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Rotational Spectrum And Ring Structures Of Silacyclohex-2-Ene And 1,1-Difluorosilacyclohex-2-Ene

Nicole T. Moon

Amanda J. Duerden

Thomas M.C. McFadden

Nathan A. Seifert

et. al. For a complete list of authors, see *https://scholarsmine.mst.edu/chem_facwork/3681*

Rotational Spectrum and Ring Structures of Silacyclohex-2-ene and 1,1-Difluorosilacyclohex-2-ene

Nicole T. Moon, Amanda J. Duerden, Thomas M. C. McFadden, Nathan A. Seifert, Gamil A. Guirgis, and G. S. Grubbs, II*

ABSTRACT: Silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene have been synthesized, and the chirped-pulse, Fourier-transform microwave spectra of each have been observed and analyzed from 4.9 to 23.1 GHz. Quantum chemical calculations have been performed at the B3LYP-D3BJ/Def2TZVP level of theory and predict μ_a to be the largest dipole moment component with a significantly larger value in this component for 1,1-difluorosilacyclohex-2-ene. In accordance with this prediction, the spectra were predominantly a-type with the observation of a few b- and c-type transitions. The signal-to-noise ratio was adequate in both spectra to observe ^{29}Si, ^{30}Si, and all singly substituted ^{13}C isotopologues in natural abundance. All spectra have been fit to a semirigid rotational Hamiltonian and are presented. Analysis of the physical meaning of the fitted parameters is explored and determined to hold for the rotational constants while being more empirical for the centrifugal distortion terms. Experimental structures of both molecules indicate that the quantum chemically calculated structures for the atoms in the ring are a very close depiction of the experimentally determined structures. The structures of each molecule are compared to similar molecules for context, where it is shown that both molecules possess a similar "half-chair" conformation to that of the all-carbon analogue, cyclohexene.
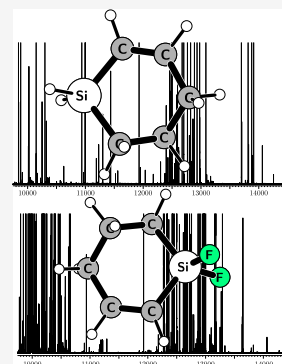
INTRODUCTION

Cyclohexene has long been known to have a predominate conformer structure of "half-chair" with C_2 symmetry.[1,2] Similar to half of the chair structure of cyclohexane, this structure is where four carbons, including the carbons of the double bond, are planar, and the two furthest sp^3 hybridized carbons from the double bond have one carbon slightly above the plane and one slightly below the plane. This structure plays a role in cyclohexene chemistry. For instance, the heat of hydrogenation for cyclohexene is greater than trans-2-butene,[3] and it is well-known that the ring interconversion for cyclohexene is less than that of cyclohexane.

In recent years, the authors have undertaken rotational spectroscopy studies that investigate the structural differences in substituting a carbon with a silicon atom.[4−9] Studies of these systems have led to interesting physiochemical results like ring-puckering motions, planar vs nonplanar ring structures, or C_2 symmetry in straight-chain alkane species where one may expect C_{2v}. In some of these systems, the potential energy surfaces of the ring-puckering motion may be flatter at the base through the puckering coordinate than the carbon analogues or may result in a double well. The results often support the understanding that silicon-containing molecular structures and chemistry are different from their all-carbon analogues.

In this work, then, we replace a carbon with a silicon in cyclohexene and a similar derivative to investigate the structure. This work is also the first known report on the microwave rotational spectra of silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene using chirped-pulse, Fourier-transform microwave (CP-FTMW) spectroscopy. Analyses of the resulting spectra and structures are aided by and compared to quantum chemical calculations while also being discussed in terms of other similar molecules, including cyclohexene.

QUANTUM CHEMICAL CALCULATIONS

Silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene structures were optimized, and a natural bond order (NBO) analysis[10] was performed utilizing the Gaussian16 program suite[11] at the B3LYP-D3BJ/Def2TZVP level. The minimum energy structures for each are presented in Figures 1 and 2 in three sets of principal axis planes (ab, ac, and bc). Both molecules have bends in the six-member ring, resulting in the ring being in the half-chair configuration.

Dipole moment components and rotational spectroscopic parameters for each molecule were also calculated. These are presented in Table 1. Besides the expected difference in the rotational constants due to the significant addition of mass from the fluorines, there are no major changes in the general structure in the inertial frame between molecules. One obvious
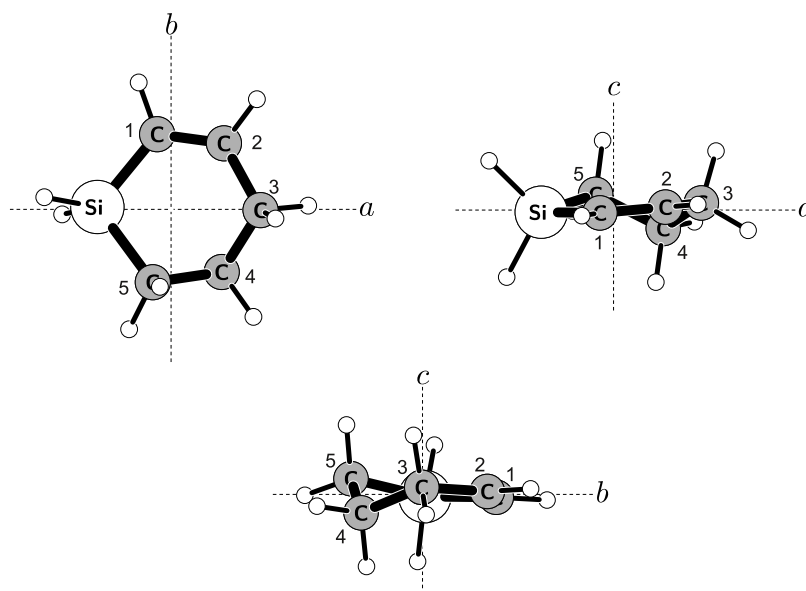
Figure 1. Quantum chemical structure of silacyclohex-2-ene presented in the *ab-*, *ac-*, and *bc*-planes. The structure has been optimized at the B3LYP-D3BJ/Def2TZVP level of theory. Carbons have been labeled for reference throughout the manuscript.

