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Ring Conformation and Barrier to Inversion of 1,3-Disilacyclobutane from Low-Frequency Vibrational Spectra[1]

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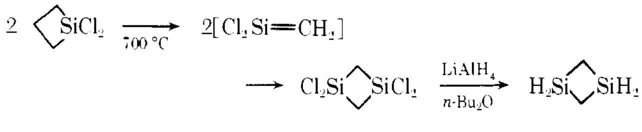
Abstract: The far-infrared and low-frequency Raman spectra of 1,3-disilacyclobutane and the far-infrared spectrum of 1,3-disilacyclobutane-*1,1,3,3-d*$_4$ have been recorded and analyzed. The spectra consist of a large number of bands between 30 and 200 cm^{-1} which correspond to transitions involving the excited states of the ring-inversion vibration. The potential energy function for this vibration was determined from the transition frequencies, and it establishes the equilibrium conformation of the ring. In the ground state, the molecule is puckered with an average dihedral angle of 24°. The barrier to inversion is 87 cm^{-1} (0.25 kcal/mol). A study of the isotopic shift in going from the d_0 to the d_4 molecule demonstrates that the SiH_2 in-phase rocking motion is coupled to the ring-inversion vibration. The syntheses of 1,3-disilacyclobutane, 1,3-disilabutane, and some related compounds are also described.

Low-frequency vibrational spectroscopy has been effectively used during the past ten years for determining the conformations and energy barriers to inversion of small ring systems.[2-7] One of the systems examined was silacyclobutane (and its 1,1-d_2 derivative), which Laane and Lord[8] showed from far-infrared studies to have a puckered ring with a dihedral angle of 35° and a barrier to inversion of 440 cm^{-1} (1.26 kcal/mol). Vapor-phase Raman spectra[7] confirmed these results. Since similar data had also been reported for cyclobutane[9-11] (dihedral angle: 33°; barrier to inversion: 515 cm^{-1}), 1,3-disilacyclobutane (and its 1,1,3,3-d_4 derivative) was prepared so that data for the three different $\overline{MH_2CH_2M'H_2CH_2}$ systems (where M and M′ are C or Si) could be used to better evaluate the intramolecular forces responsible for the conformations of these molecules.

In this report, we present the far-infrared and Raman ring-puckering spectra and the vibrational potential energy function governing the ring-inversion process for 1,3-disilacyclobutane. Calculations have been carried out on the kinetic energy (reduced mass) expansions for both molecules in order to reproduce the observed frequency shifts upon isotopic substitution and to obtain a valid representation of the ring-inversion motion. The evaluation of the degree of mixing of the SiH_2 (or SiD_2) rocking motion into the inversion coordinate was of special interest. The results obtained complement our previous studies on other four- and five-membered ring silicon systems.[7,8,12-18]

Experimental Section

Synthetic Methods. 1,3-Disilacyclobutane was prepared by the $LiAlH_4$ reduction of 1,1,3,3-tetrachloro-1,3-disilacyclobutane, which was obtained by pyrolyzing 1,1-dichloro-1-silacyclobutane[19] at 700 °C according to methods described by Nametkin and co-workers.[20] This type of pyrolysis reaction is of considerable interest in that it is postulated to go through the [$Cl_2Si{=}CH_2$] intermediate.[21]



An attempt to prepare 1,3-disilacyclobutane by reducing 1,1,3,3-tetraethoxy-1,3-disilacyclobutane with $LiAlH_4$ resulted instead in the ring-cleaved product, 1,3-disilabutane:

$$ClCH_2SiCl_3 \xrightarrow{2EtOH} ClCH_2SiCl(OEt)_2$$

$$\xrightarrow[THF]{Mg} [(EtO)_2SiCH_2]_2 \xrightarrow[n\text{-}Bu_2O]{LiAlH_4} H_3SiCH_2SiH_2CH_3$$

Direct cyclization of Cl_3SiCH_2Cl, as expected, produced only very poor yields (~2%) of 1,1,3,3-tetrachloro-1,3-disilacyclobutane.

1,1,3,3-Tetrachloro-1,3-disilacyclobutane. 1,1-Dichloro-1-silacyclobutane, prepared as previously described,[19] was pyrolyzed according to the procedure of Nametkin and co-workers[20] using a Vycor tube packed with porcelain chips and heated to 700 °C. The starting material was introduced at the rate of 3 mL/h and the pyrolysis products were collected in a series of cold temperature traps. Distillation at atmospheric pressure gave the tetrachloride (bp 169 °C) in 65% yield. The material is a solid at room temperature and very moisture sensitive.

