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Registry No. $\text{CH}_2=\text{C}=\text{CH}^+$, 12542-67-5; $\text{CH}_3\text{C}\equiv\text{C}^+$, 24858-94-4; $\text{CH}_2=\text{CH}-\text{C}^+$, 88000-25-3; $\text{CH}\equiv\text{C}-\text{CH}_2-\text{I}$, 659-86-9; $\text{CH}_3\text{C}\equiv\text{CC}$ -

H_3 , 503-17-3; $\text{HC}\equiv\text{CCH}_2\text{CH}_3$, 107-00-6; $\text{HC}\equiv\text{CCH}_2\text{Br}$, 106-96-7; $\text{HC}\equiv\text{CCH}_2\text{Cl}$, 624-65-7; $\text{CH}_3\text{C}\equiv\text{CD}$, 7299-37-8; $\text{CH}_2\text{CH}=\text{CH}$, 2781-85-3; $\text{CH}_3\text{C}\equiv\text{CH}$, 74-99-7; $\text{CH}_2\text{CH}=\text{C}^-$, 80251-77-0; $\text{CH}_2=\text{C}=\text{CH}^-$, 64066-06-4; $\text{CH}_3\text{C}\equiv\text{C}^-$, 36147-87-2; $\text{CH}_2=\text{C}=\text{CH}_2$, 463-49-0; cyclopropenium, 26810-74-2.

Polarized Infrared Spectroscopy of Matrix-Isolated Dimethylsilylene and 1-Methylsilylene

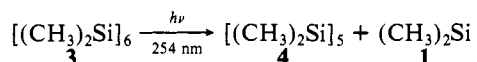
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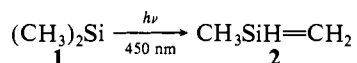
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Abstract: Dimethylsilylene (**1**) was generated in an argon matrix by irradiation of dodecamethylcyclohexasilane and photolyzed at 450 nm to produce 1-methylsilylene (**2**). Irradiation with linearly polarized light yielded matrices with both **2** and residual **1** partially oriented by photoselection. From the polarized infrared spectra of such samples, many of the absorption bands were classified as in-plane or out-of-plane polarized. Detailed assignments of the infrared spectra of **1** and **2** were made, based on comparison with spectra calculated with an MNDO program and with spectra of related molecules. The Si=C stretch in **2** falls at 988 cm^{-1} .

The reactive organosilicon species, dimethylsilylene (**1**) and 1-methylsilylene (**2**), have been produced photochemically and characterized spectroscopically in both 3-methylpentane (3-MP) glass and argon matrix.^{2,3} In these experiments **1** was obtained by 254-nm irradiation of dodecamethylcyclohexasilane (**3**):²



It is stable for hours in an argon matrix at temperatures as high as 35 K. In 3-MP glass at 77 K, the same species was obtained⁴ by irradiation of bis(trimethylstannyl)dimethylsilane, as judged by UV-vis spectrum, but in an argon matrix at 10–20 K this precursor fails to undergo significant photolysis. Bleaching of the yellow **1** by irradiation with 450-nm light induces its photoconversion to the colorless **2**:³



This species is also stable for hours in an argon matrix at 35 K and below, but warming of the bleached argon matrix to 50 K leads to its dimerization and formation of a mixture of dimethyl-1,3-disilacyclobutanes,³ identified by mass spectrometry and by comparison of several infrared absorption bands with those in the room-temperature spectra of an authentic sample.⁵ In contrast, warming of a 3-MP glass containing **2** to ~100 K in the presence of trapping agents gave products expected for the trapping of **1** rather than those expected from the trapping of **2**.³ The simplest interpretation of this result is to postulate that **2** undergoes fast thermal rearrangement to **1** at 100 K, and this was proposed as likely in ref 3. However, more recent work from several laboratories suggests that a more complex mechanism needs to be postulated: pyrolytic production of silenes appears to produce

evidence for silylene formation either not at all⁶ or only when very high temperatures are used,^{7,8} state-of-art calculations suggest that the **2** → **1** conversion is thermoneutral but has an activation barrier of about 40 kcal/mol,⁹ and the authors of an ion cyclotron resonance study suggest that the conversion is actually endothermic by 28 kcal/mol.¹⁰ The considerable discussion which this subject has generated, and the questions which have been raised¹¹ concerning the correctness of the structural assignment of **2**, make it particularly important to examine the spectra of **1** and **2** in argon matrices in more detail. In the present paper, we report a number of new bands in the infrared spectra of **1** and **2** and show that both spectra are perfectly compatible with the proposed structures. In a separate communication,¹² we reported the reactions of **1** and **2** with N_2O in argon matrix at 35 K, which suggest a possible resolution of the above described dilemma. We now consider it likely that the "thermal rearrangement" of **2** to **1** is in fact a complex process brought about by reaction with the trapping agent.

