J. Phys. Chem. A **1998,** *102,* 10261−10264

Far-Infrared, Combination Band, and Raman Spectra of the Ring-Puckering Vibration of 1,4-Disilacyclohexa-2,5-diene

Arnold del Rosario,[†] Ralf Bitschenauer,[‡] Marwan Dakkouri,[‡] Kristjan Haller,[†,§] and Jaan Laane*[,†]

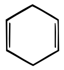
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and
Department of Chemistry, Universität Ulm, Ulm, Germany

Received: August 21, 1998; In Final Form: October 23, 1998

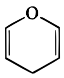
The far-infrared spectrum of 1,4-disilacyclohexa-2,5-diene shows a series of four closely spaced bands originating at 70.5 cm^{-1} resulting from the ring-puckering vibration. Four mid-infrared bands near 2214 cm^{-1} result from combinations of the puckering with the Raman active B_{2g} SiH_2 antisymmetric stretch at 2143.2 cm^{-1}, and seven difference bands near 2083 cm^{-1} result from combinations with the Raman active A_g SiH_2 symmetric stretch at 2154.0 cm^{-1}. The ring-puckering transitions result from a single-minimum potential energy function, $V(cm^{-1}) = 1.23 \times 10^4x^2 + 2.40 \times 10^4x^4$, where x is the puckering coordinate. The molecule is planar and less rigid than 1,4-cyclohexadiene, thus apparently showing no unusual interactions between the silicon atoms and the C═C π systems.

1. Introduction

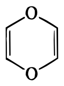
1,4-Cyclohexadiene and its analogues can be treated as pseudo-four-membered rings when their out-of-plane ring-puckering vibrations are considered.[1] This is because each of the two pairs of olefinic carbon atoms can be viewed as a single unit during this ring-bending motion. Originally 1,4-cyclohexadiene (I) was thought to be nonplanar,[2] but more recent studies on this molecule[1,3,4] clearly show it and two of its oxygen analogues, 4*H*-pyran[4] (II) and 1,4-dioxin[5] (III), to be planar. In addition, the ring-puckering potential energy functions determined for II and III showed that weak π interactions between the nonbonded oxygen orbitals and the C═C bonds are present.[4] Without these interactions, III would be expected to be nonplanar.



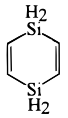
I



II

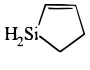


III

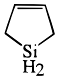


IV

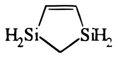
In the present study we report our results for 1,4-disilacyclohexa-2,5-diene (IV). We were especially interested in investigating whether any significant unusual interactions were present between the silicon atoms and the C═C bonds. The presence of such interactions would be expected to increase the torsional forces about the ═C−Si− bonds and hence increase the rigidity of the ring system. In previous work we have investigated the far-infrared spectra and ring-puckering potential energy functions of 2-silacyclopentene[6,7] (V), 3-silacyclopentene[8,9] (VI), and 1,3-disilacyclopent-4-ene[10] (VII). The potential energy function of V is unusually steep reflecting a rigid, planar, ring system, and this was attributed to interactions between the silicon atom orbitals and the C═C π orbitals. Molecule VI is also planar but much less rigid, and the silicon atom in this molecule is not capable of interaction with the carbon−carbon π bond. On the basis of the results for V, molecule VII could be expected to be very rigid and planar. However, while VII is planar, it is only slightly more rigid than VI.[10]



V



VI



VII

2. Experimental Section

1,4-Disilacyclohexa-2,5-diene (IV) was prepared according to the method of Maier et al.[11] The reaction of hexamethoxydisilane with acetylene produced 1,1,4,4-tetramethoxy-1,4-disilacylohexa-2,5-diene, which was then reduced with $LiAlH_4$ to produce IV. The 1,1,4,4-d_4 isotopomer was prepared using $LiAlD_4$ as the reducing agent.