Figure 2. Quantum chemical structure of 1,1-difluorosilacyclohex-2-ene presented in the *ab-*, *ac-*, and *bc*-planes. The structure has been optimized at the B3LYP-D3BJ/Def2TZVP level of theory. Carbons have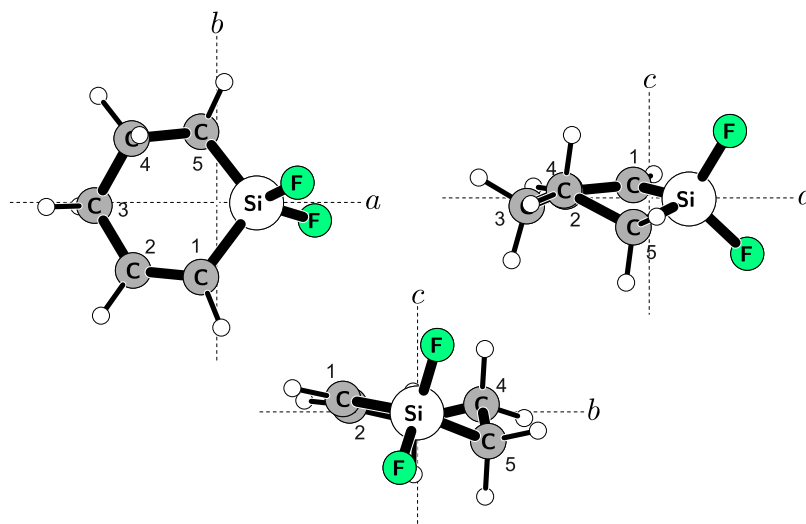 been labeled for reference throughout the manuscript. Carbon 3 in the *bc*-plane is completely eclipsed by the silicon atom.

distinction that arises between the two molecules due to the substitution of the fluorines is the significant increase in the μ_a dipole moment component. This component almost triples in magnitude upon the addition of the fluorines from 1.19 to 3.17 D. Because both were expected to be predominantly *a*-type spectra, this was viewed as a significantly favorable increase for observing isotopologues of the 1,1-difluorosilacyclohex-2-ene molecule in natural abundance in order to compare structural parameters such as both lengths and angles with quantum chemical calculations.

EXPERIMENTAL METHODS

Synthesis. The synthetic work was carried out in two steps, as shown in Scheme 1. First, 1,1-dichlorosilacyclohex-2-ene was prepared as a precursor for 1,1-difluorosilacyclohex-2-ene and silacyclohex-2-ene as previously reported,[8] with the exception of using trichlorosila-5-chloropent-2-ene. The

product 1,1-dichloro-1-silacyclohex-2-ene was obtained and purified by trap-to-trap distillation under vacuum (0.1 Torr), and the product was collected in a trap at −38 °C with a yield of 68%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 6.95 (4.19 and 3.85 Hz ^{1}H, ═C−H), 5.87 (dt, 2.0 and 2.41 Hz 1H, ═CH), 2.27 (m, CH$_2$, 2.29−2.25), 1.99 (m, CH$_2$, 2.02−1.96), 1.32 (m, CH$_2$, 2.02−1.96). ^{13}C NMR (400 MHz, CDCl$_3$): δ (ppm), 154.70, 123.37, 29.97, 20.26, 17.66. ^{29}Si NMR (400 MHz, CDCl$_3$): δ (ppm) 10.13. In addition to being used in the next step, 1,1-dichlorosilacyclohex-2-ene was also measured spectroscopically and is the focus of a future manuscript. All NMR spectra are presented in the Supporting Information.

For the second step of the 1,1-difluorosilacyclohex-2-ene synthesis, an equimolar amount of 1,1-dichlorosilacyclohex-2-ene and freshly sublimed antimony trifluoride was added to a Schlenk tube and degassed after being frozen with liquid nitrogen. The tube was allowed to come to room temperature

Table 1. Quantum Chemical Calculation Parameters for Silacyclohex-2-ene and 1,1-Difluorosilacyclohex-2-ene Using the Watson S-Reduction[a]

parameter	silacyclohex-2-ene	1,1-difluorosilacyclohex-2-ene
A_e/MHz	3980.7	2728.7
B_e/MHz	3041.9	1368.4
C_e/MHz	1875.5	1202.0
A_0/MHz	3948.4	2711.8
B_0/MHz	3023.7	1362.8
C_0/MHz	1863.1	1196.5
D_J/kHz	0.310	0.099
D_{JK}/kHz	0.043	0.350
D_K/kHz	0.636	−0.046
d_1/kHz	−0.120	−0.011
d_2/kHz	−0.024	0.008
H_J/mHz		0.033[b]
$|\mu_a|$/D	1.19	3.17
$|\mu_b|$/D	0.34	0.18
$|\mu_c|$/D	0.20	0.41

[a]See text for details. [b]Only included for comparison to experimentally fit value.

Scheme 1. Schematic for the Synthesis of 1,1-Difluorosilacyclohex-2-ene and Silacyclohex-2-ene
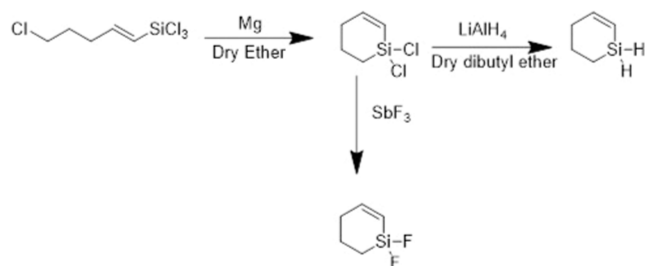
and then was heated in an oil bath to 55 °C for 2 h with stirring. The product 1,1-difluorosilacyclohex-2-ene was collected using trap-to-trap distillation with a yield of 50%. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.17 (dt, 4.44−4.24 Hz, 1H, =C−H), 5.70 (dt, 1.97−1.99 Hz, ^{1}H, =C−H), 2.25 (m, 2.27−2.22, 2H, CH$_2$), 1.98 (m, 2.01−1.94, 2H, CH$_2$), 0.96 (m, 1.00−0.95, 2H, CH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$): δ (ppm), (159.68), (t, 5.50 Hz), t 118.79, (t, 19.04 Hz), 30.40 s, 21.55 t, 9.89 (t, 1.59 Hz), ^{19}F NMR (400 MHz, CDCl$_3$) δ (ppm), −141.83. ^{29}Si NMR (400, MHz, CDCl$_3$): δ (ppm) −16.19 (t, 294.42 Hz).

As an alternative second step, silacyclohex-2-ene is prepared by the reduction of the 1,1-dichlorosilacyclohex-2-ene using lithium aluminum hydride in diethyl ether for 2 h at 40 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.88 (dt, 4.03 Hz, 2.08 Hz, 1H, =C−H), 3.91 (S, 2H, CH$_2$), 2.15 (m, 2.18−2.14, 2H, CH$_2$), 1.82 (m, 1.85−1.79, 2H, CH$_2$), (m, 0.89−0.87, 2H, CH$_2$). ^{13}C NMR (400 MHz, 2 h CDCl$_3$): δ ppm, 152.05 (s), 118.64 (s), 30.37 (s), 4.47 (s). ^{29}Si NMR (400, MHz, CDCl$_3$): δ (ppm)-52.52 (s).

