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Reactions of Silicon Atoms with Nitrogen: A Combined Matrix Spectroscopic and Density Functional Theory Study[1]

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Cocondensation of thermally generated silicon atoms with an excess of nitrogen at 12 K offers an access to new binary silicon−nitrogen compounds. In addition to the well-known linear dinitrogensilicon, SiNN (**1-T**), six new species containing one (**2**, **3**) or two silicon atoms (**4**−**7**) have been isolated and identified by matrix spectroscopy and their mutual photochemical transformations. The structural elucidation of the new compounds **2**−**7** is based on isotopic labeling experiments and density functional theory calculations.

Introduction

More than 20 years ago Weltner et al. reported on the formation of SiNN (**1-T**) in various matrices by reaction of silicon atoms with N_2.[2] From the matrix spectroscopic data (ESR, IR, UV/vis) a linear structure and a triplet ground state were derived. Some years later Margrave et al. studied the UV spectrum of **1-T** in a krypton matrix.[3] SiNN (**1-T**) is easily detectable by a very strong infrared band (NN str: 1731 cm^{-1} in Ar matrix, 1754 cm^{-1} in N_2 matrix). Indeed, this band was already observed in 1970 by Milligan and Jacox in a N_2 matrix during a vacuum UV photolysis of SiH_4, but not assigned to **1-T**.[4] As far as we know, evidence for the existence of other molecules consisting of silicon and nitrogen has only been reported in two cases: Si_3N and Si_2N have been detected in the gas phase by mass spectroscopic methods.[5−7] The structural data of a linear SiNSi species were determined by Brugh and Morse by means of high-resolution two-photon ionization spectroscopy.[8] This result is in good accordance with the ab initio study of Ornellas and Iwata, predicting this Si_2N isomer to be the global minimum on the corresponding energy hypersurface.[9]

While experimental results are rather scarce, there are numerous contributions from the theoretical side. Most deal with the SiN_2 system (**1**).[10−17] It turned out that ab initio methods including higher level electron correlation or density functional methods are necessary to predict the experimentally observed IR bands with acceptable accuracy,[12,14,15] while SCF and CISD methods failed completely.[10] A cyclic SiN_2 isomer has been considered by several authors.[16−18] Beyond the SiN_2 isomer Janoschek calculated two SiN_4 species by ab initio and DFT methods.[18] Ornellas and Iwata reported on the location of nine stationary points on the Si_2N_2 potential energy hypersurface using ab initio calculations on various levels of electron correlation.[19]

Our interest in $Si_x(N_2)_y$ species has mainly two sources. On one hand, in earlier studies on the matrix photolysis of silyl azides we had observed, in addition to SiNN (**1-T**), some additional IR bands, which probably originated from hitherto unknown silicon−nitrogen compounds.[20] On the other hand, the IR band of SiNN (**1-T**) was, due to the unavoidable presence of N_2, ubiquitous in all our experimental studies on reactions of atomic silicon with various substrate molecules in argon matrices.[21] From these experiments it was obvious that a silicon atom reacts, presumably without

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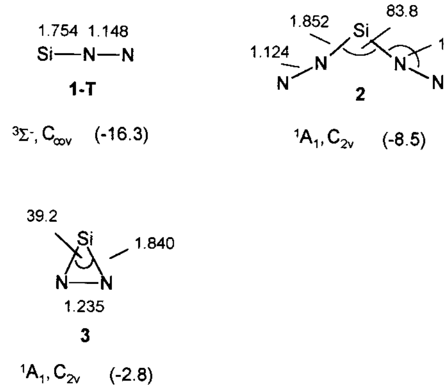
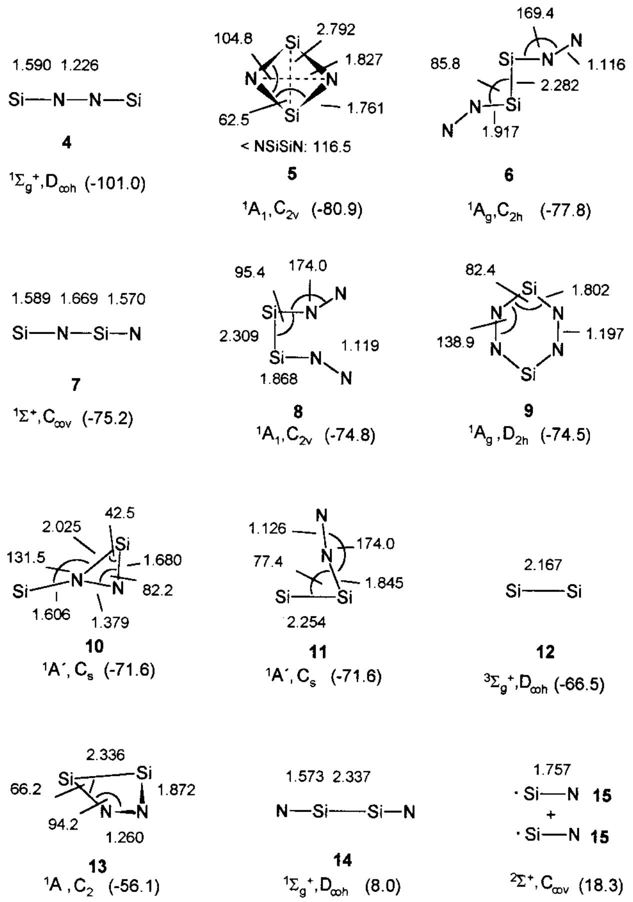
Chart 1. Calculated Geometries and Energies (kcal mol^{-1}) of Si(N$_2$)$_y$ Species (B3LYP/6-311+G, ZPE Included) Relative to ^{3}Si + (N$_2$)$_y$ (y = 1, 2)^a**



^{a} Distances are given in Å and angles in deg.

Chart 2. Calculated Geometries and Energies (kcal mol^{-1}) of Si$_2$(N$_2$)$_y$ Species (B3LYP/6-311+G, ZPE Included) Relative to 2 ^{3}Si + (N$_2$)$_y$ (y = 0−2)^a**



^{a} Distances are given in Å and angles in deg.

any activation barrier, with a nitrogen molecule. The question arose whether another N$_2$ molecule can be bound, allowing formation of a compound of the composition SiN$_4$. It was also conceivable that Si$_x$(N$_2$)$_y$ molecules with more than one Si atom may be found if the concentration of silicon atoms is increased. Such compounds are of interest with respect to the formation of solid silicon nitride (Si$_3$N$_4$) directly from the elements.[22] As shown in this paper, an expansion in both directions—formation of compounds with a lower or higher Si/N$_2$ ratio than in SiNN (**1-T**)—is indeed possible.

Generation of Si$_x$(N$_2$)$_y$ Species

The obvious entry onto Si$_x$(N$_2$)$_y$ energy hypersurfaces is the reaction of silicon atoms with nitrogen, which is deposited via a vacuum line on a CsI window at 12 K. At the same time silicon atoms, prepared by vaporization of solid silicon at ca. 1500 °C[2,23] using a boron nitride crucible, are separately condensed. It turned out that an even better method for the generation of Si atoms can be applied: namely, the resistive heating of a silicon rod to a temperature of ca. 1380 °C. The ratio Si:N$_2$ varied from 1:30 to 1:300.

