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Microwave Spectrum, Dipole Moment, Structure, and Internal Motion of 1-Silabicyclo[2.2.1]heptane

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The rotational constants of 1-silabicyclo[2.2.1]heptane in the ground vibrational state were determined to be A_0=2744.775 (2) MHz, B_0=2662.017 (2) MHz, and C_0=2145.994 (2) MHz, with the standard deviations in parentheses. Because the spectrum was very rich, the Stark effects of two transitions were analyzed by a simulation technique. The dipole moments thus obtained are $\mu_b=0.5\pm0.1$ D, $\mu_c=0.05\pm0.01$ D, and $\mu_t=0.5\pm0.1$ D. The observed spectra did not exhibit any anomalies which were due to deviations of the molecular symmetry from C_s. Three structural parameters, Si–C(7), ∠C(2)–Si–C(6), and ∠Si–C(2)–C(3), were adjusted so as to reproduce the rotational constants observed for the ground state. The Si–C(7) bond was found to be longer than Si–C(2) by 0.07 Å. Two vibrational satellites were detected and were assigned to the $v=1$ and the $v=2$ states of a torsional mode of the skeleton. A relative-intensity measurement resulted in the excitation energies of 70±25 cm^{-1} and 160±60 cm^{-1} for $v=1$ and $v=2$, respectively. The molecular structure and the internal motions were discussed in terms of intramolecular forces.

Bicyclic compounds are often characterized by highly strained structures of their skeletons, which involve three-, four-, and/or five-membered rings in most cases. Because two or more such rings are condensed to constitute the skeleton of a bicyclic molecule, new aspects are often introduced in the resultant structure. Bicyclo[2.2.2]octane, for example, has cyclohexane rings as constituents, and may thus be free from the strain of the valence angles. However the cyclohexane rings are forced to be of the boat form in the bicyclo[2.2.2]-octane molecule, rather than of the more stable chair form. The conformation about the three C–C bonds is thus eclipsed, provided that the molecular symmetry is D_{3h}. We might, however, expect additional lowering in energy by twisting slightly the skeleton about the symmetry axis. In fact, we have shown in our previons papers[3,4] that simple derivatives of bicyclo[2.2.2]-octane have a double-minimum potential function to the torsion of the skeleton and the height of the potential barrier which is sensitive to the substituents is explained by balance of two forces due to the valence-angle strain and to the internal-rotation potential.

Bicyclo[2.2.1]heptane or norbornane is obtained by replacing one of the three ethylene bridges by a methylene bridge. We have thus here two C–C bonds with unstable conformation. Furthermore, the methylene bridge which is introduced will cause considerable strain in the molecular skeleton. These two facts will thus favor the C_{2v} symmetry much higher than C_2 or the twisted form. In fact, electron-diffraction data on norbornane[5] are consistent with C_{2v}. Unfortunately this molecule has too small dipole moment to observe its microwave spectrum. In the present work we investigated the 1-silabicyclo[2.2.1]heptane molecule by microwave spectroscopy.

Experimental

A sample of 1-silabicyclo[2.2.1]heptane was prepared by a procedure described in Ref. 6. It is a white crystalline solid with mp of 75 °C. Because this compound sublimes easily, the sample was purified by sublimation before use. However, the vapor pressure permitted observation of the microwave spectrum only at room temperature or higher. The microwave spectrometer which was used was of conventional Stark-modulation type with a 110 kHz sine-wave or square-wave oscillator as a modulator.

Rotational Spectra

By transferring appropriate structure parameters from norbornane,[5] dimethylsilane,[7] and trimethylsilane[8] we calculated the rotational constants of 1-silabicyclo-[2.2.1]heptane on an assumption of C_s symmetry. Bond-moment consideration indicated that the *b* component of the dipole moment was much larger than the *c* component, while the *a* component was zero because of symmetry (see Fig. 1, where the heavy atoms are given numbers for identification).

