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Spectroscopic and structural characterization of three silaisocyanides: exploring an elusive class of reactive molecules at high resolution†

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Silaisocyanoacetylene, HCCNSi, silaisocyanodiacetylene, HC₄NSi, and silaisocyanogen, NCNSi, have been identified spectroscopically for the first time. All three transient species were observed at high spectral resolution at centimeter wavelengths (5–40 GHz) by microwave spectroscopy. From detection of less abundant isotopic species and high-level quantum-chemical calculations, accurate empirical equilibrium structures have been derived for HCCNSi and NCNSi. All three molecules are promising candidates for future radio astronomical detection owing in part to large calculated dipole moments.

Nitriles and isonitriles are important classes of molecules in chemistry, and molecules containing these functional groups are very prominent in a wide variety of astronomical sources, including cold clouds, star-forming regions, and circumstellar shells.¹ Near 40 of the more than 160 astronomical molecules, for example, contain or are terminated by –CN or –NC; chains as long as HC₁₁N have been reported in space,² while even longer ones (*e.g.*, up to HC₁₇N) have been detected in the laboratory.³ More complex species such as isopropylcyanide have been recently detected astronomically,⁴ as have a number of metal-containing species, such as SiCN and SiNC.⁵

In sharp contrast, the isovalent silanitrides (*R*-SiN) and silaisocyanides (*R*-NSi) have received far less attention. Much of the available information, although limited, is theoretical in nature, with calculations predicting that silaisocyanides are usually more stable by several tens of kcal mol⁻¹ than their silanitride

counterparts.⁶ Experimentally, the synthesis of silanitride or silaisocyanide has remained largely elusive, and only HNSi, the second-row counterpart to HNC, has been extensively characterized using microwave,⁷ infrared⁸ and mass spectrometric⁹ techniques. Its isomer, HSiN, is calculated to lie approximately 65 kcal mol⁻¹ higher in energy¹⁰ and has only been observed in an argon matrix,¹¹ not in the gas phase.

Only very recently has even the existence of more complex silaisocyanides been established by experiment. Two such compounds, vinyl isocyanide,¹² C₂H₃NSi, and silaisocyanoacetylene,¹³ HCCNSi, were produced in a crossed molecular beam apparatus by reaction of the SiN radical with either ethylene or acetylene.¹⁴ In related work, the rotational spectrum of two small silicon-nitride compounds, bent-chain silaisocyanosilylene (HSiNSi) and silyl silaisocyanide (H₃SiNS), were studied¹⁵ using Fourier transform (FT) microwave spectroscopy.

HCCNSi and silaisocyanogen (NCNSi) are isovalent to the well-known compounds HCCCN¹⁶ and NCCN,¹⁷ but there is a paucity of information on their energetics and structures, and their spectroscopic properties are essentially unknown. For HCCNSi, in addition to some calculations accompanying the crossed molecular beam experiment,¹³ there is only one other quantum chemical study,¹⁸ in which extensive density functional theory calculations of the [H, Si, 2C, N] potential energy surface were undertaken, work that predicted this isomeric arrangement of atoms to be the global minimum. The situation is no better for NCNSi, it has not yet been detected experimentally, and there are only two computational studies,^{19,20} but both identify NCNSi as the most stable isomer. HC₄NSi, the next member in the series of silaisocyanoacetylenes H(C≡C)_{*n*}NSi (*n* = 1, 2, . . .), apparently has neither been characterized experimentally nor quantum-chemically.

This communication reports detection of three silaisocyanoacetylene compounds, HCCNSi, HC₄NSi, and NCNSi, in the gas-phase by FT microwave rotational spectroscopy of a supersonic molecular beam, guided by new high-level quantum chemical calculations performed at the coupled-cluster level of theory. The two smaller species are so readily produced that several of their less

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abundant isotopic species have also been observed in natural abundance. In combination with quantum-chemical calculations, it is then possible to carefully examine the geometry and chemical bonding in these compounds, and study how the N–Si bond length changes with different substituents.

Searches for the rotational spectra of HCCNSi, NCNSi and HC₄NSi were guided by high-level quantum-chemical calculations performed at the CCSD(T)²¹ level of theory. All calculations were performed using the CFOUR program package²² in combination with Dunning's hierarchies of correlation consistent polarized valence and polarized core-valence sets.²³ The best estimate equilibrium structures have been calculated at the CCSD(T)/cc-pwCVQZ level of theory (Fig. 1), which has been shown previously to yield equilibrium structures of very high quality for molecules harboring second-row elements.²⁴ Zero-point vibrational corrections ΔB_0 to the rotational constants were calculated in the frozen-core (fc) approximation at the CCSD(T)/cc-pV(T+d)Z level and ground state rotational constants were obtained as $B_0 = B_e - \Delta B_0$. Here, the equilibrium rotational constants B_e are calculated from the CCSD(T)/cc-pwCVQZ structures. The calculated spectroscopic parameters are given in Table 1.

