Reactions of Silicon Atoms with Conjugated π-Systems: A Matrix-Spectroscopic Study[‡]

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The reaction of silicon atoms with cyclopentadiene and butadiene in argon at 10 K has been studied. Addition to the conjugated π-system of cyclopentadiene occurs in a [1,4]-fashion. Upon irradiation the π-adduct **3** rearranges to the formal insertion product **2** which has an unusual structure. Remarkably, a photoequilibrium between the two *exo,endo* isomers **2** and **4** can be observed. In the case of butadiene the addition is less stereospecific. The planar [1,4]-adduct **11** is formed together with the [1,2]-adduct **14**. Surprisingly, besides **11** a second, nonplanar [1,4]-adduct **10** can be detected. The isomers **11** and **14** are transformed into **10** upon irradiation. The final photoproduct is silole **9**. The structural elucidation of the new species is based on isotopic labelling and a comparison of the experimental observations with the results from density functional calculations.

Introduction

During the past five years we have studied the reactions of thermally generated silicon atoms with low molecular weight reactants in an argon matrix. The reaction products were identified by means of IR and UV/Vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful.[1] Among the selected partner molecules those with isolated π-bonds were of special interest. It was found that acetylene and ethylene react with silicon atoms to form the corresponding π-adducts.[1b,1d] These initially formed cyclic silylenes rearrange in the matrix upon irradiation to give the ring-opened isomers ethynyl- and vinylsilylene.

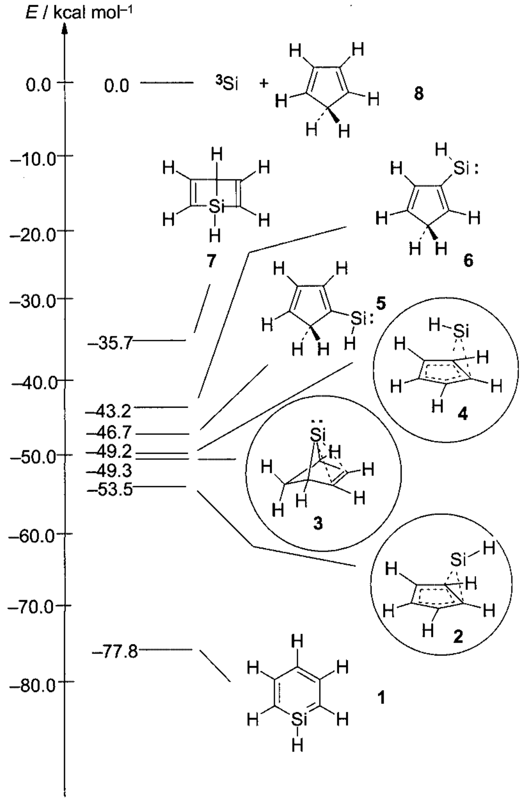
The reactions that occur when conjugated π-systems react with silicon atoms are the subject of this paper.

Reaction with Cyclopentadiene

Calculations

In order to learn something about the addition behavior of a conjugated π-system it is tempting to choose cyclopentadiene as the model. To obtain an overview of the C_5H_6Si potential energy surface, several stationary points together with the corresponding vibrational spectra were calculated with the 6-311+G** basis set and the B3LYP functional. Scheme 1 gives the calculated relative energies.

The global minimum is silabenzene (**1**), a compound prepared and identified by us several years ago.[2] The stabiliza-



Scheme 1. Calculated relative energies of some C_5H_6Si isomers (B3LYP/6-311+G**)

[‡] Hetero π-Systems, 33. Part 32: Ref.[1i]

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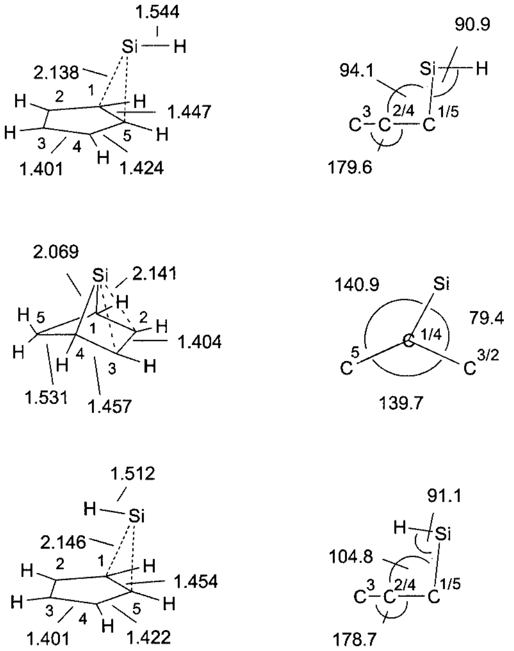
tion energy compared with the two components − triplet silicon atom and cyclopentadiene (**8**) − is 77.8 kcal·mol^{-1}. Besides **1** six other isomers (**2**−**7**), which should be formed in exothermic reactions from ^{3}Si atoms and **8**, can be expected as reaction products.

In view of the preferred [1,4]-addition of silylenes to cyclopentadiene the most reasonable candidate in the reaction with a silicon atom seems to be the [1,4]-π-adduct **3**.



Scheme 2. Calculated structural features of the C_5H_6Si isomers **2**, **3**, and **4** (B3LYP/6-311+G**; bond lengths in Å, angles in °)

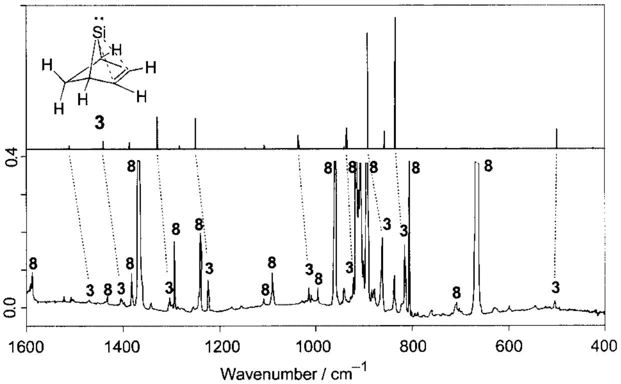


Figure 1. IR spectrum of the reaction product of Si atoms with cyclopentadiene (**8**) in an argon matrix at 10 K

Table 1. Calculated energies and vibrational spectra of some C_5H_6Si isomers (B3LYP/6-311+G**)