We first searched the spectra in the 20—30 GHz region. We observed a number of lines with nearly first-order Stark effects, which we subsequently assigned to the *b*-type *Q*-branches of high *J* and high K_{+1}. Figure 2 shows a portion of the observed spectra, which are assigned to $K_{+1}=20\leftarrow21$. Because the members of the series are weak in the limit of $J\cong K_{+1}$, it is difficult to determine the *J* numbers unambiguously. We therefore searched the *b*-type *R* branches in higher-frequency region, where the *R* branches

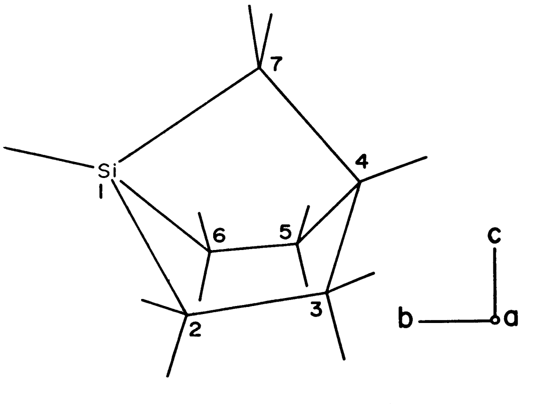

Fig. 1. 1-Silabicyclo[2.2.1]heptane. The heavy atoms are given numbers for identification.

TABLE 1. OBSERVED FREQUENCIES OF 1-SILABICYCLO[2.2.1]HEPTANE IN THE GROUND STATE (MHz)

