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Reaction of Silicon Atoms with Hydrogen Cyanide: Generation and Matrix-Spectroscopic Identification of CHNSi and CNSi Isomers

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Cocondensation of thermally generated silicon atoms with hydrogen cyanide in an argon matrix can be used as an access to compounds of the composition CHNSi and CNSi. Isolation, matrix-spectroscopic identification and photochemical behavior of these species are described. Structural assignments are made by the comparison of experimental with calculated IR spectra.

Evaporation of metal atoms and their subsequent condensation, possibly after reaction with another substrate, is the basic step in chemical vapor deposition (CVD) processes, which today are in manifold use to generate thin metallic or organic films. If the metal used is silicon, this method is essential in microelectronics industry and thus of economical importance, for the condensation of silicon vapor — alone and after reaction with substrate gases — is used for the manufacture of silicon wafers, silicon-based semiconductors, and dielectrics. A predictive understanding of the complex chemical processes involved herein requires detailed knowledge of the scope and fundamental reactions of silicon atoms.

The first work in this field goes back to Gaspar et al., who studied the reactions of recoil silicon atoms produced by nuclear transformations with silane, phosphane, and ethylene^[1]. A few years later, Skell and Owen found that silanes react with silicon atoms, which were produced by electron bombardment heating of a silicon electrode or resistance heating of a silicon rod, by successive insertion into Si–H bonds^[2].

The combination of silicon evaporation with matrix isolation techniques made possible the direct study of reactive intermediates emerging from these reactions. In 1977, Weltner et al. obtained SiNN and SiCO after cocondensation of thermally vaporized silicon with argon/N₂ and argon/CO mixtures^[3]. Margrave et al. used small hydrogencontaining molecules as reactants for silicon atoms. They observed hydroxysilylene^[4], fluorosilylene^[5], and the parent silylene^[6] after codeposition of the silicon atoms together with water, hydrogen fluoride, and hydrogen, respectively.

Experimental Procedure

Silicon is vaporized from a boron nitride crucible, which is surrounded by an aluminum oxide tube. The oven is resistively heated to temperatures of 1490–1550°C by means of a tungsten wire wound around the alumina tube. The silicon atoms are codeposited with gaseous mixtures of the substrate and argon onto a CsI window at 12 K. The substrate/argon ratio is usually in the range of 1:100. If cocondensed with argon alone, the high reactivity of the silicon atoms can be seen in the formation of many products, such as SiNN, SiCO, SiO, SiH₂, SiH₄, Si₂H₂^[7], and Si₂H₆^[8]. The formation of the silicon hydrides is most likely due to hydrogen impurities in the metal surfaces of the cryostat, whereas the other observable products may result from reactions of the silicon atoms with residual gases in the apparatus.

Results and Discussion

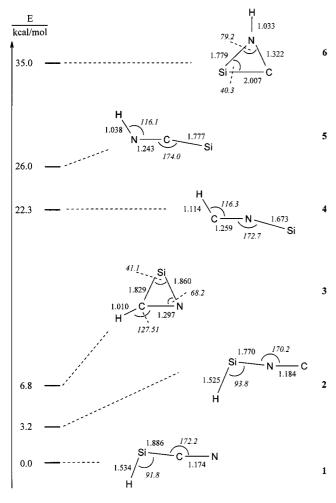
Calculations

Scheme 1 shows the relative energies of several CHNSi singlet species as calculated with the BLYP functional at the 6-311G** basis^[9]. In this system, the global minimum is not the silacyclopropenylidene system, as it is the case in many other related systems^[10]. Cyanosilylene (1) and isocyanosilylene (2) are of lower energy. Obviously, the CN group has a great stabilizing effect on an adjacent silylenic centre. Nevertheless, this stabilization does not cause much increase of the bonding angle at silicon, which according to the BLYP calculations is 92° for 1 and 94° for 2.

We now report on the cocondensation of thermally generated silicon atoms with hydrogen cyanide in an argon matrix, which led to the observation of a total of four CHNSi isomers and two CNSi isomers.