Spectroscopy. The microwave experiments were carried out at Missouri University of Science and Technology (Missouri S&T) using a multiantenna detection, chirped-pulse, Fourier-transform microwave (MAD-CP-FTMW) spectrometer in the standard CP-FTMW orientation. The details of this spectrometer are reported elsewhere.[12−14] Both sample liquids under typical laboratory conditions were introduced

into the system via a heated nozzle reservoir with a backing gas of argon at 25 psig.[15] Since the sample was volatile, no heat was applied to the reservoir as vaporization was sufficient at room temperature.

Spectra of both molecules were then acquired with 5.5−10.25, 9.75−14.5, and 14−18.75 GHz chirp ranges with 4 μs chirp widths. A Parker Hannifin Series 9 supersonic nozzle pulsed sample into the chamber at a rate of 3 Hz with 3 free induction decays (FIDs) per gas pulse. Approximately 100,000 20 μs FIDs was collected and averaged in each range for the samples except for 1,1-difluorosilacyclohex-2-ene where only 34,000 FIDs was collected before the sample was completely depleted. Fourier transformation of the FIDs was performed with Kisiel's FFTS program[16] using a Bartlett windowing function. A zoom-in view of portions of the spectra collected for both molecules is presented in Figures 3 and 4. Typical line
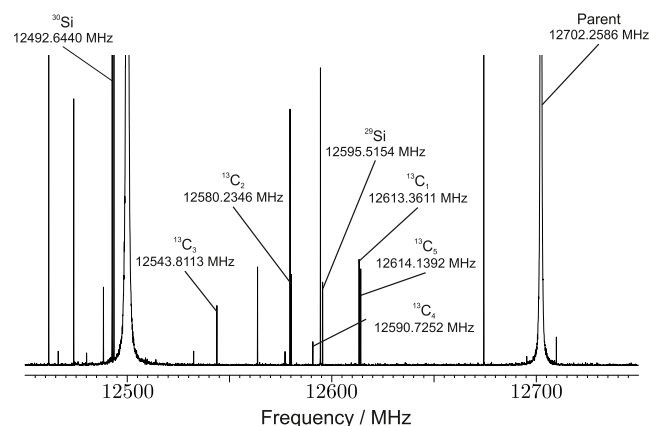

Figure 3. $J', K'_a, K'_c \leftarrow J'', K_a'', K_c'' = 3_{13}-2_{12}$ transition for all assigned isotopologue species of silacyclohex-2-ene. There is sufficient S/N on all singly substituted species for unambiguous assignment. The approximate natural abundances of each isotope are [28]Si-92.2%. [29]Si-4.7%, [30]Si-3.1%, [12]C-98.9%, [12]C-1.1%. Although the CP-FTMW experiment should provide relatively correct intensities,[17] there are inconsistencies in power across the band, giving inconsistencies in the relative intensities among the isotopologues.

widths for the spectra were 70−80 kHz with an attributed 10 kHz uncertainty for the line centers. Line center measurements are made through a mathematical routine of the AABS package that automatically reports the transition to 4 decimal places, which is used directly in the spectral fitting process.

RESULTS AND DISCUSSION

Spectra for both molecules were assigned using Kisiel's AABS package[18] used in conjunction with Pickett's SPFIT/SPCAT program suite[19] in the I^r representation. A semirigid, Watson S-reduced[20] Hamiltonian was employed for fitting of both molecular spectra. All rotational constants and quartic centrifugal distortion constants were determined for both molecules, while the sextic centrifugal distortion term H_J was determined for 1,1-difluorosilacyclohex-2-ene. As expected from quantum chemical calculations, the spectra were predominantly a-type for both species with an observation of a few b- and c-type transitions. Although 1,1-difluorosilacyclohex-2-ene was significantly stronger in intensity, Figures 3 and 4 show that the signal-to-noise ratio was sufficient on both species to observe all singly substituted [29]Si, [30]Si, and ^{13}C isotopologues in natural abundance. Determined parameters
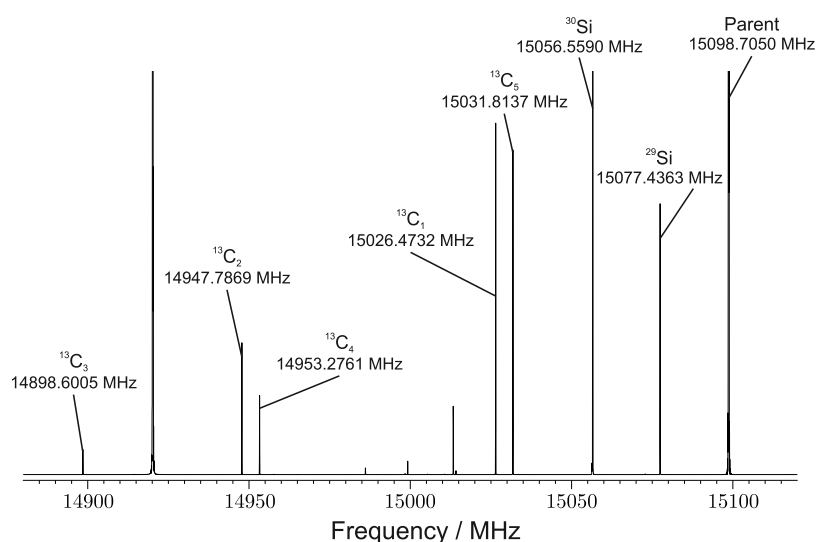
Figure 4. $J', K_a', K_c' \leftarrow J'', K_a'', K_c'' = 6_{06} - 5_{05}$ transition for all assigned isotopologue species of 1,1-difluorosilacyclohex-2-ene. There is significant S/N on all singly substituted species for unambiguous assignment. The approximate natural abundances of each isotope are ^{28}Si-92.2%. ^{29}Si-4.7%, ^{30}Si-3.1%, ^{12}C-98.9%, ^{12}C-1.1%. Although the CP-FTMW experiment should provide relatively correct intensities,[17] there are inconsistencies in power across the band, giving inconsistencies in the relative intensities among the isotopologues.

