Reactions of Silicon Atoms with Cyanogen: Generation and Matrix-Spectroscopic Identification of Five C_2N_2Si Isomers[‡]

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Dedicated to Professor Johann Weis on the occasion of his 60th birthday

Keywords: Matrix isolation / Photoisomerizations / Co-condensation / Reaction mechanisms / Silylenes

The reactions of silicon atoms with cyanogen **12** in an argon matrix at 10 K have been studied. In the initial step a triplet *n* adduct **T-13** is formed between a silicon atom and **12**. The next step needs photochemical activation. Long-wavelength irradiation yields 3-cyanoazasilacyclopropenylidene **14**, which upon irradiation with 254 nm light is transformed into three isomeric silylenes: dicyanosilylene **15**, cyano(isocyano)silylene **16**, and di(isocyano)silylene **17**. The structural elucidation of all new species is based on comparison of the experimentally obtained IR and UV/Vis spectra with the results of density functional theory calculations.

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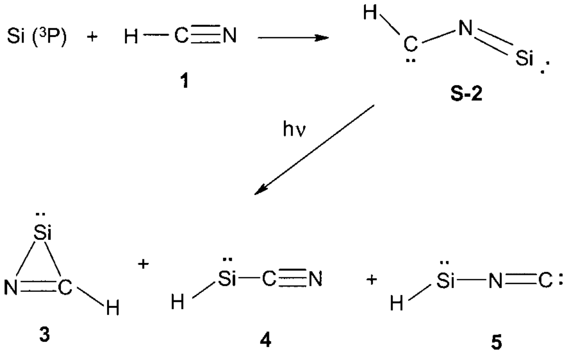
Introduction

During the past six years we have been studying the reactions of thermally generated silicon atoms with a variety of low molecular weight reactants in an argon matrix. The reaction products were identified by IR and UV/Vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful.[1] The reactions under discussion can be understood by considering the basic features of atomic silicon. Firstly, it has a triplet ground state. According to the law of spin conservation the primary reaction product should be a triplet molecule. Secondly, the silicon atom has an empty 3p orbital. As a consequence, strongly electrophilic behavior is to be expected.

No wonder then, that ($\sigma + n$) molecules, such as dimethyl ether[2] and methyl halides,[3] can easily be attacked at the free electron pair with formation of the corresponding triplet *n* adducts. Of special interest are molecules possessing *n* electrons in combination with π bonds. The reaction of silicon atoms with hydrogen cyanide **1** has already shown that in such a case the free electron pair is attacked preferentially.[4] The primarily formed (silaisocyano)carbene (**2**) can be transformed into three isomeric silylenes (azasilacyclopropenylidene **3**, cyanosilylene **4**, and isocyanosilylene **5**). In contrast to other known[1–3] *n* adducts between Si atoms and substrates containing free electron pairs, which possess triplet ground states (see also *n* adduct **T-13** below), the experimental observations provided unequivocal evidence that **2** is matrix-isolated in its singlet state **S-2**.[4]



It was therefore of interest to know the result of the reaction between Si atoms and dicyanogen $(CN)_2$ **12**. The first question was: would the corresponding *n* adduct again show the characteristics of a singlet carbene? A second aspect was even more important: in continuing our studies on carbenes[5] we had recently investigated dicyanocarbene and its isomers.[6] For their generation a different procedure had to be used, namely the photolysis of dicyanodiazomethane **6**. The first product is triplet dicyanocarbene **T-7**, which upon further photoexcitation undergoes successive isomerizations until a photoequilibrium between the five C_3N_2 isomers **T-7**, triplet cyano(isocyano)carbene **T-8**, singlet 3-cyanoazacyclopropenylidene **S-9**, singlet di(isocyano)carbene