Several inorganic silylenes have previously been characterized by infrared spectroscopy. The parent compound, SiH_2 , was first produced in an argon matrix by Milligan and Jacox.¹³ Margrave and co-workers have studied a series of halogenated and hydroxy-substituted silylenes and have provided complete vibrational analyses of these species.¹⁴ While organosilylenes have been implicated in a number of reactions,¹⁵ to our knowledge only a few direct observations have been reported,^{2,3,16} and no detailed

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vibrational spectroscopic analysis has been provided for any such species.

Silenes, which contain a silicon-carbon double bond, have been identified spectroscopically in a number of experiments. The parent compound, silene, and its deuterio and chloro derivatives have been studied by Maier et al., who reported a number of infrared bands,⁶ confirmed the photochemical conversion $1 \rightarrow 2$, and reported the reverse photochemical transformation $2 \rightarrow 1$.¹⁶ Maltsev et al.¹⁷ have examined the infrared spectra of 1,1-dimethylsilene and its deuterated derivatives. They assigned the C=Si stretch to a band at 1003 cm^{-1} and tentatively identified a band at 825 cm^{-1} as belonging to a CH_2 out-of-plane wag. A second study of this compound confirmed their observations.¹⁸ Infrared spectra of 1,1,2-trimethylsilene have been published by Chapman et al.¹⁹ and Chedekel et al.²⁰ A complex stable silene with bulky substituents has been prepared by Brook and co-workers, and an infrared band at 1135 cm^{-1} has been assigned to the C=Si stretch.²¹

Experimental Section

Dimethylsilylene was generated by the 254-nm irradiation of **3** trapped in an argon or nitrogen matrix. Upon irradiation with 450-nm light dimethylsilylene undergoes a slow photoconversion to 1-methylsilylene.

Infrared spectra were recorded on a Nicolet 7199 FT IR spectrometer with 0.5-cm^{-1} resolution before and after 254- and 450-nm irradiation in a number of experiments and stored for later analysis. Typically, 400 scans were accumulated for each spectrum.

Matrices were formed on a CsI window cooled with an Air Products Displex closed-cycle helium cryostat. The light sources used included an Ultraviolet Products, Inc., low-pressure mercury lamp, a Gates 100-W medium-pressure mercury lamp, and a PEK high-pressure mercury lamp.

Argon or nitrogen as the matrix gas was passed over crystals of **3** contained in a glass trap attached to the vacuum shroud of the cryostat. A cryostat temperature of 28 to 30 K resulted in matrices of good optical quality and suitable rigidity. Deposition rates for matrix gases were about 0.2 mmol/min. The concentration of **3** in the matrix was not measured in these experiments but was estimated to be in the range of 0.1 to 1%. Irradiation of **3** to produce **1** was sometimes carried out simultaneously with deposition and sometimes subsequent to deposition with no observable differences in the resulting spectra. Complete bleaching of **1** to produce **2** typically required 10 to 16 h of irradiation with the high-pressure mercury lamp with a Balzers K-2 interference filter to select the 450-nm light.

Experiments with polarized irradiation used a calcite prism polarizer to produce polarized 450-nm light. Polarized infrared spectra were obtained with an aluminum grid polarizer (Cambridge Physical Sciences, Ltd.) placed in the sample beam.

Results

IR Frequencies of 1 and 2. The dominant features in all spectra were the bands of the starting cyclohexasilane **3** and of the by-product, the cyclopentasilane **4**. Some of the infrared bands of **1** and **2** are well separated from these dominant spectral features while others are so strongly overlapped by these stronger bands that their presence is not easily detected. Subtraction of a spectrum taken before bleaching with 450-nm irradiation from a spectrum of the same matrix after bleaching should reveal the spectrum of **2** as positive peaks relative to the base line and that of **1** as negative peaks. However, the inevitable small intensity changes and frequency shifts that occur in the spectra of **3** and **4** during the long irradiation period result in spurious peaks in the difference spectrum, which make unequivocal assignment of