1,3-Disilacyclobutane. 1,1,3,3-Tetrachloro-1,3-disilacyclobutane (29.4 g, 0.13 mol) diluted with 25 mL of *n*-butyl ether was added dropwise to 5.0 g (0.13 mol) of lithium aluminum hydride in 100 mL of the ether in a three-necked 250-mL flask equipped with rapid magnetic stirring, a chilled water condenser, and a dry nitrogen purge. The dropping funnel was wrapped with heating tape and gently warmed to keep the chloride from recrystallizing. The reaction mixture was maintained at 0 °C with an ice bath for the duration of the 6-h addition and was then allowed to warm to room temperature after 2 h. The mixture was distilled at 0.1 Torr into a dry ice–acetone trap which was followed by a liquid nitrogen trap. Approximately 95% of the silane–ether solution (~100 mL) was caught by the dry ice–acetone trap. This solution was subsequently distilled on a spinning band column at atmospheric pressure to obtain 6.3 g (0.07 mol) of 1,3-disilacyclobutane (bp 61 °C), yield, 55%. Anal. Calcd: C, 27.22; H, 9.14. Obsd: C, 27.41; H, 9.21. None of the product resulting from ring cleavage, 1,3-disilabutane, was obtained.

1,3-Disilacyclobutane was identified from its NMR spectra (δ values of 0.38 and 4.69 for the methylene and silicon hydrogens, respectively; $J = 4.5$ Hz), mass spectrum (Table **I**), elemental analysis, and vibrational spectra (IR 2947 m, 2156 vs, 2145 vs, 1370 w, 965 s, 930 w, 900 s, 780 m, 740 w, 640 w; Raman 2915 s (P), 2150 vs (P), 1375 m, 965 m, 760 s (P), 745 m (P), 450 m (P), 380 m (P)).

1,3-Disilacyclobutane-*1,1,3,3-d*$_4$. Reaction of 31.6 g (0.14 mol) of the tetrachloride with 6.0 g (0.15 mol) of $LiAlD_4$ in the manner described above gave 6.0 g (0.06 mol) of $[D_2SiCH_2]_2$: bp 61 °C, yield 47%.

1,1,3,3-Tetraethoxy-1,3-disilacyclobutane. Direct chlorination of methyltrichlorosilane similar to the method of Kaesz and Stone[22] was used to prepare $ClCH_2SiCl_3$ in about 60% yield. The product (bp 117 °C)[23] showed an NMR singlet at δ 3.20 whereas $Cl_2CHSiCl_3$ (15% yield) has a singlet at δ 5.42. Addition of ethanol in a 2:1 molar ratio to chloromethyltrichlorosilane resulted in the expected statistical distribution of products, 1:6:12:8, of starting product (bp 66 °C), $(EtO)Cl_2SiCH_2Cl$ (bp 153 °C), $(EtO)_2ClSiCH_2Cl$ (bp 171 °C), and $(EtO)_3SiCH_2Cl$ (bp 180 °C).[23] The methylene hydrogen NMR peaks for the last three compounds, at δ 2.70, 2.84, and 3.05, respectively, are useful for characterization. The cyclization of chloromethyldiethoxychlorosilane, similar to methods described by Kriner,[24] was achieved by slow addition of a slight excess of magnesium shavings to this compound to THF. A 20% yield of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (bp 72 °C (0.025 Torr)) was obtained. Smaller quantities of the six- and eight-membered rings, $[(EtO)_2SiCH_2]_n$ for $n = 3$ and 4, were also identified. The four-membered ring can readily be identified from its methylene hydrogen NMR peak at δ 0.40 as compared to values of 0.04 and −0.20 for the six- and eight-membered rings, respectively. The high-resolution mass spectrum for 1,1,3,3-tetraethoxy-1,3-disilacyclobutane gave a molecular weight of 264.1210 (calcd 264.1213).

1,3-Disilabutane. Reduction of $[(EtO)_2SiCH_2]_2$ with $LiAlH_4$ in *n*-butyl ether at 0 °C and distillation from the reaction mixture at atmospheric pressure resulted in a 20% yield of 1,3-disilabutane (bp ~40 °C), $H_3SiCH_2SiH_2CH_3$. Elemental Anal. Calcd for $Si_2C_2H_{10}$: C, 26.6; H, 11.2. Obsd: C, 26.5; H, 11.3. No other volatile compounds were obtained. This product, resulting from ring cleavage,[25] had the expected mass spectrum (Table **I**), NMR spectrum (with a triplet and multiplet in the silicon hydrogen (downfield) region and another triplet and multiplet at high field), elemental analysis, and infrared spectrum (2980 m, 2160 vs, 1270 m, 1060 m, 950 s, 900 vs, 800 m, 770 m). The 1270-cm^{-1} band is characteristic of the $Si–CH_3$ group.

Characterization. The compounds were characterized using NMR spectra (Varian T-60), chemical analyses (Galbraith Laboratories, Knoxville, Tennessee), mass spectra (high resolution on a CEC-110 and regular on a Perkin Elmer CH7 instrument), and infrared spectra (Beckman IR-12).

Low-Frequency Spectra. The far-infrared spectra of 1,3-disilacyclobutane and its 1,1,3,3-d_4 derivative were recorded using a Digilab FTS-20 high-resolution vacuum spectrophotometer and a 15-cm metal bodied gas cell with polyethylene windows of 20-mil thickness. Vapor-phase Raman spectra were recorded on a Cary Model 82 spectrophotometer equipped with a Coherent Radiation Model 53 argon ion laser. Multireflection optics and modified gas cells[7] were utilized.