[[] $^{\circ}$] Part 26: G Maier, H. P. Reisenauer, J. Jung, H. Pacl, H. Egenolf, Eur. J. Org. Chem. 1998, 1297–1305, preceding paper.

Scheme 1. Calculated (BLYP/6-311G**) relative energies [kcal mol⁻¹] (corrected by zero point vibrational energies) of six CHNSi singlet species



Scheme 2 shows the relative energies of the three CNSi isomers, which can be expected from the dehydrogenation of the compounds shown in Scheme 1.

Scheme 2. Calculated (BLYP/6-311G**) relative energies [kcal mol⁻¹] (corrected by zero point vibrational energies) of three CNSi isomers. The products of a homolytic dissociation of 1 into 7 and a hydrogen atom lie 69.3 kcal mol⁻¹ above 1

$$Si = \frac{1.857}{7} C = \frac{1.181}{N}$$

$$7 (0.0)$$

$$36.7 Si$$

$$2.020$$

$$C = \frac{1.868}{N}$$

$$Si = \frac{1.752}{N} N = \frac{1.204}{N}$$

$$8 (2.5)$$

$$9 (12.9)$$

Spectroscopic Observations

Apart from the byproducts listed above (SiN₂ etc.) and HCN, the IR spectrum registered after cocondensation of silicon atoms and hydrogen cyanide shows various new absorptions at 2754, 1538, 977, and 735 cm⁻¹. They fit to the calculated spectrum of (silaisocyano)carbene (4)^[11]. This means, the lone pair of the nitrogen atom is more basic than the π system. This is analogous to the reaction of atomic silicon with nitrogen, leading to formation of linear SiNN^[3], instead of the cyclic diazasilacyclopropenylidene [12]. The lowering of the frequency of the N–N stretching vibration in SiNN by about 600 cm⁻¹ with respect to the N₂ molecule indicates a relatively weak N–N bond. The same holds for 4, for which the band of the C–N stretching

Table 1. Calculated (BLYP/6-311G**, C_S symmetry, absolute intensities [km mol⁻¹] in parentheses), corrected [$\nu_{corr} = \nu_{calc} \cdot \nu_{obs}$ ($^1H^1^2C_-$ 4) / ν_{calc} ($^1H^1^2C_-$ 4)], and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm⁻¹] of (silaisocyano)carbene (4)

		mode	label	$\tilde{v}_{\text{calc.}}$ (4-singlet)		$v_{\rm corr.}$	\sim $v_{ m obs.}$		$v_{\text{calc.}}$ (4-triplet)	
ν ₆	a''	SiNC		222.8	(2)		_		310.3	(11)
		def oop	D 13C	218.5 220.6	(<1) (2)					
V_5	a'	SiNC		355.3	(24)		_		291.5	(20)
		def ip	D 13C	332.3	(25)					
		G13.7 /	13C	352.9	(23)		==	/=\		/= = 4\
V_4	a'	SiN str/		708.3	(20)	734.8	734.8	(2)	521.8	(251)
		CH def	D 13C	649.2	(69)	698.7	665.3	(11)		
			¹³ C	699.9	(17)	726.1	730.3	(12)		
v_3	a'	CH def		976.8	(456)	977.0	977.0	(100)	675.7	(124)
. 5			D	836.3	(195)	836.5	854.7	(100)		` /
			D 13C	964.3	(458)	964.5	964.8	(100)		
v_2	a'	CN str	C	1568.6	(83)	1538.1	1538.1	(15)	1660.3	(412)
• 2		011 001	D	1528.0	(160)	1498.3	1485.9	(63)	1000.0	(112)
			¹³ C	1549.1	(72)	1519.0	1519.6	(16)		
V.	a′	CH str	C	2821.8	(127)	2753.5	2753.5	(20)	3157.6	(27)
v_1	а	CII sti	D	2084.9	(46)	2034.4	2059.0	(5)	3137.0	(27)
			¹³ C					(3)		
				2811.9	(127)	2743.8	2745.3	(22)		

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vibration (1538 cm⁻¹, see Table 1) is lowered by about 560 cm⁻¹ compared with that of hydrogen cyanide. It even lies below values observed for compounds with C-N double bonds (e. g., 1641 cm⁻¹ for methanimine, H₂C=NH^[13]). The value of the C-H stretching vibration frequency also is very low (2754 cm⁻¹), indicative of a rather unusual structure of 4. According to our BLYP calculations, the HCN angle in 4 is 116°. Thus, 4 can be assumed to have partly carbene character (resonance structure 4 is more important than other ones).