FT-IR and UV/vis spectra were taken of the matrices thus formed. In addition to the absorptions of SiNN (**1-T**)[2] several new bands were recorded which should originate from compounds formed by the reaction of nitrogen with silicon atoms. After cocondensation the matrices were irradiated with light from a mercury high-pressure lamp in combination with various filters or a monochromator. For irradiations with the wavelength λ = 254 nm a mercury low-pressure lamp was used. The initiated photochemical reactions were monitored by IR and UV/vis spectroscopy.

Calculations

For the identification of compounds formed in the reaction of silicon atoms with nitrogen it was necessary to obtain the calculated vibrational spectra of the expected species. In addition to earlier theoretical studies[10−19] we carried out some calculations on our own using the Gaussian package of programs.[24] To get an overview of the Si$_x$(N$_2$)$_y$ potential energy surfaces, several stationary points were calculated with the 6-311+G** basis set and the B3LYP functional. Charts 1−3 show the calculated geometries and relative energies.

The global minimum in the series containing one silicon atom (Chart 1) is triplet dinitrogensilicon (**1-T**). As already shown by Janoschek,[18] this compound has to be described as a relatively loose complex between a silicon atom and a nitrogen molecule as an electron donor (end-on complexation). The stabilization energy of **1-T** compared to the two components is 16.3 kcal mol^{-1}. The S/T gap for **1** has been calculated to amount to 13.1[13] or 15.8 kcal mol^{-1}.[17] These values are similar to that of silicon itself (on the same level of calculation used by our group ^{3}Si is 25.8 kcal mol^{-1} lower in energy than ^{1}Si).

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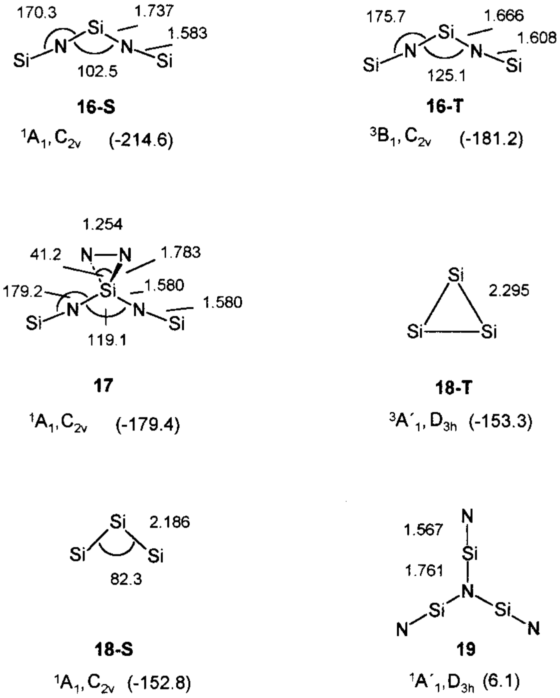
Chart 3. Calculated Geometries and Energies (kcal mol^{-1}) of $Si_3(N_2)_y$ Species (B3LYP/6-311+G, ZPE Included) Relative to 3 ^{3}Si + $(N_2)_y$ (y = 0−2)^a**



^{a} Distances are given in Å and angles in deg.

As calculated before,[18] there are two additional candidates, namely bis(dinitrogen)silicon (**2**) and 1-sila-2,3-diazacyclopropenylidene (**3**), which can be expected as reaction products of silicon atoms, since they have stabilization energies of −8.5 and −2.8 kcal mol^{-1}. Bisadduct **2** can be regarded as the addition product of excited ^{1}Si atoms with two molecules of nitrogen. Compound **3** has been calculated several times before.[16−18] Despite its high strain energy, it is more stable than the components. This may be due to the cyclic delocalization, similar to the situation in silacyclopropenylidene.[25,26]

In Chart 2 a selection of species containing two silicon atoms and 0, 1, or 2 molecules of nitrogen are summarized as a function of the energies relative to two ^{3}Si atoms and nitrogen. The global minimum is disiladiisocyanogen (**4**).[27] In comparison to the carbon analogues[28] the energetic ranking of the three isomers **4**, **7**, and **14** is reversed, because the N−N bond is stronger than the Si−N bond, which is in turn stronger than the Si−Si bond. It should also be kept in mind that silane isonitrile is more stable than silane nitrile.[29]

The cyclic isomer **5** is a very peculiar compound which has no analogy in carbon chemistry. It was first mentioned by Ornellas and Iwata[19] as a rather stable molecule with a tetrahedral-like structure. A "single bond" connects each pair of Si and N atoms, and this occurs mainly through p-type orbitals of both atoms.[19]

Table 1. Theoretical (B3LYP/6-311+G) IR Absorptions (Unscaled; Wavenumbers in cm^{-1}) of Compounds 1−19^a**

species	vibrational wavenumber
1-T ($^3\Sigma^-$)	π 315 (1); π 315 (1); σ 516 (16); σ 1809 (752)
2 ($^1A_1$)	a_1 121 (1); b_2 297 (1); b_1 312 (3); a_2 372 (0); a_1 398 (2); b_2 402 (26); a_1 514 (15); b_2 2063 (1007); a_1 2163 (258)
3 ($^1A_1$)	a_1 585 (0); b_2 730 (19); a_1 1552 (131)
4 ($^1\Sigma_g^+$)	π_u 161 (18); π_u 161 (18); π_g 413 (0); πg 413 (0); σ_g 571 (0); σ_u 1167 (93); σ_g 1617 (0)
5 ($^1A_1$)	a_1 239 (8); a_1 500 (15); a_2 517 (0); b_1 574 (35); a_1 827 (11); b_2 914 (314)
6 (^1A_g)	a_u 72 (0); b_u 85 (2); a_g 141 (0); b_g 288 (0); b_u 298 (57); a_g 327 (0); b_u 381 (12); a_u 386 (4); a_g 392 (0); a_g 522 (0); b_u 2169 (1260); a_g 2195 (0)
7 ($^1\Sigma^+$)	π 103 (2); π 103 (2); π 231 (26); π 231 (26); σ 541 (2); σ 1212 (30); σ 1381 (276)
8 ($^1A_1$)	a 95 (0); a 112 (2); b 163 (0); b 284 (0); b 329 (7); a 358 (0); a 371 (11); a 409 (0); a 450 (30); b 471 (44); b 2124 (421); a 2168 (584)
9 (^1A_g)	b_u 55 (14); a_u 223 (8); a_g 393 (0); a_g 410 (0); a_u 470 (0); b_g 481 (0); b_u 519 (99); a_g 578 (0); a_g 643 (0); b_u 725 (152); b_u 1508 (844); a_g 1822 (0)
10 ($^1A'$)	a′ 140 (6); a′ 315 (59); a" 332 (13); a′ 683 (85); a′ 910 (6); a′ 1249 (36)
11 ($^1A'$)	a′ 84 (5); a" 347 (2); a′ 389 (19); a′ 446 (12); a′ 492 (5); a′ 2093 (528)
12 ($^3\Sigma_g^-$)	σ_g 539 (0)
13 (^{1}A)	a 215 (11); b 393 (38); a 415 (0); a 528 (2); b 675 (7); a 1285 (203)
14 ($^1\Sigma_g^+$)	π_g 37 (0); π_g 37 (0); π_u 45 (40); π_u 45 (40); σ_g 295 (0); σ_u 1214 (1); σ_g 1218 (0)
15 ($^2\Sigma^+$)	σ 1174 (28)
16-S ($^1A_1$)	a_1 69 (5); b_1 147 (12); a_2 156 (0); b_2 182 (2); a_1 345 (33); b_2 568 (107); a1 574 (101); b_2 1296 (750); a_1 1327 (125)
16-T ($^3B_1$)	a_1 65 (2); b_2 170 (4); b_1 219 (43); a_2 225 (0); a_1 325 (43); a_1 525 (14); b_2 690 (1); b_2 1129 (795); a_1 1220 (0)
17 ($^1A_1$)	a_1 64 (4); b_1 105 (1); b_2 118 (1); a_2 173 (0); b_2 285 (68); b_1 298 (52); a_2 324 (0); a_1 338 (20); a_1 456 (6); b_2 693 (92); a_1 748 (5); b_1 758 (7); a_1 1360 (1); b_2 1371 (374); a_1 1502 (377)
18-T ($^3A_1'$)	e 311 (0.4); e 311 (0.4); a_1' 488 (0)
18-S ($^1A_1$)	a_1 166 (5); a_1 536 (9); b_2 538 (44)
19 ($^1A_1'$)	e′ 51 (14); e′ 51 (14); a_2' 56 (0); a_2'' 74 (44); e″115 (0); e″ 115 (0); e′ 173 (0); e′ 173 (0); a_2'' 311 (4); a_1' 383 (0); e′ 785 (179); e′ 785 (179); a_1' 1257 (0); e′ 1261 (71); e′ 1261 (71)

