The Raman, Ultraviolet, and Infrared Spectra and the $J_{\mathrm{Si=C}}$ NMR Coupling Constant of the Stable Silene (t-BuMe$_2$Si)(Me$_3$Si)Si═2-Ad. Manifestations of the Si═C Double Bond

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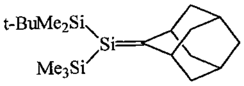
The UV, preresonance Raman, and IR spectra of the stable silene t-BuMe$_2$Si(Me$_3$Si)Si═2-Ad (**1**) have been measured as well as its $J_{\mathrm{Si=C}}$ NMR coupling constant. The normal modes involving the ν(Si═C) stretching coordinate were identified for the first time for a stable silene. The experimental data and computations of potential energy distribution and mode eigenvectors show that there is no single vibrational normal mode which can be assigned as ν(Si═C). Raman intensity enhancement on approaching resonance strongly supports the conclusion that there are five lines in the region 1000−1370 cm^{-1} which include significant contribution from the ν(Si═C) stretching coordinate. Both the Si═C force constant and the $J_{\mathrm{Si=C}}$ NMR coupling constant (as well as the Si═C bond length) indicate that the Si═C bond order is smaller in **1** than that in simpler silenes of the type R$_2$Si═CH$_2$ (R = H, Me).

Introduction

Since the presentation of the first firm evidence for the existence of compounds with a Si═C double bond (silenes) in 1967,[1] there is growing interest in the physical and chemical properties of these compounds.[2,3] Most known silenes are transient species,[2,3] and only three silenes have so far been characterized by X-ray structure analysis.[4−6] From those stable silenes the silene (t-BuMe$_2$Si)(Me$_3$Si)Si═2-Ad (**1**)[6] is the focus of this paper.



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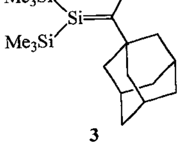
Vibrational spectroscopy was the most popular method for identifying simple transient silenes and this is why the identification of the Si═C stretching mode ν(Si═C) is important. For most known simple transient silenes, only matrix-isolated IR spectra were obtained.[2,3] These IR spectra were recently comprehensively reviewed, discussed, and analyzed on the basis of density functional theory (DFT) calculations.[7] For simple silenes of the type R$_2$Si═CH$_2$ (R = H, Me, Cl), it was shown that the ν(Si═C) mode is well localized, 80−100% in potential energy distribution (PED), exhibiting an IR band of variable intensity (from weak to strong) with its frequency lying in the region of 980−1020 cm^{-1}. However, already for the trimethyl substituted silene Me$_2$Si═CHMe (**2**), according to estimated PED data, the Si═C stretching mode appeared to be not distinguishable. In **2**, the ν(Si═C) internal vibrational coordinate gives small contributions (within 10−15%) to five calculated normal modes with frequencies extending from 780 to 1350 cm^{-1}.[7] In this situation, it is of interest to investigate the Raman spectra of silenes, because it is known that double bonds exhibit intense Raman lines due to their high polarizability.[8] Thus, one could expect a high intensity ν(Si═C) line in the Raman spectra of silenes.

To our best knowledge, the only previously reported Raman spectrum of a silene is that of (Me$_3$Si)$_2$Si═C(OSiMe$_3$)(1-Ad) (**3**) reported by Brook et al.[4] Several very intense lines were observed in this spectrum in the region of 1000−1300 cm^{-1}. However, by analogy with simple silenes of the type R$_2$Si═CH$_2$, the ν(Si═C) stretching mode was tentatively assigned to one of the three lines of medium intensity at either 935, or 975 or 1005 cm^{-1}.[4,9] In addition, Okazaki et al. have reported that the most intense Raman line of 1-silanaphthalene **4** appears at 1368 cm^{-1} (no other details were given).[10] We note, however, that the vibrational spectra of aromatic compounds strongly differ from those of molecules containing a double bond.



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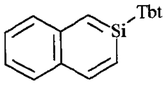

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In this paper we report the UV, preresonance Raman, and IR spectra of the stable silene **1,** as well as its $J_{\mathrm{Si=C}}$ NMR coupling constant. The normal modes involving the ν(Si═C) stretching coordinate were identified for the first time for a stable silene with bulky substituents. This was done experimentally and by computation of PED and mode eigenvectors. Both the Si═C

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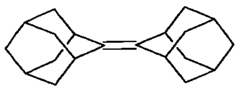
force constant and the $J_{\mathrm{Si=C}}$ NMR coupling constant (as well as the Si=C bond length) indicate that the Si=C bond order in **1** is less than in simple silenes of the type R$_2$Si=CH$_2$ (R = H, Me).