Species (pointgroup, state)[a] Energy, ZPE included [hartrees][a]	Vibrational spectrum: wavenumber (IR intensity) symmetry
1 (C_{2v}, $^1A_1$) −483.582265	275.3 (4) b_1, 363.6 (0) a_2, 428.3 (11) a_1, 444.1 (1) b_1, 492.1 (1) b_2, 577.5 (46) b_1, 713.0 (74) b_1, 721.1 (7) b_2, 767.6 (2) a_1, 787.3 (0) a_2, 861.3 (0) b_1, 894.3 (17) b_2, 899.8 (6) a_1, 969.8 (1) a_1, 984.2 (0) a_2, 1004.4 (0) b_1, 1083.3 (5) b_2, 1193.9 (0) a_1, 1215.3 (0) b_2, 1291.9 (49) b_2, 1383.7 (35) a_1, 1438.6 (6) b_2, 1535.2 (24) b_2, 1566.6 (19) a_1, 2285.9 (75) a_1, 3124.3 (12) a_1, 3127.9 (19) b_2, 3170.7 (12) a_1, 3175.2 (10) b_2, 3176.4 (8) a_1
2 (C_s, $^1A'$) −483.543625	184.8 (1) a″, 188.8 (1) a′, 370.7 (1) a″, 431.5 (45) a′, 575.2 (1) a″, 600.6 (13) a′, 768.1 (218) a′, 775.7 (2) a″, 790.2 (1) a′, 838.1 (29) a′, 846.8 (18) a′, 846.10 (0) a″, 891.6 (14) a″, 940.5 (8) a′, 1020.4 (23) a′, 1026.2 (5) a″, 1089.6 (7) a′, 1091.0 (0) a″, 1139.3 (4) a′, 1283.9 (0) a″, 1380.1 (2) a″, 1382.10 (9) a′, 1461.6 (19) a″, 1488.8 (11) a′, 1936.6 (431) a′, 3208.3 (1) a′, 3208.8 (2) a″, 3222.9 (4) a″, 3224.0 (0) a′, 3236.8 (7) a′
3 (C_s, $^1A'$) −483.536902	291.1 (0) a″, 332.2 (1) a′, 424.2 (0) a′, 500.9 (10) a′, 580.5 (0) a″, 729.5 (0) a′, 788.9 (0) a″, 834.8 (70) a′, 857.4 (9) a″, 891.7 (62) a′, 934.5 (5) a″, 936.2 (11) a″, 940.6 (1) a′, 1035.2 (4) a″, 1037.2 (7) a′, 1061.4 (0) a′, 1107.1 (2) a′, 1147.0 (1) a″, 1249.8 (16) a″, 1283.6 (2) a″, 1329.3 (17) a′, 1386.7 (3) a″, 1441.5 (4) a′, 1511.1 (2) a′, 2894.10 (189) a′, 3078.7 (28) a′, 3183.3 (19) a″, 3183.3 (2) a′, 3214.3 (0) a″, 3230.3 (2) a′
4 (C_s, 1A′) −483.536718	124.5 (1) a″, 231.5 (0) a′, 415.7 (61) a′, 498.9 (0) a″, 548.4 (1) a″, 596.9 (22) a′, 772.8 (2) a″, 772.10 (97) a′,802.7 (4) a′, 838.9 (0) a″, 839.4 (4) a′, 859.0 (164) a′, 878.3 (5) a″, 936.5 (24) a′, 1013.2 (39) a′, 1032.9 (3) a″, 1087.7 (1) a″, 1092.9 (8) a′, 1135.3 (7) a′, 1283.4 (0) a″, 1370.4 (0) a″, 1380.3 (20) a′, 1458.7 (15) a″, 1489.7 (20) a′, 2095.7 (166) a′, 3191.0 (2) a″, 3197.7 (1) a′, 3210.9 (1) a′, 3215.5 (7) a″, 3231.7 (7) a′
5 (C_s, 1A′) −483.532759	146.3 (0) a″, 212.7 (0) a′, 274.9 (0) a″, 362.2 (12) a″, 428.8 (28) a′, 535.5 (1) a″, 709.5 (32) a″, 808.4 (76) a′, 830.4 (4) a′, 863.10 (1) a′, 887.3 (6) a″, 929.1 (21) a″, 961.8 (7) a′, 976.4 (0) a″, 1024.9 (94) a′, 1088.8 (72) a′, 1122.7 (2) a′, 1124.3 (0) a″, 1244.1 (9) a′, 1282.3 (1) a′, 1384.5 (25) a′, 1394.0 (20) a′, 1474.3 (115) a′, 1592.3 (6) a′, 1988.10 (310) a′, 3014.4 (2) a′, 3034.10 (5) a″, 3179.6 (4) a′, 3193.4 (7) a′, 3214.5 (16) a′
6 (C_s, 1A′) −483.527144	121.3 (0) a″, 213.6 (0) a′, 254.2 (0) a″, 346.3 (5) a″, 423.7 (33) a′, 564.8 (9) a″, 710.7 (34) a″, 760.7 (2) a″, 805.9 (71) a′, 823.4 (4) a′, 876.8 (7) a′, 936.1 (26) a″, 941.5 (22) a′, 969.10 (0) a″, 976.6 (4) a′, 1088.6 (37) a′, 1124.9 (0) a″, 1135.2 (17) a′, 1243.6 (8) a′, 1284.2 (8) a′, 1355.10 (13) a′, 1401.9 (31) a′, 1514.8 (57) a′, 1598.4 (11) a′, 2003.10 (300) a′, 3005.5 (5) a′, 3025.5 (4) a″, 3191.2 (3) a′, 3193.5 (2) a′, 3216.1 (13) a′
7 (C_s, 1A′) −483.515290	274.0 (0) a″, 303.1 (0) a′, 389.5 (2) a′, 565.6 (34) a″, 598.2 (15) a′, 603.9 (43) a′, 669.8 (1) a″, 683.1 (44) a′, 729.1 (28) a″, 775.2 (70) a′, 786.4 (20) a′, 822.7 (139) a″, 920.8 (2) a′, 950.10 (0) a″, 968.9 (5) a′, 977.10 (0) a″, 1006.9 (16) a′, 1056.0 (0) a″, 1103.9 (23) a′, 1206.9 (2) a″, 1270.1 (2) a″, 1287.1 (26) a′, 1533.5 (22) a″, 1564.3 (10) a′, 2220.6 (159) a′, 3098.3 (30) a″, 3099.8 (43) a′, 3130.5 (18) a′, 3191.8 (19) a″, 3192.7 (8) a′

[a] ^{3}Si (^{3}P) −289.394168. C_5H_6 **8** (C_{2v}, $^1A_1$) −194.064125.

Table 2. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C$_5$H$_6$Si isomers **[H$_6$]3** (a) and **[D$_6$]3** (b)

(a) isomer **[H$_6$]3**

Sym.	Approx. description	Calculation	Experiment
a"	SiC str.	291.1 (0.5)	–
a′	SiC str.	332.2 (1.4)	–
a′	ring def.	424.2 (0.4)	–
a′	SiC str.	500.9 (10.5)	504.6 (w)
a"	ring def.	580.5 (0.3)	–
a′	ring def.	729.5 (0.4)	–
a"	ring def.	788.9 (0.3)	–
a′	CH def.	834.8 (69.7)	815.7 (s)
a"	CH def.	857.4 (9.2)	–
a′	CH def.	891.7 (61.5)	861.7 (s)
a"	CH def.	934.5 (4.8)	–
a"	CH def.	936.2 (11.0)	921.9 (m)
a′	ring breath.	940.6 (0.9)	–
a"	CC str. + CH def.	1035.2 (4.4)	–
a′	CH def.	1037.2 (7.3)	1014.5 8w)
a′	CCstr. + CH def.	1061.4 (0.2)	–
a′	CC str.	1107.1 (2.3)	–
a"	CH$_2$ twist.	1147.0 (0.9)	–
a"	CCstr. + CH def.	1249.8 (16.1)	1224.4 (m)
a"	CCstr. + CH def.	1283.6 (1.6)	1254.1 (vw)
a′	CCstr. + CH def.	1329.3 (16.9)	1303.5 (w, br.)
a"	CCstr. + CH def.	1386.7 (3.4)	1367.4 (w)
a′	CCstr. + CH def.	1441.5 (4.2)	1404.6 (w)
a′	CH$_2$ sciss.	1511.1 (2.0)	1471.0 (w)
a′	CH str.	2895.0 (188.9)	2800.9, 2784.3, 2766.5 (s, very br.)
a′	CH str.	3078.7 (27.7)	2916.7 (w)
a"	CH str.	3183.3 (18.6)	2968.4 (w)
a′	CH str.	3183.3 (1.6)	
a"	CH str.	3214.3 (0.2)	
a′	CH str.	3230.3 (1.7)	