Transition[a]	Obsd.	Δ[b]
21, 19—21, 20	21 671.60	−0.15
22, 19—22, 20	21 666.90	0.22
23, 19—23, 20	21 660.95	0.01
24, 19—24, 20	21 654.44	−0.04
25, 19—25, 20	21 647.07	−0.16
26, 19—26, 20	21 639.25	0.11
27, 19—27, 20	21 630.21	0.08
28, 19—28, 20	21 620.06	−0.08
21, 20—21, 21	22 788.34	0.19
22, 20—22, 21	22 783.50	−0.16
23, 20—23, 21	22 778.52	−0.08
24, 20—24, 21	22 772.87	−0.04
25, 20—25, 21	22 766.53	−0.02
26, 20—26, 21	22 759.43	−0.02
27, 20—27, 21	22 751.50	−0.06
28, 20—28, 21	22 742.80	−0.02
29, 20—29, 21	22 733.11	−0.06
30, 20—30, 21	22 722.56	0.01
31, 20—31, 21	22 710.94	0.07
32, 20—32, 21	22 698.14	0.06
33, 20−33, 21	22 684.13	0.02
34, 20—34, 21	22 668.96	0.10
35, 20—35, 21	22 652.25	−0.02
36, 20—36, 21	22 634.13	−0.12
37, 20—37, 21	22 614.70	−0.01
38, 20—38, 21	22 593.59	0.03
39, 20—39, 21	22 570.75	0.04
40, 20—40, 21	22 546.08	0.03
41, 20—41, 21	22 519.42	−0.07
23, 21—23, 22	23 895.59	0.01
24, 21—24, 22	23 890.47	−0.05
25, 21—25, 25	23 884.97	0.10
26, 21—26, 22	23 878.59	0.01
27, 21—27, 22	23 871.60	−0.00
28, 21—28, 22	23 863.89	0.00
29, 21—29, 22	23 855.44	0.07
30, 21—30, 22	23 845.90	−0.11
31, 21—31, 22	23 835.72	−0.02
32, 21—32, 22	23 824.56	0.05
33, 21—33, 22	23 812.14	−0.10
34, 21—34, 22	23 799.05	0.17
35, 21—35, 22	23 784.38	0.03
23, 22—23, 23	25 012.15	0.09
24, 22—24, 23	25 007.65	0.14
25, 22—25, 23	25 002.55	0.10
26, 22—26, 23	24 996.78	−0.04
27, 22—27, 23	24 990.47	−0.12
28, 22—28, 23	24 983.80	0.09
29, 22—29, 23	24 976.08	−0.05
30, 22—30, 23	24 967.62	−0.19
31, 22—31, 23	24 958.55	−0.14
32, 22—32, 23	24 948.68	−0.05
33, 22—33, 23	24 937.88	0.02
34, 22—34, 23	24 925.96	−0.08
35, 22—35, 23	24 913.44	0.23
8, 8—7, 7	34 891.37	−0.04
8, 7—7, 6	36 003.37	0.00
8, 2, 6—7, 3, 5 8, 3, 6—7, 2, 5	37 116.18	0.02 −0.12
8, 8, 0—7, 7, 1	43 739.89	−0.02
8, 8, 1—7, 7, 0	43 641.89	−0.03
8, 7, 1—7, 6, 2	43 873.25	−0.01
9, 9—8, 8	39 183.31	0.07
9, 8—8, 7	40 295.20	0.06
9, 2, 7—8, 3, 6 9, 3, 7—8, 2, 6	41 407.60	0.00 −0.01
9, 3, 6—8, 4, 5 9, 4, 6—8, 3, 5	42 522.20	0.36 −0.22
9, 4, 5—8, 5, 4	43 634.58	−0.01
9, 5, 5—8, 4, 4	43 653.92	−0.02
9, 5, 4—8, 6, 3	44 645.12	−0.01
9, 6, 4—8, 5, 3	44 943.67	0.02
9, 7, 3—8, 6, 2	46 682.80	−0.00
9, 8, 2—8, 7, 1	48 303.08	−0.01
10, 10—9, 9	43 475.00	−0.03
10, 9—9, 8	44 586.95	0.06
10, 8—9, 7	45 699.12	−0.02
10, 3, 7—9, 4, 6 10, 4, 7—9, 3, 6	46 812.66	0.03 −0.01
10, 4, 6—9, 5, 5	47 929.00	−0.05
10, 5, 6—9, 4, 5	47 931.19	0.10
10, 10, 0—9, 9, 1	54 685.26	−0.03
10, 10, 1—9, 9, 0	54 654.92	0.03
10, 9, 2—9, 8, 1	53 923.86	−0.01
10, 9, 1—9, 8, 2	54 507.37	−0.01
10, 8, 2—9, 7, 3	55 379.70	0.05
10, 8, 3—9, 7, 2	52 386.10	−0.00
11, 11—10, 10	47 766.78	0.01
11, 10—10, 9	48 878.63	0.01
11, 9—10, 8	49 990.78	0.05
11, 4, 7—10, 5, 6 11, 5, 7—10, 4, 6	52 218.93	0.04 −0.14
11, 6, 6—10, 5, 5	53 344.12	0.07
11, 5, 6—10, 6, 5	53 337.94	−0.04
11, 6, 5—10, 7, 4	54 429.43	−0.01
11, 7, 5—10, 6, 4	54 542.58	0.04
11, 7, 4—10, 8, 3	55 174.74	0.01
11, 8, 4—10, 7, 3	56 142.70	−0.01
11, 9, 3—10, 8, 2	58 111.44	−0.04
11, 11, 1—10, 10, 0	60 151.39	0.07
11, 11, 0—10, 10, 1	60 167.75	0.07
11, 10, 2—10, 9, 1	59 515.76	0.03
11, 10, 1—10, 9, 2	59 889.97	−0.03
11, 9, 2—10, 8, 3	60 510.81	0.15
11, 8, 3—10, 7, 4	62 279.29	−0.06
12, 12—11, 11	52 058.27	−0.20
12, 11—11, 10	53 170.30	−0.01
12, 10−11, 9	54 282.27	−0.07
12, 9—11, 8	55 394.80	−0.16
12, 4, 8—11, 5, 7 12, 5, 8—11, 4, 7	56 509.07	−0.02 −0.04

Table 1. (Continued)

