1–7]. Among these are a number of organosilanes

## 2. Theoretical calculations

*Ab initio* and DFT computations were carried out using the Gaussian 09 package [30]. MP2/cc-pVTZ calculations were utilized to determine the molecular structures and the conformational



including silacyclobutane (I) [8–14], 1,3-disilacyclobutane (II) [15–16], silacyclopentane (III) [17–20], 1,3-disilacyclopentane (IV) [21,22], 1-silacyclopent-3-ene (V) [10,23–25], 1-silacyclopent-2-ene (VI) [26–29], and 1,3-disilacyclopent-4-ene (VII) [21,22]. Among these, molecules I, II, IV, and VII were prepared for the first time by our laboratories. We have previously reported theoretical calculations for I [8], II [15], and VI [26]. In the present work we report on III, IV, V, and VII with a focus on theoretical calculations of the conformational energies of these molecules as governed by their low-frequency out-of-plane vibrations.

energies for different values of selected vibrational coordinates. B3LYP/cc-pVTZ calculations were used to compute the vibrational frequencies. A scaling factor of 0.985 was used for the low frequencies. From past experience we have found that the DFT calculations do a slightly better job of predicting the vibrational frequencies. The vibrational frequencies of the ring-puckering and ring-twisting motions were calculated using the DA1OPTN program [31]. The VNCOSPX program [32] was used to calculate the pseudorotational frequencies.

Fig. 1 shows the calculated structures for III and V, which we have previously not reported. III is twisted with a calculated twist angle of  $27.7^\circ$  while V is planar. The structures for IV and VII were presented previously [22].

\* Corresponding author. Tel.: +1 9798453352.

E-mail address: [LAANE@MAIL.CHEM.TAMU.EDU](mailto:LAANE@MAIL.CHEM.TAMU.EDU) (J. Laane).

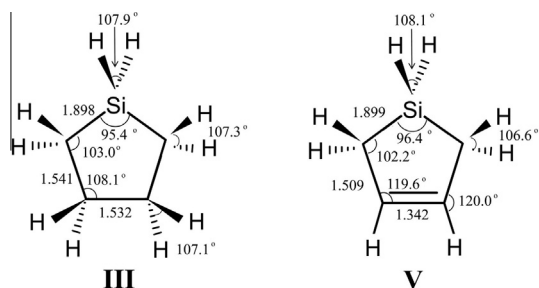


Fig. 1. Calculated structures for silacyclopentane (III) and 1-silacyclopent-3-ene (V). The twisting angle for III is 27.7°.

### 3. Experimental

The far-infrared spectra of 1,3-disilacyclopentane (IV) and 1,3-disilacyclopent-4-ene (VII) were previously recorded and published in part [21]. Additional spectra were reported in the L.F. Colegrove, Ph.D. thesis [33].

### 4. Results and discussion

#### 4.1. 1-Silacyclopent-3-ene (V)

We have previously reported the far-infrared spectrum of this molecule and determined its one-dimensional ring-puckering potential energy function [25]. At that time the reduced mass was only estimated, but some years later, after we had refined the process of carrying out reduced mass calculations [34,35], we determined an improved value [23]. That value of  $\mu = 128.64$  a.u. along with the kinetic energy expansion terms, which account for the change in reduced mass with coordinate, will be utilized here. The conformational energy of V was calculated point by point using increments of  $\Delta x = 0.008$ – $0.028$  Å for the puckering coordinate. The computations predicted a barrier of  $3.8$   $\text{cm}^{-1}$  and the calculated values were fit with the potential function in Eq. (1):

$$V(\text{cm}^{-1}) = 2.200 \times 10^5 x^4 - 0.0183 \times 10^5 x^2 \quad (1)$$

This can be compared to the function in Eq. (2) determined from the experimental data [23] and the calculated reduced mass [23]