(b) isomer **[D$_6$]3**

Sym.	Approx. description	Calculation	Experiment
a"	SiC str.	281.1 (0.4)	–
a′	SiC str.	310.2 (0.7)	–
a′	ring def.	359.2 (1.4)	–
a′	SiC str.	467.0 (2.6)	–
a"	ring def.	515.4 (0.3)	–
a′	CD def.	614.7 (0.3)	–
a"	CD def.	632.0 (1.3)	–
a′	CD def.	674.7 (89.4)	667.0/664.4 (vs, br.)
a"	CD def.	691.3 (4.0)	–
a′	ring def.	715.4 (0.8)	–
a"	CD$_2$ wagg. + CD def.	732.4 (0.0)	–
a"	CD$_2$ wagg. + CD def.	750.6 (13.1)	738.9 (m)
a′	CD def. + CC str.	759.9 (2.2)	751.2 (w)
a′	CD def. + CC str.	792.8 (4.6)	779.8 (w)
a"	CD$_2$ twist. + ring def.	821.7 (0.4)	–
a′	CD$_2$ rock. + ring breath.	882.8 (2.9)	867.8 (w)
a"	ring def. + CD$_2$ twist.	897.3 (4.3)	885.4 (m)
a′	ring breath.	977.3 (0.8)	961.5 (vw)
a"	CD def.	1009.0 (0.0)	–
a′	CD$_2$ sciss.	1125.4 (2.0)	1101.8 (w)
a"	CC str.	1145.1 (6.7)	1128.4/1123.8 (m)
a′	CC str.	1239.4 (8.9)	1216.9 (m)
a"	CC str.	1258.5 (2.7)	1233.2 (vw)
a′	CC str.	1374.4 (6.4)	1344.6 (w)
a′	CD str.	2115.0 103.2)	2049.4, 2054.7, 2065.7 2119.7 (s, br., overlapping)
a′	CD str.	2272.0 (14.4)	2191.2 (w)
a"	CD str.	2349.5 (8.7)	(2215.7 (w)
a′	CD str.	2351.1 (0.8)	
a"	CD str.	2372.8 (0.0)	
a′	CD str.	2401.3 (1.0)	

Table 3. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C$_5$H$_6$Si isomers (a) **[H$_6$]2** and (b) **[D$_6$]2**

(a) isomer **[H$_6$]2**

Sym.	Approx. description	Calculation	Experiment
a′′	Si/ring def.	184.8 (1.2)	–
a′	Si/ring def.	188.8 (0.6)	–
a′′	SiH def.	370.7 (0.9)	–
a′	SiC sym. str.	431.5 (44.6)	445.3(m)
a′′	CH o.o.p.def.	575.2 (1.1)	–
a′	CH o.o.p.def.	600.6 (13.1)	593.1(w)
a′	SiH def.	768.1 (217.6)	765.2(s)
a′′	CH o.o.p.def.	775.7 (1.7)	–
a′	CH o.o.p.def.	790.2 (1.3)	–
a′	CH o.o.p.def.	838.1 (28.8)	823.9(m)
a′	CH o.o.p.def.	846.8 (18.5)	832.2(m)
a′′	ring def. i.p.	847.0 (0.2)	–
a′′	CH o.o.p.def.	891.6 (14.0)	875.6(w)
a′	CH o.o.p.def.	940.5 (8.4)	–
a′	HCH i.p.def.	1020.4 (23.4)	1005.4(m)
a′′	HCH i.p.def.	1026.2 (4.8)	–
a′	HCH i.p.def.	1089.6 (7.5)	1069.1(w)
a′′	HCH i.p.def.	1091.0 (0.0)	–
a′	CC str. (ring breath.)	1139.3 (3.7)	1114.0(w)
a′′	HCH i.p.def.	1283.9 (0.0)	–
a′′	CC str.+ HCH i.p.def.	1380.1 (1.7)	–
a′	CC str.+ HCH i.p.def.	1383.0 (9.4)	1361.2(w)
a′′	CC str.+ HCH i.p.def.	1461.6 (18.5)	1430.7(w)
a′	CC str.+ HCH i.p.def.	1488.8 (11.4)	1458.8(w)
a′	SiH str.	1936.6 (430.6)	1902.3(w),[a] 1891.5(vs),[a] 1851.8(m)[a]
a′	CH str.	3208.3 (0.8)	–
a′′	CH str.	3208.8 (1.8)	–
a′′	CH str.	3222.9 (4.1)	–
a′	CH str.	3224.0 (0.2)	–
a′	CH str.	3236.8 (6.7)	–

(b) isomer **[D$_6$]2**

Sym.	Approx. description	Calculation	Experiment
a′′	Si/ring def.	164.4 (0.7)	–
a′	Si/ring def.	178.4 (0.7)	–
a′′	CD o.o.p. def.	303.0 (1.1)	–
a′	SiC sym. str.	399.2 (17.2)	–
a′	CD o.o.p. def.	505.3 (0.3)	–
a′′	SiC as. str.	513.2 (0.0)	–
a′′	CD o.o.p. def.	572.9 (1.2)	–
a′	SiD def.	576.6 (144.5)	578.2(vs), 575.7(vs)
a′	CD o.o.p. def.	606.9 (1.4)	–
a′	CD o.o.p. def.	639.4 (59.3)	633.9(s)
a′′	CD o.o.p. def.	697.1 (9.9)	683.5(m)
a′	DCD i.p.def.	734.1 (2.3)	–
a′′	DCD i.p.def.	752.2 (0.2)	–
a′	DCD i.p.def.	779.9 (21.1)	757.1(m)
a′′	DCD i.p.def.	782.6 (3.7)	771.0(w)
a′	DCD i.p.def.	789.6 (1.4)	778.2(w)
a′′	DCD i.p.def.	862.7 (0.7)	–
a′	DCD i.p.def.	865.1 (3.8)	854.2(w)
a′′	DCD i.p.def.	1009.2 (0.0)	–
a′	CC str. (ring breath.)	1076.8 (6.8)	1058.3(w)
a′′	CC str.	1307.5 (0.1)	–
a′	CC str.	1313.8 (0.7)	–
a′′	CC str.	1371.9 (12.7)	1347.7(w),[b] 1340.4(w)[b]
a′	SiD str.	1392.2 (194.8)	1375.2(s)[b]
a′	CC str.	1413.0 (53.4)	1385.7(s)[b]
a′	CD str.	2366.4 (0.8)	–
a′′	CD str.	2368.6 (1.9)	–
a′′	CD str.	2387.6 (3.0)	–
a′	CD str.	2388.1 (0.7)	–
a′	CD str.	2411.2 (4.8)	–

[a] Very broad and split (at least 3 different matrix sites). [b] Broad and split (several overlapping bands and different matrix sites; unambiguous assignment not possible).

According to the calculations the silylene bridge in **3** is strongly coordinated to the double bond. Astonishingly, two other isomers (**2** and **4**) are calculated to have similar stabilities. Both compounds contain an SiH group but they are not to be regarded as simple silylenes (formal insertion products). In accordance with this structural prerequisite it might be possible to isolate **3** together with the two distinct *exo*/*endo* isomers **2** and **4** (circled in Scheme 1).

The insertion products **5** and **6** are additional candidates for experimental verification. Remarkably, calculations predict that no [1,2]-addition product should be found as a reaction product. The list is completed by the Dewar silabenzene **7** which, according to our earlier studies,[2] is formed upon irradiation of silabenzene **1**.

As far as the reaction mechanism is concerned it can be anticipated that in the first step a triplet [1,2]- or [1,4]-π-adduct is formed. Both can lead by intersystem crossing to more stable singlet silylenes, which should be detected as the final products.

The calculated structural features of **2**, **3**, and **4** are given in Scheme 2. For **2** and **4** theory demands distinct electron delocalization in the five-membered ring and, at the same time, a threefold coordination of the silicon atom. The carbon and hydrogen atoms are practically all lying in one plane. The bond alternation is small. The bond angles H−Si−C(1,5) and Si−C(1,5)−C(2,4) are close to 90°, therefore **2** and **4** can be regarded as two *exo*,*endo* isomers in which an SiH unit is complexed to one side of a delocalised cyclopentadienyl radical. In the [1,4]-adduct two normal Si−C bonds (2.069 Å) are found for the connection with carbon atoms 1 and 4. Additional coordination with C(2) and C(3) is revealed by the bond lengths (2.141 Å) and by the small Si−C(1,4)−C(3,2) angle of only 79.4°.