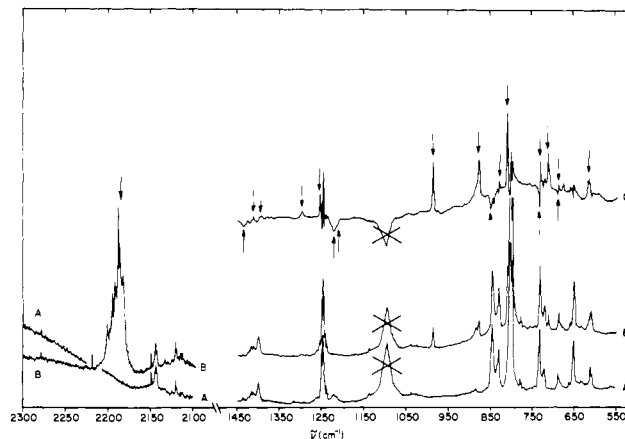


Figure 1. IR spectrum of an argon matrix (28 K) containing dodecamethylcyclohexasilane (**3**): A, after partial conversion to dimethylsilylene (**1**) and decamethylcyclopentasilane (**4**) with 254-nm light; B, after subsequent conversion of **1** to 1-methylsilylene (**2**) with 450-nm light. The difference spectrum C is shown on top, with upward arrows indicating the peaks of **1** and downward arrows indicating the peaks of **2**.

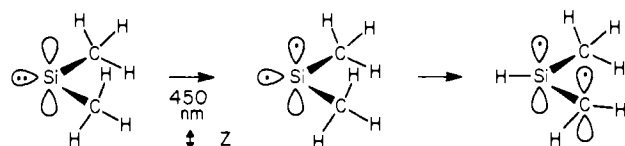


Figure 2. The photoconversion of dimethylsilylene (**1**) to 1-methylsilylene (**2**). The absorbing transition moment is oriented along z .

the complete infrared spectrum of the silylene less straightforward than one would wish. In Figure 1 a sample spectrum indicates the nature of the original and difference spectra for a typical experiment.

A total of nine different experiments were performed, and the resulting difference spectra were compared to determine the common features attributable to **1** and **2**. Slight matrix shifts of a few wavenumbers were observed in comparing spectra in argon matrices with those in nitrogen. The bands identified as a result of these comparisons are listed in Tables I and II.

Polarization Measurements. In the usual electric dipole approximation, absorption probability is proportional to the square of the projection of the absorbing transition dipole moment into the direction of the electric vector of the light. We shall define a molecular system of orthogonal axes such that the absorbing transition moment is oriented along z , while x and y are chosen arbitrarily. Molecules of **1** produced in the matrix by the irradiation of **3** with unpolarized light will therefore have a random orientation relative to all directions perpendicular to the direction of propagation of the photolyzing light and as a result will exhibit no linear dichroism when observed along the latter direction. If, however, **1** is partially bleached by linearly polarized 450-nm irradiation whose electric vector lies along the Z axis in the laboratory frame, those molecules whose z axis lies nearly parallel to Z will be preferentially excited and converted to **2**. Therefore, the remaining molecules of **1** will be partially oriented with their z direction mostly tilted away from the Z axis of the sample. Unless the photochemical process induces an essentially random rotation of the molecule, the resulting molecules of **2** will be partially oriented in a complementary fashion, with their z axis tilted towards the Z axis of the sample. Both sets of molecules, **1** and **2**, will exhibit dichroism in the UV-vis as well as the IR regions. These orienting effects of light are well known under the name of photoselection.²² A more quantitative treatment of the particular photoselection process of interest presently is available²³ but will not be needed presently.

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Table I. Dimethylsilylene (1) Vibrations

	calculated			observed		
	wavenumber, cm ⁻¹	intensity, cm ² /mol	assignment	wavenumber, cm ⁻¹	intensity (relative)	polarization
1	3335	4	a ₁ CH ₃ stretch			
2	3334	3	b ₁ CH ₃ stretch			
3	3261	307	a ₁ CH ₃ stretch			
4	3260	330	b ₁ CH ₃ stretch			
5	3256	592	b ₂ CH ₃ stretch			
6	3254	0	a ₂ CH ₃ stretch			
7	1442	37	b ₂ as CH ₃ deformation	1435 ^a	m	
8	1439	0	a ₂ as CH ₃ deformation			
9	1431	48	a ₁ as CH ₃ deformation			
10	1429	23	b ₁ as CH ₃ deformation			
11	1394	1300	a ₁ sym CH ₃ deformation	1220 ^b	s	in plane
12	1389	1515	b ₁ sym CH ₃ deformation	1210 ^b	m	in plane
13	841	5870	a ₁ in-plane CH ₃ rock	850 ^c	s	
14	831	8870	b ₁ in-plane CH ₃ rock	806 ^c	vs	
15	754	566	a ₁ sym Si-C stretch	690 ^d	m	
16	699	424	b ₁ as Si-C stretch	735 ^d	m	
17	635	0	a ₂ out-of-plane CH ₃ rock			
18	608	21	b ₂ out-of-plane CH ₃ rock			
19	293	1635	a ₁ C-Si-C bend			
20	0.1	14	b ₂ torsion			
21	0.03	0	a ₂ torsion			

^a This observed band could correspond to one or more of the calculated vibrations: 7, 9, and 10. ^b The assignment of these two bands to calculated vibrations 11 and 12, respectively, could also be interchanged (12 and 11, respectively). ^c The assignment of these two bands to calculated vibrations 13 and 14, respectively, could also be interchanged (14 and 13, respectively). ^d The assignment of these two bands is reversed compared with the calculated order, so that the b₁ stretch is assigned to the higher frequency.