^{a} Absolute intensities (km mol^{-1}) are given in parentheses.

The other Si_2N_2 isomers **10**, **11**, and **13** require no further comment. Nevertheless, all of them can be formed in a exothermic reaction of silicon atoms with nitrogen. The adducts **6** and **8** of the composition Si_2N_4 formally represent *cis*,*trans* isomers of bis end-on nitrogen complexes of disilicon **12**. They may be formed via the monoadduct **11** as an intermediate. Both **6** and **8** have about the same energy as the cyclic isomer **9**.

Chart 3 shows some members (**16**−**19**) of the family $Si_3(N_2)_y$ (y = 0−2). It is not very likely that compounds containing three silicon atoms are directly generated under our reaction conditions. However, it cannot be excluded that such species may be formed upon annealing of the matrices (see below).

Results and Discussion

IR Spectroscopic Observations. Table 1 summarizes the calculated IR spectra of all calculated species **1**−**19**, from which only **1-T** has been identified so far.[2]

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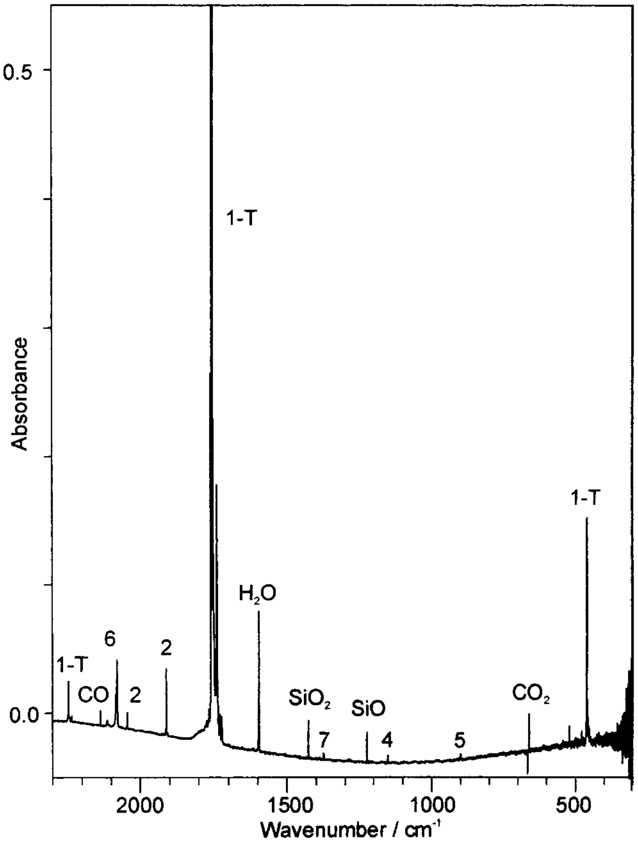


Figure 1. IR spectrum after cocondensation of silicon atoms and nitrogen (1:30) at 12 K.

Table 2. Theoretical and Experimental (Ar and N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of Triplet Dinitrogensilicon (1-T)

	sym	calcd[a]	calcd[b]	exptl (Ar, 12 K)[c]	exptl (N_2, 12 K)[c]
ν_{NN}	σ	1859.0[b]	1809.3 (752)[c]	1731.6 (vs)	1754.7 (vs)
δ_{SiNN}	π	336.0	315.3 (1)		
ν_{SiN}	σ	429.0	515.9 (16)	484.3 (vw)	461.6 (vw)

[a] CCSD(T)/cc-pVQZ.[17] [b] B3LYP/6-311+G** (absolute intensities (in km mol^{-1}) in parentheses). [c] Major trapping site.

In Figure 1 the “standard” IR spectrum registered at 12 K after cocondensation of silicon atoms and nitrogen (ratio 1:30) is presented. The strongest bands belong to the known[2] dinitrogensilicon (**1-T**). The experimental bands fit quite well with the absorptions calculated with the B3LYP/6-311+G** method (Table 2), which was therefore used throughout our work. Table 3 contains a list of the spectra of all isotopomers of **1-T** observed in our experiments. In each case the two most intense fundamental vibrations ν_{NN} and ν_{SiN} can be detected. The other experimental absorptions belong to combination bands and overtones. It should be added that the mixed isotopomers $Si^{14}N^{15}N$ and $Si^{15}N^{14}N$ were prepared by microwave discharge of a mixture of $^{14}N_2$ and $^{15}N_2$. The accordance between the calculated and experimental absorptions (Figure 2) is convincing. The splitting of the measured bands is caused by matrix effects, as could be shown by changing the population of the different matrix sites by irradiation or annealing experiments.

The bands of bis(dinitrogen)silicon (**2**) at 2045.0 and 1912.9 cm^{-1} were already present after cocondensation. Their intensities were enhanced when the concentration of nitrogen was raised (Si:N_2 = 1:300). Therefore, it is reasonable to assume that this molecule contains only one Si atom. Upon irradiation of the matrix with λ = 313 nm, surprisingly, the amount of **2** is increased at the beginning and then its concentration remains constant for a long time; finally the bands of **2** diminish and those belonging to 1-sila-2,3-diazacyclopropenylidene (**3**) become stronger. Thus, it seems as if **2** is an intermediate in the photoisomerization **1-T** → **3**. One can assume that an electronic transition in SiNN (**1-T**) promotes the molecule to an excited triplet state, which subsequently undergoes intersystem crossing to a singlet state, which in turn dissociates to ^1Si and N_2, followed by nitrogen addition to the ^1Si atoms and ending with the formation of **2**. If **3** is irradiated with λ = 254 nm, a back-reaction to **1-T** occurs.