Experimental Section

The kinetically stable silene **1** was synthesized as reported previously.[6] 2,2′-biadamantylidene **5** was obtained as a byproduct in the thermolysis of 1,2-disilacyclobutane and was purified by column chromatography.[11] Adamantane was commercially available and was purified by sublimation before use. All experiments with **1** were carried out under high vacuum or under strictly inert atmosphere to prevent reaction with oxygen and sample decomposition. We found that **1** can be easily sublimed in high vacuum (10^{-4} Torr) at 35−40 °C. Sublimed crystals, sealed in a capillary, were used for the Raman measurements. The UV spectrum was obtained for the mull of **1** in Apiezon, which was prepared under inert atmosphere, as well as for the solution of **1** in pentane, dried over CaCl$_2$, and degassed. To obtain the IR spectrum, the substance was sublimed on a cooled (by liquid nitrogen) CsI window in a vacuum cryostat. Annealing of this sample was performed before registration of the IR spectrum.



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The UV absorption spectra of solid **1** and its solution in pentane were recorded with a computerized Carl Zeiss M-40 and a HP 8452A diode-array spectrophotometers, respectively. The Raman spectra of **1** were registered with a U-1000 and a T-64000 Jobin-Yvon laser Raman spectrometers, using excitation by 514.5 and 457.9 nm lines of an Ar$^+$ laser of type SP-2020. The IR spectrum was measured on a computerized Carl Zeiss M-82 spectrophotometer.

The NMR coupling constant $J_{\mathrm{Si=C}}$ was determined with a Bruker AC-200 instrument from the ^{13}C NMR spectrum of silene **1** in C$_6$D$_6$ solution, using the POWGATE program.

Molecular orbital calculations were carried out using the GAUSSIAN 98[12] series of programs. The geometries of all molecules of interest were optimized using the hybrid−density functional[13] B3LYP level of theory[14] with the 6-31G(d) basis set. Frequency calculations were performed at the same level of theory for all molecules, to characterize the stationary points as minima or saddle points. These calculations also involved determination of harmonic vibrational frequencies and normal mode eigenvectors. Transformation of the output obtained in Cartesian coordinates into internal vibrational coordinates was carried out using the NCA-99 program.[15] The resulting force constants were used for further model normal coordinate analysis (NCA),[16] which was accomplished with the program elaborated by Gribov and Dement'ev and updated for IBM-PC compatible computers.[17] UV transitions were calculated with the time-dependent-B3LYP (TD-B3LYP) method.[18]

Results and Discussion

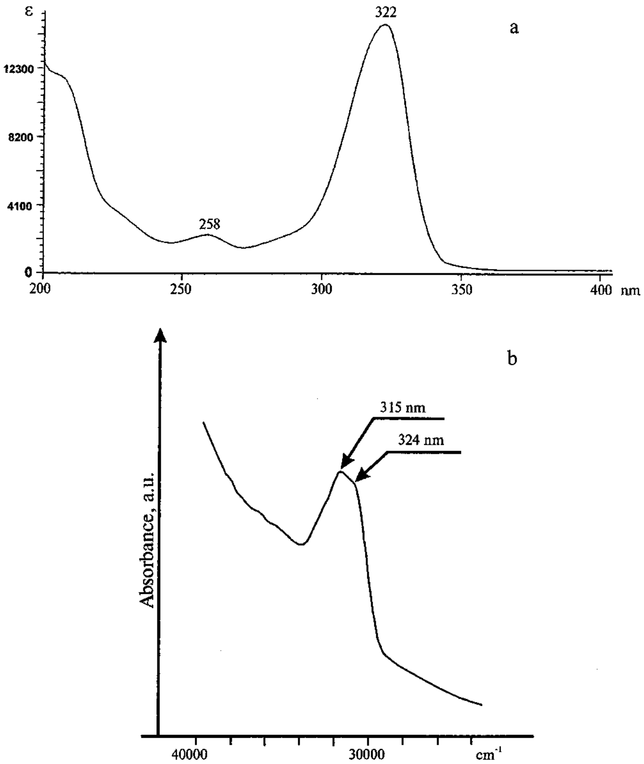


Figure 1. (a) UV spectrum of **1** in pentane solution (4.9 × 10^{-5}M), (b) UV spectrum of solid **1**.