Table II. 1-Methylsilene (2) Vibrations

	calculated			observed		
	wavenumber, cm ⁻¹	intensity, cm ² /mol	assignment	wavenumber, cm ⁻¹	intensity (relative)	polarization
1	3413	80	a' sym CH ₂ stretch			
2	3383	72	a' as CH ₂ stretch			
3	3351	163	a' sym CH ₃ stretch			
4	3287	140	a' as CH ₃ stretch			
5	3277	250	a'' as CH ₃ stretch			
6	2280	330	a' Si-H stretch	2188	s	in plane
7	1433	47	a'' as CH ₃ deformation	1412 ^a	m	
8	1429	125	a' as CH ₃ deformation	1397 ^a	m	
9	1425	114	a' CH ₂ scissoring	1300	m	
10	1384	1700	a' sym CH ₃ deformation	1254	s	in plane
11	1049	2150	a' Si=C stretch	988	s	in plane
12	992	333	a'' CH ₂ out-of-plane wag	830	s	
13	863	8740	a' CH ₂ + SiH in-plane bend	880 ^b	s	in plane
14	831	2820	a' in-plane CH ₃ rock	812 ^b	vs	in plane
15	769	2550	a'' out-of-plane CH ₃ rock	714	m	out of plane
16	747	1300	a' Si-C stretch	732 ^c	m	in plane
17	681	2360	a' SiH + CH ₂ in-plane bend	688 ^c	w	in plane
18	599	12000	a'' CH ₂ twist + SiH out-of-plane bend	615	m	out of plane
19	329	28200	a'' SiH out-of-plane bend + CH ₂ twist			
20	224	18600	a' C-Si-C bend			
21	46	495	a'' CH ₃ torsion			

^a The assignment of these two bands to calculated vibrations 7 and 8, respectively, could also be reversed (8 and 7, respectively). ^b The assignment of these two bands to calculated vibrations 13 and 14, respectively, could also be reversed (14 and 13, respectively). ^c The assignment of these two bands to calculated vibrations 16 and 17, respectively, could also be reversed (17 and 16, respectively).

The electronic transition in **1** can be safely assumed to be similar to that of the parent silylene,²⁴ in which an electron is promoted from the lone pair in a hybrid orbital of σ symmetry into the empty p orbital of π symmetry. This defines the z direction as the one perpendicular to the C-Si-C plane (Figure 2). Thus, in the infrared spectrum of **2** the out-of-plane (z) polarized vibrations will have greater absorption E_Z for light polarized along the sample axis Z , while the in-plane (x,y) polarized vibrations will have greater absorption E_Y for light whose electric vector lies perpendicular to Z . Conversely, in the IR spectrum of the remaining **1**, the (x,y)-polarized vibrations will preferentially contribute to E_Z and the z -polarized vibrations will preferentially contribute to E_Y .

In three experiments dimethylsilylene was bleached with 450-nm radiation polarized along Z . Infrared spectra were then recorded with the infrared beam both parallel and perpendicular to Z . These spectra exhibited the expected infrared linear dichroism indicative of partial orientation of **1** and **2**. While the signal-to-noise ratio in the $E_Z - E_Y$ spectra (Figure 3) was not sufficient to determine dichroic ratios for all of the spectral bands, it was possible to identify certain bands as being either in-plane- (z) or out-of-plane- (x,y) polarized vibrations. These symmetry identifications are included in Tables I and II.

IR Spectra—MNDO Calculations. The vibrational frequencies and normal modes were calculated with an MNDO program developed by Dewar and collaborators²⁵ and modified in our labo-

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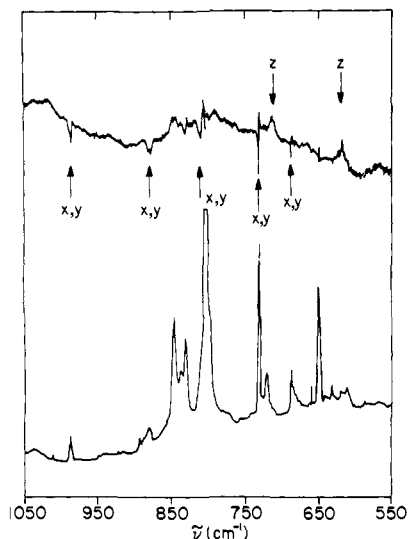