IR Spectroscopic Observations

Table 1 summarizes the calculated IR spectra of some relevant isomers with the elemental composition C_5H_6Si.

The FT-IR spectrum of the reaction products after cocondensation of silicon atoms and cyclopentadiene in argon (ratio 1:100) is shown in Figure 1. The calculated spectrum of adduct **3** is also shown for comparison. It is obvious that, besides SiH_4, Si_2H_6, and SiN_2 − the products of silicon atoms with unavoidable amounts of hydrogen or nitrogen − cyclopentadiene (**8**) yields the [1,4]-adduct **3** exclusively.

A detailed analysis of the calculated and experimental IR spectra of the primarily formed [1,4]-adduct is given in Table 2, a (protonated compound **[H$_6$]3**). In order to confirm the results we also studied the reaction of perdeuterated cyclopentadiene **[D$_6$]8**. These data can be found in Table 2, b. The good agreement between theory and experiment indicates that the structural elucidation of the reaction product is correct.

Upon irradiation with light of wavelength 313 nm the bands of **3** disappear and a set of new absorptions can be detected. Again, comparison with the calculated spectra (Table 3, a, b) shows that the photoproduct has to be isomer **2**, which means that photoexcitation transforms the π-adduct **3** into the formal insertion product **2**. The presence of an Si−H group is shown by a strong Si−H stretching vibration at an astonishingly low frequency (1891.5 cm^{-1}).

By subsequent change of the wavelength to 366 nm it is possible to create a third isomer, which reverts back to the starting material when irradiated at 290 nm. This mutual photoinduced interconversion is best demonstrated by the difference spectrum shown in Figure 2. From the comparison with the calculated spectra (Table 4, a and b) it follows that the secondary photoproduct has structure **4**. Most bands of **2** and **4** are very close to each other, and only the Si−H stretching vibration of **4** shows a distinct shift to higher frequency (ca. 2069 cm^{-1}).

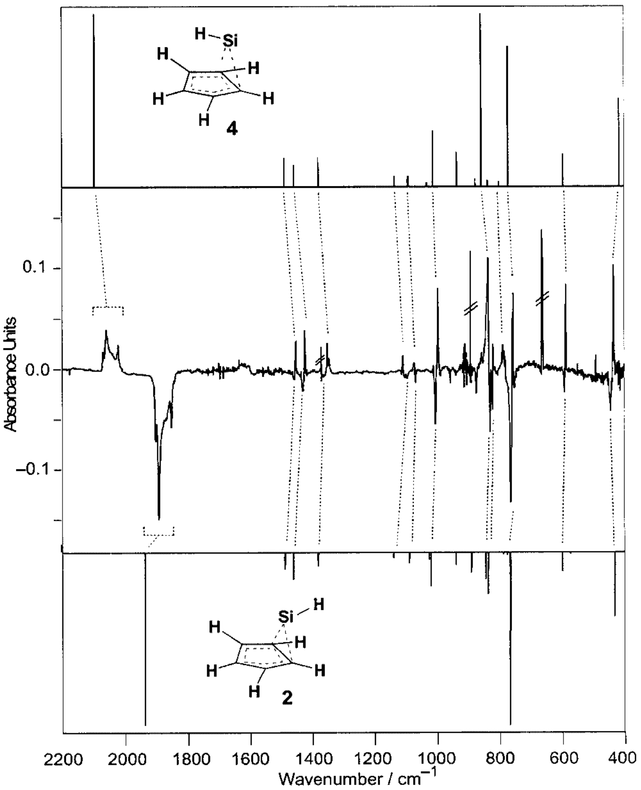
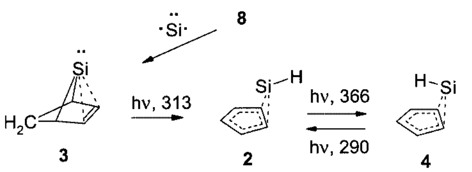


Figure 2. Top: Calculated (B3LYP/6-311+G**) IR spectrum of insertion product **4**; center: difference FT-IR spectrum of the photoreaction **4** → **2** (obtained by subtraction of the spectra taken before and after irradiation with 290 nm for 2 h); bottom: calculated IR spectrum (B3LYP/6-311+G**) of insertion product **2**



To sum up it can be concluded that the π-adduct **3** gives the *exo* insertion product **2** upon irradiation, which then establishes a photoequilibrium with the *endo* isomer **4**.

Table 4. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C_5H_6Si isomers (a) **[H_6]4** and)b) **[D_6]4**

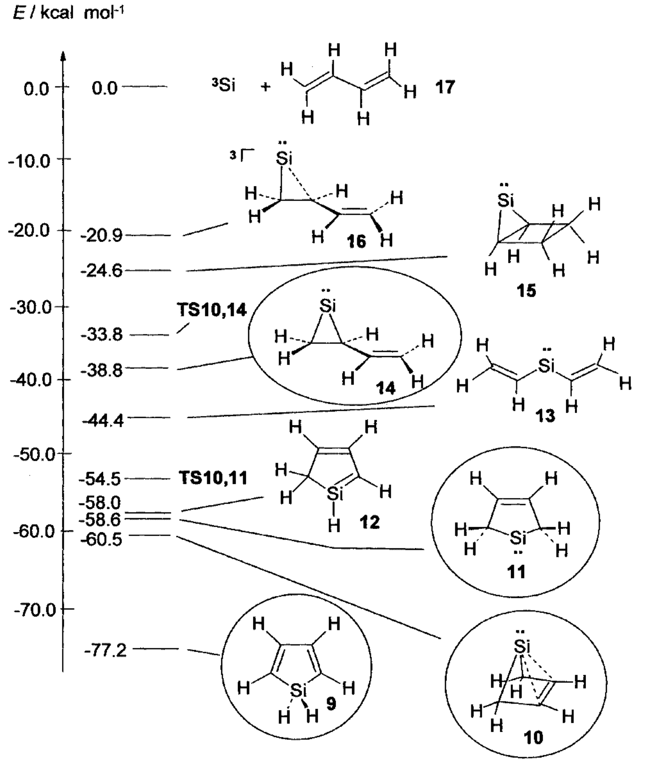
(a) isomer **[H_6]4**

Sym.	Approx. description	Calculation	Experiment
a"	Si/ring def.	124.5 (0.8)	–
a′	Si/ring def.	231.5 (0.3)	–
a′	SiH def.	415.7 (60.7)	434.4(s),[a] 433.4(s)[a]
a"	SiC sym. str.	498.9 (0.3)	–
a"	CH oop def.	548.4 (0.8)	–
a′	CH oop def.	596.9 (22.5)	588.3(s)
a"	SiH def.	772.8 (2.0)	–
a′	CH oop def.	773.0 (97.3)	665.2(s),[a] 663.6(s)[a]
a′	CH oop def.	802.7 (3.8)	791.2(w)
a"	CH oop def.	838.9 (0.4)	–
a′	CH oop def.	839.4 (4.2)	–
a′	ring def.	859.0 (163.6)	837.5(vs)
a"	CH oop def.	878.3 (5.3)	–
a′	CH oop def.	936.5 (23.8)	–
a′	HCH ip def.	1013.2 (38.6)	996.2(s)
a"	HCH ip def.	1032.9 (3.0)	–
a"	HCH ip def.	1087.7 (0.6)	–
a′	HCH ip def.	1092.9 (7.7)	1073.7(w)
a′	ring breath.	1135.3 (7.3)	1109.1(w)
a"	HCH ip def.	1283.4 (0.2)	–
a"	CC str.+ HCH ip def.	1370.4 (0.0)	–
a′	CC str.+ HCH ip def.	1380.3 (20.3)	1351.4(m)
a"	CC str.+ HCH ip def.	1458.7 (15.1)	1424.1(m)
a′	CC str.+ HCH ip def.	1489.7 (20.1)	1453.2(m)
a′	SiH str.	2095.7 (165.5)	2069.5(m),[a] 2059.8(m),[a] 2055.5(m),[a] 2021.7(w)[a]
a"	CH str.	3191.0 (2.1)	–
a′	CH str.	3197.7 (1.3)	–
a′	CH str.	3210.9 (0.6)	–
a"	CH str.	3215.5 (7.4)	–
a	CH str.	3231.7 (7.4)	–