UV Spectrum of 1. As Raman intensity is closely related to the position of the electronic absorption bands, it was necessary to study the UV spectrum of **1**. In pentane solution, silene **1** exhibits a main band at 322 nm with an $\epsilon = 15000$,[19] and a second, significantly less intense band at 258 nm (Figure 1a). The UV spectrum of solid **1** (as an Apiezon mull, Figure 1b), shows a broad absorption band with smoothed structure which include submaxima at 315 and 324 nm, in good accord with the spectrum of **1** in solution. Usually the lowest energy UV transition of simple silenes, corresponding to the $\pi-\pi^*$ transition, is located below 300 nm.[3c] However, the lowest energy absorption band measured for **1** (322 nm) is significantly red-shifted compared to that for H$_2$Si=CH$_2$ (258 nm), MeHSi=CH$_2$ (260 nm), or Me$_2$Si=CH$_2$ (244 nm). It should be noted, however, that the band of **1** at 322 nm is quite similar to that of **3** (339 nm).[3c,4,6] Ab initio calculations for model compounds confirm that the lowest energy transition in all silenes studied is indeed due to a $\pi-\pi^*$ transition and suggest that the batochromic shifts observed in the UV spectra of **1** and **3** are due to the bis-silyl substitution at the sp^2 silicon atom of these silenes. The calculations show that the π orbital of **1** is localized on the C=Si bond,[20a] while the π^* orbital is significantly delocalized between the C=Si bond and the silyl groups. TD-B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) calculations for **1** predict the lowest energy UV transition in **1** to be at 323 nm in excellent agreement with the experimental value.[20b] For comparison, predicted first UV transition in model (H$_3$Si)$_2$Si=CMe$_2$ (**6**) is 304 nm at the same level. The contour of the band at 322 nm is not symmetric with an asymmetry from the short-wavelength side up to 270 nm (Figure 1a). According to TD-B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) calculations, weak absorptions at 291, 284, and 282 nm could be hidden in this wing.

Raman Spectrum of Solid 1. The Raman spectrum of solid **1** excited by the 514.5 nm line of an Ar$^+$ laser is presented in Figure 2a along with the Raman spectra of 2,2′-biadamantylidene **5** (Figure 2b) and of adamantane (Figure 2c) recorded under the same conditions. The lines in the region below 700 cm^{-1} are surprisingly weak compared to those in the region 1000−1400 cm^{-1}. The most salient features in the spectrum of

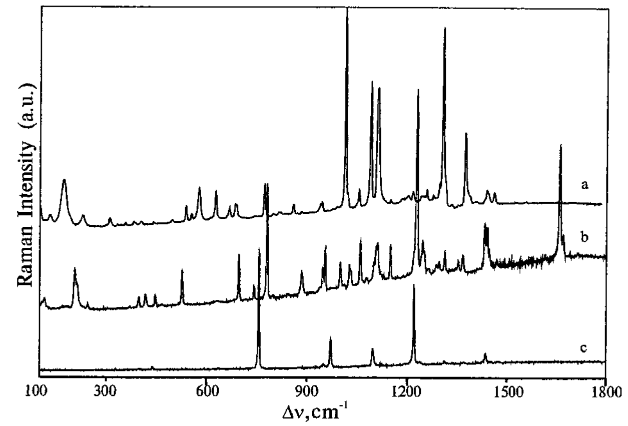


Figure 2. The Raman spectra of (a) solid **1**, (b) **5**, and (c) adamantane, excited by the 514.5 nm line of an Ar^+ laser and recorded under the same conditions.

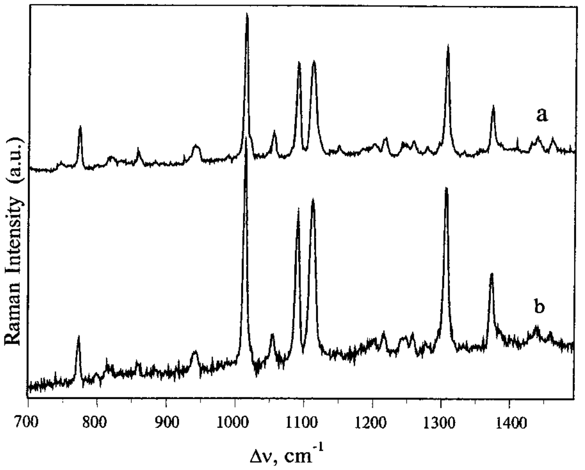


Figure 3. The Raman spectra of **1** obtained with different excitation lines. (a) $\lambda = 514.5$ nm; (b) $\lambda = 457.9$ nm.