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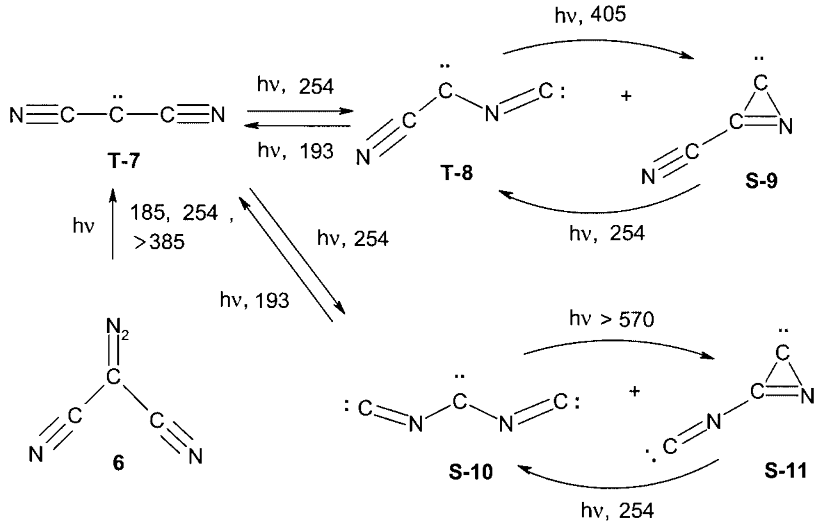


S-10, and singlet 3-(isocyano)azacyclopropenylidene **S-11** is reached.

The species C_2N_2Si expected from the reaction between cyanogen **12** and silicon atoms should offer an ideal opportunity to elucidate the typical features of silylenes in comparison to the corresponding carbenes.

Results and Discussion

Calculations

The relevant parts of the C_2N_2Si potential energy surface were investigated by use of the Gaussian package of programs.[7] Several stationary points were located with the 6-311+G(3df,3pd) basis set and the B3LYP functional and were characterized by calculation of their vibrational spectra. Scheme 1 shows the calculated relative energies and structures of some minima. Additionally, TD//6-311+G(3df,3pd) calculations were used in order to predict their electronic transitions (Table 1). The structural identification of the generated C_2N_2Si species was carried out by comparison of the experimentally obtained and the calculated vibrational spectra (Table 2, Table 3, Table 4, Table 5, and Table 6).

The global minimum is di(isocyano)silylene **17**. The two next higher isomers on the energy scale are cyano(isocyano)silylene **16** and dicyanosilylene **15**.[8] Like all silylenes they each have a singlet ground state. According to B3LYP/6-311G(d) calculations the corresponding triplet states are higher in energy in all cases [T/S gaps: 30.1 (**15**), 37.6 (**16**), and 47.1 (**17**) kcal mol^{-1}]. The next higher candidate is 3-cyanoazasilacyclopropenylidene **14**, followed by the expected primary reaction product between cyanogen **12** and a silicon atom, namely the *n* adduct **13**. In this case the T/S gap is 8.5 kcal mol^{-1} in favor of **T-13** and the geometry of **S-13** is no longer linear. As a result of this, one may expect **T-13** instead of **S-13** to be the first detectable product in the reaction between ^{3}Si atoms and **12**. Excited ^{1}Si atoms (T/S gap ^{3}Si/^{1}Si amounts to 25.8 kcal mol^{-1}; B3LYP/6-311G(d)) would give **S-13** without spin inversion, but these are not available when the atoms are generated by evaporation of bulk silicon. Another member of the C_2N_2Si family, 3-(isocyano)azasilacyclopropenylidene **18**, could also be formed in an exothermic reaction from **12** and Si atoms, but no obvious reaction pathway leads to this isomer.