Table I. Mass Spectra of 1,3-Disilacyclobutane and 1,3-Disilabutane

M/e	$Si_2C_2H_8$ intensity	Primary species	$Si_2C_2H_{10}$ intensity
92		$[M^+ (^{30}Si)$	1
91		$[M^+ (^{30}Si) - 1$	4
90	5	$M^+ (^{30}Si\text{ etc.})], [Si_2C_2H_{10}$	11
89	9	$M^+ (^{29}Si\text{ etc.})], [Si_2C_2H_9$	77
88	56	$Si_2C_2H_8$	42
87	19	$Si_2C_2H_7$	19
86	100	$Si_2C_2H_6$	35
85	22	$Si_2C_2H_5$	11
84	12	$Si_2C_2H_4$	3
83	7	$Si_2C_2H_3$	3
82	3	$Si_2C_2H_2$	1
81	10	Si_2C_2H	3
80	3	Si_2C_2	1
77		$[^{28}Si^{30}SiCH_7$	4
76		$[^{28}Si^{29}SiCH_7$	6
75	1	Si_2CH_7	40
74	1	Si_2CH_6	9
73	7	Si_2CH_5	20
72	3	Si_2CH_4	10
71	14	Si_2CH_3	12
70	10	Si_2CH_2	8
69	30	Si_2CH	24
68	3	Si_2C	2
60	3	SiC_2H_8	5
59	12	SiC_2H_7	42
58	8	SiC_2H_6	21
57	6	SiC_2H_5	11
56	3	SiC_2H_4	3
55	6	SiC_2H_3	4
54	2	SiC_2H_2	1
53	10	SiC_2H	5
47		$[^{30}SiCH_5$, etc.	3
46		$[^{29}SiCH_5$, etc.	5
45	12	$SiCH_5$	58
44	7	$SiCH_4$	31
43	42	$SiCH_3$	100
42	14	$SiCH_2$	27
41	3	$SiCH$	15

Potential and Kinetic Energy Calculations

The matrix method used for calculating the energy levels for different potential energy functions has been described[4] as has been the determination of kinetic energy expansions,[26] If we choose x to represent the ring-puckering coordinate,[27] the Hamiltonian representing the one-dimensional ring puckering becomes

$$\mathcal{H}(x) = -(\hbar^2/2)(\mathrm{d}/\mathrm{d}x)\mu(x)^{-1}(\mathrm{d}/\mathrm{d}x) + V(x) \quad (1)$$

where

$$\mathcal{H}(x)\Psi(x) = E\Psi(x) \quad (2)$$

and where the potential energy is assumed to have the form

$$V(x) = ax^4 + bx^2 \quad (3)$$

The reciprocal of the reduced mass[28] $\mu(x)^{-1}$ is expressed as an expansion in terms of the puckering coordinate, and this is evaluated for an assumed ring-puckering motion at various values of x. This expansion is dominated by the fixed term ${\mu_0}^{-1}$.

The calculation of the energy levels is for mathematical purposes carried out in reduced (undimensional) form. The following reduced Schrödinger equation is used:[26]

$$-A \sum_{i=0}^{3} {G_{44}}^{(2i)} \frac{\mathrm{d}}{\mathrm{d}Z} Z^{2i} \frac{\mathrm{d}}{\mathrm{d}Z} \Psi + A(Z^4 + BZ^2)\Psi = E\Psi \quad (4)$$

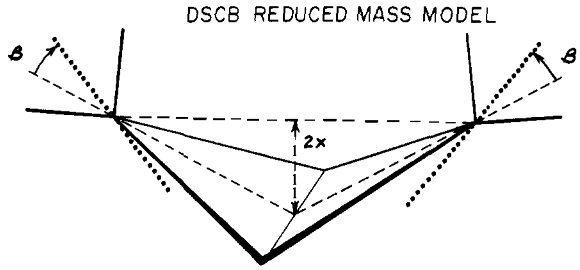


Figure 1. Definition of puckering (x) and rocking (β) coordinates.

where $Z = \alpha^{1/6}a^{1/6}x$; $\alpha = 2\mu_0/\hbar^2$; $A = \alpha^{-2/3}a^{1/3}$; $B = \alpha^{1/3}a^{-2/3}b$; $G_{44}^{(2i)} = (\alpha a)^{-i/3}\mu_0^{(2i-3)/3}g_{44}^{(2i)}$, and where $g_{44}^{(2i)}$ represents the coefficient of the x^{2i} term in the reciprocal reduced mass expansion.[28]

The reduced mass expansions were calculated for ring-puckering models of various types. First, the basic bisector model[26] was assumed. This model assumes all of the bond distances to remain constant with the HCH and CCC bond angles maintaining a common bisector throughout. This model allows for different amounts of bending about the two ring diagonals and the parameter ω is used[30] to measure the relative amounts of bending.