Table 2. Determined Spectroscopic Parameters for Silacyclohex-2-ene

parameter	$SiH_2CH = CHCH_2CH_2CH_2$	$^{29}SiH_2CH = CHCH_2CH_2CH_2$	$^{30}SiH_2CH = CHCH_2CH_2CH_2$	$SiH_2^{13}CH = CHCH_2CH_2CH_2$
A_0/MHz	3978.8253(6)[a]	3978.706(1)	3978.604(1)	3911.49(1)
B_0/MHz	3040.3460(5)	3002.687(1)	2966.756(1)	3038.967(1)
C_0/MHz	1879.6657(4)	1865.199(1)	1851.272(1)	1864.023(1)
D_J/kHz	0.326(6)	0.29(4)	0.39(4)	[0.326]
D_{JK}/kHz	0.058(6)	[0.058][d]	[0.058]	[0.058]
D_K/kHz	0.644(9)	0.60(2)	0.65(3)	[0.644]
d_1/kHz	−0.122(1)	−0.128(5)	−0.125(9)	[−0.122]
d_2/kHz	−0.0256(7)	−0.018(2)	−0.022(4)	[−0.0256]
N^b	167	52	31	7
microwave RMS[c]/kHz	14.2	11.6	12.0	4.7
parameter	$SiH_2CH = {}^{13}CHCH_2CH_2CH_2$	$SiH_2CH = CH{}^{13}CH_2CH_2CH_2$	$SiH_2CH = CHCH_2^{13}CH_2CH_2$	$SiH_2CH = CHCH_2CH{}^{13}CH_2$
A_0/MHz	3928.49(1)	3978.37(1)	3928.50(1)	3913.31(2)
B_0/MHz	3019.279(1)	2984.286(1)	3019.728(1)	3035.890(2)
C_0/MHz	1860.440(1)	1858.260(1)	1862.492(1)	1864.698(2)
D_J/kHz	[0.326]	[0.326]	[0.326]	[0.326]
D_{JK}/kHz	[0.058]	[0.058]	[0.058]	[0.058]
D_K/kHz	[0.644]	[0.644]	[0.644]	[0.644]
d_1/kHz	[−0.122]	[−0.122]	[−0.122]	[−0.122]
d_2/kHz	[−0.0256]	[−0.0256]	[−0.0256]	[−0.0256]
N^b	8	8	8	9
microwave RMS[c]/kHz	7.9	7.3	4.7	12.5

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure. [b]Number of observed transitions used in the fit. [c]Microwave RMS is defined as $\sqrt{\left(\sum [(obs - calcd)^2]/N \text{ lines}\right)}$. [d]Value in brackets held to the parent determined value.

for each isotopologue of both species are presented in Tables 2 and 3 with quality of fit details and assigned transition quantum numbers being reported in the Supporting Information.

Although all fits were achieved with acceptable experimental accuracy, it is important to discuss the quality of these fits and the physical meaning of the constants. For silacyclohex-2-ene, we compare the fitted parameters in Table 2 to the theoretical values reported in Table 1. From this comparison, it is observed that the equilibrium rotational constants and centrifugal distortion constants for the parent are very comparable to the fitted, experimental rotational and

centrifugal distortion constants as expected from previous use of this method and basis set.[21] It is important to note that the attempts at fitting higher order centrifugal distortion terms were made, but they both did not significantly impact the microwave root mean square (RMS) nor were they determinable to a value where the error in the value was less than 20% of the entire parameter value. During these trials, however, it was noticed that the D_{JK} and D_K terms would vary greatly, giving some indication that their values may be more empirical than physical. D_J did also vary, but not to the degree of D_{JK} and D_K.

Table 3. Determined Spectroscopic Parameters for 1,1-Difluorosilacyclohex-2-ene

parameter	$SiF_2CH=CHCH_2CH_2CH_2$	$^{29}SiF_2CH=CHCH_2CH_2CH_2$	$^{30}SiF_2CH=CHCH_2CH_2CH_2$	$SiF_2\,^{13}CH=CHCH_2CH_2CH_2$
A_0/MHz	2742.0553(4)[a]	2742.041(2)	2742.079(2)	2709.92(5)
B_0/MHz	1379.1798(2)	1376.931(1)	1374.7185(4)	1378.627(1)
C_0/MHz	1209.0375(3)	1207.3059(9)	1205.6110(5)	1202.692(1)
D_J/kHz	0.084(3)	0.084(8)	0.080(4)	0.08(1)
D_{JK}/kHz	0.341(2)	0.61(2)	0.37(3)	0.39(3)
D_K/kHz	−0.10(1)	[−0.10][d]	[−0.10]	[−0.10]
d_1/kHz	−0.01195(9)	−0.024(6)	[−0.01195]	[−0.01195]
d_2/kHz	0.00725(4)	[0.00725]	[0.00725]	[0.00725]
H_J/Hz	−0.14(1)	[−0.14]	[−0.14]	[−0.14]
N[b]	300	49	35	34
microwave RMS[c]/kHz	15.0	11.6	6.7	14.3
parameter	$SiF_2CH=\,^{13}CHCH_2CH_2CH_2$	$SiF_2CH=CH\,^{13}CH_2CH_2CH_2$	$SiF_2CH=CHCH_2\,^{13}CH_2CH_2$	$SiF_2CH=CHCH_2CH_2\,^{13}CH_2$
A_0/MHz	2716.36(3)	2741.71(4)	2719.12(3)	2709.44(2)
B_0/MHz	1369.0360(7)	1357.9809(9)	1368.8934(7)	1377.6553(5)
C_0/MHz	1196.3364(8)	1192.800(1)	1196.8417(8)	1203.3727(5)
D_J/kHz	0.095(7)	0.074(9)	0.083(6)	0.085(5)
D_{JK}/kHz	0.32(3)	0.33(4)	0.33(2)	0.36(3)
D_K/kHz	[−0.10]	[−0.10]	[−0.10]	[−0.10]
d_1/kHz	[−0.01195]	[−0.01195]	[−0.01195]	[−0.01195]
d_2/kHz	[0.00725]	[0.00725]	[0.00725]	[0.00725]
H_J/Hz	[−0.14]	[−0.14]	[−0.14]	[−0.14]
N[b]	33	35	33	31
microwave RMS[c]/kHz	9.1	11.8	8.6	5.9