(b) isomer **[D_6]4**

Sym.	Approx. description	Calculation	Experiment
a′′	Si/ring def.	117.2 (0.6)	–
a′	Si/ring def.	216.8 (0.6)	–
a′′	SiD def.	381.5 (0.5)	–
a′	SiC sym. str.	397.4 (36.6)	412.1(m)
a′′	SiC as. str.	494.5 (0.1)	–
a′	CD o.o.p. def.	505.7 (17.1)	502.2(m)
a′′	CD o.o.p. def.	567.5 (1.5)	–
a′	SiD def.+ CD def.	573.1 (51.0)	570.5(s), 568.8(s)
a′	SiD def.+ CD def.	607.0 (44.3)	591.1(m)
a′	CD o.o.p. def.	635.6 (82.7)	628.1(s)
a′′	CD o.o.p. def.	686.9 (3.1)	672.9(vw)
a′	CD i.p. def.	734.1 (3.1)	733.1(w)
a′′	CD i.p. def.	752.7 (0.1)	–
a′	CD i.p. def.	782.6 (42.7)	767.2(vs)
a′′	CD i.p. def.	787.9 (3.1)	775.1(w)
a′	CD i.p. def.	791.4 (2.8)	790.9(w)
a′′	CD o.o.p. def.	856.0 (1.2)	843.8(w)
a′	CD i.p. def.	862.8 (3.9)	850.7(m)
a′′	CD i.p. def.	1008.9 (0.1)	–
a′	CC str.(ring breath.)	1071.2 (14.0)	1049.8(m)
a′′	CC str.	1296.8 (0.6)	1275.2(vw)
a′	CC str.	1306.3 (1.3)	1284.4(w)
a′′	CC str.	1364.2 (6.3)	–
a′	CC str.	1415.3 (40.6)	1388.9(s)
a′	SiD str.	1508.4 (87.1)	1505.8(m),[b] 1498.7(m),[b] 1487.3(m),[b] 1472.9(s)[b]
a′′	CD str.	2354.8 (2.1)	–
a′	CD str.	2358.4 (1.4)	–
a′	CD str.	2377.2 (2.7)	–
a′′	CD str.	2381.9 (5.0)	–
a′	CD str.	2406.4 (5.0)	–

[a] Very broad and split (at least 3 different matrix sites). [b] Broad and split (several overlapping bands and different matrix sites; unambiguous assignment not possible.



Scheme 3. Calculated relative energies of some C_4H_6Si isomers (B3LYP/6-311+G**)

Reactions with Butadiene

Calculations

A prerequisite for [1,4]-addition to a conjugated system is the *s,cis* orientation of the two double bonds. However, condensed butadiene at 10 K consists almost exclusively of the *s,trans* conformer. Therefore it can be anticipated that in case of butadiene silicon atoms may not yield the [1,4]-adduct **10** but the [1,2]-adduct **14**. This is especially true if the silicon atoms add in a concerted manner.

Calculations show that both compounds **10** and **14** represent minima on the C_4H_6Si energy hypersurface. Both isomers can be formed in an exothermic reaction from the starting materials (Scheme 3, Table 5). Most interestingly, the calculations indicate that two different [1,4]-adducts can exist. In addition to folded **10**, which is similar to adduct **3** in the case of addition to cyclopentadiene, a structure with C_s symmetry, a second [1,4]-adduct **11** with a planar geometry (C_{2v} symmetry) is calculated as a minimum. Comparison of the energies of the two "folding isomers" shows that the planar form **11** is only 1.9 kcal·mol^{-1} less stable than the bent form **10**. The global minimum is silole **9**. Scheme 3 also shows the isomers **13** and **15**, although there is no obvious route for their formation.

According to the calculations silicon atoms (having a triplet ground state) should generate, in the initial step, a triplet [1,2]-type adduct **16** with butadiene. This species has to be regarded as a 1,3-diradical in which the silicon atom

Table 5. Calculated energies and vibrational spectra of some C_4H_6Si isomers (B3LYP/6-311+G**)