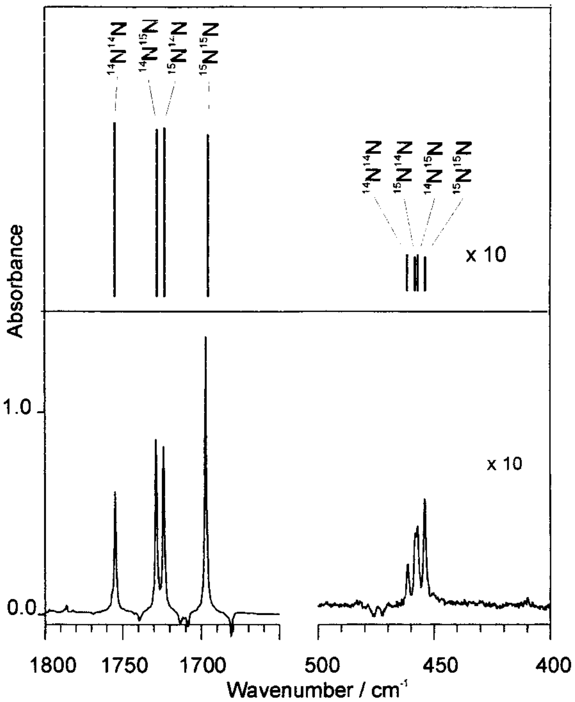
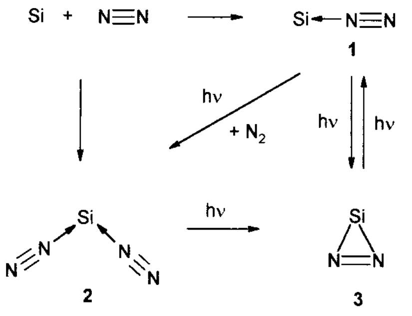


Figure 2. Comparison of experimental (N_2, 12 K; bottom) and theoretical (B3LYP/6-311+G**; top; scaled as in Table 3) IR spectra of triplet dinitrogensilicon ([$^{14}N_2$]**1** + [$^{15}N_2$]**1** + [$^{14,15}N_2$]**1**). The isotopic distribution was achieved by microwave discharge of a mixture of $^{14}N_2$ and $^{15}N_2$.



The interplay between **1-T**, **2**, and **3** can be taken as a structural hint for the compounds involved. More convincing for the correct description of **2** are again the isotopic studies (Figure 3, Table 4). The spectra of [$^{14}N_2$][$^{14}N_2$]**2** and [$^{15}N_2$][$^{15}N_2$]**2** show good accordance with the theoretical band positions. In the case of [$^{14}N_2$][$^{15}N_2$]**2**

Table 3. Theoretical (B3LYP/6-311+G) and Experimental (Ar and N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of Triplet Dinitrogensilicon (1-T)**

isotopomer		calcd	scaled[a]	exptl site 1[b]	exptl site 2[c]	exptl site 3[d]	exptl site 4[e]	exptl site 5[f]
$^{28}Si^{14}N^{14}N$	$2\nu_{NN}$	3618.6		3456.1	3426.5	3483.9	3494.8	
	$\nu_{NN} + \nu_{SiN}$	2325.2		2246.4	2247.7	2258.3		
	ν_{NN}	1809.3		1754.7	1739.5	1769.0	1774.7	1736.4
	δ_{SiNN}	315.3						
	ν_{SiN}	515.9		461.6	480.4	459.5		
$^{28}Si^{14}N^{15}N$	$2\nu_{NN}$	3563.2	3403.2	3405.9	3376.6		3440.8	
	$\nu_{NN} + \nu_{SiN}$	2292.3	2214.6	2215.0	2216.6			
	ν_{NN}	1781.6	1727.8	1728.7	1713.5	1742.7	1748.2	1710.9
	δ_{SiNN}	307.9						
	ν_{SiN}	510.7	456.9	457.1	475.9			
$^{28}Si^{15}N^{14}N$	$2\nu_{NN}$	3553.2	3393.6	3396.7	3368.0		3432.3	
	$\nu_{NN} + \nu_{SiN}$	2288.7	2211.1	2211.5	2213.2			
	ν_{NN}	1776.6	1723.0	1723.9	1708.7	1738.1	1743.4	1706.0
	δ_{SiNN}	312.6						
	ν_{SiN}	512.1	458.2	458.1	476.8			
$^{28}Si^{15}N^{15}N$	$2\nu_{NN}$	3496.6	3339.6	3344.7	3316.4	3372.3	3387.0	
	$\nu_{NN} + \nu_{SiN}$	2255.5	2179.0	2179.6	2181.6			
	ν_{NN}	1748.3	1695.5	1697.1	1681.2	1710.9	1716.6	1679.5
	δ_{SiNN}	305.2						
	ν_{SiN}	507.2	453.8	454.1	472.5			

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(Si^{14}N^{14}N)/\nu_{calcd}(Si^{14}N^{14}N)$; $C(2\tilde{\nu}_{NN}) = 0.9551$; $C(\tilde{\nu}_{NN} + \tilde{\nu}_{SiN}) = 0.9661$; $C(\tilde{\nu}_{NN}) = 0.9698$; $C(\tilde{\nu}_{SiN}) = 0.8947$. [b] Major trapping site. [c] Minor trapping site. [d] Photochemically generated trapping site ($\lambda = 254$ nm). [e] Interstitial site, generated by irradiation ($\lambda = 254$ nm) or annealing to 27 K. [f] Interstitial site, generated by irradiation ($\lambda = 254$ nm).

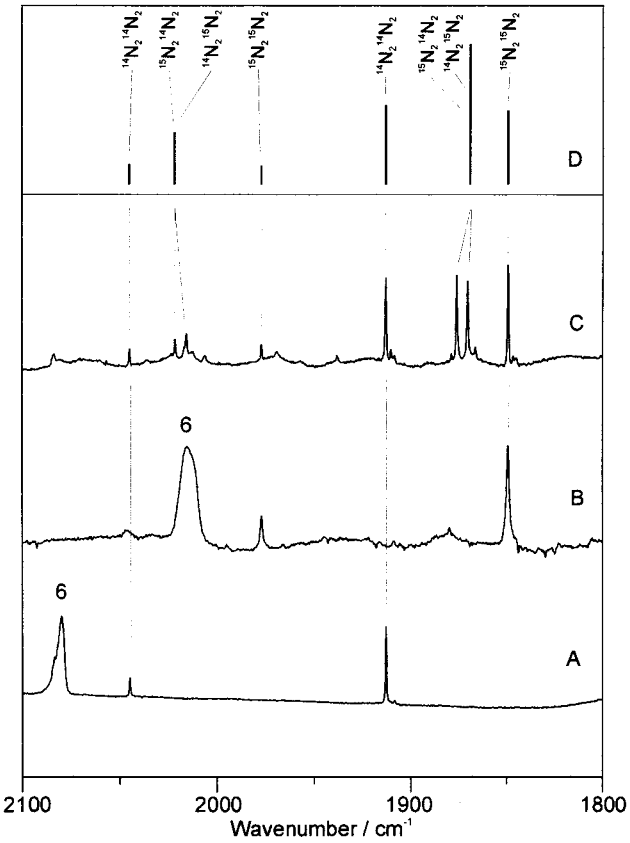


Figure 3. Comparison of experimental (N_2, 12 K) and theoretical (B3LYP/6-311+G**; scaled as in Table 4) IR spectra of bis(dinitrogen)silicon (**2**): (A) spectrum after cocondensation of Si atoms and $^{14}N_2$. (B) spectrum after cocondensation of Si atoms and $^{15}N_2$; (C) spectrum after cocondensation of Si atoms and a mixture of $^{14}N_2$ and $^{15}N_2$ (these bands diappeared upon irradiation (λ >400 nm)); (D) theoretical (B3LYP/6-311+G**) spectrum of a mixture of [$^{14}N_2$,$^{14}N_2$]**2**, [$^{15}N_2$,$^{15}N_2$]**2**, and [$^{14}N_2$,$^{15}N_2$]**2**.