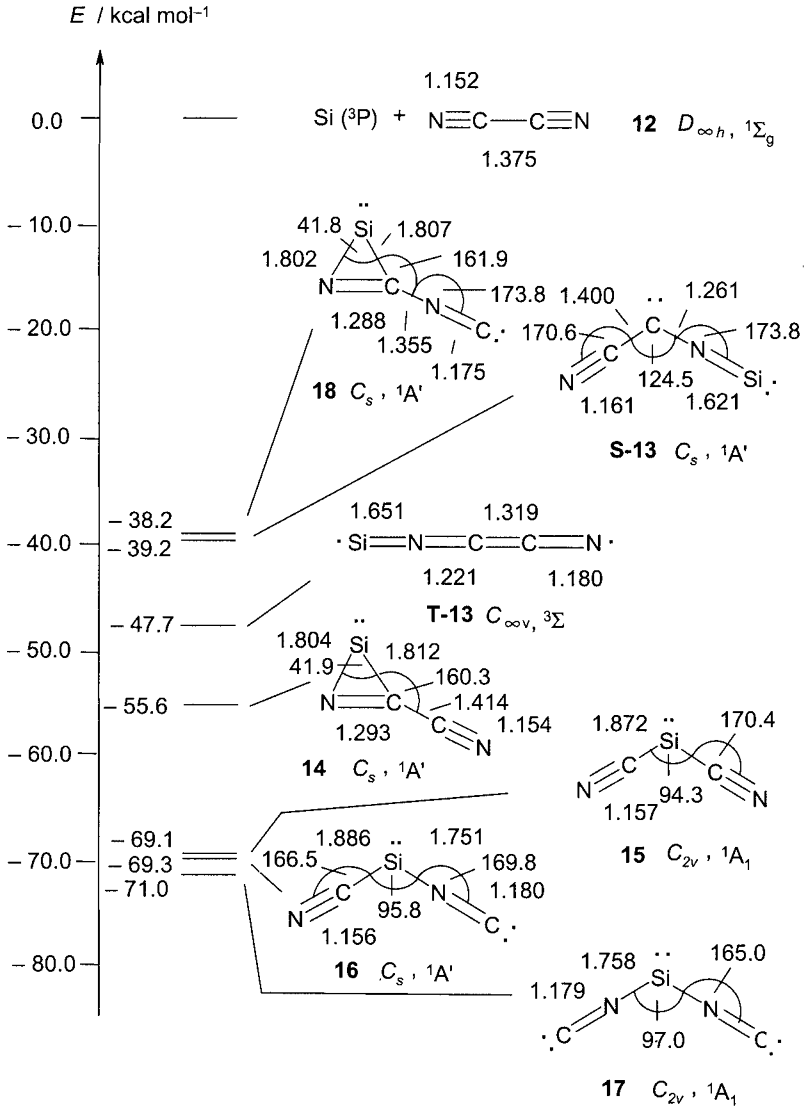
Matrix Experiments

In the standard experiments a gaseous mixture of cyanogen **12** and argon was deposited together with silicon atoms (generated by resistive heating of a silicon rod to a temperature of ca. 1380 °C) onto a CsI window at 10 K. FT-IR and UV/Vis spectra were taken of the matrices. Subsequent photochemical transformations were initiated by irradiating the matrices with light of the appropriate wavelength.

Upon simultaneous co-condensation of silicon atoms together with cyanogen **12** (ratio **12**:Ar = 1:1000) on a spectroscopic window at 10 K, beside the bands of cyanogen **12** and as well as those of SiNN, SiH_2, SiH_4, Si_2H_2, and H_2O (normal byproducts in co-condensations with Si atoms), new intense absorptions are observed (Figure 1). Two strong IR bands at 1955.5 and 1726.0 cm^{-1}, together with a weak absorption at 1022.7 cm^{-1}, belong to *n* adduct **13** (Figure 1, Table 2; bands are split into doublets by matrix effects).

This structural elucidation is supported by a look at the difference spectrum (Figure 2) of the photoreaction of **13**. Beyond that, comparison between the calculated (Table 2) and the experimentally observed (Figure 2) bands leaves no doubt that the initial product is the triplet *n* adduct **T-13**, possessing a linear geometry, and not the singlet isomer **S-13**. For the latter a completely different IR spectrum would be expected [B3LYP/6-311+G(3df,3pd): 2216.3(8), 1603.6(54), 1011.0(3), 743.5(117) 525.9(14), 379.1(12), 329.3(21), 213.4(0), 120.5(1) cm^{-1} (km mol^{-1})].