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure. [b]Number of observed transitions used in the fit. [c]Microwave RMS is defined as $\sqrt{\left(\sum[(obs-calcd)^2]/N\text{ lines}\right)}$. [d]Value in brackets held to the parent determined value.
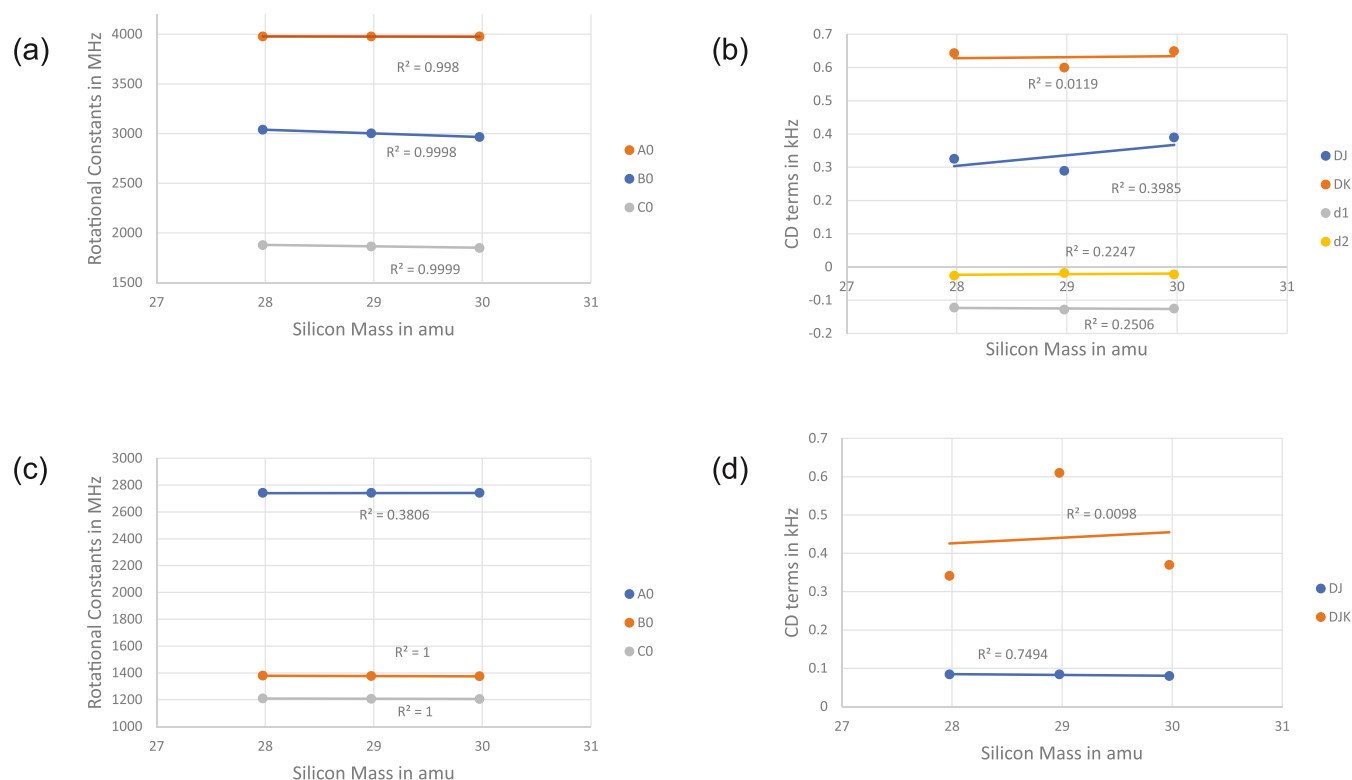
Figure 5. Variance of the rotational constants and centrifugal distortion terms versus silicon mass for silacyclohex-2-ene (a and b) and 1,1-difluorosilacyclohex-2-ene (c and d) with their linear trendline R^2 values. See the text for additional details.

For 1,1-difluorosilacyclohex-2-ene, we compare Tables 3−1. Again, the equilibrium rotational and centrifugal distortion constants for the parent are very comparable to the fitted experimental values, with the largest discrepancy being D_K, which differs by approximately a factor of 2. The real interesting note of these fits is that H_J was needed. We included the theoretical value of H_J for comparison. This is questionable for two reasons. The first is that this molecule,

Table 4. Comparisons of Kraitchman Coordinates with Costain Errors[22,25] for Silacyclohex-2-ene and 1,1-Difluorosilacyclohex-2-ene to that of Theory

silacyclohex-2-ene atom	a-coordinate/Å		b-coordinate/Å		c-coordinate/Å	
	experiment	theory	experiment	theory	experiment	theory
Si-29	−1.4509(10)[a,b]	−1.4552	0.049(31)	0.047	−0.040(37)	−0.043
Si-30	−1.4509(10)	−1.4552	0.046(32)	0.047	−0.041(36)	−0.043
C(1)	−0.2627(57)	−0.2752	1.4842(10)	1.4838	−0.054(28)	−0.058
C(2)	1.0560(14)	1.0440	1.2970(12)	1.3038	0.067(22)	0.060
C(3)	1.76743(85)	1.76630	0.000(20)[c]	−0.015	0.143(10)	0.143
C(4)	0.9805(15)	1.0000	−1.2376(12)	−1.2372	−0.3814(39)	−0.3710
C(5)	−0.3627(42)	−0.3609	−1.4280(11)	−1.4391	0.3303(46)	0.3163

1,1-difluorosilacyclohex-2-ene atom	a-coordinate/Å		b-coordinate/Å		c-coordinate/Å	
	experiment	theory	experiment	theory	experiment	theory
Si-29	0.7767(19)	0.7788	−0.032(47)	−0.010	0.00(21)	−0.02
Si-30	0.7775(19)	0.7788	0.000(57)	−0.010	0.00(14)	−0.02
C(1)	−0.2876(60)	−0.3107	−1.4592(12)	−1.4600	0.2578(68)	0.2532
C(2)	−1.64009(97)	−1.63696	−1.3288(12)	−1.3303	0.104(15)	0.127
C(3)	−2.39093(69)	−2.39412	0.000(28)	−0.061	−0.165(10)	−0.161
C(4)	−1.64837(96)	−1.66489	1.2485(13)	1.2494	0.160(10)	0.148
C(5)	−0.2769(56)	−0.3085	1.3737(11)	1.3827	−0.5846(26)	−0.5727

[a]Numbers in parentheses give Costain errors[25] in units of the least significant figure. [b]Kraitchman analyses give absolute value coordinates. Signs have been assigned based on the corresponding theoretical coordinate positions. [c]Imaginary values from the Kraitchman analysis are assigned a coordinate value of 0 Å for reporting.

being an asymmetric top, would typically have sextic centrifugal distortion constants H_{JK} and H_{KJ} be the easier constants to determine. The second is that, although H_J is determinable, it is both off by 2 orders of magnitude and opposite in sign from its predicted value. To account for if a mistake had been made in arriving at our presented fit, other fit combinations using various permutations of H_J, H_{JK}, and H_{KJ} were tried, but the fits either lowered the overall quality of the fit as measured by microwave RMS or were concluded with D_K becoming an undeterminable parameter. The latter observation led the authors to try holding D_K to its theoretical value, but this also did not improve either the quality of the fits or their overall agreement with the theoretical values. Although the presented fit in Table 3 would be referred to as the best fit of the data set for 1,1-difluorosilacyclohex-2-ene, this exercise, combined with the large disagreement in centrifugal distortion terms, leads the authors to believe that H_J is more of an empirical fitting term rather than one with much physical meaning. Furthermore, the variance of D_K when trying different combinations also provides evidence that its value is also probably more empirical than physical.