$$\omega = (1 - \rho)/(1 + \rho) \tag{5}$$

where

$$\rho = [\Delta(x_{\text{Si}})^2/\Delta(y_{\text{C}})^2]$$

The coordinates x_{Si} and y_{C} represent motions relative to the center of the planar ring (i.e., the x axis passes through both silicon atoms and the y axis passes through both carbon atoms for the planar ring structure). The limits of ρ are 0 and ∞ with corresponding limits on ω of 1 and -1. The positive limit of ω represents puckering entirely about the silicon–silicon axis with no change in SiCSi angle. The value of $\omega = -1$ corresponds to puckering entirely about the carbon–carbon axis with no bending of the CSiC angle. The value of ω is determined by the relative values of the angle bending force constants at carbon and silicon. Since it is easier to bend angles at silicon atoms than at carbon atoms, a positive ω value is expected for 1,3-disilacyclobutane. Consequently, calculations were carried out using ω values from 0.0 to 0.6. It should be noted that the value of ω has no effect on the dominant term $\mu_0(x)^{-1}$ in the kinetic energy expansion, but only on the higher order terms $g_{44}^{(2i)}$. Consequently, the selected value of ω has little effect on the calculated frequencies or the potential energy parameters.

In addition to the basic bisector model, we also carried out calculations for ring inversions which allowed mixing of the in-phase SiH_2 rocking motion with the puckering motion. The rocking was defined by

$$\beta = Rx \tag{6}$$

where β is the angle between CSiC and HSiH angle bisectors at each silicon atom, R is a selected rocking parameter, and x is the ring-puckering coordinate. Figure 1 shows the definition of β and x. The proportionality constant R may be positive or negative, representing rocking with or against the puckering motion. As an example of magnitude, a rocking parameter of 0.5 represents a rocking of 5.0° when the dihedral angle of puckering is 30°.

The reduced mass expansion $\mu(x)$, including the dominant term μ_0, is very sensitive to the choice of rocking parameter. Consequently, the calculated isotope shift between the spectra of two isotopic forms of the same molecule (such as 1,3-disilacyclobutane-d_0 and -*1,1,3,3*-d_4) can be adjusted by selection of the rocking parameters for the two species.

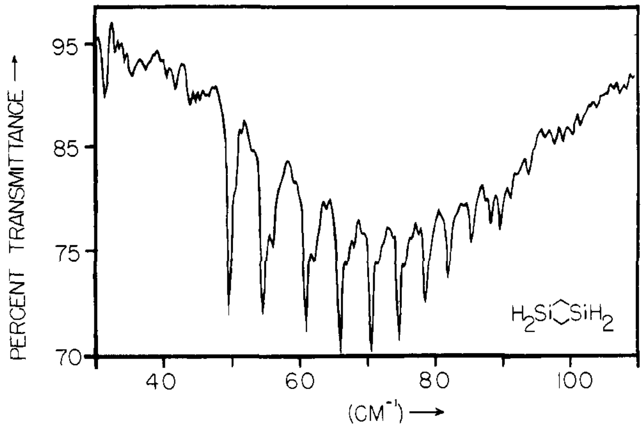


Figure 2. Far-infrared spectrum of 1,3-disilacyclobutane: vapor pressure, 140 Torr; path length, 15 cm; resolution, 0.5 cm^{-1}.

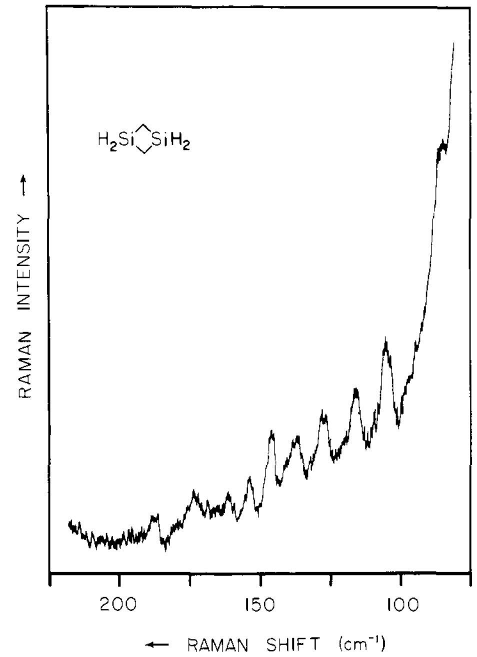


Figure 3. Raman spectrum of 1,3-disilacyclobutane: vapor pressure, 160 Torr; resolution, 3.0 cm^{-1}.

Although the one-dimensional model does not allow for the calculation of a reduced mass expansion which is asymmetric about the origin (this is required for a structure which has an initial rocking for the planar configuration), the dominant term μ_0 can be calculated. Since the reduced mass is much more sensitive to the nature of the motion than the exact molecular structure, the initial rocking has a negligible effect on μ_0 (<0.03 for a 5° rocking).