Table 4. Theoretical (B3LYP/6-311+G), Scaled and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of Bis(dinitrogen)silicon (2) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{14}N^{14}N^{28}Si^{14}N^{14}N$	$\nu(s)_{NN}$	a_1	2162.6		2045.0
	$\nu(as)_{NN}$	b_2	2063.1		1912.9
$^{14}N^{15}N^{28}Si^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2147.3	2030.5	
	$\nu(as)_{NN}$	a’	2043.6	1894.8	1897.8/1895.5
$^{15}N^{14}N^{28}Si^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2147.7	2030.9	
	$\nu(as)_{NN}$	a’	2041.8	1893.2	1894.8/1892.4
$^{14}N^{15}N^{28}Si^{15}N^{14}N$	$\nu(s)_{NN}$	a_1	2126.2	2010.6	2011.3
	$\nu(as)_{NN}$	b_2	2030.1	1882.3	1883.5
$^{14}N^{15}N^{28}Si^{14}N^{15}N$	$\nu(s)_{NN}$	a’	2126.3	2010.7	2011.3
	$\nu(as)_{NN}$	a’	2028.5	1880.8	1881.4
$^{15}N^{14}N^{28}Si^{14}N^{15}N$	$\nu(s)_{NN}$	a_1	2126.5	2010.9	2011.3
	$\nu(as)_{NN}$	b_2	2027.0	1879.4	1879.4
$^{15}N^{15}N^{28}Si^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2137.6	2020.7	2021.4/2015.6
	$\nu(as)_{NN}$	a’	2016.6	1869.8	1876.1/1870.4
$^{14}N^{15}N^{28}Si^{15}N^{15}N$	$\nu(s)_{NN}$	a’	2111.2	1996.4	1997.7
	$\nu(as)_{NN}$	a’	2008.3	1862.1	1865.8/1863.9
$^{15}N^{14}N^{28}Si^{15}N^{15}N$	$\nu(s)_{NN}$	a’	2111.1	1996.3	1994.5
	$\nu(as)_{NN}$	a’	2007.1	1861.0	1862.5/1860.8
$^{15}N^{15}N^{28}Si^{15}N^{15}N$	$\nu(s)_{NN}$	a_1	2089.4	1975.8	1977.0
	$\nu(as)_{NN}$	b_2	1993.4	1848.3	1849.4

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{14}N^{14}N^{28}Si^{14}N^{14}N)/\tilde{\nu}_{calcd}(^{14}N^{14}N^{28}Si^{14}N^{14}N)$; $C(s) = 0.9456$; $C(as) = 0.9272$.

one also expects two NN valence vibration bands (scaled: 2020.7 and 1869.8 cm^{-1}). However, in practice two split bands at 2021.4/2015.6 and 1876.1/1870.4 cm^{-1} are found. This result has two implications. First, the molecule has to contain two nitrogen molecules. Second, **2** loses the calculated C_{2v} symmetry if it is embedded in a matrix.

For 1-sila-2,3-diazacyclopropenylidene (**3**) three fundamental vibrations are expected, but only two of them have enough intensity to be detectable. Therefore, the structural elucidation has to rely on the bands for the NN and SiN stretching vibrations calculated to lie at 1551.8 and 729.9 cm^{-1}. The experimental absorptions are positioned at 1475.0 and 716 cm^{-1}. The deviation of the NN valence stretch is acceptable. Additional proof for structure **3** stems from the measured isotopic shifts, which are consistent with those obtained from the scaled theoretical wavenumbers (Figure 4, Table 5).

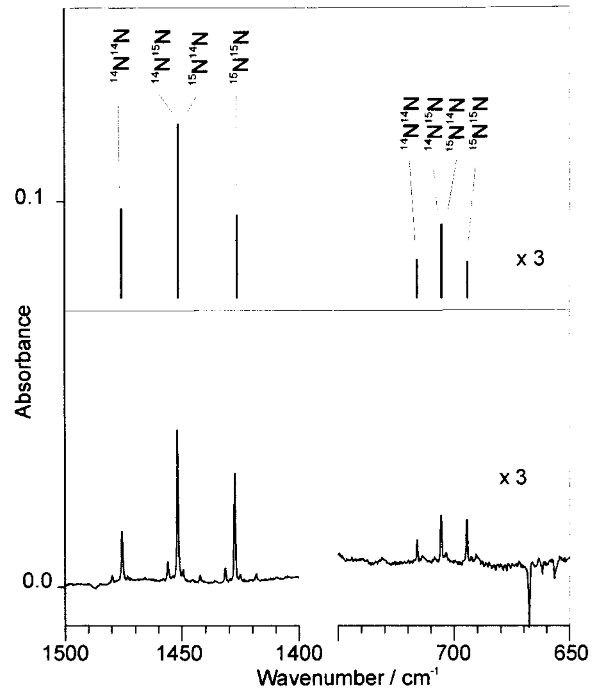


Figure 4. Comparison of experimental (N_2, 12 K; bottom) and theoretical (B3LYP/6-311+G**; top; scaled as in Table 5) IR spectra of 1-sila-2,3-diazacyclopropenylidene ([$^{14}N_2$]-**3** + [$^{15}N_2$]**3** + [$^{14,15}N_2$]**3**). The experimental bands are derived from a difference spectrum of the photoreaction **1** → **3** (λ = 280−420 nm). The isotopic distribution was achieved by microwave discharge of a mixture of $^{14}N_2$ and $^{15}N_2$.

Table 5. Theoretical (B3LYP/6-311+G), Scaled, and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of 1-Sila-2,3-diazacyclopropenylidene (3) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{28}Si^{14}N^{14}N$	ν_{NN}	a_1	1551.8		1475.6
	δ_{SiNN}	b_2	585.0		
	ν_{SiN}	a_1	729.9		716.0
$^{28}Si^{14}N^{15}N$	ν_{NN}	a_1	1526.3	1451.4	1452.0
	δ_{SiNN}	a_1	579.6		
	ν_{SiN}	a_1	719.0	705.3	705.6
$^{28}Si^{15}N^{15}N$	ν_{NN}	a_1	1500.2	1426.5	1427.8
	δ_{SiNN}	b_2	574.8		
	ν_{SiN}	a_1	707.7	694.2	694.6

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{28}Si^{14}N^{14}N)/\tilde{\nu}_{calcd}(^{28}Si^{14}N^{14}N)$; $C(\tilde{\nu}_{NN}) = 0.9509$; $C(\tilde{\nu}_{SiN}) = 0.9809$.