At the applied level of theory, the triplet form of 4 is 3.7 kcal/mol lower in energy than the singlet form, but this order is reversed when using more sophisticated methods. CAS (4,6)/6-31G** calculations predict the singlet to be 5.9 kcal/mol more stable than the triplet. The experimental observations provide unequivocal evidence that only the singlet species is formed (Table 1), as is the case in other reactions of silicon atoms investigated^[14]. The calculated IR spectrum of the triplet is not compatible with the observed bands of 4.

The photochemical behavior of 4 is unusual. With light of wavelengths >700 nm, 4 can be quickly transformed into 2-aza-1-silacyclopropenylidene (3, Table 2). A rough estimation of the excitation energy to the lowest electronically excited state by means of a CIS/6-31 G** calculation predicts a weak absorption maximum for 4 at 1006 nm representing the HOMO-LUMO transition. The HOMO of 4 is not the 3s Si orbital, as it is usually the case for silylenes, but represents a lone pair at the C atom, typical for a singlet carbene.

Table 2. Calculated (BLYP/6-311G**, $C_{\rm S}$ symmetry, absolute intensities \sim [km mol⁻¹] \sim in parentheses), corrected [$\nu_{\rm corr} = \nu_{\rm calc} \cdot \nu_{\rm obs}.(^{1}{\rm H}^{12}{\rm C}\text{-3})$], and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm⁻¹] of singlet azasilacyclopropenylidene (3)

		-	_	_			-	
		1	1 1 1	~		~	~	
		mode	label	$v_{\rm calc.}$		$v_{\rm corr.}$	$v_{ m obs.}$	
ν ₅	a′	ring def		586.6	(32)	635.5	635.5	(96)
			D	553.8	(33)	599.7	591.6	(100)
			^{13}C	584.5	(32)	632.9	633.2	(100)
V_4	a′	SiC str		735.2	(28)	769.8	769.8	(100)
			D	679.1	(28)	711.1	718.3	(48)
			¹³ C	723.2	(26)	757.2	757.9	(92)
v_6	a"	CH def		799.8	(16)	820.6	820.6	(95)
		oop	D	625.4	(7)	641.7	634.1	(2)
			¹³ C	793.2	(16)	813.8	814.2	(73)
v_3	a′	CH def i	р	1104.7	(35)	1124.7	1124.7	(94)
			D	919.3	(6)	935.9	944.0	(10)
			¹³ C	1094.4	(37)	1114.2	1114.4	(99)
v_2	a′	CN str		1465.3	(9)	1466.2	1466.2	(22)
			D	1443.7	(10)	1444.6	1452.2	(13)
			^{13}C	1436.8	(8)	1437.7	1439.0	(26)
v_1	a′	CH str		2977.7	(40)	2974.2	2974.2	(28)
			D	2208.5	(17)	2205.9	_	
			^{13}C	2967.9	(40)	2964.4	2962.8	(43)

Upon the irradiation mentioned above also a small amount of a second photoproduct is formed. By comparison with its calculated IR spectrum it can be identified as cyanosilylene (1, Table 3). Upon irradiation with light of wavelengths 366 or >395 nm, the bands of 3 and 1 disap-