Figure 3. IR absorption (bottom) and dichroic difference ($E_z - E_y$, top) spectra of 1-methylsilene (**2**) obtained by irradiation of argon-matrix-isolated dimethylsilylene (**1**) with Z-polarized 450-nm light. Arrows indicate IR polarization directions: z, parallel to the 450-nm transition moment; x, y perpendicular to it. Peaks which are unmarked do not appear reproducibly.

ratory to yield also intensities and transition moment directions.²⁶

Discussion

An assignment of the observed vibrational bands to characteristic group frequencies can be made on the basis of comparison with the assignments for related molecules and comparison with the calculated vibrational spectrum. These assignments are included in Tables I and II. In the spectrum of **3** the CH stretching region above 2900 cm^{-1} consists of two broad bands. The width of these features renders difficult the observation of distinct C-H stretching modes for **1** and **2**, although some changes in this region are observed upon bleaching. No spectra were recorded below 400 cm^{-1} . The following discussion focuses on the bands observed in the region between 400 and 2500 cm^{-1} .

Dimethylsilylene (1). This molecule has C_{2v} symmetry with 21 vibrations distributed among irreducible representations as shown in Table I. The normal modes may be assigned to nominal group frequencies as indicated in Table I, but it should be recognized that for vibrations of similar frequency there is considerable mixing of these usual group frequencies so that the assignment to a single group vibration is only a convenient approximation.

The approximate frequencies of the various normal modes can be estimated by examination of the spectra of molecules of similar structure. The only known molecule that is exactly isostructural with **1** appears to be dimethylstannylene whose matrix-isolation infrared spectrum has been reported very recently,²⁷ and another quite suitable molecule for comparison is dimethyl sulfide.²⁸ In the spectra of both of these, the C-H stretches occur near 2900 cm^{-1} . The antisymmetric methyl deformations have not been observed in $(\text{CH}_3)_2\text{Sn}$ and appear above 1400 cm^{-1} in $(\text{CH}_3)_2\text{S}$. The symmetric methyl deformations lie at a strikingly low frequency for $(\text{CH}_3)_2\text{Sn}$, 1182 and 1187 cm^{-1} , while in $(\text{CH}_3)_2\text{S}$ they are above 1300 cm^{-1} . Methyl rocks are near 750 cm^{-1} in $(\text{CH}_3)_2\text{Sn}$ and near 1000 cm^{-1} in $(\text{CH}_3)_2\text{S}$. The C-Sn stretching vibrations lie near 460 cm^{-1} and the C-S stretching vibrations near 700 cm^{-1} . The CSC bend is at 282 cm^{-1} and the b_2 torsion at 182 cm^{-1} .

Vibrational frequencies for **1** and related molecules calculated by using the MNDO program are included in Table I and Figure 4 along with the experimental frequencies. The calculated fre-

quencies are systematically higher than the experimental frequencies, and Dewar et al. have published a list of correction factors for a wide range of molecules.²⁹ The calculated polarizations provide a unique assignment of each vibration to the appropriate symmetry species.

In Figure 4, the calculated and experimental spectra of **1**, dimethylsilane,³⁰ and dimethyl sulfide²⁸ and the reported spectrum of dimethylstannylene²⁷ are displayed for purposes of comparison. The antisymmetric methyl deformation modes for the first three molecules are clustered in the 1430- to 1480- cm^{-1} region, and the calculated positions are quite close to the observed frequencies. The symmetric methyl deformation modes occur at frequencies that are lower by 150 to 220 cm^{-1} than those of the antisymmetric deformations. In this case, the calculated frequencies are significantly higher than the observed frequencies. The low frequencies of the silane and silylene modes compared with the sulfide agree with the calculated spectra for those compounds, which also place these vibrations lower than those in dimethyl sulfide, but the calculated difference is not nearly large enough. The similarity of these frequencies in $(\text{CH}_3)_2\text{Si}$ and $(\text{CH}_3)_2\text{Sn}$ is striking. It appears that a lower electron density on the central atom leads to a decrease in the symmetric methyl deformation frequency, presumably due to the involvement of the methyl group in hyperconjugative electron density donation.