The *n* adduct **T-13** is photolabile. Irradiation with long-wavelength light ($\lambda > 570$ nm) gives rise to the cyclic silylene **14** (Figure 2, Table 3). Consistently with calculation,



Scheme 1. Calculated relative energies (zero-point vibrational energies included) and structural features (point group, state, angles in degrees, distances in Å) of some C_2N_2Si isomers [B3LYP/6-311+G(3df,3pd)].

Table 1. Calculated electronic excitations of some C_2N_2Si species [TD//B3LYP/6-311+G(3df,3pd)].

Species	Wavelength [nm] (oscillator strength)
SiNCCN **T-13**	609.3 (0.0000), 609.3 (0.0000), 570.2 (0.0000), 377.0 (0.2821), 294.8 (0.0078), 294.8 (0.0078), 280.0 (0.0000), 280.0 (0.0000), 273.1 (0.0104), 273.1 (0.0104), 267.2 (0.0000), 248.6 (0.4414)
SiNC)ring-CN **14**	$^1A''$ 408.5 (0.0006), $^1A''$ 396.9 (0.0000), $^1A''$ 276.5 (0.0001), $^1A''$ 257.5 (0.0531), $^1A'$ 234.3 (0.0562), $^1A'$ 213.9 (0.0108)
NCSiCN **15**	$^1B_1$ 448.1 (0.0206), $^1A_2$ 316.4 (0.0000), $^1B_1$ 259.2 (0.0044), $^1B_2$ 257.0 (0.0604), $^1A_2$ 252.6 (0.0000), $^1A_1$ 235.3 (0.0233)
NCSiNC **16**	$^1A''$ 400.0 (0.0292), $^1A''$ 308.3 (0.0004), $^1A''$ 272.6 (0.0002), $^1A'$ 239.8 (0.0409), $^1A''$ 224.8 (0.0001), 1A'' 209.2 (0.0066)
CNSiNC **17**	$^1B_1$ 350.5 (0.0442), $^1A_2$ 293.4 (0.0000), $^1B_1$ 258.7 (0.0006), $^1A_2$ 228.7 (0.0000), $^1B_2$ 210.6 (0.0058), $^1A_1$ 194.7 (0.0011)

which predicts two weak bands at 474 and 702 cm^{-1}, only absorptions of low intensity at 462.9 and 692.6 cm^{-1} are found. An additional experimentally observed tiny band at 1086.1 cm^{-1} may correspond to the calculated vibration at 1082 cm^{-1}.

The cyclic silylene **14** can be used as a photochemical source of the wanted open-chain silylenes **15**, **16**, and **17**. If the matrix containing **14** is irradiated with 254 nm light its bands diminish and new absorptions appear. These can be assigned to a mixture of *n* adduct **T-13** and the three isomeric silylenes **15**, **16**, and **17**. The individual bands of these three species can be extracted from their reversible photoisomerizations with light of specific wavelengths.

Upon irradiation with 405 nm light, dicyanosilylene **15** is transformed into a mixture of cyano(isocyano)silylene **16** and di(isocyano)silylene **17**. The difference spectrum allows the determination of the bands belonging to dicyanosilylene

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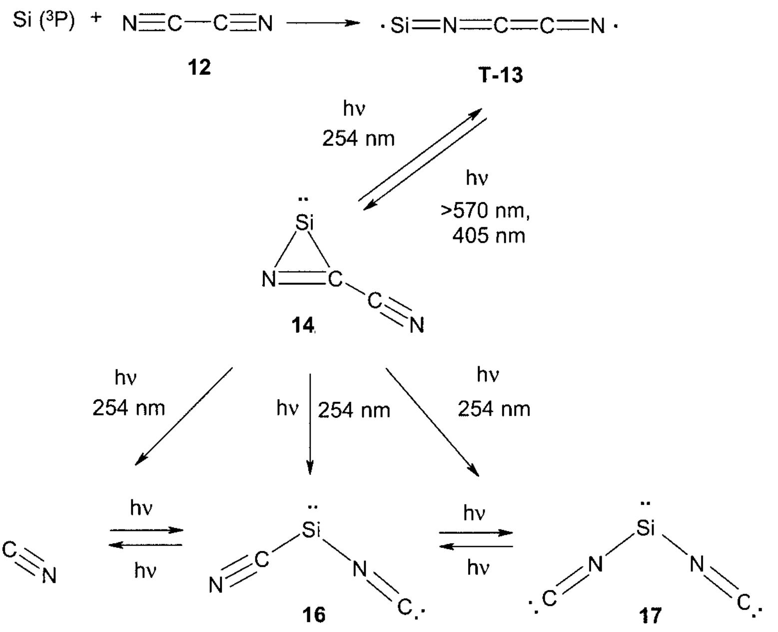