$$V(\text{cm}^{-1}) = 2.130 \times 10^5 x^4 - 0.0054 \times 10^5 x^2 \quad (2)$$

The experimentally determined function in Eq. (2) has a barrier of only  $0.3$   $\text{cm}^{-1}$ . Thus both functions produce a miniscule barrier. So, for all practical purposes the molecule is planar and very nearly a pure quartic oscillator. Fig. 2 compares the two functions and the agreement can be seen to be excellent. Table 1 compares the observed experimental frequencies to those calculated from Eqs. (1) and (2). The latter fits the data very well since the potential energy parameters were refined to fit the spectroscopic data. Moreover, the excellent agreement is gratifying since it also confirms that our model [34,35] for calculating the reduced mass for the puckering has produced a very accurate value. The frequencies calculated for Eq. (1) agree remarkably well with the experimental values considering that the potential energy function was generated directly from the *ab initio* data. As seen from Eq. (1), the slightly higher (but still tiny) barrier for this function causes the lowest two energy levels to move closer together and produces a lower transition frequency by  $5.9$   $\text{cm}^{-1}$ . All of the other frequencies from the *ab initio* calculation function of Eq. (1) wind up  $1.3$ – $2.9$   $\text{cm}^{-1}$  lower than those from Eq. (2). It is remarkable that the *ab initio* prediction is as good as it is, and it is interesting that the barrier difference of  $3.5$   $\text{cm}^{-1}$  does have a significant effect on the observed values. It

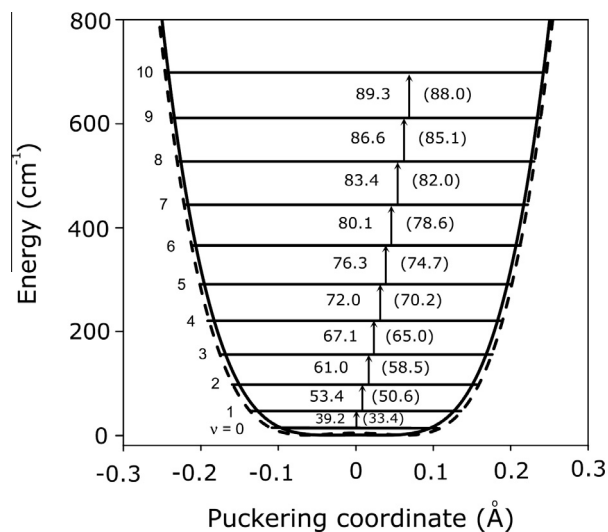


Fig. 2. Experimental (solid line) and theoretical (dashed line) potential energy functions for the ring-puckering vibration of 1-silacyclopent-3-ene (V). The values in parentheses are the calculated values.

Table 1

Observed and calculated ring-puckering transitions for 1-silacyclopent-3-ene.

Transition	Frequency ( $\text{cm}^{-1}$ )		
	Obs.	Calc. <sup>a</sup>	Calc. <sup>b</sup>
0–1	39.2	39.1	33.3
1–2	53.4	53.5	50.6
2–3	61.0	61.2	58.5
3–4	67.1	67.3	65.0
4–5	72.0	72.3	70.2
5–6	76.3	76.5	74.7
6–7	80.1	80.3	78.6
7–8	83.4	83.6	82.0
8–9	86.6	86.6	85.1
9–10	89.3	89.3	88.0

<sup>a</sup>  $V(\text{cm}^{-1}) = 2.130 \times 10^5 x^4 - 0.0054 \times 10^5 x^2$  (experimental fit).

<sup>b</sup>  $V(\text{cm}^{-1}) = 2.220 \times 10^5 x^4 - 0.0183 \times 10^5 x^2$  (*ab initio*).

is also noteworthy that the Gaussian 09 program predicts a transition frequency from the DFT calculation of  $62$   $\text{cm}^{-1}$ , which is higher than the experimental value of  $39.2$   $\text{cm}^{-1}$ . The theoretical value is based on the assumption of harmonic forces but, as we have seen, the puckering vibration is very nearly pure quartic.

#### 4.2. 1,3-Disilacyclopent-4-ene (VII)

The calculations for VII were carried out in similar fashion as for V. The previously reported potential function for the puckering determined from the experimental data [21] was

$$V(\text{cm}^{-1}) = 1.48 \times 10^5 x^4 + 0.030 \times 10^5 x^2 \quad (3)$$

The function determined from the *ab initio* calculations is

$$V(\text{cm}^{-1}) = 1.83 \times 10^5 x^4 + 0.020 \times 10^5 x^2 \quad (4)$$

Both functions are shown in Fig. 3 and the agreement is very good. Although the quartic constant in Eq. (4) is about 20% higher than that in Eq. (3), this is somewhat compensated for by a lower quadratic constant. Table 2 also shows the comparison between the observed transition frequencies and those calculated from Eqs. (3) and (4). The generally higher values resulting from the *ab initio* calculation result from the higher quartic potential energy constant. Nonetheless, it is obvious that the theoretical calculation again does a

Download English Version:

<https://daneshyari.com/en/article/5373664>

Download Persian Version:

<https://daneshyari.com/article/5373664>

[Daneshyari.com](https://daneshyari.com)