The three infrared active methyl rocking motions appear in the neighborhood of 1000 cm^{-1} for $(\text{CH}_3)_2\text{S}$, at 739, 745, and 774 cm^{-1} in $(\text{CH}_3)_2\text{Sn}$, and near 850 cm^{-1} for $(\text{CH}_3)_2\text{SiH}_2$. We observe only two bands for **1** which can be assigned to methyl rocking motions, at 806 and 850 cm^{-1} , fairly close to the $(\text{CH}_3)_2\text{Sn}$ bands and to the calculated frequencies. It is worth noting that the calculated frequencies of the a_2 and b_2 modes for $(\text{CH}_3)_2\text{Si}$ fall considerably lower, between 600 and 700 cm^{-1} . The normal coordinate displacements resulting from the MNDO calculations involve some mixing of the methyl rocking motions and the skeletal stretches, particularly in the case of $(\text{CH}_3)_2\text{Si}$.

For **1** the assignments of the antisymmetric C-Si stretch at 735 cm^{-1} and the symmetric stretch at 690 cm^{-1} are consistent with the assignments for $(\text{CH}_3)_2\text{SiH}_2$, $(\text{CH}_3)_2\text{Sn}$, and $(\text{CH}_3)_2\text{S}$, but we cannot be sure that they are not reversed. The calculated normal coordinate displacements indicate that b_1 -type methyl rock and C-Si stretching vibrations are strongly mixed and, in fact, suggest that the calculated band at 699 cm^{-1} is predominately the methyl rock, while the calculated band at 831 cm^{-1} is predominately the C-Si antisymmetric stretch.

1-Methylsilene (2). Previous calculations of the geometry of silenes indicate a planar geometry about the silicon atom.³¹ Planar 1-methylsilene would have 14 in-plane and 7 out-of-plane vibrations as indicated in Table II, and a reasonable model molecule would be propene.

The propene spectrum is well known although there are some discrepancies in the published vibrational assignments.³² The assignment of the normal modes for propene is displayed in Figure 5. If the bonding conditions are similar, we may expect a slight shifting of frequencies in **2** for those vibrations involving only carbon and hydrogen and a substantial reduction in frequency for the bands of vibrations involving the silicon atom.

The optimized MNDO geometry is distinctly pyramidal at the silicon atom. Since no other calculations that we are aware of predict a nonplanar geometry at silicon,³¹ we are on less safe

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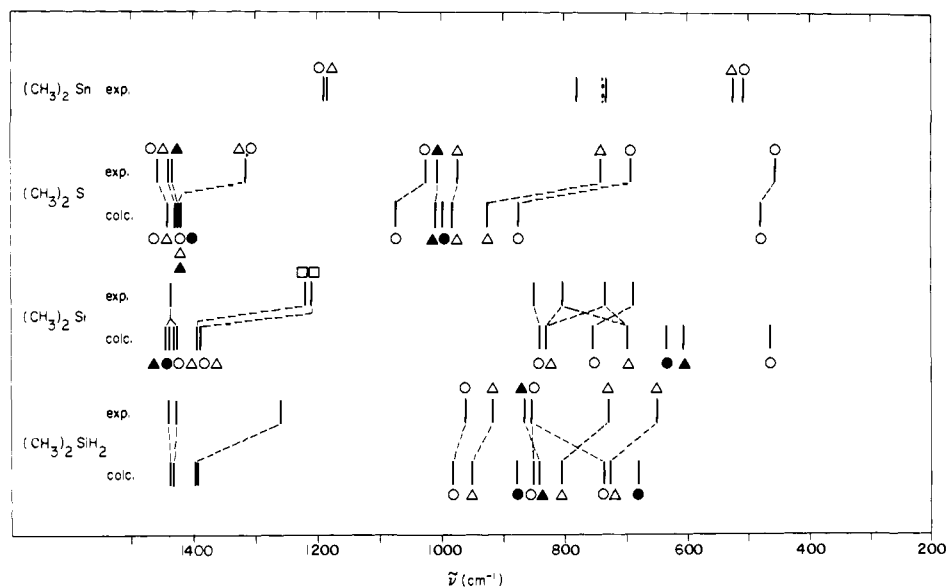


Figure 4. IR frequencies of vibrations: observed and calculated (MNDO). Symmetry code: (○) a_1 , (●) a_2 , (Δ) b_1 , (▲) b_2 , (□) out of C-Si-C plane, (■) in plane.