Results

Figures 2 and 3 show the far-infrared and low-frequency Raman spectra of 1,3-disilacyclobutane in the vapor phase. In addition to the main band series of ring-puckering transitions in Figure 2, a few side bands resulting from ring-puckering transitions in the SiH_2 in-phase rocking first excited state can also be seen. The infrared (single quantum transitions) and Raman (double quantum jumps) frequencies for the primary transitions are listed in Table II. The infrared side-band frequencies resulting from the excited state of the SiH_2 rocking are presented in Table III. The assignment of the frequencies is not obvious without the observation of the 2 → 3 transition near 31 cm^{-1}. This is a weak band in a region with a relatively poor signal to noise ratio for the spectrophotometer, and the band is not prominent in all recorded spectra. However, the observation of sum and difference bands in the SiH_2 stretching

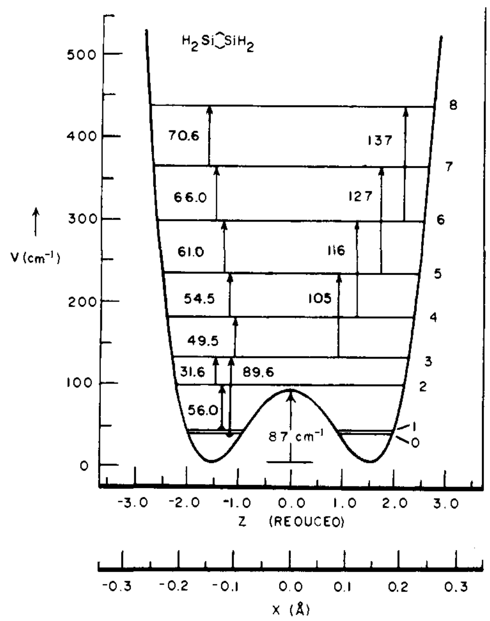


Figure 4. Potential energy function showing the infrared ($\Delta v = 1$ or 3) and Raman ($\Delta v = 2$) transitions of 1,3-disilacyclobutane.

Table II. Ring-Puckering Spectra of 1,3-Disilacyclobutane

Transition	Frequency, cm^{-1} Obsd	Calcd[a]	Δ	Rel intensity Obsd	Calcd
		Infrared			
0-1		2.99			0.01
1-2	56.0	56.1	−0.1	0.56	0.50
2-3	~31.6	31.3	0.3	~0.4	0.38
3-4	49.5	50.0	−0.5	1.33	0.86
4-5	54.5	55.0	−0.5	1.10	0.95
5-6	61.0	61.1	−0.1	(1.00)	1.00
6-7	66.0	66.1	−0.1	0.98	0.95
7-8	70.6	70.6	0.0	0.87	0.84
8-9	74.7	74.7	0.0	0.77	0.71
9-10	78.5	78.3	0.2	0.56	0.58
10-11	82.0	81.7	0.3	0.46	0.45
11-12	85.3	84.9	0.4	0.28	0.34
12-13	88.2	87.8	0.4	0.21	0.25
13-14	91.2	90.6	0.6	0.11	0.18
14-15	93.9	93.2	0.7	0.11	0.13
0-3	89.6	90.4	−0.8	0.27	0.40
		Raman			
0-2		59.1			
1-3	86	87.4	−1.4	0.3	0.57
2-4	~80	81.3	−1.3	~0.1	0.46
3-5	105	105.0	0.0	1.7	0.84
4-6	116	116.1	−0.1	1.1	0.94
5-7	127	127.3	−0.3	(1.0)	(1.00)
6-8	137	136.8	0.2	0.8	0.97
7-9	146	145.3	0.7	1.1	0.89
8-10	153	153.0	0.0	0.7	0.78
9-11	161	160.0	1.0	0.5	0.65
10-12	~168	166.6	1.4	~0.3	0.53
11-13	173	172.6	0.4	0.6	0.41
12-14	~180	178.3	1.7	~0.2	0.32
13-15	187	183.7	3.3	0.4	0.23

[a] $V = 15.188(Z^4 - 4.798Z^2)$ cm^{-1}; $\omega = 0.2$, $R = 0.4$.

region[31] corresponding to this transition confirm this frequency. Furthermore, the 0 → 3 transition at 89.6 cm^{-1} is additional evidence for the 2 → 3 energy spacing. Since the 1 → 2 transition occurs at 56.0 cm^{-1} and since the 0-1 spacing is calculated to be about 3 cm^{-1}, the 2-3 spacing must be near 31 cm^{-1}.