A sensitive FT microwave spectrometer,^{3,25} which employs a low-repetition rate pulsed discharge nozzle source (6 Hz), was used to detect rotational lines of the new silaisocyanides. Because the frequency range (5–42 GHz) is well-coupled to the low rotational temperature ($T_{\text{rot}} \sim 3$ K) in the expansion,

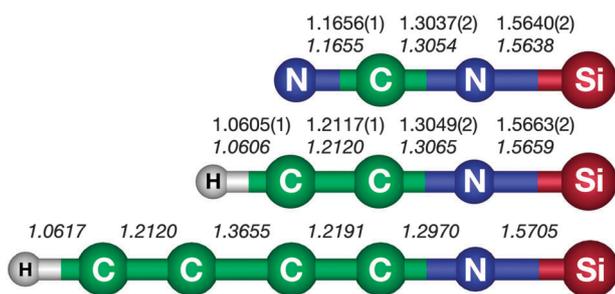


Fig. 1 Molecular structures of the three silaisocyanides studied here (in Å). Semi-experimental equilibrium parameters (r_e^{exp}) are given in plain text, while those derived at the CCSD(T)/cc-pwCVQZ level of theory are given in italics. See the ESI† for further details.

Table 1 Calculated and experimental rotational constants and calculated zero-point vibrational corrections of HCCNSi and NCNSi and their isotopologues (in MHz)

Species	B_0	ΔB_0^a	Species	B_0	ΔB_0^a
HCCNSi	2842.735 ^b	+2.451	NCNSi	2907.141 ^b	+1.776
HCCNSi	2844.82943(14)	+2.451	NCNSi	2909.42284(9)	+1.776
HCCN ²⁹ Si	2802.48249(22)	+2.399	N ¹³ CNSi	2885.45388(18)	+1.723
HCCN ³⁰ Si	2762.64147(35)	+2.350	N ¹³ C ¹⁵ NSi	2885.17079(17)	+1.790
HCC ¹⁵ NSi	2844.68517(24)	+2.477	¹⁵ N ¹³ CNSi	2798.24419(32)	+1.626
H ¹³ CCNSi	2754.02718(15)	+2.426	¹⁵ NC ¹⁵ NSi	2819.17542(12)	+1.743
HC ¹³ CNSi	2821.46479(16)	+2.385	¹⁵ NC ¹⁵ N ²⁹ Si	2775.51184(15)	+1.693
DCCNSi	2664.15573(12)	+1.478	¹⁵ NC ¹⁵ N ³⁰ Si	2734.43050(22)	+1.646

^a fc-CCSD(T)/cc-pV(T+d)Z, see the text. ^b Best estimate, see the text; see Table 2 and the ESI for nuclear quadrupole coupling constants.

this type of spectroscopy has proven to be one of the most powerful techniques to detect small new molecules in the gas phase. For HCCNSi, rotational lines were observed through a discharge consisting of only methyl cyanide, CH₃CN (formally carrying the HCCN structural motif), and silane, SiH₄ (serving as the source of silicon), both diluted to 1% in neon. NCNSi was first detected using a three-component mixture of HC₃N, SiH₄, and N₂ in neon, while a mixture of HC₃N and SiH₄ in neon yielded lines of HC₄NSi. For all three, the discharge potential was typically in the 1.0–1.2 kV range, and the stagnation pressure behind the nozzle was 2.5 kTorr (3.2 atm).

On the basis of the calculated rotational constant of HCCNSi (Table 1), a search for its $J = 3-2$ transition, predicted near 17 GHz and covering some 60 MHz ($\sim 0.4\%$, see the ESI†), was carried out. Several lines were detected, but the strongest feature was only observed when both CH₃CN and SiH₄ were present in the discharge mixture, and it displays a closely-spaced line structure, very similar to that predicted from the theoretical nitrogen quadrupole constant $eQq(\text{N})$. Soon afterwards, a number of harmonically-related lines at lower (Fig. 2) and higher frequencies were found. In total, the lowest six rotational transitions were detected between 5 and 34 GHz.