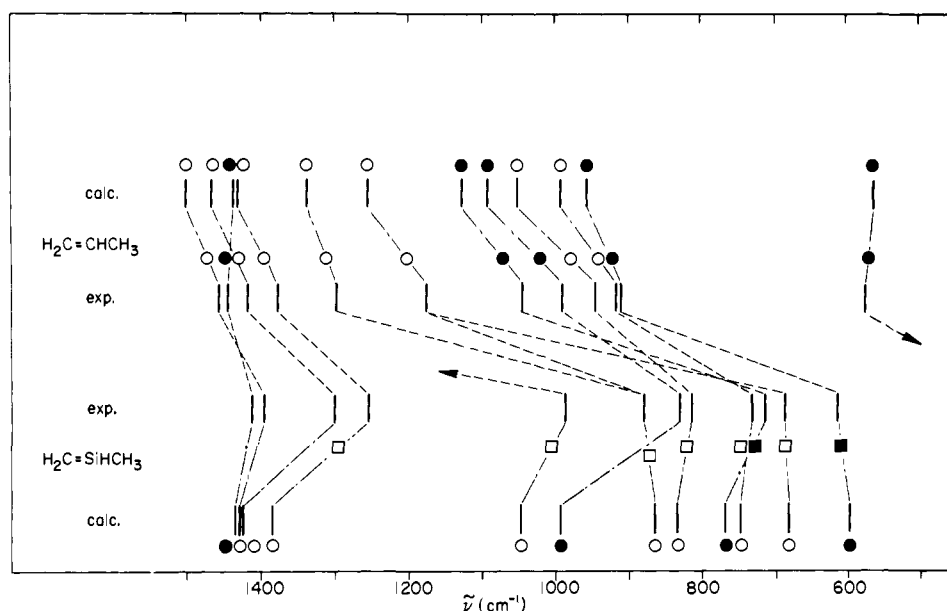


Figure 5. IR frequencies of vibrations: observed and calculated (MNDO). Symmetry code: see caption to Figure 4.

ground in an attempt to use the calculated vibrational properties for this molecule as a guide for vibrational assignments than was the case for dimethylsilylene.

The bands at 880, 998, and 2188 cm^{-1} stand out clearly upon bleaching of dimethylsilylene. The other bands listed in Table II are clearly visible in the subtracted spectrum and in general are more readily characterized than the bands of **1**.

The Si-H stretch at 2188 cm^{-1} is a broad band with several maxima between 2180 and 2200 cm^{-1} . Si-H stretching modes fall between 2100 and 2150 cm^{-1} for silanes, and Maier et al.⁶ report bands at 2219 and 2239 cm^{-1} for the parent silene. The propene C-H stretch at 3017 cm^{-1} is 39 cm^{-1} below the average of the CH_2 stretches in ethylene,³² while the 2188- cm^{-1} band in **2** is 41 cm^{-1} below the average of the two bands reported⁶ for silene. We attribute the broad, multip peaked nature of this band in our experiments to the influence of different matrix sites. The polarized infrared spectrum shows that this band belongs to an in-plane motion.

Twelve bands in the region from 500 to 1500 cm^{-1} are assigned as vibrations of silapropene. Seven of these bands are clearly due to in-plane vibrations, and two are out-of-plane vibrations. We were not able to determine the polarization of the other three bands.

The antisymmetric methyl deformation vibrations occur at 1397 and 1412 cm^{-1} and the symmetric deformation at 1254 cm^{-1} , values which are considered typical³³ for CH_3 attached to Si. The band at 1300 cm^{-1} is assigned to the CH_2 scissoring motion by analogy to propene.

The Si=C stretch appears at 988 cm^{-1} and is calculated by the MNDO program to be at 1048 cm^{-1} . This band is observed to be an in-plane vibration with the less intense satellites due to ^{29}Si and ^{28}Si occurring at 981 and 975 cm^{-1} , respectively. The MNDO calculated isotopic shift for this vibration is 4 cm^{-1} for ^{29}Si , somewhat less than the 7 cm^{-1} observed.

The in-plane Si-H and CH_2 bends are mixed in the calculated normal coordinate displacements. Bands at 688 and 880 cm^{-1} (or possibly, 812 cm^{-1}) are assigned to these motions with the lower

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frequency best identified as the Si-H bend.

Methyl rocking modes occur at 812 cm^{-1} (or possibly, 880 cm^{-1}) for the in-plane rock and 714 cm^{-1} for the out-of-plane rock. The latter band is lower than the usual frequency for such vibrations. Our assignment is based on the observed out-of-plane polarization and the calculated frequency this vibration, 769 cm^{-1} .

The in-plane vibration at 732 cm^{-1} is assigned to the Si-C single-bond stretch and that at 688 cm^{-1} to a combined Si-H and CH_2 in-plane bend. The Si-C stretch value is close to the b_1 stretch in **1** at 735 cm^{-1} . A less likely but possible assignment is the reverse, the Si-C stretch at 688 cm^{-1} and the bend at 735 cm^{-1} .