Table 3. Calculated (BLYP/6-311G**, C_S symmetry, absolute intensities ~ [km mol⁻¹]~ in parentheses), corrected [$\nu_{corr} = \nu_{calc} \cdot \nu_{obs} (^1H^{12}C-1) / \nu_{calc} (^1H^{12}C-1)]$, and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm⁻¹] of singlet cyanosilylene (1)

		mode	label	$v_{\rm calc.}$		$v_{\rm corr.}$	$v_{\rm obs.}$	
ν ₆	a''	SiCN def	D	205.7 203.9	(4) (4)	_	_	
v_1	a′	SiH def	¹³ C	200.0 264.8 250.9	(4) (1) (2)	_	_	
v_2	a′	SiC str	D 13C D	258.5 538.2 523.9	(1) (56) (33)	563.5 548.5	563.5 547.3	(10)
ν_3	a′	SiH def/ SiCN def ip	¹³ C	533.4 811.2 635.0	(55) (79) (76)	558.5 826.4 646.9	555.1 826.4 642.1	(12) (87) (46)
v_4	a′	SiH str	13C	807.6 1987.2 1429.8	(77) (197) (107)	822.7 2026.7 1458.2	823.3 2026.7 1470.0	(39) (100) (100)
v_5	a′	CN str	¹³ C D ¹³ C	1987.3 2131.0 2131.0 2083.6	(197) (38) (39) (34)	2026.8 2142.7 2142.7 2095.0	2024.5 2142.7 2143.2 2095.7	(100) (74) (34) (17)

Table 4. Calculated (BLYP/6-311G**, C_S symmetry, absolute intensities ~ [km mol⁻¹]~ in parentheses), corrected [$\nu_{\rm corr} = \nu_{\rm calc} \cdot \nu_{\rm obs}$, ($^1{\rm H}^{12}{\rm C}$ -2) / $\nu_{\rm calc}$, ($^1{\rm H}^{12}{\rm C}$ -2)], and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR ab sorptions [cm⁻¹] of singlet isocyanosilylene (2)

		mode	label	v _{calc.}		$v_{\rm corr.}$	$v_{\rm obs.}$	
ν ₆	a''	SiNC def		157.4	(1)		_	
		oop	D	154.4	(1)			
		•	^{13}C	155.8	(1)			
v_5	a′	SiNC def ip		214.7	(<1)		_	
			D	208.3	(<1)			
			^{13}C	212.3	(<1)			
v_4	a′	SiN str		601.3	(86)	622.0	622.0	(41)
			D	583.2	(32)	603.3	607.4	(13)
			¹³ C	594.5	(83)	615.0	615.5	(31)
ν_3	a′	SiH def		842.3	(98)	867.9	867.9	(30)
			D	647.5	(119)	667.2	662.6	(35)
			¹³ C	842.2	(98)	867.8	867.8	(25)
v_2	a′	SiH str		1960.4	(296)	2017.8	2017.8	(100)
			D	1412.2	(144)	1453.5	1470.1	(24)
			$^{13}C^{[a]}$	1967.2	(186)	2024.8	2024.6	(47)
ν_1	a′	CN str		1998.1	(244)	2039.5	2039.5	(77)
			D	1996.6	(277)	2038.0	2035.9	(100)
			$^{13}C^{[a]}$	1952.4	(353)	1992.9	1994.1	(100)

[[]a] Better described as SiH_{str} + CN_{str}.

pear, whereas four small absorptions already present grow rapidly. These can be assigned to isocyanosilylene (2, Table 4). An independent proof for structure 2 stems from the observation that the same compound is formed on irradiation of triazidomethylsilane $10^{[15]}$ in an argon matrix. Triazidosilane 10 loses four molecules of nitrogen upon matrix irradiation with $\lambda=254$ nm. The reaction sequence initiated by photoexcitation is relatively complex. The main product after longer irradiation is silylisocyanide (13; $v_{N=C}=2098~\text{cm}^{-1}$), which exists in a photoequilibrium with the already known^[16] silylcyanide (14; $v_{C=N}=2200~\text{cm}^{-1}$). It is hard to believe that 13 can be a photoproduct

of 10. One has to assume the intermediacy of silanitrile 11, which can undergo a methyl migration under formation of silaisonitrile 12 ($v = 1467, 1410 \text{ cm}^{-1}$). A subsequent threefold 1,3 H-shift gives silylisocyanide 13, the most stable isomer on the CH₃NSi energy surface. Parallel to this isomerization a dehydrogenation occurs. Product is the same species 2, which has already been discussed above. But there is a remarkable difference. The photoisomerization $3 \rightarrow 2$ delivers the isocyanosilylene (2) in the matrix cage without any partner molecule, but in case of the H₂-elimination 12 \rightarrow 2·H₂ silylene 2 has to be "complexed" with a hydrogen molecule. That is indeed so, as can be seen from the band shifts of 2·H₂ compared to free 2. In the presence of hydrogen the relevant IR absorptions are registered at 2056, 2037, 852, and 605 cm⁻¹.