Transition[a)]	Obsd.	Δ[b)]	Transition[a)]	Obsd.	Δ[b)]
12, 5, 7—11, 6, 6	57 626.82	−0.02	13, 9—12, 8	60 799.67	−0.12
12, 6, 7—11, 5, 6	57 627.52	0.07	13, 5, 8—12, 6, 7 13, 6, 8—12, 5, 7	61 915.75	0.03 −0.02
12, 7, 6—11, 6, 5	58 764.23	0.05	13, 6, 7—12, 7, 6	63 036.99	0.05
12, 6, 6—11, 7, 5	58 748.06	−0.10	13, 7, 7—12, 6, 6	63 038.76	−0.00
12, 7, 5—11, 8, 4	59 804.40	0.07	13, 8, 6—12, 7, 5	64 196.21	0.02
12, 12, 1—11, 11, 0	65 644.36	−0.05	13, 7, 6—12, 8, 5	64 157.92	−0.07
12, 12, 0—11, 11, 1	65 653.19	0.10	13, 8, 5—12, 9, 4	65 146.46	−0.10
12, 11, 2—11, 10, 1	65 077.92	−0.02	13, 9, 5—12, 8, 4	65 587.20	0.02
12, 11, 1—11, 10, 2	65 307.95	−0.16	13, 9, 4—12, 10, 3	65 311.59	0.06
12, 10, 3—11, 9, 2	63 841.73	0.03	14, 14—13, 13	60 641.76	0.07
12, 9, 4—11, 8, 3	61 839.44	0.03	14, 13—13, 12	61 753.55	0.02
12, 8, 5—11, 7, 4	60 037.59	0.05	14, 12—13, 11	62 865.44	−0.03
12, 8, 4—11, 9, 3	60 304.52	−0.08	14, 11—13, 10	63 977.70	−0.03
13, 13—12, 12	56 350.24	0.13	14, 10—13, 9	65 090.80	0.05
13, 12—12, 11	57 461.88	−0.07	15, 15—14, 14	64 933.20	−0.02
13, 11—12, 10	58 574.10	0.18			
13, 10—12, 9	59 686.38	0.05			

a) J', $K_{+1}'-J''$, K_{+1}'' for the degenerate transitions and J', K_{-1}' $K_{+1}'-J''$, K_{-1}'', K_{+1}'' for the non-degenerate transitions. b) Obsd−Calcd. The calculated frequencies are obtained using the constants listed in Table 2.

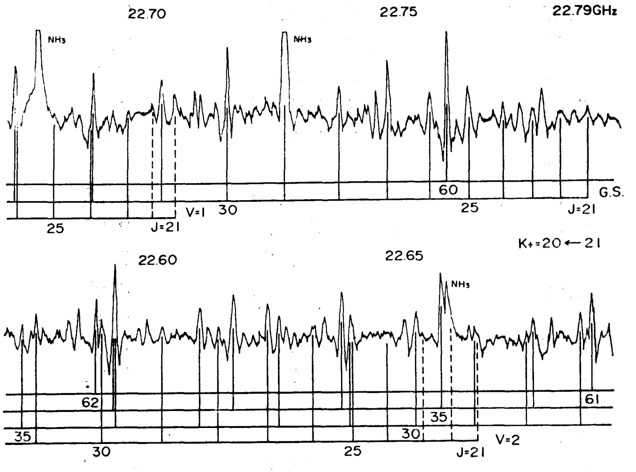

Fig. 2. A part of the *b*-type *Q*-branch spectra of 1-silabicyclo[2.2.1]heptane, recorded at room temperature with the AC modulation field of 20—40 V/cm superposed on the DC Stark field of 160—200 V/cm and with the time constant of 0.4 s.

were stronger than the *Q* branches. The *R* branches of $K_{+1}\cong J$ were degenerate and showed the first-order Stark effects. We observed peculiar lineshapes for transitions with small *K*-type splittings, that is, stronger Stark components between weaker zero-field doublets. This is due to Stark mixing of the *K* doublets, which induces forbidden transitions at finite Stark fields. Table 1 lists the observed frequencies of the assigned transitions, which we analyzed by a least-squares method taking into account the centrifugal distortion effects to the first order. In addition to those given in Table 1 we also observed the following transitions, but did not include them in a least-squares analysis; *Q* branches of $K_{+1}=19\leftarrow20$, $J=29$—44, of $K_{+1}=20\leftarrow21$, $J=42$—62, of $K_{+1}=21\leftarrow22$, $J=36$—67, of $K_{+1}=22\leftarrow23$, $J=36$—71, of $K_{+1}=23\leftarrow24$, $J=48$—75, of $K_{+1}=27\leftarrow28$, $J=29$—32, of $K_{+1}=52\leftarrow53$, $J=54$—83, of $K_{+1}=54\leftarrow55$, $J=66$—80, and of $K_{+1}=55\leftarrow56$, $J=57$—83, and four *R* branches, $5_{24}\leftarrow4_{13}$, $5_{14}\leftarrow4_{23}$, $5_{05}\leftarrow4_{14}$, and $5_{15}\leftarrow4_{04}$ (the latter two are degenerate). Table 2 lists the rotational constants and the centrifugal distortion constants which are thus derived. We set arbitrarily the τ_{aabb} constant to be zero. The transition frequencies which are calculated using the constants of Table 2 are compared with the observed frequencies in Table 1.