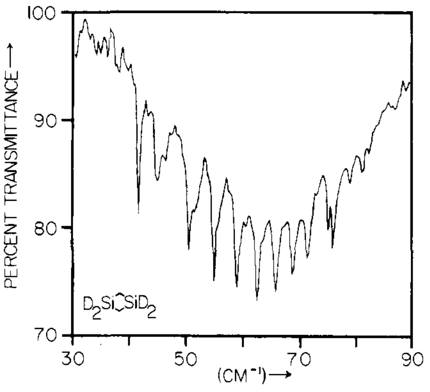


Figure 5. Far-infrared spectrum of 1,3-disilacyclobutane-*1,1,3,3-d*$_4$: vapor pressure, 140 Torr; path length, 15 cm; resolution, 0.5 cm^{-1}.

Table III. Infrared Side Bands of 1,3-Disilacyclobutane

Transition	Frequency, cm^{-1} Obsd	Calcd[a]	Δ
3-4	~50.5	50.5	0.0
5-6	62.0	62.0	0.0
6-7	67.0	66.7	0.3
7-8	71.5	71.5	0.0
8-9	75.4	75.6	−0.2
9-10	~79.5	79.8	−0.3

[a] $V = 15.1(Z^4 - 4.80Z^2)$ cm^{-1}; fixed reduced mass model.

For preselected ring-inversion motions, the potential energy functions having the form of eq 3 were determined in order to calculate transition frequencies which best reproduce those observed. The calculated frequencies are compared to the observed ones in Table II. Table IV summarizes the potential parameters as well as the models used to determine the kinetic energy expansions. It should be noted that the kinetic energy expansions have only a very small effect on the calculated frequencies and on the reduced potential parameters A and B in eq 4. The selection of the ring-puckering model primarily affects the calculated reduced mass, μ_0, and the dimensioned parameters a and b in eq 3. Consequently, the calculated frequencies listed in Table II, which are determined from the $\omega = 0.2$, $R = 0.4$ calculation, are virtually identical for all of the models shown in Table IV. Figure 4 shows the potential energy function determined for the undeuterated 1,3-disilacyclobutane.

Figure 5 shows the far-infrared spectrum of 1,3-disilacyclobutane-*1,1,3,3-d*$_4$ and Table V lists the observed and calculated (for $\omega = 0.2$, $R = 0.4$) frequencies for this molecule. Very few side bands were observed in the d_4 spectra. Figure 6 shows the potential energy function for the d_4 molecule.

For all models, the reduced potential for the d_0 molecule is

$$V_{C_2H_4Si_2H_4} = (15.20 \pm 0.07)[Z^4 - (4.79 \pm 0.02)Z^2]\ \text{cm}^{-1} \quad (7)$$

and for the deuterated species

$$V_{C_2H_4Si_2D_4} = (12.92 \pm 0.09)[Z^4 - (5.15 \pm 0.02)Z^2]\ \text{cm}^{-1} \quad (8)$$

Use of the transformations in eq 4 and the appropriate reduced mass, μ_0, calculated for a particular vibrational model results in the dimensioned potential function of the form of eq 3. In the one-dimensional approximation, the d_0 and d_4 molecules should have the same dimensioned potential. This fact can be used to understand which vibrational models are most realistic. Figure 7 shows how the potential parameters a and b calcu-

Table IV. Ring-Puckering Parameters for 1,3-Disilacyclobutane-d_0 and -d_4[a]

			$V = A(Z^4 - BZ^2)$		$V = ax^4 - bx^2$			
ω	R	μ_0	A, cm^{-1}	B	a, cm^{-1}/Å^4	b, cm^{-1}/Å^2	Barrier to inversion, cm^{-1}	Dihedral angle, deg.
					DSCB-d_0			
0	0	123.86	15.297	4.777	1.931×10^5	8.211×10^3	87.27	24.82
0.2	0	123.86	15.260	4.784	1.917×10^5	8.183×10^3	87.31	24.87
0.4	0	123.86	15.261	4.784	1.918×10^5	8.184×10^3	87.32	24.87
0.6	0	123.86	15.299	4.776	1.932×10^5	8.212×10^3	87.24	24.82
0.2	0	123.86	15.260	4.784	1.917×10^5	8.183×10^3	87.31	24.87
0.2	0.2	130.23	15.260	4.784	2.119×10^5	8.604×10^3	87.31	24.25
0.2	0.4	137.29	15.188	4.798	2.322×10^5	9.011×10^3	87.41	23.70
0.2	0.6	145.05	15.155	4.805	2.576×10^5	9.493×10^3	87.47	23.09
					DSCB-d_4			
0	0	150.00	13.007	5.133	1.741×10^5	7.725×10^3	85.63	25.37
0.2	0	150.00	12.957	5.154	1.718×10^5	7.685×10^3	86.05	25.47
0.2	0.2	162.51	12.911	5.164	1.999×10^5	8.296×10^3	86.07	24.52
0.2	0.4	176.40	12.866	5.167	2.331×10^5	8.955×10^3	85.87	23.58
0.2	0.6	191.66	12.836	5.175	2.733×10^5	9.683×10^3	85.94	22.63

[a] Typical expansion $g_{44}(x) = 8.07394 \times 10^{-3} - 1.13226 \times 10^{-2}x^2 - 4.92114 \times 10^{-2}x^4 + 2.0189 \times 10^{-2}x^6$ (DSCB-d_0: $\omega = 0$, $R = 0$).