1 are five lines at 1011, 1087, 1109, 1304 and 1371 cm^{-1}. A similar Raman pattern was reported for **3**.[4,9] It is evident from comparison of the three spectra in Figure 2 that the five intense lines mentioned above cannot belong to internal vibrations of the substituting adamantane moiety alone.[21,22]

Excitation of the Raman spectrum of **1**, with its lowest energy absorption band at ca. 320 nm (ν_e), by the green laser line at 514.5 nm (ν) brings about the so-called "preresonance" conditions: ($\nu_e - \nu \approx 11800$ cm^{-1}).[23] This should result in Raman intensity enhancement, primarily of the lines corresponding to normal modes involving the fragment where the lowest energy $\pi-\pi^*$ electronic transition is localized, that is, the Si=C bond. The Raman patterns observed by us for **1** (Figure 2a) and also those reported for **3**[4] allows us to suggest that the Si=C stretch is not localized, but is heavily mixed with adamantane vibrations, the internal ν(Si=C) stretching coordinate participating in several normal modes. This result is in agreement with the calculated data for **2**.[7] Significant contribution from the ν(Si=C) stretch into eigenvectors of the five normal modes indicated above leads to an intensity enhancement of the latter due to preresonance. To confirm this conclusion, it was reasonable to change the exiting line for a blue one, 457.9 nm, thus approaching resonance (in this case $\nu_e - \nu \approx 9400$ cm^{-1}). The excitation dependence obtained for the Raman region 700−1500 cm^{-1} is presented in Figure 3. To exclude the intensity increase due to the ν^4 scattering law, the spectra in Figure 3 are normalized so as to equalize approximately the intensities of the lines in the region 1400−1460 cm^{-1} belonging to deformational δ_{CH} modes localized in CH_2 and CH_3 groups. The latter Raman lines should not be affected by a change in the excitation line from green to blue, because the electronic transitions which determine the intensity of these lines are situated in the far UV region. Indeed, in the Raman spectrum, excited by the blue line (Figure 3b), the five lines mentioned above grew in intensity, in contrast to, e.g., the line at 773 cm^{-1} belonging to the normal mode known as a breathing vibration of the adamantane moiety.[22]

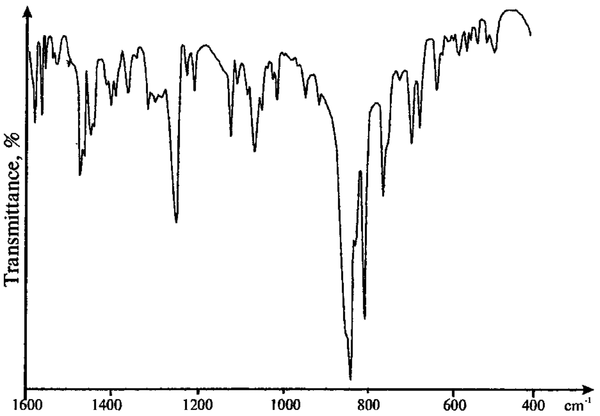


Figure 4. IR spectrum of solid **1** sublimed on a cooled target in a vacuum cryostat.

Two lines at 360 and 495 cm^{-1} are very weak with green excitation, but grow significantly in intensity with blue excitation. Evidently, they could be assigned to the ν(Si−Si) stretching modes in the trisilane fragment of **1** (by analogy with similar values for Si_4Me_{10}, which are at 365 and 474 cm^{-1}).[24] For those Raman lines, the $\sigma-\sigma^*$ electronic transition localized in trisilane fragment is effective. Their observed intensity enhancement seems to be due to preresonance conditions reached.