Table 2. Rotational constants and centrifugal distortion constants of 1-silabicyclo[2.2.1]heptane (MHz)[a)]

Constant	G. S.	$v=1$	$v=2$
A	2744.775 (2)	2745.94 (2)	2746.88 (5)
B	2662.017 (2)	2662.79 (2)	2663.59 (6)
C	2145.994 (2)	2148.779 (3)	2150.931 (6)
τ_{aaaa}	−0.00116 (4)	−0.0008 (4)	−0.0032 (7)
τ_{bbbb}	−0.00075 (3)	−0.0007 (2)	−0.0020 (4)
τ_{cccc}	−0.00075 (2)	−0.00078 (4)	−0.00060 (6)
τ_{bbcc}	0.0141 (3)	0.016 (4)	−0.014 (9)
τ_{aacc}	−0.0178 (4)	−0.020 (5)	0.02 (1)

a) Values in parentheses denote the standard deviations and apply to the last digits of the constants. The τ_{aabb} constant is fixed to zero.

In addition to the ground-state spectra we observed two prominent sets of the vibrational satellites. Based on the frequency shifts from the ground-state spectra and on the relative intensities, which are observed, we assigned these two to the first and the second excited states of the lowest normal mode, probably the skeletal torsion. We listed the observed transitions in Table 3, and the rotational constants and the centrifugal distortion constants, which were derived by a least-

TABLE 3. OBSERVED FREQUENCIES OF 1-SILABICYCLO[2.2.1]HEPTANE IN THE EXCITED VIBRATIONAL STATES (MHz)