The out-of-plane CH_2 wag presents a problem. This motion has a calculated frequency of 992 cm^{-1} which would appear to correspond to the observed band at 880 cm^{-1} . However, this band clearly has in-plane polarization. The only remaining plausible candidate for this assignment is the 830-cm^{-1} band whose polarization has not been determined unambiguously because of the presence of substantial dichroism in the spectrum of residual **3** at this frequency. Such an assignment by default is less satisfactory than the rest and will have to remain tentative until additional experimental data are available. Some of the discrepancy between the calculated and assigned frequency of this vibration may be related to the fact that the calculated geometry of silapropene is pyramidal at the Si atom and therefore does not have a plane of symmetry which we assume in our discussion. If the molecule were indeed nonplanar, then the observed polarizations could deviate significantly from those expected for normal modes of a planar molecule.

The band at 615 cm^{-1} has out-of-plane polarization and is assigned to a motion which includes both CH_2 twist and Si-H out-of-plane bends. The other combination of these two motions is calculated to occur at 329 cm^{-1} , outside the range of the present study.

In view of the interest in the properties of the Si=C double bond relative to the C=C double bond, a brief summary of the comparison with propene is called for (Figure 5). The calculated spectrum of propene compares well with its observed frequencies except that the calculated C=C stretch is at 1825 cm^{-1} , much higher than the experimental frequency at 1650 cm^{-1} . Since there is a discrepancy in the description of some of the normal modes in previous analyses³² and the MNDO calculations provide normal coordinate displacements that represent mixtures of various simple group vibrations, the descriptions we provide are approximations based on the MNDO calculations.

The most interesting feature of the spectrum of **2** is the Si=C stretch at 988 cm^{-1} . This frequency is considerably lower than the C=C stretch at 1650 cm^{-1} . The ratio of C=C to C-C stretching frequencies in propene is 1.81 while that for Si=C to Si-C in **2** is 1.35. These comparative values are consistent with a weaker Si=C π bond which can be attributed to the larger size of the Si atom. In the parent silene Maier *et al.*⁶ reported a weak band at 985 cm^{-1} , which shifts to 952 cm^{-1} upon dideuteration on silicon, and this presumably also corresponds to the Si=C stretch. In 1,1-dichlorosilene, they reported a stronger band at

1008 cm^{-1} , presumably of the same origin. Two studies of dimethylsilene^{17,18} have assigned the Si=C stretch in this compound to a band at 1003 cm^{-1} . The isobutene C=C stretch at 1660 cm^{-1} is 10 cm^{-1} higher than that of propene, so the 15-cm^{-1} difference in the C=C stretching frequency of 1,1-dimethylsilene and **2** is not unexpected. An ab initio calculation³³ of the structure of the parent silene predicted its Si=C stretch at 1140 cm^{-1} , while a more recent calculation³⁴ gave 1069 cm^{-1} . These results are consistent with our assignment for **2**.

The methyl deformations are shifted to lower frequencies in **2** as is the case for $\text{CH}_3\text{-Si}$ groups in other compounds when compared with the corresponding $\text{CH}_3\text{-C}$ vibrations.³⁵ The methyl rocks also occur at frequencies lower than those in propene, but the order of the in-plane and out-of-plane rocks is reversed in **2** with the in-plane rock appearing 100 cm^{-1} higher than the out-of-plane rock.

The Si-H in-plane and out-of-plane bends are strongly mixed with the CH_2 bends in the MNDO calculations and as expected occur at a lower frequency than the corresponding CH_2 vibrations in propene.

Conclusion

The infrared spectral measurements reported here confirm the earlier structural assignments^{2,3} for **1** and **2**.

The infrared spectrum of **1** shows considerable resemblance to that of dimethylstannylene and dimethyl sulfide. The most significant differences between the three compounds are observed in the frequency of the symmetric methyl deformation vibration, which is much lower in $(\text{CH}_3)_2\text{Si}$ and $(\text{CH}_3)_2\text{Sn}$ than in $(\text{CH}_3)_2\text{S}$.

The infrared spectrum of 1-methylsilene (**2**) is rather similar to that for propene but with the absorption bands generally shifted to lower frequencies. As expected, the largest shifts are found for the absorptions in which the silicon atom is directly involved. The observed shifts probably reflect lower force constants for Si-C modes as well as the greater mass of silicon compared to carbon. The very large shift of the double bond stretching absorption from 1650 cm^{-1} in propene to 988 cm^{-1} in **2** is consistent with a much lower π -bond strength for Si=C than for C=C.

The Si-H stretch in **2** falls at a high frequency, about 100 cm^{-1} above the usual Si-H stretching region in trialkylsilanes. This frequency difference is similar to that found for vinylic C-H stretching modes and suggests that in silenes as in alkenes the σ bonds to hydrogen are strengthened by increased s-orbital participation. This is consistent with the contrasting unusually low Si-H frequencies found in silylenes^{14,16} in which the σ bonds to hydrogen have decreased s-orbital participation.

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