Species (pointgroup, state)[a] Energy, ZPE included [hartrees][a]	Vibrational spectrum: wavenumber (IR intensity) symmetry
9 (C_{2v}, $^1A_1$) −445.473218	246.5 (0) b_1, 375.2 (0) a_2, 500.2 (17) a_1, 548.2 (2) b_1, 618.7 (2) b_2, 675.6 (0) a_2, 709.3 (13) b_2, 731.7 (185) b_1, 749.9 (0) a_1, 763.5 (0) a_2, 888.7 (91) b_2, 933.8 (21) a_1, 962.2 (94) a_1, 993.7 (0) a_2, 997.9 (0) b_1, 1109.0 (11) a_1, 1118.8 (2) b_2, 1309.2 (5) b_2, 1364.2 (12) a_1, 1532.10 (4) a_1, 1610.0 (4) b_2, 2218.0 (113) b_1, 2220.6 (107) a_1, 3135.4 (10) b_2, 3149.9 (32) a_1, 3196.1 (8) b_2, 3197.6 (2) a_1
10 (C_s, $^1a'$) −445.446664	269.6 (4) a', 399.1 (0) a'', 412.5 (4) a', 483.9 (4) a'', 539.3 (17) a', 725.4 (5) a'', 755.8 (16) a'', 829.4 (54) a', 876.7 (26) a', 924.2 (5) a'', 983.5 (20) a', 990.6 (36) a', 1009.8 (1) a'', 1028.7 (11) a'', 1071.5 (12) a', 1160.1 (5) a'', 1191.4 (2) a', 1383.0 (1) a'', 1475.6 (1) a'', 1485.2 (12) a', 1521.7 (2) a', 3071.3 (24) a', 3082.4 (11) a'', 3153.4 (4) a'', 3157.6 (4) a', 3166.8 (9) a'', 3178.4 (13) a',
11 (C_{2v}, $^1A_1$) −445.443584	109.3 (2) b_1, 318.3 (0) a_2, 478.10 (22) a_1, 528.9 (1) b_1, 557.5 (0) a_2, 573.1 (26) b_2, 636.3 (14) a_1, 746.7 (67) b_1, 769.10 (2) b_2, 931.4 (0) a_1, 952.3 (15) b_2, 970.2 (0) a_2, 1103.7 (0) a_2, 1105.3 (1) b_1, 1117.4 (31) a_1, 1178.7 (24) b_2, 1218.0 (11) a_1, 1364.4 (3) b_2, 1407.6 (20) b_2, 1409.10 (0) a_1, 1667.5 (18) a_1, 2973.8 (30) b_2, 2975.9 (11) a_1, 2986.10 (0) a_2, 2990.3 (15) b_1, 3124.2 (8) b_2, 3148.7 (52) a_1
12 (C_1, $^1A_1$) −445.442702	104.7 (29) a_1, 362.4 (20) a_1, 459.8 (16) a_1, 507.4 (8) a_1, 592.4 (18) a_1, 656.8 (7) a_1, 684.0 (48) a_1, 729.1 (27) a_1, 785.1 (9) a_1, 804.5 (23) a_1, 920.9 (31) a_1, 951.7 (12) a_1, 966.2 (7) a_1, 1023.9 (8) a_1, 1050.9 (8) a_1, 1117.6 (10) a_1, 1187.6 (2) a_1, 1249.1 (11) a_1, 1383.4 (2) a_1, 1402.4 (17) a_1, 1557.9 (2) a_1, 2249.10 (82) a_1, 2992.5 (2) a_1, 3083.6 (7) a_1, 3149.6 (16) a_1, 3180.6 (14) a_1, 3212.0 (3) a_1
13 (C_{2v}, $^1A_1$) −445.420965	48.5 (1) b_1, 103.1 (0) a_2, 138.5 (0) a_1, 315.5 (1) b_2, 340.7 (1) a_1, 419.7 (0) a_2, 506.0 (16) b_1, 657.5 (138) b_2, 687.7 (52) a_1, 999.8 (0) b_2, 1019.0 (0) a_2, 1019.10 (63) b_1, 1025.2 (14) a_1, 1031.3 (0) a_2, 1040.2 (46) b_1, 1282.2 (0) b_2, 1296.3 (0) a_1, 1421.6 (78) b_2, 1425.9 (6) a_1, 1608.7 (38) b_2, 1620.0 (0) a_1, 3081.5 (5) b_2, 3081.7 (39) a_1, 3097.4 (51) b_2, 3098.8 (6) a_1, 3172.7 (22) a_1, 3173.1 (7) b_2
14 (C_1, $^1A_1$) −445.412011	104.9 (0) a_1, 149.4 (1) a_1, 270.2 (1) a_1, 415.5 (19) a_1, 496.4 (3) a_1, 547.7 (9) a_1, 617.8 (34) a_1, 682.5 (14) a_1, 834.6 (9) a_1, 871.9 (18) a_1, 896.6 (50) a_1, 958.9 (1) a_1, 988.9 (4) a_1, 1021.10 (10) a_1, 1103.5 (34) a_1, 1202.1 (37) a_1, 1297.1 (0) a_1, 1330.9 (2) a_1, 1414.9 (6) a_1, 1456.3 (5) a_1, 1665.0 (75) a_1, 3073.5 (6) a_1, 3087.3 (2) a_1, 3101.3 (19) a_1, 3130.9 (6) a_1, 3143.10 (6) a_1, 3216.5 (15) a_1
15 (C_s, $^1a'$) −445.389506	131.2 (0) a'', 206.5 (1) a', 524.6 (7) a', 561.2 (33) a'', 681.4 (10) a'', 782.4 (3) a', 846.6 (19) a', 894.5 (1) a', 911.5 (1) a'', 929.10 (2) a'', 976.6 (4) a', 1002.6 (6) a', 1070.6 (4) a'', 1073.2 (6) a', 1203.0 (2) a'', 1205.8 (6) a', 1213.8 (0) a'', 1263.5 (9) a'', 1284.4 (2) a', 1493.0 (1) a'', 1513.2 (1) a', 3016.7 (57) a'', 3025.8 (108) a', 3060.6 (1) a'', 3079.9 (36) a', 3100.1 (23) a'', 3112.3 (28) a'
16 (C_1, $^3A_1$) −445.383500	96.2 (2) a_1, 211.3 (0) a_1, 291.0 (1) a_1, 302.6 (9) a_1, 404.9 (15) a_1, 514.4 (2) a_1, 597.4 (4) a_1, 746.0 (4) a_1, 845.4 (1) a_1, 874.7 (52) a_1, 888.8 (49) a_1, 911.6 (8) a_1, 991.0 (15) a_1, 1014.5 (7) a_1, 1199.5 (9) a_1, 1236.1 (9) a_1, 1290.4 (5) a_1, 1359.9 (1) a_1, 1460.0 (1) a_1, 1494.6 (14) a_1, 1552.6 (15) a_1, 3090.0 (3) a_1, 3134.10 (3) a_1, 3141.1 (2) a_1, 3148.8 (4) a_1, 3176.9 (1) a_1, 3235.7 (6) a_1
TS10,11 (Cs, $^1a'$) −445.437040	−209.1 (3) a', 332.8 (10) a', 396.3 (0) a'', 563.9 (19) a'', 605.10 (42) a', 682.2 (2) a'', 720.3 (32) a', 781.4 (1) a'', 788.5 (11) a', 935.2 (1) a', 947.5 (9) a'', 970.3 (2) a'', 1083.9 (6) a', 1096.0 (8) a'', 1123.1 (38) a', 1179.8 (1) a'', 1207.3 (19) a', 1359.7 (2) a'', 1449.1 (5) a'', 1454.6 (2) a', 1640.5 (8) a', 2971.7 (44) a', 2974.9 (20) a'', 3073.9 (25) a'', 3074.4 (4) a', 3135.5 (7) a'', 3158.5 (41) a'
TS10,14 (C_1, $^1A_1$) −445.404042	−156.9 (2) a_1, 148.7 (0) a_1, 275.8 (2) a_1, 380.1 (15) a_1, 516.10 (4) a_1, 579.7 (33) a_1, 628.5 (4) a_1, 664.2 (6) a_1, 790.5 (13) a_1, 860.8 (8) a_1, 949.8 (44) a_1, 959.9 (4) a_1, 1010.6 (13) a_1, 1027.8 (9) a_1, 1104.5 (6) a_1, 1158.4 (36) a_1, 1281.7 (0) a_1, 1334.5 (4) a_1, 1417.10 (5) a_1, 1439.1 (3) a_1, 1672.2 (23) a_1, 3053.2 (7) a_1, 3074.1 (5) a_1, 3106.6 (23) a_1, 3124.4 (14) a_1, 3145.6 (6) a_1, 3206.8 (19) a_1

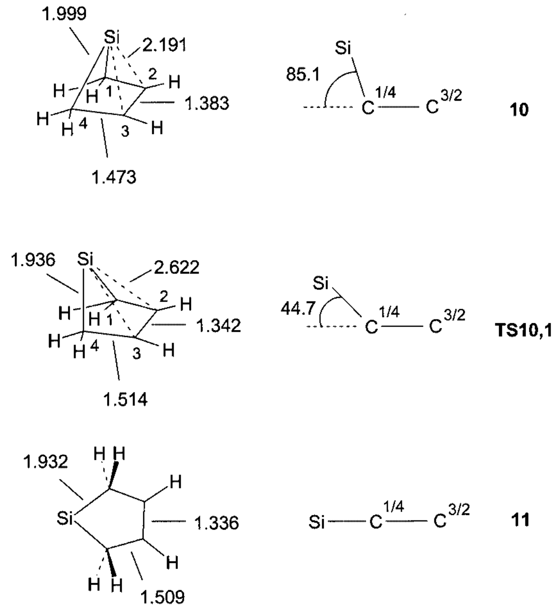
[a] ^3Si (^3P) −289.394168. C_4H_6 **17** (C_2h,$^1A_1$) −155.956078.

is normally bonded to the carbon atom at the end of the chain (Si−C distance 2.05 Å), but has only a very weak nonbonding interaction with the adjacent carbon atom (Si−C distance 2.33 Å). Diradical **16** could be a precursor not only for [1,2]-adduct **14** but also for the [1,4]-isomers **10** and **11**. The four isomers **9**, **10**, **11**, and **14** (circled in Scheme 3) should therefore be considered as reasonable candidates for matrix isolation.

The calculated structural features of the two peculiar C_4H_6Si isomers **10** and **11** as well as of transition state **TS10,11** are given in Scheme 4. The fact that, depending on the folding of the molecule, two [1,4]-adducts can exist is a strange situation and originates probably from the tendency of the bivalent silicon atom in **11** to demand higher coordination. By folding of the ring in the planar conformer the silicon atom comes via **TS10,11** into the sphere of the π-bond and the molecule is stabilized by coordination to the double bond, resulting in a new minimum **10**.