Transition[a)]	$v=1$		$v=2$	
	Obsd	Δ[b)]	Obsd	Δ[b)]
24, 20—24, 21			22 643.28	0.24
25, 20—25, 21			22 636.44	−0.07
26, 20—26, 21			22 628.94	−0.29
27, 20—27, 21			22 621.20	0.06
28, 20—28, 21			22 612.20	0.01
29, 20—29, 21			22 602.14	−0.16
30, 20—30, 21	22 647.50	−0.02	22 591.44	0.03
31, 20—31, 21	22 635.76	−0.01	22 579.34	−0.11
32, 20—32, 21	22 622.82	−0.08	22 566.34	−0.02
33, 20—33, 21	22 608.84	0.02	22 552.06	0.02
34, 20—34, 21	22 593.52	0.06	22 536.48	0.06
35, 20—35, 21	22 576.74	0.01	22 519.48	0.06
36, 20—36, 21	22 558.60	0.05	22 501.10	0.16
37, 20—37, 21	22 538.80	−0.04	22 481.04	0.13
38, 20—38, 21	22 517.46	−0.03	22 459.14	−0.07
39, 20—39, 21	22 494.40	−0.01	22 435.76	0.01
40, 20—40, 21	22 469.62	0.12	22 410.48	0.06
41, 20—41, 21	22 442.42	−0.23	22 382.80	−0.30
42, 20—42, 21	22 413.82	0.07	22 353.70	0.02
43, 20—43, 21	22 382.80	0.12	22 322.08	0.04
44, 20—44, 21	22 349.26	−0.06	22 288.04	0.02
45, 20—45, 21	22 313.50	−0.04	22 251.46	−0.05
46, 20—46, 21	22 275.26	0.06	22 212.38	0.05
48, 20—48, 21	22 190.24	−0.02		
10, 10—9, 9	43 528.93	0.07	43 571.00	0.23
10, 9—9, 8	44 637.02	−0.05	44 676.26	−0.09
10, 8—9, 7	45 745.61	−0.05	45 782.28	−0.04
10, 3, 7—9, 4, 6	46 855.52	0.00	46 889.50	−0.07
10, 4, 7—9, 3, 6		−0.04		−0.12
10, 4, 6—9, 5, 5	47 968.46	0.13	47 999.84	0.08
10, 5, 6—9, 4, 5	47 970.47	0.03	48 002.00	0.04
10, 6, 5—9, 5, 4	49 122.58	−0.05		
10, 5, 5—9, 6, 4	49 071.52	−0.08		
11, 11—10, 10	47 826.21	0.05	47 872.41	−0.02
11, 10—10, 9	48 934.39	0.04	48 978.08	0.09
11, 9—10, 8	50 042.82	0.00	50 083.79	−0.03
11, 8—10, 7			51 190.34	−0.17
11, 4, 7—10, 5, 6	52 263.81	0.09	52 299.48	−0.01
11, 5, 7—10, 4, 6		−0.10		−0.21
11, 5, 6—10, 6, 5	53 379.06	−0.14	53 412.28	−0.02
11, 6, 6—10, 5, 5	53 385.34	−0.15	53 419.04	0.18
11, 7, 5—10, 6, 4	54 582.51	0.28		
11, 6, 5—10, 7, 4	54 466.15	0.11		
12, 12—11, 11	52 123.39	−0.02	52 174.08	0.02
12, 11—11, 10	53 231.54	−0.06	53 279.53	−0.06
12, 10—11, 9	54 340.00	0.02	54 385.34	0.01
12, 9—11, 8	55 449.02	0.06	55 491.86	0.18
12, 4, 8—11, 5, 7	56 559.49	−0.02	56 599.50	−0.07
12, 5, 8—11, 4, 7		−0.03		−0.09
12, 5, 7—11, 6, 6	57 673.77	0.12	57 711.00	−0.14
12, 6, 7—11, 5, 6	57 674.40	0.11	57 711.90	0.08
12, 6, 6—11, 7, 5	58 791.20	−0.09	58 826.09	0.12
12, 7, 6—11, 6, 5	58 807.68	−0.20	58 843.53	0.27
12, 7, 5—11, 8, 4	59 841.69	−0.02		
12, 8, 5—11, 7, 4	60 081.00	−0.11		

Table 3. (Continued)

Transition[a]	$v=1$ Obsd	$v=1$ Δ[b]	$v=2$ Obsd	$v=2$ Δ[b]
13, 13—12, 12	56 420.63	0.03	56 475.60	−0.04
13, 12—12, 11	57 528.60	−0.19	57 581.09	−0.07
13, 11—12, 10	58 637.25	0.13	58 686.88	0.05
13, 10—12, 9	59 745.77	−0.12	59 792.91	−0.04
13, 9—12, 8	60 855.83	0.10	60 900.06	−0.09
13, 5, 8—12, 6, 7 13, 6, 8—12, 5, 7	61 968.15	0.08 0.03	62 010.00	0.12 0.06
13, 6, 7—12, 7, 6	63 085.74	0.00	63 125.06	0.12
13, 7, 7—12, 6, 6	63 087.49	−0.15	63 126.91	−0.05
13, 8, 6—12, 7, 5	64 242.51	0.05	64 279.94	−0.22
13, 7, 6—12, 8, 5	64 202.95	0.03	64 238.82	−0.15
14, 14—13, 13	60 717.80	0.06	60 777.07	−0.10
14, 13—13, 12	61 825.91	−0.03	61 882.50	−0.19
14, 12—13, 11	62 934.08	−0.15	62 988.30	−0.01
14, 11—13, 10	64 042.73	−0.12	64 094.18	−0.09
14, 10—13, 9	65 152.53	0.28	65 201.50	0.48

a) $J', K_{+1}'-J'', K_{+1}''$ for the degenerate transitions and $J', K_{+1}', K_{-1}'-J'', K_{+1}'', K_{-1}''$ for the non-degenerate transitions. b) Obsd−Calcd. The calculated frequencies are obtained using the constants listed in Table 2.