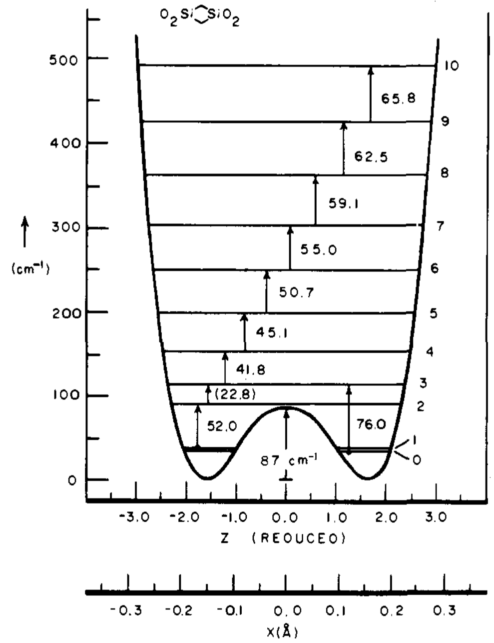


Figure 6. Potential energy function showing the infrared transitions of 1,3-disilacyclobutane-*1,1,3,3*-d_4.

lated for each isotopic form depend on the choice of rocking parameter R. These values have no dependence on ω since μ_0 is independent of this parameter. The first conclusion which is clear from Figure 7 is that vibrational models which allow no rocking are inconsistent with the isotopic data; that is, for $R = 0$ the a and b parameters for the d_0 and d_4 molecules are significantly different. On the other hand, for $R = 0.44$ the calculated values of both a and b are nearly identical for the two isotopic forms. It is this model that has been used for the calculation in Tables II and V and it represents a realistic situation. However, this is not the only model consistent with the isotopic data. It is quite likely that different amounts of SiH_2 and SiD_2 rocking motions are mixed into the ring-puckering normal coordinate for the d_0 and d_4 molecules. As a result, a large number of other models, which have different rocking parameters for the two isotopic forms, can be found to be consistent with the isotopic data. For example, if $R = 0.0$ (no rocking) is assumed for the d_0 molecule, the use of $R = 0.15$ will closely produce the observed isotopic shift for the d_4 species. It should be evident from Table IV that the rocking parameter has a negligible effect on the calculation of the barrier to inversion, but that it does affect the calculated dihedral angle for the ground state. The barrier is accurately

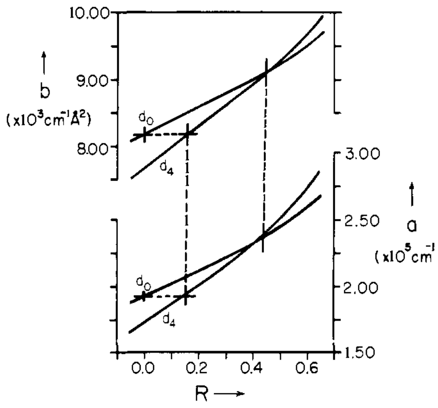


Figure 7. Dependence of the potential energy parameters a and b (in $V = ax^4 - bx^2$) on the rocking parameter R for 1,3-disilacyclobutane-d_0 and -*1,1,3,3*-d_4.

Table V. Ring-Puckering Infrared Spectra of 1,3-Disilacyclobutane-*1,1,3,3*-d_4[a]

	Frequency cm^{-1}			Rel intensity	
Transition	Obsd	Calcd	Δ	Obsd	Calcd
0-1		1.63			0.004
1-2	52.0	52.0	0.0	0.46	0.43
2-3		22.8			0.26
3-4	41.8	41.9	−0.1	0.94	0.76
4-5	45.1	45.3	−0.2	0.54	0.88
5-6	50.7	50.9	−0.2	0.92	1.00
6-7	55.0	55.3	−0.3	(1.00)	(1.00)
7-8	59.1	59.2	−0.1	0.84	0.95
8-9	62.5	62.7	−0.2	0.81	0.86
9-10	65.8	65.9	−0.1	0.65	0.74
10-11	68.7	68.8	−0.1	0.49	0.62
11-12	71.4	71.6	−0.2	0.41	0.50
12-13	75.2	74.2	1.0	0.33	0.38
13-14	~77sh	76.6		~0.2	0.31
14-15	79.0	78.9	0.1	0.17	0.24
15-16	81.2	81.0	0.2	0.16	0.17
0-3	76.0	76.5	−0.5	0.46	0.38

[a] $V = 12.866(Z^4 - 5.167Z^2)$ cm^{-1}; $\omega = 0.2$, $R = 0.4$.