The differences between the calculated and experimental spectral parameters in both molecules, particularly among the centrifugal distortion constants, warrant additional investigation in order to assess their physical meaning. To better evaluate this, we plotted the complete set of the determinable constants from the least-squares fits for each molecule for the silicon series against their respective silicon masses in amu in Figure 5. Not all centrifugal distortion terms are plotted because only those terms that were fully independently determinable across the silicon isotopologues were taken into account. The rotational constants, with the exception of A_0 in 1,1-difluorosilacyclohex-2-ene follow a very linear trend with R^2 values being reported as 1 in some cases because the value is greater than 0.9999. It is presumed that the large variance in A_0 in 1,1-difluorosilacyclohex-2-ene is due to the atom sitting very close to or on the a-axis as presented in Table 4. This is

supported by A_0 also having the worst mass linearity dependence in silacyclohex-2-ene and the silicon atom also being positioned very close to the a-axis in that molecule. The centrifugal distortion terms, however, do not follow this linear trend. A few common mathematical functionalities were tried, and the only one that fit the data well in some cases was a generic polynomial function. The only centrifugal distortion term that had a relatively linear trend was the D_J term of 1,1-difluorosilacyclohex-2-ene. Coincidentally, this value also agrees well with the predicted value from theory. These deviations from mass dependence in the centrifugal distortion terms provide further evidence to support that these values are probably more empirical than physical. However, it should be noted here that these data sets use centrifugal distortion terms determined while holding other centrifugal distortion values to the parent isotopologue instead of holding the values to the calculated isotopologue values. Both approaches will affect the ultimate determined value. While holding to the experimental parent value is the common practice, it is unclear which approach would be a better choice, as both approaches have inherent uncertainties.

The ability to observe and fit isotopologue spectra in natural abundance allowed for comparisons of the experimental structures of the molecules to each other, to similar molecules, and with theory. To start, comparisons are made with theory. It should be noted, though, that comparisons between calculated equilibrium (r_e) structures and isotopic substitution (r_S) structures are not direct and should only be used as a guide for determining how close visual representations of theory- i.e., Figures 1 and 2, are to the determined experimental structures. This is because r_e is the structure at the bottom of the potential energy surface while r_S structures are derived from the isotopic substitution of specific nuclei from molecules in their lowest vibrational state. For experimental structure parameters, Kraitchman coordinates[22] were determined for all singly substituted atoms using Kisiel's KRA program from the PROSPE Web site.[23,24] Output files

Table 5. Comparisons of Determinable r_S Parameters for Silacyclohex-2-ene and 1,1-Difluorosilacyclohex-2-ene to that of Theory

parameter	silacyclohex-2-ene		1,1-difluorosilacyclohex-2-ene	
	experiment r_S	theory r_e	experiment r_S	theory r_e
^{29}Si−C(1)/Å	1.863(24)[a]	1.860	1.799(48)	1.835
^{30}Si−C(1)/Å	1.866(25)	1.860	1.825(50)	1.835
^{29}Si−C(5)/Å	1.872(25)	1.880	1.851(75)	1.851
^{30}Si−C(5)/Å	1.869(26)	1.880	1.828(62)	1.851
C(1)=C(2)/Å	1.3374(66)	1.3366	1.3674(63)	1.3385
C(2)−C(3)/Å	1.481(18)	1.506	1.550(24)	1.506
C(3)−C(4)/Å	1.557(16)	1.531	1.489(24)	1.531
C(4)−C(5)/Å	1.5320(48)	1.5380	1.5656(70)	1.5418
∠C(1) ^{29}SiC(5)/deg	103.80(37)	104.06	108.1(16)	106.9
∠C(1) ^{30}SiC(5)/deg	103.80(37)	104.06	108.0(11)	106.9
∠^{29}SiC(1) C(2)/deg	121.35(66)	121.43	119.6(17)	119.8
∠^{30}SiC(1) C(2)/deg	121.30(67)	121.43	119.0(14)	119.8
∠C(1) C(2) C(3)/deg	126.93(40)	126.59	125.48(53)	126.73
∠C(2) C(3) C(4)/deg	115.84(43)	116.13	116.08(33)	116.31
∠C(3) C(4) C(5)/deg	112.66(35)	113.43	113.59(56)	113.48
∠C(4) C(5) ^{29}Si/deg	108.65(75)	109.02	106.7(39)	108.2
∠C(4) C(5) ^{30}Si/deg	108.67(75)	109.02	107.0(27)	108.2
dihedral ∠^{29}SiC(1) C(2) C(3)/deg	3.9(38)	3.4	−5.6(76)	−3.4
dihedral ∠^{30}SiC(1) C(2) C(3)/deg	3.9(38)	3.4	−5.3(52)	−3.4
dihedral ∠C(1) C(2) C(3) C(4)/deg	19.3(28)	19.8	−18.6(17)	−20.5
dihedral ∠C(2) C(3) C(4) C(5)/deg	−56.7(12)	−56.1	56.9(11)	56.3
dihedral ∠C(3) C(4) C(5) ^{29}Si/deg	63.5(12)	62.2	−63.0(52)	−60.6
dihedral ∠C(3) C(4) C(5) ^{30}Si/deg	63.6(12)	62.2	−63.6(36)	−60.6
dihedral ∠C(4) C(5) ^{29}SiC(1)/deg	−37.0(20)	−35.6	36.(10)	34.0
dihedral ∠C(4) C(5) ^{30}SiC(1)/deg	−37.1(19)	−35.6	36.3(68)	34.2
dihedral ∠C(5) ^{29}SiC(1) C(2)/deg	5.3(32)	5.1	−4(12)	−4
dihedral ∠C(5) ^{30}SiC(1) C(2)/deg	5.4(32)	5.1	−5(8)	−4

[a]Numbers in parentheses give the errors derived using the Costain errors[25] in units of the least significant figure.

from this program are in the Supporting Information. Coordinates with Costain errors[25] are reported for both molecules and compared to theoretical coordinates in Table 4. Signs for the coordinates are not determined by Kraitchman analyses and have been assigned based on the coordinate values from theory. All of the determined coordinates for both molecules are in good agreement with the theoretical structures.