IR Spectrum. The IR spectrum of solid **1** is given in Figure 4. This spectrum is similar to that of **3**.[4] The IR counterparts of the most intense Raman lines involving the ν(Si=C) stretch are very weak, or not observed at all. Thus, the IR spectrum is much less informative for identification of the Si=C bond than the Raman spectrum. The most intense lines in the IR spectrum are the bands in the region of 800 cm^{-1} (rocking vibrations in the R_3Si groups) and those at 1250 and 1450 cm^{-1} (CH deformations).[8b,21a]

Quantum Chemical Calculations and Normal Coordinate Analysis (NCA). To confirm the conclusion gained from the Raman spectrum and to obtain quantitative characteristics of the vibrational coupling of the ν(Si=C) with other internal coordinates, we have carried out quantum mechanical DFT calculations[13] at the B3LYP/6-31G(d) level of theory.[14] The calculations were carried out for $(Me_3Si)_2Si{=}Ad$ (**7**) which serves as a simpler and more symmetric model to **1**. Substitution of a (t-Bu)Me_2Si group in **1** for a Me_3Si group in **7** should not affect significantly the spectral characteristics of the Si=C bond.

The force constant of the Si=C bond, $F_{Si=C}$, calculated for **7** as 4.55 mdyn/Å is significantly lower than that in simple silenes of the type $R_2Si{=}CH_2$, where R = H, Me (5.52−5.54 mdyn/Å)[7] or in **2** (5.36 mdyn/Å),[7] calculated analogously, but it is significantly higher than the force constant of the Si−C single bond (2.96 mdyn/Å for Me_4Si,[21a] 2.75 mdyn/Å for Si_6Me_{12}[25]). The calculated Si=C bond length in **7** is 1.754 Å, close to the experimental value of 1.741 Å for **1**[6] or to the calculated value of 1.755 Å for **1** (1.734 Å at HF/6-31G(d)[6]). The smaller $F_{Si=C}$ value in **7** as well as the longer Si=C bond lengths in **1** (and

TABLE 1: Calculated Frequencies and Potential Energy Distribution (PED) for Silene 7 and the Model Fragment 8[a]

B3LYP/6-31G(d) results for silene **7**		NCA for the model **8** $F_{\mathrm{Si=C}}$ = 4.55mdyn/Å		NCA for the model **8** $F_{\mathrm{Si=C}}$ = 5.36 mdyn/Å	
ν, cm^{-1}	PED (%)	ν, cm^{-1}	PED (%)	ν, cm^{-1}	PED (%)
292	CCC (25), Si−Si (20), SiSiC (16), **Si═C (4)**	262	Si−Si (30), C−C (9), SiSiC (9), **Si═C (7)**	265	Si−Si (32), C−C (8), SiSiC (6), **Si═C (5)**
549	**Si═C (22)**, Si−Si (12), C−C (10), CCC (9)	554	CCC (40), CC (24), **Si═C (13)**, Si−Si (12)	560	CCC (41), CC (25), **Si═C (11)**, Si−Si (11)
703	C−C (22), CCH (9), **Si═C (8),** CCC (5)	707	C−C (41), CCC (31), CCH (26), **Si═C (6)**	710	C−C (44), CCC (29), CCH (19), **Si═C (5)**
866	C−C (66), **Si═C (6)**	863	C−C (70), CCH (15), CCC (9), **Si═C (2)**	865	C−C (70), CCH (15), CCC (9), **Si═C (1.5)**
957	C−C (34), CCH (12), CCC (10), **Si═C (4)**	935	C−C (45), CCH (37), CCC (14), **Si═C (2)**	936	C−C (44), CCH (37), CCC (14), **Si═C (1.5)**
1030	CCC (23), C−C (16), **Si═C (15)**, CCH (8)	992	CCC (60), CCH (25), C−C (8), **Si═C (3)**	992	CCC (61), CCH (25), C−C (7), **Si═C (1.5)**
1112	CCC (40), **Si═C (18)**, CCH (16), C−C (10)	1103	CCC (30), **Si═C (27)**, CCH (25), C−C (7)	1122	CCH (70), **Si═C (14)**, C−C (6)
1137	Si═C (32)	1144	CCH (60), CCC (19), C−C (8), **Si═C (7.5)**	1155	CCH (51), CCC (18), **Si═C (16)**, C−C (8)
1255		1211	CCH (88), **Si═C (4.5)**, C−C (3)	1217	CCH (80), **Si═C (8)**, C−C (5)
1349	CCH (24), CCC (16), C−C (8),**Si═C (3)**	1333	CCH (71), C−C (16), **Si═C (2.5)**	1337	CCH (72), C−C (15), **Si═C (3.5)**
1426	CCH (57), C−C (8), **Si═C (4)**	1385	CCH (51), C−C (30), **Si═C (8)**	1399	CCH (42), C−C (30), **Si═C (14)**

[a] Only modes, in which the contribution from the ν(Si═C) coordinate in PED is more than 2%, are presented.