Table VI. Ring-Puckering Potential Energy Functions

	Function $V = ax^4 - bx^2$				
Molecule	a, $\mathrm{cm^{-1}/\AA^4}$	b, $\mathrm{cm^{-1}/\AA^2}$	Inversion barrier, $\mathrm{cm^{-1}}$	Dihedral angle, deg.	Ref
$\mathrm{CH_2CH_2CH_2CH_2}$	7.6×10^5	39.6×10^3	515	33	11
$\mathrm{CH_2CH_2CH_2SiH_2}$	3.5×10^5	24.9×10^3	440	37	8
$\mathrm{CH_2SiH_2CH_2SiH_2}$	2.3×10^5	9.0×10^3	87	24	This work

determined as $87 \pm 1\ \mathrm{cm^{-1}}$, but the dihedral angle has a larger uncertainty at $24 \pm 2°$. The dimensioned potential parameters a and b are the most sensitive to the value of R and, therefore, are least well determined. Without additional data, such as rotational constant dependence on ring-puckering state, we must state our potential energy function (assuming $\omega = 0.2$, $R = 0.4$ as an optimal choice) with considerable uncertainty,

$$V\,(\mathrm{cm^{-1}}) = (2.3 \pm 0.4) \times 10^5 x^4 - (9.0 \pm 1.0) \times 10^3 x^2$$

Discussion

Previous investigations on the ring-puckering vibrations of cyclobutane and unsaturated five-membered rings[11,32] have considered the mixing of $\mathrm{CH_2}$ rocking motions into the ring-inversion coordinate. Although these support the view that the rocking motion couples with the ring-puckering mode, observed isotope shifts have not been explainable exclusively with this picture. For 1,3-disilacyclobutane, however, we can clearly conclude that the contribution of the $\mathrm{SiH_2}$ rocking motion to the ring inversion accounts for the observed isotope shift. This is not surprising in that $\mathrm{SiH_2}$ rocking motions have much lower natural frequencies (~450 vs. ~800 $\mathrm{cm^{-1}}$) than $\mathrm{CH_2}$ rockings and consequently are likely to couple to a much greater extent with the low-frequency ring-puckering mode.

In addition to gaining insight into the ring-inversion process, we have also determined the barrier to inversion, dihedral angle, and (less accurately) the parameters of the potential energy function. Table VI presents the results and compares these to data for cyclobutane and silacyclobutane. The potential parameters a and b listed in the table for all three molecules have relatively large uncertainties for reasons discussed earlier. As is well established,[2] the conformation of a four-membered ring is determined by the relative balance between angle strain forces, which tend to keep a ring near its planar conformation, and by torsional forces, which generally tend to twist the ring into a puckered structure. Furthermore, the parameters a and b in the potential function have been shown to arise primarily from angle strain and torsional forces, respectively.[5,13,30,33] Since ring angles at silicon atoms are more easily deformed than at carbon atoms, the angle strain is expected to be largest for cyclobutane and least for 1,3-disilacyclobutane among the three molecules. This is reflected in the magnitude of the potential constant a. For torsional forces, $\mathrm{-CH_2-CH_2-}$ interactions are greater than $\mathrm{-CH_2-SiH_2-}$ interactions.[34] As a result, the parameter b is largest for cyclobutane and least for 1,3-disilacyclobutane. For cyclobutane the four torsional interactions between methylene groups is sufficient to overcome the angle strain and pucker the ring by 33° and to give a barrier to inversion of 515 $\mathrm{cm^{-1}}$ (1.47 kcal/mol). Silacyclobutane has two $\mathrm{-CH_2-CH_2-}$ interactions and two $\mathrm{-CH_2-SiH_2-}$ interactions. The decrease in torsional forces is roughly balanced by the decrease in angle strain and the barrier is seen to only drop slightly to 440 $\mathrm{cm^{-1}}$ (1.26 kcal/mol). 1,3-Disilacyclobutane has just $\mathrm{-CH_2-SiH_2-}$ torsional interactions and the decrease in these forces is not counterbalanced by the decrease in angle strain achieved by the addition of a second silicon atom to the ring. The barrier is thus seen to decrease to 87 $\mathrm{cm^{-1}}$ (0.25 kcal/mol), and the dihedral angle is decreased to a floppy 24°, i.e., the ring conformation is very nonrigid and the dihedral angle vibrates between approximately ±10 and ±40°. In fact, the vibrational spectra in the mid-infrared and Raman are expected to not differ markedly from D_{2h} (planar structure) selection rules.

In summary, we have found 1,3-disilacyclobutane to be a puckered molecule with a 0.25-kcal potential barrier at the planar configuration. Its dihedral angle of puckering has been determined, and the puckering motion has been found to be coupled to the $\mathrm{SiH_2}$ rocking mode. Although the exact degree of rocking has not been established, we hope to do this by examining the spectra of the $\mathrm{SiH_2}$ rocking and combining this data with the puckering data to carry out a two-dimensional analysis.

Acknowledgment. The authors wisk to thank the Robert A. Welch Foundation for financial support. The Digilab FTS-20 instrument was purchased with the aid of NSF Grant GP-37029 to Texas A&M University. J. F. Blanke and S. F. Moore carried out parts of the synthetic work described.

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