Far-infrared and mid-infrared spectra were recorded on a Bomem DA8.02 Fourier transform interferometer equipped with a liquid-helium-cooled germanium bolometer as a detector. Gas samples with 1−10 Torr of vapor pressure were contained in a 5 m multipath cell with polyethylene windows. Vapor- and liquid-phase Raman spectra were recorded on an ISA JY U-1000 double monochromator equipped with a Coherent Radiation DPSS 532-400 frequency-doubled Nd:YAG laser operating at 532 nm with about 450 mW of power. For vapor spectra the high-temperature cell previously described was utilized.[12]

3. Results and Discussion

Figure 1 shows the far-infrared spectrum of IV recorded with 0.1 cm^{-1} resolution. Four bands at 70.5, 71.2, 71.6, and 72.1 cm^{-1} can be resolved as transitions between the different ring-puckering quantum states. The Raman spectrum of the vapor shows a broad unresolved band with a maximum at 141 cm^{-1}. This corresponds to overlapping double quantum jump transi-

---

* To whom correspondence should be addressed.

[†] Texas A&M University.

[‡] Universität Ulm.

[§] Permanent address: Institute of Physics, University of Tartu, Tartu, Estonia.

10.1021/jp983439a CCC: $15.00 © 1998 American Chemical Society
Published on Web 11/20/1998

TABLE 1: SiH_2 Stretching Bands and Combinations with the Ring-Puckering Vibration of 1,4-Disilacyclohexa-2,5-diene[a]

	ν (cm^{-1})			
SiH_2 vibration	vapor	liquid	inferred	combination
$\nu_2(A_g)$ symmetric stretch (i.p.)	2154.6 R	2146 R	2154.0	B_{1u} (type C)
$\nu_{13}(B_{2g})$ antisymmetric stretch (o.p.)	~2143 R	2129 R	2143.2	B_{3u} (type A)
$\nu_{22}(B_{1u})$ symmetric stretch (o.p.)	2143 IR			A_g
$\nu_{32}(B_{3u})$ antisymmetric stretch (o.p.)	2150 IR			B_{2g}

[a] R, Raman; IR, infrared; i.p., in-phase; o.p., out-of-phase.

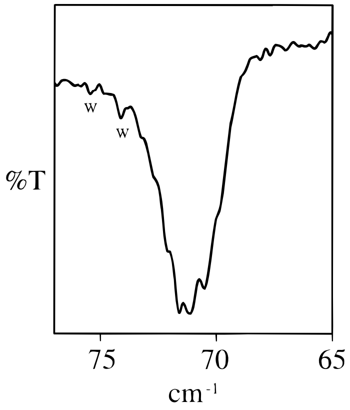


Figure 1. Far-infrared spectrum of 1,4-disilacyclohexa-2,5-diene, 10 Torr in a 5 m cell.

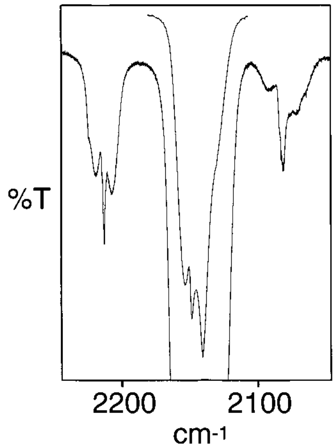


Figure 2. Infrared combination band spectrum of 1,4-disilacyclohexa-2,5-diene, 0.5 and 10 Torr in a 5 m cell.