TABLE 2: Comparison of Experimental Raman Bands (in cm^{-1}) with Calculated Values for 1 and 7[a]

	7		**1**	
exptl band	band	deviation (%)	band	deviation (%)
1011	999	−1.2	1002	−0.8
1087	1079	−0.8	1084	−0.2
1109	1103	−0.5	1107	−0.2
1304	1309	0.3	1312	0.6
1371	1383	0.9	1386	1.1

[a] B3LYP/6-31G(d), scaled by a factor of 0.97[29]

7), compared to simple silenes R$_2$Si═CH$_2$ (1.689−1.707 Å),[7] or to the parent H$_2$Si═CH$_2$ (1.704 Å)[26] may be attributed to the special substitution in **1** and **7**, namely, to the bissilyl substitution at the doubly bonded silicon atom.[6,27]

Classical normal coordinate analysis (NCA)[16] was carried out for a simplified model fragment Si$_2$Si═2-Ad (**8**) of C_{2v} symmetry. The normal-mode frequencies and eigenvectors as well as PED were calculated for this fragment using the experimental geometry of **1**.[6] The initial force field for the adamantane moiety was transferred from the NCA calculations reported in ref 22. The $F_{\mathrm{Si-Si}}$ value was taken as 1.70 mdyn/Å from the NCA calculations for Si$_2$Me$_6$.[28] The $F_{\mathrm{Si=C}}$ value was varied within reasonable limits starting from 5.36 mdyn/Å reported for **2**[7] to 4.55 mdyn/Å, obtained in this work for **7**. The calculated frequencies of some fundamentals and the corresponding PED data obtained using these procedures are summarized in Table 1. Comparison of the experimental Raman frequencies with the calculated values is given in Table 2.

We did not expect strict coincidence between the observed and the calculated frequencies either those obtained from the DFT calculations with its harmonic force field, or, the more so, from the approximate model NCA calculations. Our aim was to elucidate mode eigenvectors and to analyze the effect of variation of some important parameters on the frequencies values and on the degree of vibrational coupling. As can be seen from Table 2, the DFT calculations reproduce the position of the Raman lines of interest rather well, with a maximal absolute error of less than 1.2% (using a scaling factor 0.97[29]).

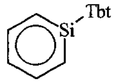
The main conclusion from the calculations is that the ν(Si═C) vibration is not localized and that the corresponding internal coordinate participates in *many* normal modes. This is clearly seen in Table 1, where the calculated frequencies and PED, obtained by DFT and by NCA calculations (the latter with two different values of $F_{\mathrm{Si=C}}$), are presented for the modes in which the contribution from the ν(Si═C) coordinate is notable. Comparison of the last two columns in Table 1 demonstrates the dependence of the PED values on the $F_{\mathrm{Si=C}}$ value used.

According to all calculations, the highest participation of the ν(Si═C) coordinate is in two normal modes with frequencies in the region of 1100 cm^{-1}. This result is in good agreement with the Raman experiment. Interestingly, not all the frequencies of the modes whose calculated contributions from the ν(Si═C) coordinate are the highest, correspond to the most enhanced Raman lines. For instance, all calculations point to a mode in the region ca. 550 cm^{-1} as involving from 11 to 22% of the ν(Si═C) stretch in PED, whereas **1** shows no intense Raman line in this region, and vice versa, the calculated contribution from the ν(Si═C) into the modes in the region of 1300−1400 cm^{-1} is only 3−4% in PED, while experimentally these lines are strongly enhanced. This fact can be partly rationalized in terms of the mode eigenvectors.[8c,16]

Let us consider, e.g., the eigenvector of the normal mode at about 550 cm^{-1}, which strongly involves the ν(Si═C) (Table 1). The eigenvector element for the ν(Si═C) stretch participation in this mixed mode is 0.06 whereas that for the ν(Si−Si) stretch is −0.10. These two elements have opposite signs and therefore the corresponding contributions to the intensity are subtracted, and the resulting intensity could be small. Some other modes with frequencies below 900 cm^{-1} could be treated analogously. It should be also remembered that all the PED values given in Table 1 are approximate due to the complexity of the molecule studied, and uncertainty in eigenvector determination. Thus, the PED data of Table 1 seem to be of only qualitative importance.