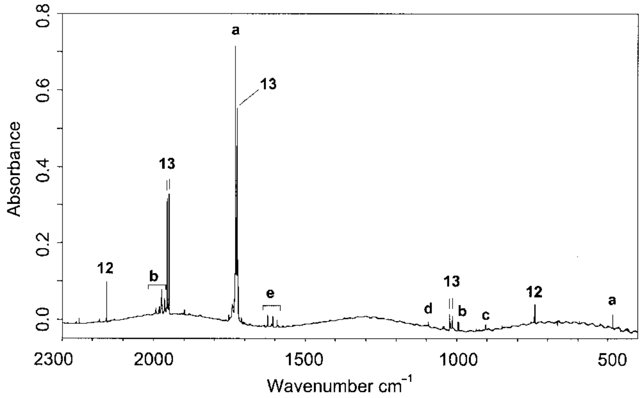

Figure 1. IR spectrum of the products of the co-condensation of silicon atoms with a cyanogen **12**/Ar gas mixture (1:1000) at 10 K. **a**) SiNN, **b**) SiH_2, **c**) SiH_4, **d**) Si_2H_2, **e**) H_2O.

Table 2. Comparison of the calculated (B3LYP/6-311+G(3df,3pd); absolute intensities [km mol^{-1}] in parentheses) IR absorptions of triplet *n* adduct **T-13** with the observed IR bands (Ar, 10 K; relative intensities in parentheses) of **T-13** after co-condensation of cyanogen **12** with silicon atoms.

No.	Sym.	Approx. descr.	**T-13**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]	**T-13**, $\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1	σ	str.	2018 (438)	1955.5 (vs)[a]
ν_2	σ	str.	1824 (539)	1726.0 (vs)[a]
ν_3	σ	str.	1052 (97)	1022.7 (w)[a]
ν_4	σ	str.	554 (2)	–
ν_5	π	bend.	426 (2)	–
ν_6	π	bend.	332 (13)	–
ν_7	π	bend.	104 (3)	–

[a] Split by matrix effects; only wavenumber of the strongest band is given.

15 (Figure 3, Table 4). The observed strong CSiC stretching vibrations at 571.8 and 599.7 cm^{-1} and the less intense CN stretching vibrations at 2158.5 and 2164 cm^{-1} correspond with the calculated data for **15**.

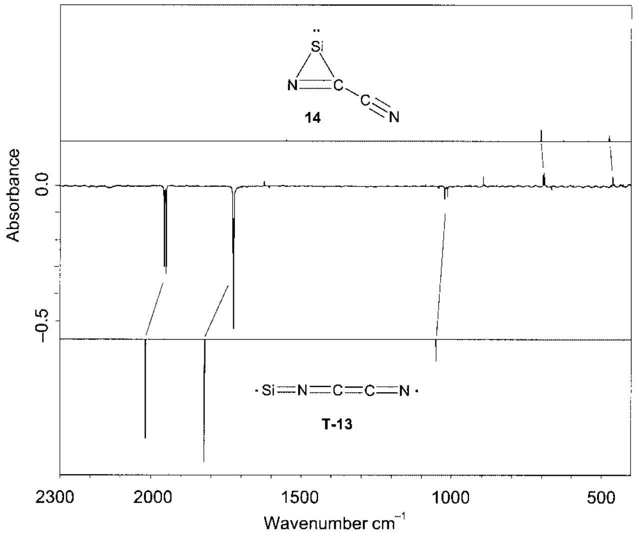

Figure 2. Top: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectrum of singlet 3-cyanoazasilacyclopropenylidene **14**. Center: Difference FT-IR spectrum originating from the photoreaction **T-13** → **14** (obtained by subtraction of the spectra after and before irradiation with > 570 nm for 15 h). Bottom: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectrum of triplet *n* adduct **T-13**.