IR Spectroscopic Observations

Cocondensation of silicon atoms and butadiene with an excess of argon (ratio 1:100) at 10 K leads to an IR spectrum showing, besides the absorptions of the excess of butadiene, two groups of bands which can be differentiated by their photochemical behavior. Upon irradiation with light of wavelength 435 nm the intensities of bands belonging to the first group decrease whereas those of the other group increase. The corresponding difference spectrum is presented in Figure 3. By comparison with the calculated IR spectra it can be concluded that the bands of the photoactive species have to be attributed to a mixture of the planar [1,4]-adduct **11** and [1,2]-adduct **14**. Both isomerize upon excitation with 435 nm-light to the tetracoordinated [1,4]-adduct **10** (Table 6, a and b). Since the absorptions of **10** are already present − but with weaker intensity − in the IR spectrum before irradiation, it is evident that the original



Scheme 4. Calculated features of the two peculiar C_4H_6Si isomers **10** and **11** as well as of transition state **TS10,11**

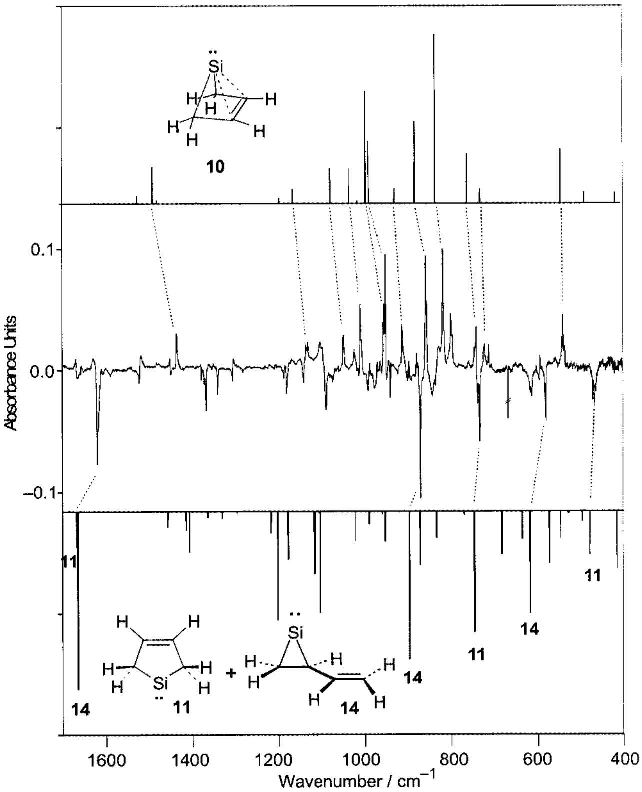


Figure 3. Top: calculated (B3LYP/6-311+G**) IR spectrum of the tetracoordinated [1,4]-adduct **10**; center: difference FT-IR spectrum of the photoreaction **11** + **14** → **10** (obtained by subtraction of the spectra taken after and before irradiation with 435 nm for 2 h); bottom: calculated IR spectrum (B3LYP/6-311+G**) of a 1:1 mixture of planar [1,4]-adduct **11** and [1,2]-adduct **14**

condensate contains all three adducts **10**, **11**, and **14**. It should also be noted that the presence of **14** is much clearer in the spectra of the reaction of silicon atoms with perdeuterated butadiene.

Table 6. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C_4H_6Si isomers (a) **[H$_6$]10** and (b) **[D$_6$]10**

(a) isomer **[H$_6$]10**

Sym.	Approx. description	Calculation	Experiment
a′	def.	269.6 (4)	–
a"	SiC as str.	399.1 (0)	–
a′	def.	412.5 (4)	–
a"	SiC as str.	483.9 (4)	–
a′	SiC sym str.	539.3 (17)	540.4, 536.3 (m)
a"	CC str.	725.4 (5)	721.5 (w)
a"	CH_2 twist.	755.8 (16)	745.3, 740.7 (w)
a′	CH oop def.	829.4 (54)	818.5, 816.4 (s)
a′	CH oop def.	876.7 (26)	858.2, 856.2 (s)
a′′	CH oop def.	924.2 (5)	913.4, 911.7 (m)
a′	CH_2 wag.	983.5 (20)	951.0 (s)
a′	CH_2 wag.	990.6 (36)	956.3 (m)
a"	CH def.	1009.8 (1)	–
a"	CC str.	1028.7 (11)	1048.7 (m)
a′	CC str.	1071.5 (12)	1137.0, 1132.9 (w)
a"	CC str.	1160.1 (5)	–
a′	CH ip def.	1191.4 (2)	–
a"	CH ip def.	1383.0 (1)	–
a"	CH_2 scis.	1475.6 (1)	–
a′	CH_2 scis.	1485.2 (12)	1437.1 (m)
a′	CC str.	1521.7 (2)	–
a′	CH str.	3071.3 (24)	–
a"	CH str.	3082.4 (11)	–
a"	CH str.	3153.4 (4)	–
a′	CH str.	3157.6 (4)	–
a"	CH str.	3166.8 (9)	–
a′	CH str.	3178.4 (13)	–

(b) isomer **[D$_6$]10**

Sym.	Approx. description	Calculation	Experiment
a′	SiC str.	237.5 (2.7)	–
a′	SiC str.	360.1 (1.3)	–
a′′	SiC str.	369.7 (1.0)	–
a′′	SiC str.	423.1 (1.2)	–
a′	SiC str.	503.4 (7.3)	–
a′′	CD_2 def.	556.9 (8.4)	549.9 (m)
a′′	CCC def.	622.0 (2.0)	–
a′	CD_2 rock.	661.0 (17.6)	645.7, 649.3 (w)
a′	CD_2 oop def.	666.8 (42.9)	675.3, 685.5 (vs)
a′′	CD_2 oop def.	715.4 (0.6)	–
a′	CD_2 def.	754.3 (39.0)	735.2, 740.8 (vs)
a′	CD_2 def.	782.3 (7.4)	–
a′′	CD_2 def.	811.9 (9.3)	799.8 (w)
a′′	CD_2 def.	843.6 (4.4)	827.3, 830.8 (m)
a′	CD_2 ip def.	861.4 (0.2)	–
a′′	CC str.	956.2 (1.6)	–
a′	CC str.	958.8 (3.7)	940.2, 944.8 (vw)
a′′	CD_2 def.	1065.5 (1.8)	1077.8, 1040.8 (vw)
a′	CC str. + CD_2 sciss.	1153.6 (10.9)	1031.1, 1032.0 (m)
a′′	CC str.	1248.6 (7.6)	1228.0, 1231.1, 1232.0 (m)
a′	CC str.	1468.7 (4.7)	1432.4, 1439.6 (vw)
a′	CD str.	2231.2 (7.0)	–
a′′	CD str.	2239.9 (3.6)	–
a′′	CD str.	2329.7 (0.0)	–
a′	CD str.	2346.0 (2.7)	–
a′′	CD str.	2349.5 (6.5)	2268.6 (w, br.)
a′	CD str.	2356.3 (7.6)	–

The symmetric Si−C vibration of **10** at 540.4/536.3 cm^{-1} is clearly detectable. According to the coordination the C=C band is expected at a very low frequency (1521.7

cm^{-1}). Unfortunately, this absorption cannot be detected experimentally. The C=C band should appear at much higher frequency in case of the planar [1,4]-adduct **11** or [1,2]-adduct **14**. As can be derived from Figure 3 the C=C double bonds of **11** and **14** absorb in the normal range. In agreement with theory the C=C vibration of **14** is rather intense.

Irradiation of the condensation product at a shorter wavelength (254 nm) for 6 h generates another species, which can be identified unequivocally by comparison of the experimental and calculated spectra as silole **9** (Figure 4, Table 7, a and b). This means that not only isomer **10** but also **11** and **14** are finally transformed into **9** upon irradiation with 254 nm-light.