Figure 1. Difference IR spectrum (Ar matrix, 12 K) of the photoreaction (> 700 nm) $4 \rightarrow 1 + 2 + 3$. Bands due to hydrogen cyanide, carbon dioxide, and SiNN have been crossed

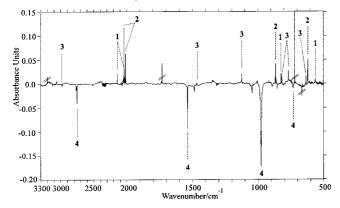
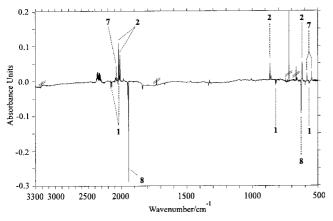


Figure 2. Difference IR spectrum (Ar matrix, 12 K) of the photoreaction (366 nm) $1 + 8 \rightarrow 2 + 7$. Bands due to hydrogen cyanide, carbon dioxide, and SiNN have been crossed



$$H - \ddot{C} - C \equiv N \qquad \stackrel{hv}{\longleftarrow} \qquad \ddot{C} - N = C: \qquad H - \ddot{C} - Si \equiv N$$

$$15 \qquad \qquad H$$

$$16 \qquad \qquad 17$$

Mechanistic Considerations and a Comparison between Silylenes and Carbenes

Small amounts of 1, 2, and 3 can be observed immediately after the cocondensation of silicon atoms and hydrogen cyanide. But it can be assumed that these products are not formed directly from these reagents in a thermal reaction, but that they originate from photochemically induced isomerizations of the primarily formed adduct 4. In this context it is important to know, that the amount of 1, 2, and 3 can be lowered by protecting the matrix from daylight during the codeposition. Obviously even the comparatively low energy of near IR light is sufficient for the isomerizations of $4^{[17]}$.

The photochemical behavior of silylenes 1 and 2 finds its parallel in the relationship between the two carbenes 15 and 16^[18], which we examined recently^[18]. Cyanocarbene 15 has a triplet ground state with a nearly linear geometry. The lowest electronic transition lies around 300 nm, the CH stretching vibration is found near 3300 cm⁻¹. The spectroscopic properties of the isocyanocarbene 16, which can be generated by irradiation of 15, are completely different. On the other hand they resemble very closely the data found for (silaisocyano)carbene 4. The lowest electronic transition for 16 can be measured as a weak and very broad absorption band in the near IR region (700-1100 nm) and the CH stretching vibration is registered at 2700 cm⁻¹. So it is no surprise that upon irradiation with visible or near IR light 16 is easily retransformed into 15. The reason for the large differences in the spectroscopic properties of 15 and 16 lies in the electronic structure and the resulting geometry of isocyanocarbene 16. This compound represents - like the silaanalogue 4 - a strongly bent singlet carbene.

The second possibility of substituting a carbon atom in 16 by a silicon atom results in isocyanosilylene 2, which is very low in energy and shows the "normal" properties of a silylene (singlet multiplicity, HSiN angle of about 90°). Formal substitution of one carbon atom by silicon in cyanocarbene 15 leads either to cyanosilylene (1) — which we found in the experiment — or to (silacyano)carbene 17. This compound is calculated to lie 115 kcal/mol higher in energy than 1 (BLYP/6-311G**), reflecting the carbenic nature of 17 and the unfavourable SiN triple bond. No wonder, that spectroscopic indications for 17 were not found.

CNSi Isomers

If 2 is irradiated with light of wavelength 254 nm, its absorptions decrease to about one third of their original intensity, and two new bands appear, which can be assigned to the SiNC radical (8, Table 5, Figure 2). Upon irradiation with light of wavelength 366 nm 8 isomerizes to the SiCN radical (7, Table 6), probably via the cyclic form 9^[19].