The spectra of **16** and **17** can be derived by measuring the changes in the IR signals during irradiation with 370 nm light (Figure 4, Table 5, and Table 6). Isomer **16** is characterized by stretching vibrations of the SiC bond (571.8 cm^{-1}), the isocyano (very strong; 2039.4 cm^{-1}), and the cyano group (2163.9 cm^{-1}).

For isomer **17** (Table 6) it is logical that two NSiN stretching vibrations at 633.6 and 659.2 cm^{-1}, as well as an asymmetric and symmetric stretching vibration of the isocyano groups at 2034.7 (strongest band) and 2058.7 cm^{-1}, are detected. The accordance between the theoretically cal-

Table 3. Comparison of the calculated (B3LYP/6-311+G(3df,3pd); absolute intensities [km mol^{-1}] in parentheses) IR absorptions of 3-cyanoazasilacyclopropenylidene **14** with the observed IR bands (Ar, 10 K; relative intensities in parentheses) of **14** after long-wavelength irradiation of **T-13**.

No.	Sym.	Approx. descr.	**14**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]	**14**, $\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1	a′	CN str.	2305 (3)	–
ν_2	a′	CN str., ring	1550 (5)	–
ν_3	a′	SiC/NC str., ring	1082 (2)	1086.1 (vw)[a]
ν_4	a′	SiN str., ring	702 (44)	692.6 (s)[a]
ν_5	a′	CC str.	629 (4)	–
ν_8	a″	CCN bend.	546 (1)	–
ν_6	a′	CCN bend.	474 (22)	462.9 (s)[a]
ν_9	a″	CCN bend.	211 (10)	–
ν_7	a′	CCN bend.	181 (5)	–

[a] Split by matrix effects; only wavenumber of the strongest band is given.

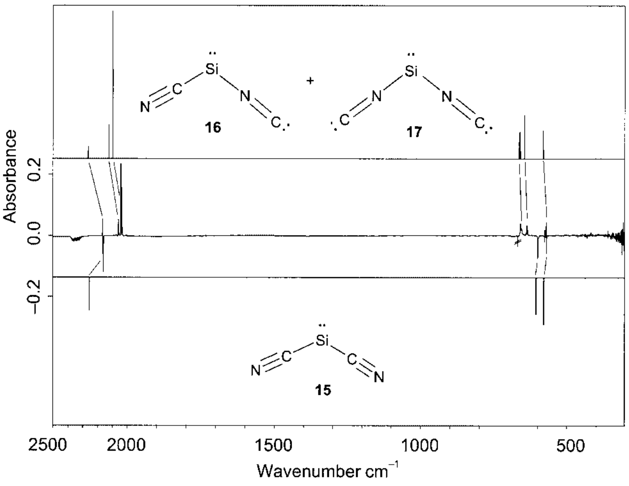

Figure 3. Top: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectra of singlet cyano(isocyano)silylene **16** and di(isocyano)silylene **17**. Center: Difference FT-IR spectrum originating from the photoreaction **15** → **16** + **17** (obtained by subtraction of the spectra after and before irradiation with 405 nm for 30 min). Bottom: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectrum of singlet dicyanosilylene **15**.

Table 4. Comparison of the calculated (B3LYP/6-311+G(3df,3pd); absolute intensities [km mol^{-1}] in parentheses) IR absorptions of dicyanosilylene **15** with the observed IR bands (Ar, 10 K; relative intensities in parentheses) of **15** after irradiation of **15** with 405 nm light.