Table 6. Theoretical (B3LYP/6-311+G), Scaled and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of Disiladiisocyanogen (4) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{28}Si^{14}N^{14}N^{28}Si$	ν_{SiN}	σ	1166.7		1153.3
$^{28}Si^{14}N^{15}N^{28}Si$	ν_{SiN}	σ	1152.8	1139.5	1139.8
$^{28}Si^{15}N^{15}N^{28}Si$	ν_{SiN}	σ	1140.6	1127.5	1127.9

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{28}Si^{14}N^{14}N^{28}Si)/\tilde{\nu}_{calcd}(^{28}Si^{14}N^{14}N^{28}Si)$; $C(\tilde{\nu}_{SiN}) = 0.9885$.

From the studied photoisomerizations it also follows that **3** is characterized by a UV maximum at 256 nm. This weak absorption is difficult to detect because the UV spectrum of the condensate is dominated by the much stronger UV bands of **1-T**, but it parallels the appearance and disappearance of the IR bands of **3**.

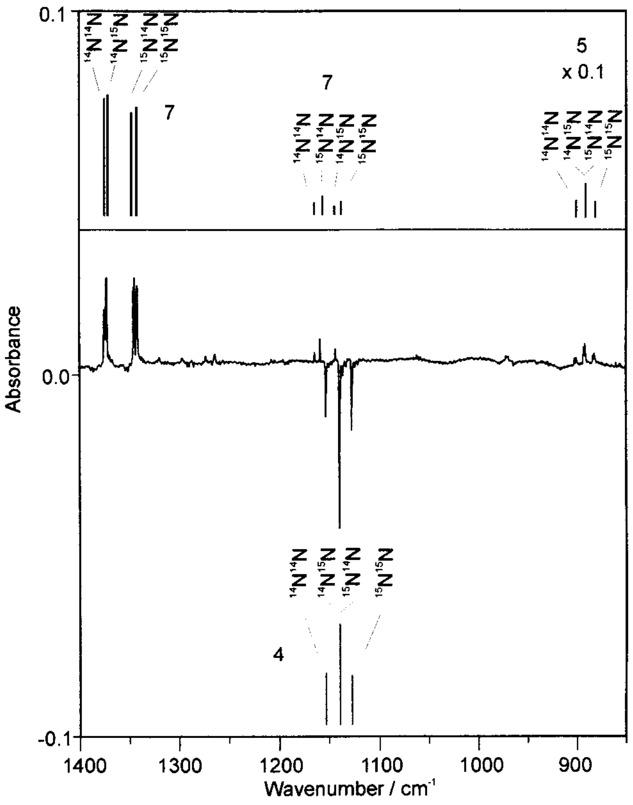


Figure 5. Comparison of experimental (N_2, 12 K) and theoretical (B3LYP/6-311+G**; scaled as in Table 6, Table 7 and Table 8) IR spectra of disiladiisocyanogen (**4**), cyclo-Si_2N_2 (**5**), and disilaisocyanogen (**7**). In the center is a difference spectrum of the photoreaction **4** → **5** + **7** (λ = 254 nm). The bands with negative values diminished, while those with positive values were enhanced upon irradiation. At the bottom, bars give the theoretical (B3LYP/6-311+G**; scaled as in Table 6) IR spectra of the isotopomers of **4**. At the top, bars give the theoretical (B3LYP/6-311+G**; scaled as in Table 7 and Table 8) IR spectra of the isotopomers of **5** and **7**. The isotopic distribution was achieved by microwave discharge of a mixture of $^{14}N_2$ and $^{15}N_2$.

Table 7. Theoretical (B3LYP/6-311+G), Scaled, and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of cyclo-Si_2N_2 (5) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{28}Si^{28}Si^{14}N^{14}N$	ν_{SiN}	b_2	914.0		900.9[b]/902.6[c]
$^{28}Si^{28}Si^{14}N^{15}N$	ν_{SiN}	a'	904.5	891.5	891.8[b]/893.6[c]
$^{28}Si^{28}Si^{15}N^{15}N$	ν_{SiN}	b_2	894.6	881.7	882.4[b]/884.0[c]

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{28}Si^{14}N^{14}N^{28}Si)/\tilde{\nu}_{calcd}(^{28}Si^{14}N^{14}N^{28}Si)$; $C(\tilde{\nu}_{SiN}) = 0.9857$. [b] Major matrix trapping site. [c] Minor matrix trapping site.

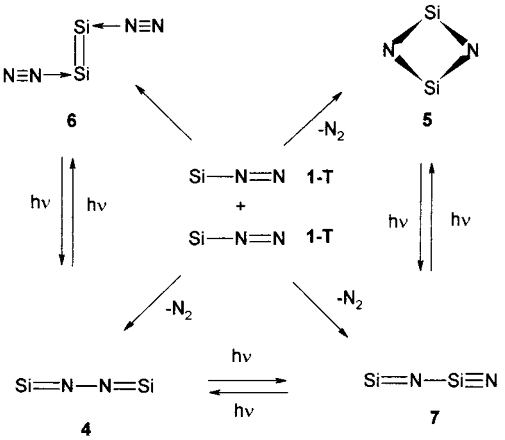
The IR band at 1153.3 cm^{-1} (Figure 5, Table 6), which we attribute to disiladiisocyanogen (**4**), is present after cocondensation. We are aware of the fact that it is dangerous to argue on the basis of one single band. However, one point is clear: the compound has to have two N atoms in symmetrically equivalent positions. Otherwise, one could not observe a triplet for the three isotopomers (Figure 5). Comparison of the calculated and observed wavenumbers together with the isotopic splittings (Table 6) strongly suggests structure **4** with $D_{\infty h}$ symmetry. The intensity of the band at 1153.3 cm^{-1} is enhanced upon subsequent irradiation with λ = 280−420 nm. Surprisingly, at the same time the bands of

Table 8. Theoretical (B3LYP/6-311+G), Scaled, and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of Disilaisocyanogen (7) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{28}Si^{14}N^{28}Si^{14}N$	ν_{NSi}	σ	1380.7		1374.7
	ν_{SiN}	σ	1212.4		1164.4
$^{28}Si^{14}N^{28}Si^{15}N$	ν_{NSi}	σ	1377.2	1371.2	1372.6
	ν_{SiN}	σ	1191.4	1144.3	1143.6
$^{28}Si^{15}N^{28}Si^{14}N$	ν_{NSi}	σ	1353.4	1347.5	1345.7
	ν_{SiN}	σ	1203.8	1156.2	1158.8
$^{28}Si^{15}N^{28}Si^{15}N$	ν_{NSi}	σ	1348.2	1342.3	1342.6
	ν_{SiN}	σ	1184.5	1137.7	1139.0

[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{28}Si^{14}N^{28}Si^{14}N)/\tilde{\nu}_{calcd}(^{28}Si^{14}N^{28}Si^{14}N)$; $C(\tilde{\nu}_{SiN}) = 0.9605$; $C(\tilde{\nu}_{NSi}) = 0.9957$.

bis(dinitrogen)disilicon (**6**) diminish. It is difficult to understand the phototransformation **6** → **4.** In this context it is important to realize that the four species **4**−**7** are photochemically interconverted upon matrix irradiation and the concentration of the different individual species depends on the applied wavelength. A clear-cut example is the photoisomerization of disiladiisocyanogen (**4**) into disilamonoisocyanogen (**7**) and cyclo-Si_2N_2 (**5**) with $\lambda = 254$ nm (Figure 5).