Atomic coordinate positions are not always easy to understand structurally in the context of the entire molecule. To clarify this, bond lengths, angles, and dihedral angles have been analyzed for every atom determined using Kraitchman coordinates and Kisiel's EVAL program.[23,24] Structural parameters for both molecules have been reported and compared with the corresponding theoretical values in Table 5. Inspection of Table 5 reveals some interesting insights into the two systems. The first is the C(1)−SiC(5) bond angle. It is expected that the geometries should remain the same upon substitution of ^{29}Si or ^{30}Si because the geometry should not depend on the number of neutrons. In 1,1-difluorosilacyclohex-2-ene, the angle is measured to be 108.1(16) or 108.0(11)° depending on if ^{29}Si or ^{30}Si is used, respectively. This is in good agreement with the theoretical value of 106.9° and is close to that of the common tetrahedral bond angle of 109.5°. However, the C(1) SiC(5) bond angle is significantly reduced for silacyclohex-2-ene to a value of 103.80(37)° for both substitution species (^{29}Si and ^{30}Si); further away from the common tetrahedral angle of 109.5°. This is particularly

interesting given that there are not significant differences in the Si−C(1) and Si−C(5) bond lengths among the molecules.

In order to help provide an explanation for this widening of the bond angle, we performed an NBO analysis on each molecule. For silacyclohex-2-ene, the silicon atom is assigned a charge of +1.120, while C(1) and C(5) have values of −0.649 and −0.833, respectively. In 1,1-difluorosilacyclohex-2-ene, the value for silicon has increased dramatically to +2.155 in response to the electron-withdrawing nature of the fluorine atoms. Even though C(1) and C(5) changed to −0.755 and −0.933, respectively, it is much more subtle, showing that much of the adjustment to the electron-withdrawing fluorines is happening directly on the silicon. Interpreting silicon as the most electropositive atom, the NBO analysis reveals a shift in s and p orbital contributions, resulting in the widening of the bond angle as a result of Bent's rule.[26] In silacyclohex-2-ene, the characteristics of the hybridized orbitals participating in the Si−H bonds on the silicon atom are $sp^{3.12}$ and $sp^{3.15}$. The corresponding silicon hybridized orbitals for Si−C(1) and Si−C(5) are $sp^{2.84}$ and $sp^{2.82}$, respectively. In 1,1-difluorosilacyclohex-2-ene, however, the electronegativity of the fluorines pull electron density, causing a large shift in the Si−F hybridization of silicon to $sp^{3.59}$ and $sp^{3.62}$, representing a large increase in p orbital contribution. This, in turn, corresponds to an increase in s contribution on the silicon atom hybridizations for Si−C(1) and Si−C(5). These hybridized orbitals are now $sp^{2.46}$ and $sp^{2.40}$, respectively. The higher s character of these hybridized orbitals of silicon leads to an increase in the bond

Table 6. Comparisons of Second Moments for Multiple Parent Isotopologues of Similar Molecules to Silacyclohex-2-ene and 1,1-Difluorosilacyclohex-2-ene

molecule	P_{aa}/uÅ^2	P_{bb}/uÅ^2	P_{cc}/uÅ^2	reference
silacyclohex-2-ene	154.03673(3)[a]	114.82970(3)	12.18744(3)	this work
1,1-difluorosilacyclohex-2-ene	300.06446(6)	117.93664(6)	66.37000(6)	this work
silacyclohexane	154.4244(7)	122.3362(7)	17.1515(7)	28
cyclohexene	100.8992(8)	96.3294(8)	10.3098(8)	1
cyclohexene	100.899(1)	96.329(1)	10.310(1)	2
1-fluoro-1-silacyclohexane (axial)	214.20745(6)	122.21878(6)	46.91095(6)	29
1-fluoro-1-silacyclohexane (equatorial)	274.8381(1)	121.9286(1)	21.2112(1)	29
cyclohexane-d_2	110.95119(5)	102.57538(5)	16.54449(5)	30
1-methyl-1-silacyclohexane (axial)	219.09864(6)	123.53275(6)	53.31346(6)	31
1-methyl-1-silacyclohexane (equatorial)	282.96261(7)	123.49348(7)	23.27675(7)	31
1,1-difluorosilacyclopent-2-ene	227.27110(12)	83.037692(12)	67.164670(12)	8
1,1-difluorosilacyclopentane	227.27110(12)	83.037692(12)	67.164670(12)	5

[a]Numbers in parentheses give standard errors (1σ, 67% confidence level) in units of the least significant figure.

angle according to Bent's rule, which aligns with our experimental observation.

Further inspection of Table 4 provides interesting insights. The first is that there is a significantly different value in the C(1)=C(2) bond length of the experimentally determined structures for silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene versus that of theory. Silacyclohex-2-ene is determined to be 1.3374(66) Å, while 1,1-difluorosilacyclohex-2-ene is determined to be 1.3674(63) Å. Theory has this parameter to be essentially the same between the molecules at 1.3366 and 1.3385 Å, respectively. While that may not be drastically different, it is interesting that the molecule with the heavily electron-withdrawing groups has the slight elongation of this bond despite not having significantly different values in the Si—C bonds. To explain this, we again use the NBO analysis. Silacyclohex-2-ene has carbon values in the double bond that are closer in charge (−0.125 and −0.649) than 1,1-difluorosilacyclohex-2-ene (−0.755 and −0.097) possibly lending itself to a sligthly more covalent bond with a shorter bond length.

The final measurements of interest involve the planarity of the ring itself. These are addressed by evaluating the dihedral angles formed from atoms as one navigates around the ring. Theoretical calculations for both structures have SiC(1) C(2) and C(3) very close to planar with C(4) and C(5) having positions above or below this plane (depending on ring orientation). This is confirmed from the experimental structure with the exception that some atoms, particularly the silicon, are very near the b and c axis, both complicating the accuracy of the Kraitchman coordinate position and giving larger errors in those coordinates. This proximity and large uncertainty in the dihedral angle is very similar to that observed in 1,1-difluorosilacyclopent-3-ene,[7] which had doubling in some transitions possibly due to an unidentified motion. No such doubling was observed in these spectra, however, which led the authors to conclude that the large uncertainty in any dihedral angle is just due to the uncertainty in the coordinate positions as the determined values, ignoring the errors, are very close to the theoretical structures. From this evidence, it can be concluded that the theoretical structure of the silicon and carbon atoms is a close approximation of the experimental structures presented.

It is important to put the structure of silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene into context with similar molecules. The most direct comparison will be that with a previous

Raman study of silacyclohex-2-ene.[27] This work found that the "ring-twisting angle", most comparable to dihedral ∠C(4) C(5) SiC(1), was 38.5 or 38.6° depending on the analytical approach taken. This Raman study value is in good agreement with the dihedral ∠C(4) C(5) ^{29}SiC(1) value of −37.0(20)° and dihedral ∠C(4) C(5) ^{30}SiC(1) value of −37.1(19)° determined in this work.