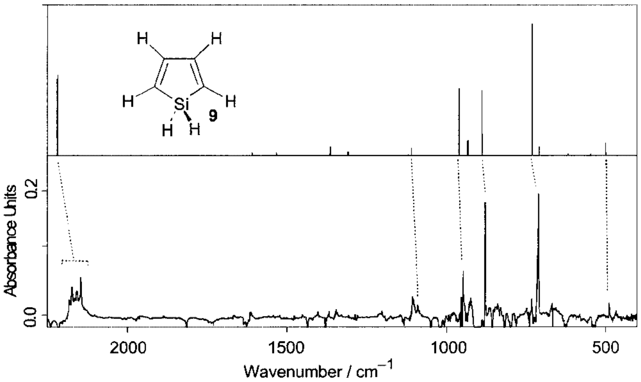


Figure 4. Top: calculated (B3LYP/6-311+G**) IR spectrum of silole **9**; bottom: experimental IR spectrum of **9** (obtained after irradiation of the reaction products of Si atoms with butadiene, **11** and **14**, with 254- nm light for 6 h)

Silole **9** has been prepared and identified before by Michl et al.[3] The reported calculated and experimental spectra agree with our results, although we were not able to detect the other bond-shift isomers of **9** − for instance silacyclopentadiene **12** − described by these authors.

Conclusion

The reaction of silicon atoms with butadiene **17** is not as clear-cut as with cyclopentadiene (**8**). The *transoid* conformation of butadiene **17** enforces the initial formation of the [1,2]-adduct in the triplet state **16**, which then can undergo an intersystem crossing to the singlet state **14**. It needs only 5 kcal·mol^{-1} to overcome **TS10,14** and to reach the bridged [1,4]-adduct **10**.

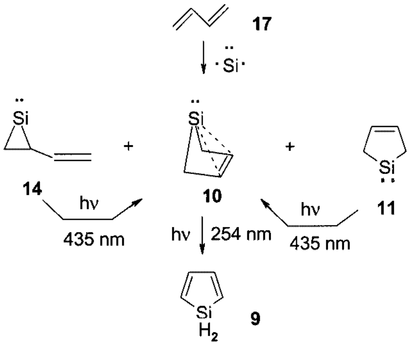


Table 7. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C$_4$H$_6$Si isomers (a) **[H$_6$]9** and (b) **[D$_6$]9**

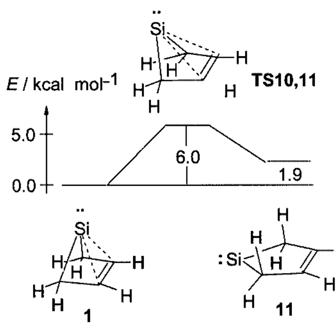
(a) isomer **[H$_6$]9**

Sym.	Approx. description	Calculation	Experiment
b_1	ring oop def.	246.5 (0.3)	–
a_2	ring oop def.	375.2 (0.0)	–
a_1	ring ip def.	500.2 (17.5)	489.6 (w)
b_1	SiH2 rock.	548.2 (2.0)	–
a_1	SiCC asym. str.	618.7 (2.4)	–
a_2	SiH2 twist.	675.6 (0.0)	–
a_1	SiH2 wag.	709.3 (12.7)	–
b_1	CH oop def.	731.7 (185.2)	711.8 (s)
a_1	SiCC sym. str.	749.9 (0.2)	–
a_2	CH oop def.	763.5 (0.0)	–
a_1	ring ip def.+ SiH$_2$ wag.	888.7 (91.4)	879.0 (s)
a_1	CC str.	933.8 (20.8)	–
a_1	SiH$_2$ sciss.	962.2 (94.3)	947.4 (s)
a_2	CH oop def.	993.7 (0.0)	–
b_1	CH oop def.	997.9 (0.2)	–
a_1	CH ip def.	1109.0 (10.5)	1089.7 (w)
a_1	CH ip def.	1118.8 (2.3)	–
a_1	CH ip def.	1309.2 (4.9)	–
a_1	CH ip def.	1364.2 (11.9)	–
a_1	CC str.	1533.0 (3.9)	–
a_1	CC str.	1610.0 (4.0)	–
b_1	SiH str.	2218.0 (112.8)	2146.6 (s), 2145.0 (m)
a_1	SiH str.	2220.6 (107.4)	2182.7 (m), 2174.2 (s), 2158.6 (m)
a_1	CH str.	3135.4 (10.4)	–
a_1	CH str.	3149.9 (32.1)	–
b_2	CH str.	3196.1 (8.4)	–
a_1	CH str.	3197.6 (2.1)	–

(a) isomer **[D$_6$]9**

Sym.	Approx. description	Calculation	Experiment
b_1	ring oop def.	200.4 (0.1)	–
a_2	ring oop def.	299.2 (0.0)	–
b_1	ring oop def.	430.7 (0.6)	–
a_1	SiCC sym. def.	481.9 (10.0)	477.0 (w)
a_2	ring twist.	515.4 (0.0)	–
b_2	SiD$_2$ rock.	526.1 (10.7)	–
b_1	SiD$_2$ rock + CD oop def.	576.9 (114.3)	564.0 (vs)
b_2	SiC asym. str.	601.8 (6.5)	–
a_2	SiD$_2$ twist.	601.9 (0.0)	–
a_1	SiD$_2$ scis. + CD ip def.	654.2 (11.6)	–
a_1	SiD$_2$ scis.	692.2 (48.1)	690.6 (m)
b_2	SiD$_2$ wag. + CD ip def.	735.6 (32.7)	729.9 (m)
b_1	CC str. + CD def.	783.1 (1.1)	–
a_1	CD ip def.	796.3 (8.8)	–
a_2	ring oop def.	816.9 (0.0)	–
a_1	ring breath.	832.8 (11.5)	–
b_2	CD ip def. + CC str.	874.9 (24.4)	–
b_2	CD ip def. + CC str.	1065.8 (0.6)	–
a_1	CC str.	1185.2 (7.4)	170.3 (m)
a_1	CC str.	1510.9 (2.2)	–
b_2	CC str.	1555.9 (6.2)	–
a_1	SiD str.	1589.5 (68.1)	1554.4 (w)
b_1	SiD str.	1602.8 (68.2)	1580.0, 1575.4, (w, br.)
b_2	CD str.	2313.4 (6.2)	–
a_1	CD str.	2323.4 (14.6)	–
b_2	CD str.	2367.3 (2.3)	–
a_1	CD str.	2371.5 (4.2)	–

The same species **10** can also easily be formed from isomer **11** via **TS 10,11** with an activation energy of only 4.1 kcal·mol^{-1}. The existence of two such "folding isomers" (Scheme 5) is unique and a peculiar characteristic of the C_4H_6Si energy hypersurface. The folding angle of the five-membered ring changes from 0° in planar **11** to 44.7° in **TS10,11** and finally to 85.1° in the bent stereoisomer **10**.



Scheme 5

With regard to the low energies of **TS 10,11** and **TS10,14** it is no surprise that all three isomers **10**, **11**, and **14** are directly formed in the reaction of butadiene **17** with silicon atoms. This process delivers enough energy to overcome the barriers of the mutual interconversions, even at 10 K.

Experimental Section

General: The cryostat for matrix isolation was a closed-cycle compressor unit RW2 with coldhead base unit 210 and extension module ROK from Leybold. The matrix window was CsI and the spectrometer was an FTIR instrument IFS 85 from Bruker. The light sources used were a mercury high-pressure lamp (HBO, 200 from Osram) with a monochromator (Bausch and Lomb) and a mercury low-pressure spiral lamp with a Vycor filter (Gräntzel). For the production of silicon atoms a 0.7 × 2 × 22 mm rod was cut out from a highly doped silicon wafer and heated resistively with a current of 10 A at 10 V. Under these conditions the surface temperature amounted to 1350−1380 °C.

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