tions. Further information on the puckering levels can be obtained from combination bands in the SiH_2 stretching region. Table 1 lists the four different SiH_2 stretching modes and the infrared and Raman frequencies observed for the vapor and liquid samples. The table also shows the symmetry species of the combinations that can be expected between the puckering and each stretching mode. Figure 2 shows the infrared spectrum in the 2050−2250 cm^{-1} region. The $\nu_{22}(B_{1u})$ and $\nu_{32}(B_{3u})$ stretching modes can be seen at 2143 and 2150 cm^{-1}, respectively. The R branch of the type A 2150 cm^{-1} band is also evident; the P branch lies under the 2143 cm^{-1} Q branch. In addition, sum and difference bands can be seen near 2214 and 2083 cm^{-1}, respectively. These combination bands can arise from either the Raman active $\nu_2(A_g)$ mode as B_{1u} infrared bands (type C) or from the Raman active $\nu_{13}(B_{2g})$ mode as B_{3u} infrared bands (type A). To ascertain which vibrations are in combination with the puckering, the Raman spectra of both the vapor and liquid spectra were recorded. Figure 3 shows the vapor-phase Raman spectrum of IV in the SiH_2 stretching region. The totally symmetric $\nu_2(A_g)$ band is observed at 2154.6 ± 1.0 cm^{-1}, while the $\nu_{13}(B_{2g})$ band is centered at 2143 ± 3 cm^{-1}. The latter is not evident when parallel polarization is utilized but accounts for most of the intensity when the $\nu_2(A_g)$ band intensity is greatly reduced with perpendicular polarization. The $\nu_{13}(B_{2g})$ band lacks a Q branch, and the maxima of the rotational envelopes are separated by approximately 13 cm^{-1}. A computed simulation[13] of the vapor-phase Raman band type produces a very similar calculated band structure with a center gap and a rotational envelope separation of 11 cm^{-1}. We also recorded the Raman spectrum of the liquid in this region. Figure 4 shows the perpendicularly polarized spectrum in which the $\nu_2(A_g)$ band intensity is considerably reduced. Deconvolution of the spectrum shows the ν_2 and ν_{13} bands to be at 2146 ± 2 and 2129 ± 2 cm^{-1}, respectively. The frequency difference of 17 cm^{-1} between the two bands for the liquid is significantly larger than

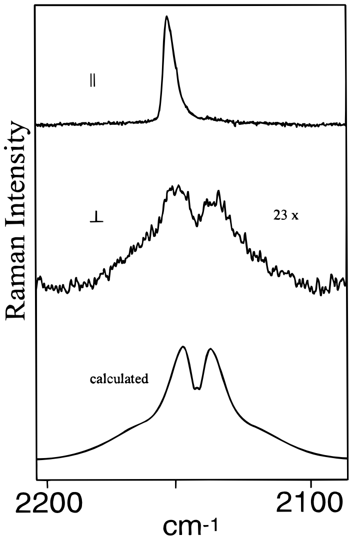


Figure 3. Vapor-phase Raman spectra of 1,4-disilacyclohexa-2,5-diene, 2 Torr at 100 °C. Top spectrum, parallel polarization; middle spectrum, perpendicular polarization; bottom spectrum, computed contour for B_{2g} band.

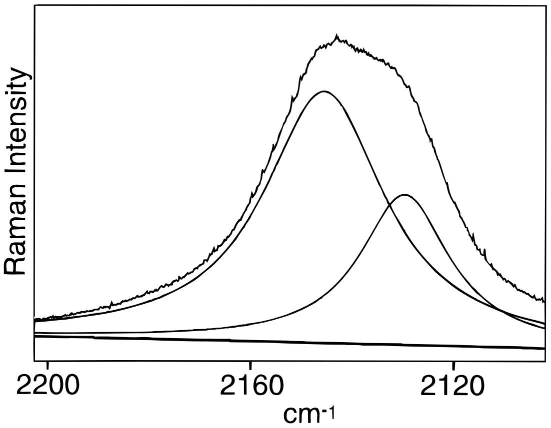


Figure 4. Liquid-phase Raman spectrum of 1,4-disilacyclohexa-2,5-diene with perpendicular polarization. The deconvolution of the spectrum into its components is also shown.