The Character of the Si═C Bond in 1. *(a) $J_{Si=C}$ Coupling Constant*. The measured $J_{\mathrm{Si=C}}$ coupling in the NMR of **1** is 73 Hz. This value is in the same range as other reported $J_{\mathrm{Si=C}}$ values for Si═C double bonds; i.e., 84 Hz for **3**,[4] 76 and 92 Hz for the single and double bonds of **4**,[10] respectively, and 83 Hz for **9**.[30]

The closest reference compounds for a related Si−C single bond is probably $(Me_3Si)_2SiMe_2$, where J_{Si-C} is 37 Hz, but the range of J_{Si-C} values for Si−C single bonds is very large, from 37 Hz to more than 100 Hz with ordinary values being around 50 Hz.[31] Thus, the $J_{Si=C}$ value measured for **1** is smaller than expected for a true double bond and it is even less than the value $J_{Si=C}$ in silaaromatic compounds, where the Si=C bond order is expected to be less than 2. Yet the $J_{Si=C}$ value of **1** is clearly much larger than that of typical Si−C single bonds.



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(b) Si=C Bond Order. According to Wiberg bond index,[32a] the Si=C bond order in the model compound $(H_3Si)_2Si{=}CMe_2$ is 1.46. According to NRT analysis,[32b] the bond order is 1.83, being composed of a covalent contribution of 1.30 and an ionic contribution of 0.52. All values are at MP2/6-31G(d)//B3LYP/6-31G(d).[32c]

The relatively small $J_{Si=C}$ NMR coupling constant, the relatively low calculated value of the force constant $F_{Si=C}$ (4.55 mdyn/Å, compared to 5.52 mdyn/Å for simpler silenes[7]), the relatively long Si=C bond length (1.741 Å,[6] compared to 1.704 Å[26] for the parent $H_2Si{=}CH_2$) and the calculated bond orders, all point to the fact that Si=C double bond in **1** is weaker than the corresponding bond in the parent $H_2Si{=}CH_2$.

Conclusions

The results of the calculations confirm the experimental conclusion that there is no single vibrational normal mode which can be assigned as ν(Si=C). This coordinate is heavily mixed with internal vibrations of the adamantane part of the molecule and with the stretching motions in the silyl substituents; it makes modest contributions to several normal modes. Raman intensity enhancement on approaching resonance strongly supports the conclusion that there are five lines in the region 1000−1370 cm^{-1} which include significant contribution from the ν(Si=C) stretching coordinate. The close similarity of the Raman and IR spectra of **1** and **3**[4] suggests that the same conclusion holds also for silene **3**. Taking into account the vibrational coupling of ν(Si=C) in **2**,[7] it seems reasonable to infer that the ν(Si=C) stretching mode is well-localized only for simple silenes of the type $R_2Si{=}CH_2$ (R = H, Me). For more highly substituted silenes, the ν(Si=C) coordinate "crawls' over several normal modes. In contrast, in alkenes the ν(C=C) stretching mode is more localized.[8,21a] Our results parallel those for disilenes.[33] Thus, also in the vibrational spectra of $Mes_2Si{=}SiMes_2$ and Mes(*t*-Bu)Si=Si(*t*-Bu)Mes there is no normal mode which is well localized in the Si=Si bond.[33]

Several criteria, experimental and theoretical, point to the conclusion that the Si=C double bond in **1** is significantly weaker than in the parent $H_2Si{=}CH_2$ or in other simple silenes. This is attributed mainly to the silyl substituents at the silicon end of the double bond which reduce substantially the inherent polarity of the Si=C double bond.[27]

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References and Notes

(1) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864.

(2) For the most recent comprehensive review, see: Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, Chapter 16.

(3) For previous reviews, see: (a) Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 17. (b) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(4) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Change, Y.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5668.

(5) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

(6) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

(7) Khabashesku, V. N.; Kudin, K. N.; Margrave, J. L. *J. Mol. Structure* **1998**, *443*, 175.

(8) (a) Turrell, G., Corset, J., Eds. *Raman Microscopy. Developments and Applications*; Academic Press: London, 1996. (b) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Academic Press: New York, 1990. (c) Hester R. E. In *Raman Spectroscopy*; Szymanski, H. A., Ed.; Plenum Press: New York, 1967; Chapter 4.