The photobehavior of **4** also gives a hint to the suggested structure. When the central N−N bond is split, the thus formed •Si≡N radicals can recombine either to **7** or **5**. An alternative photochemical pathway for **4** is its transformation into **6**. Since the irradiations are carried out in a nitrogen matrix, it is no surprise that N_2 can be captured and compound **6** with the elemental composition Si_2N_4 can be integrated into the circle together with the Si_2N_2 isomers **4**, **5**, and **7**. The third cyanogen-type isomer **14** cannot be involved as a detectable species within this photochemical cycle because of its high energy content (Chart 2).

The identification of cyclo-Si_2N_2 (**5**) is burdened with the same difficulties already dicussed for **4**. After cocondensation a band at 901 cm^{-1} is detected. This rather low position together with the isotopic shifts (Table 7) and the mutual photointerconversions indicate that this band can be attributed to the cyclic molecule **5**. This is an exotic compound which cannot be described by classical Lewis structures. It resembles a “partially opened tetrahedron”.

After cocondensation also an IR band at 1374.7 cm^{-1} appears which is connected with a second absorption at 1163.4 cm^{-1} (Figure 5, Table 8). Such a pair is calculated for disilaisocyanogen (**7**). The isotopic pattern should show four bands, resulting from the fact that now the two N atoms are nonequivalent. The experimental spectrum fulfills this prediction (Figure 5, Table 8). Together with the genetic connections with the isomers **4** and **5** the structure of **7** is on safe ground.

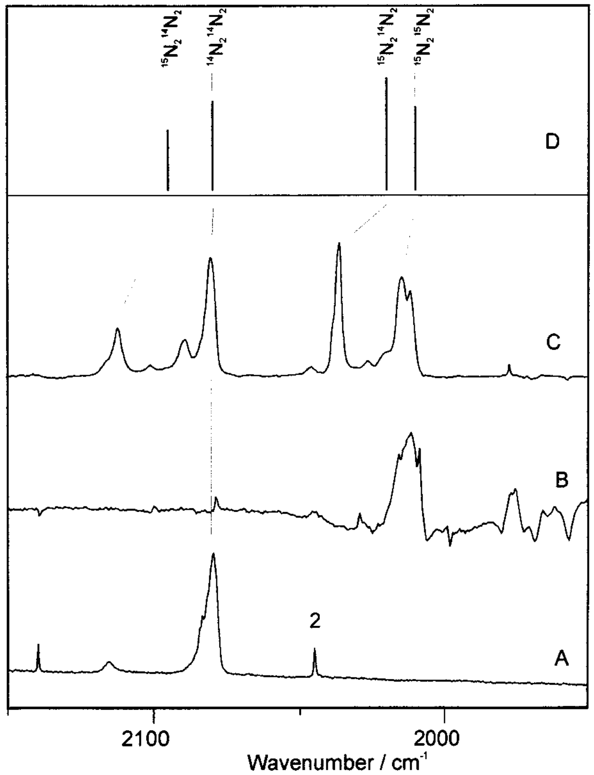


Figure 6. Comparison of experimental (N_2, 12 K) and theoretical (B3LYP/6-311+G**; scaled as in Table 9) IR spectra of 1,2-bis(dinitrogen)disilicon (**6**): (A) spectrum after cocondensation of Si atoms and $^{14}N_2$; (B) spectrum after cocondensation of Si atoms and $^{15}N_2$; (C) spectrum after cocondensation of Si atoms and a mixture of $^{14}N_2$ and $^{15}N_2$; (D) theoretical (B3LYP/6-311+G**) spectrum of a mixture of $[^{14}N_2,^{14}N_2]$**6**, $[^{15}N_2,^{15}N_2]$**6**, and $[^{14}N_2,^{15}N_2]$**6**.

In the IR spectrum of the cocondensate (Figure 1) the strongest band, except for those belonging to **1-T**, is found at 2080 cm^{-1}. This absorption is relatively broad. This may be taken as an indication that the compound is very sensitive to the solid environment (matrix effects). The arguments for structure **6** are as follows. First, only the complexes **6** and **11** of Si_2 with nitrogen show in the calculated spectrum a strong absorption in this region (Figure 6, Table 9). Second, in a mixture of $^{14}N_2$ and $^{15}N_2$ (without microwave discharge) in addition to the antisymmetric NN stretching vibrations of $[^{14}N_2][^{14}N_2]$**6** and $[^{15}N_2][^{15}N_2]$**6** a new band appears at 2036 cm^{-1}. From this observation one has to conclude that the compound contains more than one nitrogen molecule. Third, the isotopomer $[^{14}N_2]Si_2[^{15}N_2]$ has lost the C_{2h} symmetry of **6**. Therefore, this species shows the second NN stretching vibration at 2112 cm^{-1}. Last but not least, the bis(dinitrogen) adduct **6** is very photolabile. Upon irradiation with λ >300 nm nitrogen is eliminated and the bands of **4** and **5** grow in intensity.

Annealing Experiments. All the species **1**−**7** discussed above are stable under matrix conditions. As soon as the matrix softens and the trapped molecules

Table 9. Theoretical (B3LYP/6-311+G), Scaled, and Experimental (N_2, 12 K; Wavenumbers in cm^{-1}) IR Absorptions of 1,2-Bis(dinitrogen)disilicon (6) Isotopomers**

isotopomer		sym	calcd	scaled[a]	exptl
$^{14}N^{14}N^{28}Si_2{}^{14}N^{14}N$	$\nu(s)_{NN}$	a_g	2195.3[b]		
	$\nu(as)_{NN}$	b_u	2168.9	2080	
$^{14}N^{15}N^{28}Si_2{}^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2186.3	2097.0	2112
	$\nu(as)_{NN}$	a’	2142.5	2055.0	2066
$^{15}N^{14}N^{28}Si_2{}^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2186.3	2097.0	2112
	$\nu(as)_{NN}$	a’	2140.1	2052.7	2065
$^{14}N^{15}N^{28}Si_2{}^{15}N^{14}N$	$\nu(s)_{NN}$	a_g	2159.3[b]		
	$\nu(as)_{NN}$	b_u	2134.1	2046.9	2046
$^{14}N^{15}N^{28}Si2^{14}N^{15}N$	$\nu(s)_{NN}$	a’	2158.6	2070.4	2068
	$\nu(as)_{NN}$	a’	2132.5	2045.4	2046
$^{15}N^{14}N^{28}Si_2{}^{14}N^{15}N$	$\nu(s)_{NN}$	a_g	2157.8[b]		
	$\nu(as)_{NN}$	b_u	2131.0	2043.9	2046
$^{15}N^{15}N^{28}Si_2{}^{14}N^{14}N$	$\nu(s)_{NN}$	a’	2184.3	2095.1	2112
	$\nu(as)_{NN}$	a’	2106.1	2020.1	2036
$^{14}N^{15}N^{28}Si_2{}^{15}N^{15}N$	$\nu(s)_{NN}$	a’	2150.5	2062.7	2068
	$\nu(as)_{NN}$	a’	2104.5	2018.5	2032
$^{15}N^{14}N^{28}Si2^{15}N^{15}N$	$\nu(s)_{NN}$	a’	2148.6	2060.8	2067
	$\nu(as)_{NN}$	a’	2104.1	2018.1	2032
$^{15}N^{15}N^{28}Si_2{}^{15}N^{15}N$	$\nu(s)_{NN}$	a_g	2121.1[b]		
	$\nu(as)_{NN}$	b_u	2095.6	2010.2	2014