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Table 5. Calculated (BLYP/6-311G**, $C_{\rm ov}$ symmetry, absolute intensities [km mol⁻¹] in parentheses), corrected [$\nu_{\rm corr} = \nu_{\rm calc} \cdot \nu_{\rm obs} (^1{\rm H}^{12}{\rm C}\text{-8})$], and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm⁻¹] of the SiNC radical (8)

		mode	label	v _{calc.}		v _{corr.}	v _{obs.}	
ν_4	π	SiNC def ^[a]		155.3	(1)		_	
ν ₃	π	SiNC def ^[a]	¹³ C	153.5 247.1	(1) (<1)		_	
ν ₂	σ	SiN str	¹³ C	244.4 616.5	(<1) (58)	629.1	629.1	(54)
-			¹³ C	609.8	(56)	622.3	622.9	(47)
v_1	σ	C-N str	¹³ C	1878.4 1841.0		1945.2 1906.5	1945.2 1907.3	(100) (100)

[[]a] For species with a $^{2}\pi$ ground state the degeneracy of the bending vibration is lost (Renner-Teller effect).

Table 6. Calculated (BLYP/6-311G**, C_{∞_V} symmetry, absolute intensities [km mol $^{-1}$] in parentheses), corrected [$v_{\text{corr}} = v_{\text{calc}} \cdot v_{\text{obs}}(^{1}\text{H}^{12}\text{C-7})$ / $v_{\text{calc}}(^{1}\text{H}^{12}\text{C-7})$], and experimental (Ar matrix, 12 K, intensities relative to the strongest band in parentheses) IR absorptions [cm $^{-1}$] of the SiCN radical (7)

	mode	label	v _{calc.}	v _{corr.}	v _{obs.}	
ν ₄ π	SiCN def ^[a]	13 C	197.0 191.4		_	
ν_3 π	SiCN def ^[a]	¹³ C	285.0 276.9	(1)	_	
v_2 σ	SiC str			(54) –	584.6/548 571.8	8.1 (100) ^[b] (100)
ν_1 σ	C-N str	¹³ C	2046.1	(15) 2077.3 (13) 2031.5	2077.3 2032.2	(40) (28)

[[]a] For species with a $^2\pi$ ground state the degeneracy of the bending vibration is lost (Renner-Teller effect). - [b] Probably split by anharmonic resonance.

Conclusion

Cocondensation of silicon atoms with hydrogen cyanide in an argon matrix leads to the formation of (silaisocyano)carbene (4). By irradiation of this compound with visible or UV light three isomeric silvlenes [cyanosilylene (1), isocyanosilylene (2) and azasilacyclopropenylidene (3)] as well as the CNSi radical 8 can be obtained. In all cases the structural assignment is based on the comparison between the experimental and calculated IR spectra of the parent compounds including the corresponding D and ¹³C isotopomers.

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Experimental Section

Equipment Used for Matrix Isolation, Photolyses, and Pyrolyses: See Ref. [20].

Pulsed Flash Pyrolyses and High Vacuum Flash Pyrolyses: For a description see Ref. [20].

General: See Ref.[20].

- [1] [1a] P. P. Gaspar, S. A. Bock, W. C. Eckelman, *J. Am. Chem. Soc.* **1966**, 88, 3878–3879. [1b] P. P. Gaspar, S. A. Bock, C. A. Levy, *Chem. Commun.* **1968**, 1317–1318. [1c] P. P. Gaspar, S. A. Bock, W. C. Eckelman, J. Am. Chem. Soc. 1968, 90, 6914 - 6922
- (2) [2a] P. S. Skell, P. W. Owen, J. Am. Chem. Soc. 1967, 89, 3933–3934. [2b] P. S. Skell, P. W. Owen, J. Am. Chem. Soc. 1972, 94, 5434–5438. [2c] P. S. Skell, P. W. Owen, XXIII. Internat. Congress Pure Appl. Chem., Boston 1971, Abstracts Special Lectures Vol. 4, 215–221, Butterworths, London 1971.
- [3] R. R. Lembke, R. F. Ferrante, W. Weltner, Jr., J. Am. Chem.
- Soc. 1977, 99, 416–423.
 Z. K. Ismail, R. H. Hauge, L. Fredin, J. W. Kauffman, J. L. Margrave, J. Chem. Phys. 1982, 77, 1617–1625.