Table 4. RELATIVE INTENSITIES OF VIBRATIONAL SATELLITES[a]

Transition $J', K_{+1}'-J'', K_{+1}''$	$v=1$	$v=2$
14, 13−13, 12	0.75	
13, 13—12, 12	0.71	0.43
13, 12—12, 11	0.67	
13, 11—12, 10		0.45
13, 10—12, 9	0.75	
12, 11—11, 10	0.67	0.42
12, 10—11, 9	0.73	0.54
Av.	$0.71_3\pm0.093$	0.46 ± 0.14
E_v (cm^{-1})[b]	70±25	160±60

a) Referred to the ground-state transitions, at room temperature. Errors are 2.5 times standard deviations.
b) $kT=207$ cm^{-1} or $T=298$ K.

squares analysis, in Table 2. Although we included only the observed lines of $J\leqq48$ in a least-squares analysis, we measured additional lines which were mainly high J and K_{+1} transitions as in the case of the ground state. The intensities of the satellites were compared with those of the ground-state spectra at room temperature, as shown in Table 4. We thus determined the excitation energies to be 70±25 cm^{-1} and 160±60 cm^{-1} for $v=1$ and $v=2$, respectively. We did not observe any anomalies in the rotational spectra, even for the vibrational satellites, which were due to deviations of the molecular symmetry from C_s.

Dipole Moment

Because the spectrum is rich and weak, it is difficult to resolve the Stark components completely. We thus analyzed the Stark effects by a simulation technique similar to that described in our previous paper.[9] We made the following assumptions: (1) the line-widths of the Stark components are the same as that of the zero-field line, (2) the Stark components have the

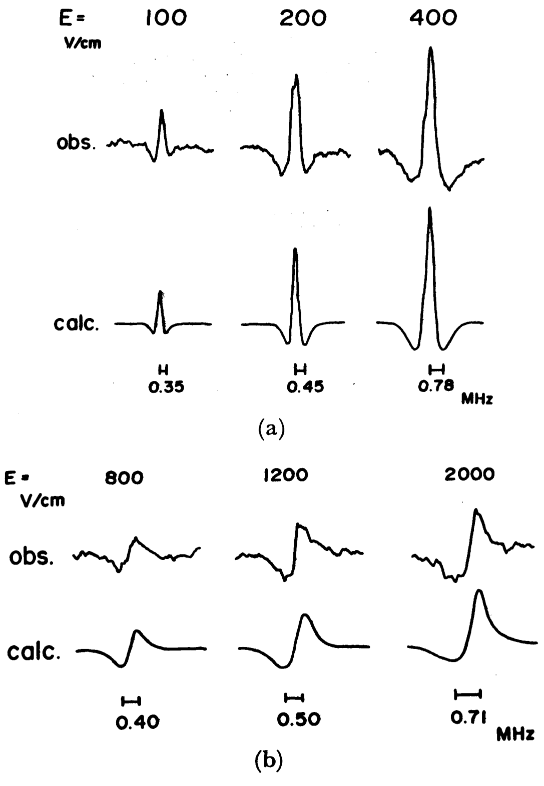

Fig. 3. Analysis of the Stark effects by a simulation method.
(a) $J, K_{+1}=13, 13\leftarrow12, 12$. Calculated spectra are obtained using $\Delta\nu$(HWHM)=0.26 MHz and $\mu_c=0.05$ D.
(b) $J_{K_{-1},K_{+1}}=11_{11,1}\leftarrow10_{10,0}$. Calculated spectra are obtained using $\Delta\nu=0.25$ MHz, $\mu_b=0.5$ D, and $\mu_c=0.05$ D.