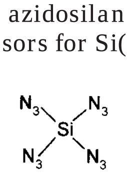
[a] $\tilde{\nu}_{scaled} = C(\tilde{\nu}_{calcd}(\text{isotopomer}))$; $C = \tilde{\nu}_{obsd}(^{14}N^{14}N^{28}Si^{214}N^{14}N)/\tilde{\nu}_{calcd}(^{14}N^{14}N^{28}Si_2{}^{14}N^{14}N)$; $C(as) = 0.9591$. [b] IR inactive; for scaling the same factor as for the asymmetric vibration was used.

become mobile, reactions occur and their chemical behavior can be studied. The most prominent bands of **1-T** disappear upon warmup to 27 K. After 3 h 50% of **1-T** has reacted, which increases to more than 75% after 17 h. As the bands of **1-T** decrease, those of **2** and the compounds containing two silicon atoms such as **4**−**6** increase. Thus, it is tempting to assume that **1-T** undergoes stabilization by addition of a second nitrogen molecule, by dimerization to form **6**, or by loss of nitrogen and subsequent reactions of the newly formed silicon atoms (see reaction scheme given above).

At temperatures higher than 30 K we observed several times an “explosive” reaction of the matrix-isolated molecules and the solid became brownish. The IR spectrum of the solid remaining after evaporation of the nitrogen showed a broad band at 1050 cm^{-1}. The spectrum was similar but not identical with that of solid Si_3N_4.

Irradiation of Silyl Azides. Because many of the structures identified above were based on a limited number of bands, independent means of forming the various molecules were sought.

The azidosilanes **20**−**22** can be used as additional precursors for $Si(N_2)_y$ molecules. Each of these starting materials was sublimed together with nitrogen onto a CsI spectroscopic window at 12 K. Matrix irradiation with $\lambda = 254$ nm generated SiNN (**1-T**) in all cases. Secondary irradiation with $\lambda = 313$ or 366 nm formed N_2SiN_2 (**2**), which disappeared again at longer irradiation times. Parallel to this process, the bands of siladiazacyclopropenylidene (**3**) appeared in the spectrum.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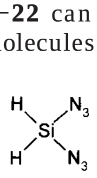
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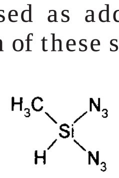
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It can easily be rationalized that **1-T** is a photoproduct of tetraazidosilane (**20**). In the case of diazidosilane (**21**) and diazidomethylsilane (**22**) not only two molecules of nitrogen but also dihydrogen or methane is eliminated.

Conclusion

In reactions of silicon atoms in a nitrogen matrix at 12 K the nitrogen lone pair serves as a Lewis base rather than the π system. This is demonstrated by the isolation and spectroscopic identification of the end-on adducts **1-T**, **2**, and **6**.

A second Si atom can also be involved, as shown by detection of the Si_2N_2 species **4**, **5**, and **7**, which are also present in the condensate. The formal π adduct **3** is not directly formed by reaction of a silicon atom with nitrogen but can be generated by photoisomerization of **1-T**.

The present study illustrates once more the great potential of matrix isolation spectroscopy in combination with quantum chemical calculations.

Experimental Section

Equipment used for matrix isolation, photolyses, and pyrolyses has been described before.[30] In our early experiments silicon was vaporized from a boron nitride crucible which was surrounded by an aluminum oxide tube. The oven was resistively heated to temperatures of 1490−1550 °C by means of a tungsten wire wound around the alumina tube. In later runs a rod in the size of 0.7 × 2 × 22 mm was cut out from a highly doped silicon wafer and heated resistively by using an electric current of 10 V/10 A. Under these conditions the surface temperature amounted to 1350−1380 °C.

The amount of silicon atoms was established by applying a quartz crystal microbalance incorporated into the cryogenic sample holder.[31] The amount of nitrogen was determined by measuring the pressure decrease in the nitrogen storage flask.

Annealing experiments were carried out by warmup of the matrix to 27−38 K.

The preparation of the azidosilanes followed the procedure described earlier for the synthesis of monoazidosilane.[32]

Tetraazidosilane (20).[33] A 0.8 g (2.3 mmol) amount of degassed and HBr-free $SiBr_4$ (Aldrich) was condensed at −196 °C into a flask which already contained 4.0 g (12 mmol) of degassed $n$$Bu_3SnN_3$.[34] The reaction mixture was magnetically stirred, starting at −78 °C and afterward at −30 °C, until a clear, mobile liquid was formed. This reaction mixture was used for the matrix experiments without any further purification. *Caution!*[33,35] MS (m/e (%)): 196 (8) [M^+], 152 (34) [$M^+ - N_3$], 70 (29) [$M^+ - 3N_3$], 43 (100). IR (cm^{-1}; N_2, 10 K): 2112 (w), 2184 (vs), 2179 (vs), 2162 (vs), 2149 (vs), 1333 (s), 1326 (s), 1320 (s), 789 (m), 766 (m), 603 (w).

Diazidosilane (21). The reaction of 0.75 g (4.0 mmol) of SiH_2Br_2[36] with 3.3 g (10.0 mmol) of $n$$Bu_3SnN_3$ followed the procedure described for **20**. The product was fractioned by stepwise condensation and gave 0.4 g (82%) of diazidosilane (**21**) as a colorless liquid. MS (m/e (%)): 113.003 95 (calcd 113.003 197) (29) [$M^+ - H$], 71 (3) [$M^+ - H,N_3$], 43 (100). IR

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(cm^{-1}; N_2,10 K): 2248 (m), 2243 (w), 2233 (w), 2214 (w), 2181 (vs), 2159 (vs), 2153 (vs), 1333 (s), 1326 (s), 1323 (s), 950 (m), 947 (m), 897 (s), 895 (s), 740 (m), 738 (m), 654 (m), 580 (m), 570 (m).

Diazidomethylsilane (22). Reaction of 0.8 g (4.0 mmol) of $H_3CSiHBr_2$[36] with 3.3 g (10.0 mmol) of *n*Bu_3SnN_3 followed the procedure described for **20**. A 0.3 g (59%) amount of diazidosilane (**22**) was isolated as a colorless liquid. ^{1}H NMR (CD_2Cl_2, 60 MHz): δ 4.9 (q, 1 H, Si−H), 0.4 (d, 3 H, C−H). MS (*m*/*e* (%)): 127 (95) [$M^+ - H$], 85 (2) [$M^+ - H,N_3$], 70(35) [$M^+ - H,CH_3,N_3$], 43 (100). IR (cm^{-1}; N_2, 10 K): 2199 (w), 2188 (w), 2176 (vs), 2153 (vs), 1405 (w), 1330 (s), 1324 (s), 1321 (s), 1313 (s), 1264 (m), 902 (m), 895 (m), 859 (s), 851 (m), 777 (m), 773 (m), 771 (m), 707 (m), 700 (m), 578 (m), 571 (m), 553 (m).

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