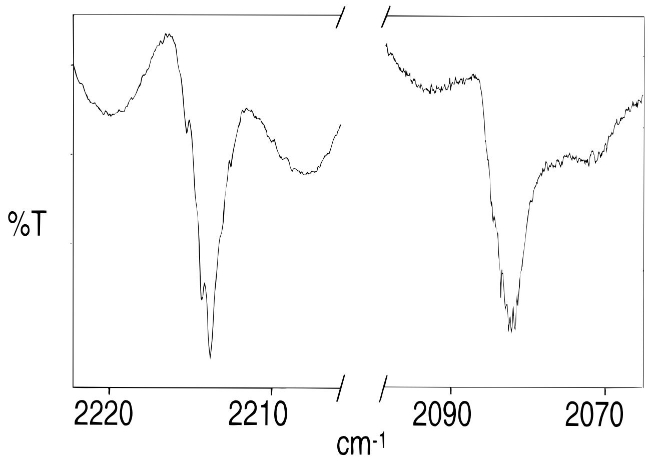


Figure 5. Infrared sum and difference bands of 1,4-disilacyclohexa-2,5-diene vapor.

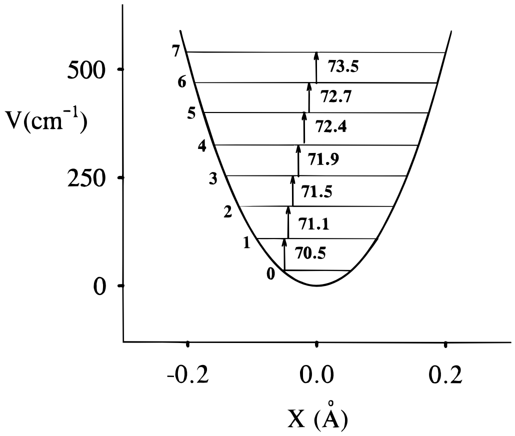


Figure 6. Ring-puckering potential energy function of 1,4-disilacyclohexa-2,5-diene.

TABLE 2: Far-Infrared and Combination Band Spectra (cm^{-1}) of the Ring-Puckering Vibration of 1,4-Disilacyclohexa-2,5-diene

	ν_{FIR}		ν_{SUM}		ν_{DIFF}	
transition	obsd	calcd[a]	obsd	ν_{SUM} − 2143.2	obsd	2154.0 − ν_{DIFF}
0−1	70.5	70.6	2213.7	70.5	2083.5	70.5
1−2	71.2	71.1	2214.3	71.1	2082.9	71.1
2−3	71.6	71.5	2214.7	71.5	2082.5	71.5
3−4	72.1	72.0	2215.2	72.0	2082.1	71.9
4−5		72.4			2081.6	72.4
5−6		72.7			2081.3	72.7
6−7		73.1			2080.8	73.5

the 11 cm^{-1} value for the vapor, but the spectrum is nonetheless compatible with the assignments in the vapor spectrum. Consideration of all this information shows that the infrared sum bands originate from $\nu_2(A_g)$ at 2154.0 cm^{-1} (inferred) and that the difference bands originate from $\nu_{13}(B_{2g})$ at 2143.2 cm^{-1} (inferred). Figure 5 shows the sum and difference regions expanded, and Table 2 compares the frequencies derived from the sum and difference bands to those observed in the far-infrared region. These results made it possible to determine the first seven transitions of the ring-puckering vibration. It is clear from the close spacing between the transitions that this mode is very nearly harmonic. Of the molecules previously studied, I and II also have nearly harmonic functions, whereas III, V, VI, and VII had a considerable amount of quartic character.

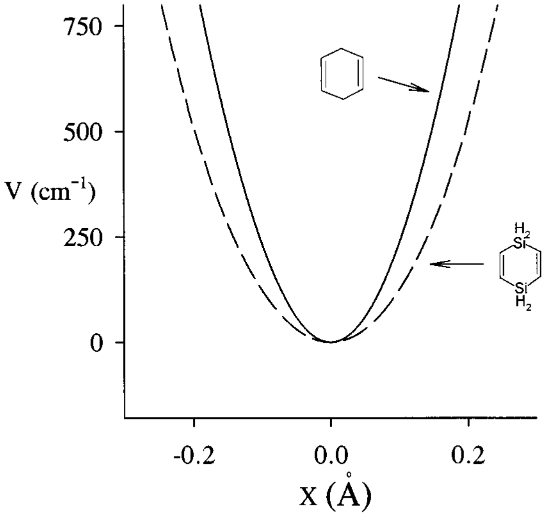


Figure 7. Comparison of the ring-puckering potential energy functions of 1,4-disilacyclohexa-2,5-diene and 1,4-cyclohexadiene.