- Margrave, J. Chem. Phys. 1982, 77, 1617–1625.
 Z. K. Ismail, L. Fredin, R. H. Hauge, J. L. Margrave, J. Chem. Phys. 1982, 77, 1626–1631.
 L. Fredin, R. H. Hauge, Z. K. Ismail, J. L. Margrave, J. Chem. Phys. 1985, 82, 3542–3545.
 G. Maier, H. P. Reisenauer, A. Meudt, H. Egenolf, Chem. Ber./Recueil, 1997, 130, 1043–1046.
 Strikingly, the link between Si₂H₂ and Si₂H₆, namely Si₂H₄, seems to be absent. A close examination on this "phenomenon" is still under progress. It is tempting to assume that an unidentified band at 746 cm^{-1[7]} originates from such a species.
 GAUSSIAN 94, Revision B.I, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W.Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, Gaussian, Inc., Pitts-
- burgh, PA, 1995. [10] [$^{[10a]}$ C₂H₂Si: G. Frenking, R. B. Remington, H. F. Schaefer III. J. Am. Chem. Soc. **1986**, 108, 2169–2173. – G. Vacek, B. T. Colegrove, H. F. Schaefer III, *ibid.* **1991**, 113, 3192–3193. – [10b] C₂H₄Si₂: G. Maier, H. P. Reisenauer, A. Meudt, Eur. J. Org. Chem. **1998**, 1291–1295, Part 25 of this series – [10c] C₃H₄Si:
- Chem. 1998, 1291–1295, Part 25 of this series ¹¹⁰³ C₃H₄Si: G. Maier, H. P. Reisenauer, J. Jung, H. Egenolf, Eur. J. Org. Chem. 1998, 1297–1305, Part 26 of this series.
 [11] Preliminary report: G. Maier, H. P. Reisenauer, H. Egenolf, Organosilicon Chemistry III From Molecules to Materials, (Eds. N. Auner, J. Weis), VCH, Weinheim 1998, pp. 31–35.
 [12] Diazasilacyclopropenylidene can be formed upon irradiation of the linear SiNN molecule with light of wavelength 313 nm in a nitrogen matrix. G. Maier, H. P. Paigenauer, J. Glatthage, H.
- nitrogen matrix: G. Maier, H. P. Reisenauer, J. Glatthaar, H.
- Egenolf, to be published.

 [13] M. E. Jacox, D. E. Milligan, *J. Mol Spectrosc.* **1975**, *56*, 333–356.
- [14] G. Maier, H. P. Reisenauer, H. Egenolf, Eur. J. Org. Chem. 1998,
- 1313–1317, following paper.

 [15] G. Maier, J. Glatthaar, Organosilicon Chemistry II From Molecules to Materials, (Eds. N. Auner, J. Weis), VCH, Weinheim **1994**, S. 131–138.

- [16] A. G. MacDiarmid, J. Inorg. Nucl. Chem. 1956, 2, 88.
 [17] The activation barrier for the reaction 4 → 3 has been calculated to be 22.6 kcal/mol (BLYP/6-311G**).
 [18] [18a] G. Maier, H. P. Reisenauer, K. Rademacher, to be published. [18b] K. Rademacher, Ph. D. Thesis, University of Ciclos. 1007 Gießen, 1997.
- ^[19] Not observed. The calculated wavenumbers are: $v_{SiC} = 345(19)$, $v_{\rm SiN} = 531.4(24)$, and $v_{\rm CN} = 1698.4(35)$ cm⁻¹. [20] G. Maier, H. P. Reisenauer, A. Meudt, *Eur. J. Org. Chem.* **1998**,
- 1285-1290, Part. 24 of this series.

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