(9) The Raman spectrum reported by Brook and co-workers[4] was measured by M. Moscovits (University of Toronto). The excitation line was not reported.[4]

(10) (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; von Schleyer, P.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; von Schleyer, P.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951.

(11) Apeloig, Y.; Bravo-Zhivotovskii, D.; Zharov, I.; Panov, V.; Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 1398.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Koch, W.; Holthausen M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: New York, 2000.

(14) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(15) The program was elaborated by V. A. Sipachev[15a] and refined by V. Novikov and M. Tafipol'sky. (a) Sipachev, V. A. *J. Mol. Struct. (THEOCHEM)* **1985**, *121*, 143.

(16) (a) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: Mineola, NY, 1980. (b) Mayants L. S. *The Theory and Computation of Molecular Vibrations*; USSR Academy of Sciences Publishing House: Moscow, 1961 (in Russian). (c) Vol'kenstein, M. V.; Gribov, L. A.; Elyashevich, M. A.; Stepanov, B. I. *Molecular Vibrations*; Nauka: Moscow, 1972 (in Russian).

(17) Gribov L. A.; Dement'ev V. A. *Simulation of Vibrational Spectra of Complex Compounds with a Computer*; Nauka: Moscow, 1989 (in Russian).

(18) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218.

(19) The ϵ value for the band at 322 nm reported here was determined more precisely than the previously reported value of 6300.[6]

(20) (a) For a detailed discussion of the HOMO orbital of silene **1**, see: Bendikov, M.; Solouki, Auner, N.; Apeloig, Y. *Organometallics* **2002**, *21*, 1349. (b) The UV of disilenes is also well reproduced by TD-B3LYP/6-311++G(d, p)//B3LYP/6-31G(d) calculations: see, Takahashi, M.; Kira, M.; Sakamoto, K.; Müller, T.; Apeloig, Y. *J. Comput. Chem.* **2001**, *22*, 1536.

(21) The frequency of the ν(C=C) mode for **5** has a value of 1659 cm^{-1}, somewhat lower than that for tetra-alkyl substituted ethylenes (1680 cm^{-1}).[21a] (a) Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, 1973.

(22) Eliashberg, M. E.; Karasev, Yu, Z.; Dement'ev, V. A.; Gribov, L. A. *Interpretation of Vibrational Spectra of Hydrocarbons; Cyclohexane and Cyclopentane Derivatives*; Nauka: Moscow, 1988; p 191 (in Russian).

(23) (a) Shorygin, P. P. *Uspekhi Khimii* **1950**, *19*, 419; *Uspekhi Khimii* **1971**, *40,* 694 (in Russian). (b) Shorygin, P. P., Krushinskij, L. L. *J. Raman Spectrosc.* **1997**, *28*, 383.

(24) Ernst, C. A.; Allred, A. L.; Ratner, M. A. *J. Organomet. Chem.* **1979**, *178*, 119.

(25) Hassler, K. *Spectrochim. Acta, Part A* **1981**, *37A*, 541.

(26) Baileux, S.; Bogey, M.; Demaison, J.; Burger, H.; Senzlober, M.; Breidung, J.; Thiel, W.; Fajgar, R.; Pola, J. *J. Chem. Phys.* **1997**, *106*, 10016.

(27) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

(28) Fontal, B.; Spiro, T. *Inorg. Chem.* **1971**, *10*, 9.

(29) Scale factors of 0.96[29a] and 0.98[29b] were proposed for B3LYP/6-31G(d) frequencies, and we have therefore used the median scale factor of 0.97. (a) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1997**, *270*, 419. (b) Bauschlicher, C. W., Jr. *Chem. Phys. Lett*. **1995**, *246*, 40. Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys*. **1995**, *103*, 1788. Urban, J.; Schreiner, P. R.; Vacek, G.; Schleyer, P. v. R.; Huang, J. Q.; Leszczynski, J. *Chem. Phys. Lett*. **1997**, *264*, 441.

(30) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 634.

(31) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Vol. 1, p 511.

(32) (a) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 1996. (b) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593. (c) For smaller model silenes the bond orders calculated at MP2/6-31G(d)//B3LYP/6−31G(d) and at B3LYP/6−31G(d)//B3LYP/6−31G(d) are similar.

(33) Leites, L. A.; Bukalov, S. S.; Garbuzova, I. A.; West, R.; Mangette, J.; Spitzner, H. *J. Organomet. Chem.* **1997**, *536/537,* 425.