TABLE 5. MOLECULAR STRUCTURE OF 1-SILABICYCLO[2.2.1]HEPTANE[a)]

Assumed:	Si-C(2)	1.868 Å	∠C(2)-C(3)-C(4)	106.5°
	C(2)-C(3)	1.5527 Å	∠C(3)-C(4)-C(5)	111.0°
	C(3)-C(4)	1.5362 Å	∠H-Si-C(7)	109.4°
	C(4)-C(7)	1.5579 Å	∠H-C(4)-C(7)	109.4°
	C(4)-H	1.11 Å	∠H-C-H	109.4°
	other C-H	1.11 Å	CH_2 plane bisects C-C-C	
	Si-H	1.489 Å	or Si-C-C angles	
	C_s symmetry			
Fitted:	Si-C(7)	1.9431 Å	∠C(2)-Si-C(6)	104.1°
			∠Si-C(2)-C(3)	102.8°

a) See Fig. 1 for the atom numbers.

Lorentzian lineshape, and (3) the inhomogeneity of the Stark field may be neglected. We calibrated the Stark field using the $J=1\leftarrow0$ transition of OCS as a reference.

To determine the μ_c component we analyzed a K-degenerate transition $J, K_{+1}=13, 13\leftarrow12, 12$. Its first-order Stark effect is determined by the μ_c component at low Stark fields. Overall fitting may be judged by two parameters, the intensity and the difference between the peak frequencies of the zero-field and of the Stark components. We obtained best fitting using the linewidth parameter $\Delta\nu$ (HWHM) of 0.26 MHz and μ_c of 0.05 D. The calculated spectrum thus obtained is compared with the observed in Fig. 3a. The error of μ_c is ±0.01 D. We determined the μ_b component from a similar analysis of the $11_{11,1}\leftarrow10_{10,0}$ transition. The two parameters which were derived are $\Delta\nu=0.25$ MHz and $\mu_b=0.5\pm0.1$ D. The total dipole moment is 0.5 ± 0.1 D.

Molecular Structure

As stated above we did not observe any deviations of the molecular symmetry from C_s. An assumption of the C_s symmetry leaves nine parameters as independent to determine the heavy-atom skeleton. We adjusted three of the nine parameters, Si–C(7), ∠C(2)–Si–C(6), and ∠Si–C(2)–C(3), so as to reproduce the observed rotational constants, while others were fixed to the values of the related molecules.[5,7,8] Table 5 summarizes the fitted as well as the assumed parameters.

Discussion

We have recently shown[10] that the 1-silabicyclo[2.2.2]octane molecule has a double-minimum potential function to the skeletal torsion and the potential hump ($212\ \text{cm}^{-1}$) is even higher than that ($67\ \text{cm}^{-1}$) in 1-halogenobicyclo[2.2.2]octane.[3] The present work shows that replacement of one ethylene bridge by a methylene bridge removes the hump from the torsional potential function, and the 1-silabicyclo[2.2.1]heptane molecule actually belongs to C_s symmetry. This result is in accord with our expectation; the number of the C–C bonds with unstable *cis* conformation is decreased from three to two and the skeleton is more strained, and both factors favor the untwisted conformation. We have, however, still one silacyclohexane ring with unstable boat conformation. It may thus be easy to twist the molecular skeleton. In fact, we found that the frequency of the skeletal torsion was as low as $70\ \text{cm}^{-1}$. It may be interesting to compare this value with the torsional frequency of $132\ \text{cm}^{-1}$ obtained for 7-thiabicyclo[2.2.1]heptane.[11]

We estimated only three structure parameters. The two angles, ∠C(2)–Si–C(6) and ∠Si–C(2)–C(3), may be compared with the corresponding angles, 103.5° and 104.3°, in norbornane.[5] It is interesting to note that Si–C(7) is considerably longer than Si–C(2) or the Si–C length (1.868 Å) in trimethylsilane.[8] The ∠Si–C(7)–C(4) angle is calculated to be 87.1° using the parameters of Table 5.

The dipole moment of 1-silabicyclo[2.2.1]heptane is close to that of trimethylsilane (0.525 D),[8] although methylsilane[12] and dimethylsilane[7] have the dipole moments of about 0.2 D larger.

The calculation in the present work is carried out at the Computation Center of Kyushu University.

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