No.	Sym.	Approx. descr.	**15**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]	**15**, $\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1	a_1	CN sym. str.	2253 (36)	2164 (vw)[a]
ν_7	b_2	CN asym. str.	2252 (87)	2158.5 (w)[a]
ν_2	a_1	CSiC sym. str.	605 (97)	599.7 (s)[a]
ν_8	b_2	CSiC asym. str.	578 (123)	571.8 (s)[a]
ν_3	a_1	CSiC bend.	421 (96)	–
ν_9	b_2	NCSi bend.	277 (2)	–
ν_5	a_2	NCSi twist.	219 (0)	–
ν_6	b_1	NCSi bend.	203 (11)	–
ν_4	a_1	NCSi bend.	104 (9)	–

[a] Split by matrix effects; only wavenumber of the strongest band is given.

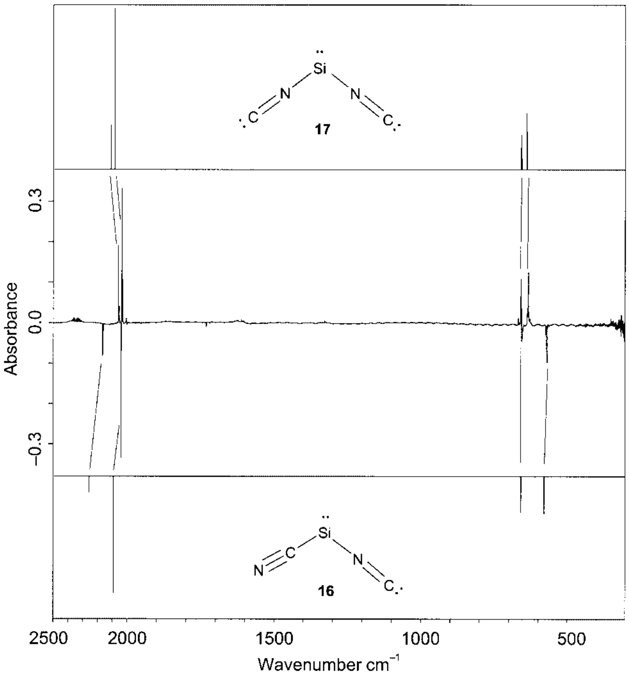

Figure 4. Top: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectrum of singlet di(isocyano)silylene **17**. Center: Difference FT-IR spectrum originating from the photoreaction **16** → **17** (obtained by subtraction of the spectra after and before irradiation with 370 nm for 40 h). Bottom: Calculated [B3LYP/6-311+G(df,3pd)] FT-IR spectrum of singlet cyano(isocyano)silylene **16**.

Table 5. Comparison of the calculated (B3LYP/6-311+G(3df,3pd); absolute intensities [km mol^{-1}] in parentheses) IR absorptions of cyano(isocyano)silylene **16** with the observed IR bands (Ar, 10 K; relative intensities in parentheses) of **16** after irradiation of **16** with 370 nm light.

No.	Sym.	Approx. descr.	**16**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]	**16**, $\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1	a′	CN str.	2261 (63)	2163.9 (vw)[a]
ν_2	a′	NC str.	2095 (465)	2039.4 (vs)[a]
ν_3	a′	SiN str.	660 (141))	–
ν_4	a′	SiC str.	581 (147)	571.8 (m)[a]
ν_5	a′	CSiN bend.	401 (1)	–
ν_6	a′	NSiC/CNSi bend.	232 (2)	–
ν_8	a″	NCSi bend.	203 (5)	–
ν_9	a″	CNSi bend.	160 (3)	–
ν_7	a′	NCSi/CNSi bend.	104 (8)	–

[a] Split by matrix effects; only wavenumber of the strongest band is given.

culated and the experimentally measured spectra of **16** and **17** is again very satisfying.

The IR results are supported by UV/Vis measurements. Cyanogen **12** itself does not absorb in the UV/Vis region, so the substrate molecule **12** is absolutely photostable under the applied irradiation conditions. For *n* adduct **T-13**, strong absorptions with vibrational fine structure in the 380–440 nm range are observed, together with less intense bands at 320–340 and 250–270 nm (band origins at 435, 333, and 265 nm) (Figure 5). This pattern fits with the calculated transitions (Table 1). The predicted long-wavelength

Table 6. Comparison of the calculated (B3LYP/6-311+G(3df,3pd); absolute intensities [km mol^{-1}] in parentheses) IR absorptions of di(isocyano)silylene **17** with the observed IR bands (Ar, 10 K; relative intensities in parentheses) of **17** after irradiation of **16** with 370 nm light.