The far-infrared spectrum of the 1,1,4,4-d_4 isotopomer was also recorded. A broad unresolved band with a maximum at 63 cm^{-1} was observed.

To evaluate the potential energy function governing this vibration, it was necessary to calculate the reduced mass for this motion as a function of its coordinate. This was done using methods we have previously described.[3] The reciprocal reduced mass functions $g_{44}(x)$ calculated for the 1,4-disilacyclohexa-2,5-diene and its d_4 derivative are, respectively

$$g_{44}{}^{H} = 0.005906 - 0.004953x^2 - 0.05854x^4 + 0.1561x^6 \tag{1}$$

and

$$g_{44}{}^{D} = 0.004688 + 0.002556x^2 - 0.06909x^4 + 0.1367x^6 \tag{2}$$

Using the observed data and the kinetic energy function of eq 1, the potential energy function for 1,4-disilacyclohexa-2,5-diene was determined to be

$$V(cm^{-1}) = 1.23 \times 10^4x^2 + 2.40 \times 10^4x^4 \tag{3}$$

where x is the puckering coordinate in angstroms, as previously defined.[3] This function and the observed transitions are shown in Figure 6. Table 2 compares the calculated frequencies with those observed, and the fit can be seen to be excellent. When the potential function of eq 3 is used together with the kinetic energy function for the d_4 isotopomer in eq 2, a puckering frequency (0−1) for the deuteride of 62.8 cm^{-1} is calculated; the higher transitions are predicted to be at 63.2, 63.6 cm^{-1}, etc. This is in good agreement with the broad infrared band observed at 63 cm^{-1}.

Figure 7 compares the 1,4-disilacyclohexa-2,5-diene ring-puckering potential energy function with that of cyclohexadiene. The curves show that the cyclohexadiene molecule is considerably more rigid than the silicon compound. This is what is expected if no unusual forces are present since angle bending and torsional forces involving silicon atoms are typically less than those involving carbon atoms. It can thus be concluded that there are no unusual significant interactions, such as π interactions, between the silicon atoms and the C=C units. Why such interaction seems to be significant for 2-silacyclopentene

(V), relatively small for 1,3-disilacyclopent-4-ene (VII), and essentially absent for 1,4-disilacyclohexa-2,5-diene (IV) remains a mystery.

Acknowledgment. The authors thank the National Science Foundation, Robert A. Welch Foundation, and the Texas Advanced Research Program for financial support.

References and Notes

(1) Laane, J.; Lord, R. C. *J. Mol. Spectrosc.* **1971**, *39*, 340−344.
(2) Oberhammer, H.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 10−16.
(3) Strube, M. M.; Laane, J. *J. Mol. Spectrosc.* **1988**, *129*, 126−139.
(4) Choo, J.; Laane, J.; Majors, R.; Villarreal, J. *J. Am. Chem. Soc.* **1993**, *115*, 8396−8400.
(5) Lord, R. C.; Rounds, T. C. *J. Chem. Phys.* **1973,** *58*, 4344−4349.
(6) Laane, J. *J. Chem. Phys.* **1970**, *52*, 358−360.
(7) Kelly, M. B.; Laane, J. *J. Phys. Chem.* **1988**, *92*, 4056−4059.
(8) Laane, J. *J. Chem. Phys.* **1969**, *50*, 1946−1951.
(9) Killough, P. M.; Laane, J. *J. Chem. Phys.* **1984**, *80*, 5475−5480.
(10) Colegrove, L. C.; Laane, J. *J. Phys Chem.* **1991**, *95*, 6494−6499.
(11) Maier, G.; Schottler K.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *34*, 4079.
(12) Haller, K.; Chiang, W.-Y.; del Rosario, A.; Laane, J. *J. Mol. Struct.* **1996**, *379*, 19−23.
(13) Sakurai, S.; Laane, J. To be published.