Finally, it is useful to look at how these structures compare to similar carbon and silicon-containing molecules, including cyclohexene. To aid in this, Table 6 presents the planar moments of a few similar molecules. These are quantifications of the mass distributions out of a plane. P_{aa} will quantify the mass distribution out of the bc-plane, P_{bb} will quantify the mass distribution out of the ac-plane, and P_{cc} quantifies the mass distribution out of the ab-plane. P_{bb} and P_{cc} are the particular planar moments for these discussions and have been boldfaced in Table 6 for ease of reference. Comparisons in these values are not always direct, as the inertial frame shifts, but they can give some qualitative insights between similar molecules. General explanations on how to interpret and utilize second moments can be found in ref 32. The first interesting comparison is in the P_{cc} values of silacyclohex-2-ene (12.18744(3) uÅ^2) and cyclohexene (10.3098(8) uÅ^{21} or 10.310(1) uÅ^{22}). To provide perspective to this difference, a typical −CH$_2$/−CH$_3$ group has contributions from 1.5 to 1.8 uÅ^{2},[32] and so this is significantly different. Figure 1 shows that the C(4) and C(5) atoms are the heavy atoms furthest from the ab-plane, very similar to the half-chair structure of cyclohexene,[1,2] and the similarity in the values supports this. The addition of the fluorines in 1,1-difluorosilacyclohex-2-ene complicates this direct comparison, but because the theoretical structures have been determined to be an accurate depiction of the experimental structure, we take the theoretical c-coordinate positions and subtract the fluorines' contribution to P_{cc} resulting in an approximate value of 11.19 uÅ^2 for the remaining atoms, very similar to silacyclohex-2-ene and cyclohexene (this calculation is shown in the Supporting Information). Figure 6 shows the half-chair structure as determined for the molecules in this work.

The next interesting comparison is that of the P_{bb} values of multiple six-membered rings with silicon. All values are near 120 uÅ^2 for the molecules presented, but the first molecules known to be studied with a double bond in the ring from this work are significantly lower in this value. This is because the molecules without a double bond exist in traditional chair
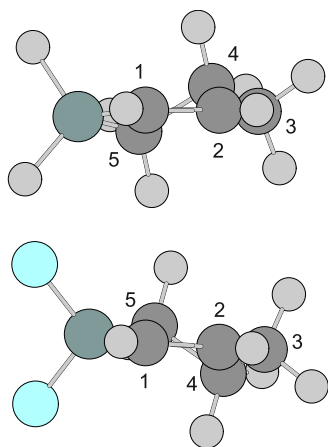
Figure 6. Silacyclohex-2-ene (top) and 1,1-difluorosilacyclohex-2-ene (bottom) looking directly into the double bond. Both molecules have a half-chair configuration, like cyclohexene.

conformations with slightly more contribution originating from one of the carbons being further along the *b*-axis, outside the *ac*-plane. However, it should be noted that the value being near 120 uÅ^2 does separate it from five-membered rings because these are all much different in value from 1,1-difluorosilacyclopent-2-ene[8] and 1,1-difluorosilacyclopentane.[8]

CONCLUSIONS

The experimental rotational spectrum and structures of silacyclohex-2-ene and 1,1-difluorosilacyclohex-2-ene have been performed and are reported here for the first time. The molecules were synthesized at the College of Charleston with subsequent spectroscopy being performed at Missouri S&T. From this work, it is apparent that two major conclusions can be drawn about the species. The first is that while the experimentally derived rotational parameters seem to have solid physical meaning, many of the centrifugal distortion constants determined in the fitting of the data sets are probably more empirical than physical. If this is true, then why are these data sets requiring empirical parameters? For this, the authors are not entirely sure because there was no additional splitting observed in either spectrum to provide a case for some form of large amplitude motion. It has been observed by the authors previously in similar systems that curious motions can exist in these silicon ring molecules,[7] but there was no direct evidence here. This could be due to the frequency range of the experiment and warrants further study, but it was outside the capabilities available to the authors. Certainly, a greater frequency range would help with the determination of the centrifugal distortion constants and more reliably address H_J.

The other conclusion drawn from this work is the structure. The molecules closely resemble the half-chair configuration of cyclohexene. This was quantitatively determined using both substitution structures and second moment analysis. The double bond in the six-membered ring is the reason for this structure, as the other six-membered silicon rings take on the traditional chair form. Other similar ring structures, especially silacyclohex-3-ene and its derivatives, would be an interesting comparator to see whether this trend.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.3c04027.

Transition measurements, quantum number assignments, obs-calcd, blends, fits, and standard errors for all measured isotopologues of silacyclohex-2-ene; quantum number assignments reported are given in J', K_a', $K_c' \leftarrow J''$, K_a'', K_c'' format as is needed for SPFIT (Tables S1−S8); transition measurements, quantum number assignments, obs-calc, blends, fits, and standard errors for all measured isotopologues of 1,1-difluorosilacyclohex-2-ene; quantum number assignments reported are given in J', K_a', $K_c' \leftarrow J''$, K_a'', K_c'' format as is needed for SPFIT (Tables S9−S16); output of Kraitchman analysis for silacyclohex-2-ene from KRA program (Table S17); output of Kraitchman analysis for 1,1-difluorosilacyclohex-2-ene from KRA program (Table S18); silacyclohex-2-ene NMR Data: (a) ^{1}H (b) ^{13}C (c) ^{29}Si (Figure S1a−c); 1,1-difluorosilacyclohex-2-ene NMR Data: (a) ^{1}H (b) ^{13}C (c) ^{19}F (d) ^{29}Si (Figure S2a−d); 1,1-dichlorosilacyclohex-2-ene NMR data: (a) ^{1}H (b) ^{13}C (c) ^{29}Si (Figure S3a−c); calculation of P_{cc} for 1,1-difluorosilacyclohex-2-ene subtracting the fluorine contribution (ZIP)

AUTHOR INFORMATION

Corresponding Author

  G. S. Grubbs, II − *Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States;* orcid.org/0000-0002-1162-8819; Email: grubbsg@mst.edu

Authors

  Nicole T. Moon − *Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States*
  Amanda J. Duerden − *Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, United States*
  Thomas M. C. McFadden − *Department of Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina 29424, United States*
  Nathan A. Seifert − *Department of Chemistry and Chemical & Biomedical Engineering, University of New Haven, West Haven, Connecticut 06516, United States*
  Gamil A. Guirgis − *Department of Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina 29424, United States;* orcid.org/0000-0002-2202-0964

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpca.3c04027

Notes

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