No.	Sym.	Approx. descr.	**17**, $\tilde{\nu}_{calcd.}$ [cm^{-1}]	**17**, $\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1	a_1	NC sym. str.	2115 (179)	2058.7 (vw)[a]
ν_7	b_2	NC asym. str.	2089 (769)	2034.7 (vs)[a]
ν_2	a_1	NSiN sym. str.	659 (138)	659.2 (w)[a]
ν_8	b_2	NSiN asym. str.	641 (226)	633.6 (w)[a]
ν_3	a_1	NSiN bend.	378 (4)	–
ν_9	b_2	CNSi bend.	202 (0.1)	–
ν_5	a_2	CNSi twist.	164 (0)	–
ν_6	b_1	CNSi bend.	145 (4)	–
ν_4	a_1	CNSi bend.	106 (7)	–

[a] Split by matrix effects; only wavenumber of the strongest band is given.

absorptions are too weak for direct detection, but are responsible for the isomerization **T-13** → **14** upon irradiation with $\lambda > 570$ nm.

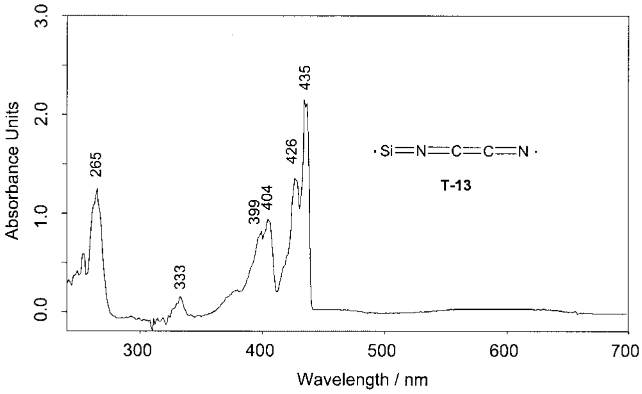

Figure 5. Difference UV/Vis spectrum of *n* adduct **T-13** originating from co-condensation of cyanogen **12** with silicon atoms and subsequent irradiation with > 570 nm for 15 h; the positive bands disappear during irradiation.

For cyclic silylene **14** the strongest absorptions are calculated to lie at 234 and 258 nm. The three open-chain silylenes should exhibit bands at 257/448 (**15**), 240/400 (**16**), and 351 (**17**) nm. On the one hand it turned out to be difficult to measure these absorptions directly. On the other hand, these data are in agreement with the observed photoisomerizations **14** → **15** + **16** + **17** (254 nm), **15** → **16** + **17** (405 nm), and **16** → **17** (370 nm).

Conclusions

From the experimental and theoretical findings the reactions between Si atoms and cyanogen **12** in an argon matrix can be summarized as follows. The first reaction product is linear triplet *n* adduct **T-13**. Upon irradiation with light of the appropriate wavelength, four different isomers of the elemental composition C_2N_2Si have been identified. The formal reorganization of the silicon atom and two CN fragments is astonishing. The mechanism of these mutual transformations is still not known.

Experimental Section

The cryostat for matrix isolation was a helium closed-cycle refrigeration system (RW2 compressor unit with coldhead base unit 210 and extension module ROK) from Leybold. The matrix IR spectra were measured with a FT-IR instrument (IFS 85 or IFS 55 from Bruker) and the UV/Vis spectra were taken with a Hewlett–Packard HP 8453 diode-array spectrophotometer. 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 rod of size 0.7 × 2 × 22 mm was cut out from a highly doped silicon wafer and heated resistively by use of a current of 10 A at 10 V. Under these conditions the surface temperature amounted to 1350–1380 °C. For experimental details see ref.[1].

Cyanogen **12**[9] was degassed by several freeze-pump-thaw cycles and mixed with argon (Messer Griesheim; 9.4).

Acknowledgments

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