In addition to the parent molecule, six rare isotopic species were also observed (Table 1) using isotopically-enriched samples of CH₃CN: ¹³CH₃CN, CH₃¹³CN, CH₃C¹⁵N, and CD₃CN, while HCCN²⁹Si and HCCN³⁰Si were observed in natural abundance (²⁹Si: 4.7% and ³⁰Si: 3.1%). Tabulations of line frequencies, along with best-fit spectroscopic constants, are summarized in the ESI.†

With a calculated dipole moment in excess of 5 D (5.41 D), NCNSi is a prime target for detection by microwave spectroscopy, despite a complex hyperfine structure (hfs) from two nitrogen nuclei, which should produce a dense, closely-spaced line pattern; hfs will be resolved at the high spectral resolution (0.1 ppm) of our spectrometer. Only one prominent feature was found in a 60 MHz survey centered at the predicted frequency of its $J = 2-1$ transition (11.6 GHz; Fig. 3), and its line structure is qualitatively similar to that found for other carbon chains containing two nitrogen atoms, e.g. NCCNH⁺.²⁶ On this basis, four confirming transitions were quickly found, and the closely-spaced

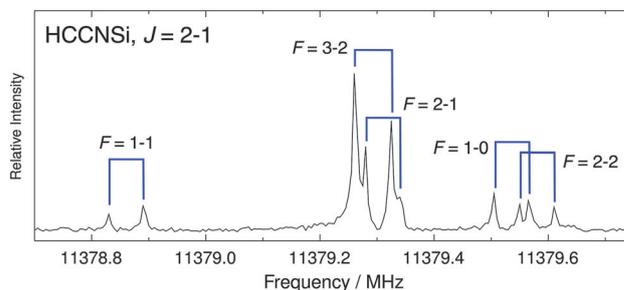


Fig. 2 The $J = 2-1$ transition of HCCNSi showing well-resolved hyperfine structure from the nitrogen nucleus ($I = 1$). The Doppler splitting (blue) arises because the supersonic jet propagates along the axis of the Fabry–Perot resonator. The spectrum is a composite of four spectra, each of 0.3 MHz bandwidth. At a repetition rate of 6 Hz, the total integration time was 5 min 30 s.

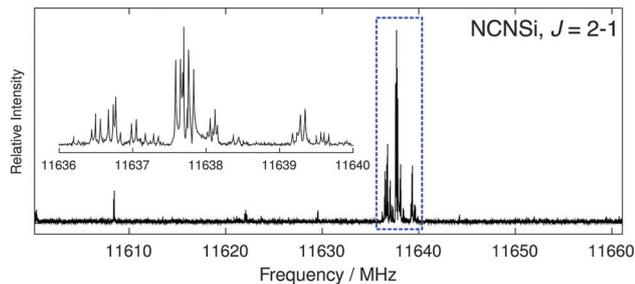


Fig. 3 Original survey for the $J = 2-1$ transition of NCNSi. The inset shows an expanded view of the feature near 11638 MHz, which exhibits complex hyperfine structure from the two nitrogen nuclei.

line structure of each was analyzed and assigned using the calculated quadrupole coupling constants as an initial guess (see the ESI[†]). Like HCCNSi, strong lines of NCNSi were also observed using CH₃CN instead of HC₃N, which allowed extensive isotopic spectroscopy to be undertaken; a total of seven isotopologs were ultimately observed and analyzed using this precursor and ¹⁵N₂ (Table 1).

By comparing line intensities of HCCNSi and NCNSi with those of a stable molecule at a known abundance (0.2% OCS in argon), and taking into account differences in rotational partition functions and dipole moments, we estimate that both silaisocyanides are produced in excess of 10¹¹ molecules per gas pulse. This abundance is relatively high compared to many reactive species produced using the same discharge source, a clear indication that both species are synthesized efficiently. Motivated by this finding, a search was then undertaken for HC₄NSi based on calculations at a similar level of theory to that employed for HCCNSi. The calculated structure of HC₄NSi is summarized in Fig. 1 and $eQq(N)$ is predicted to be almost identical to that of HCCNSi. Using an analogous search strategy, a total of six harmonically-related rotational lines were found within 0.1% of the theoretical prediction; the derived spectroscopic constants [*i.e.*, B , D , $eQq(N)$] are in very good agreement with those predicted (see the ESI[†]).

The experimental quadrupole coupling constants $eQq(N)$ of the silaisocyanides provide a direct probe of the chemical bonding at the nitrogen nucleus in each chain because this quantity is directly proportional to the electric field gradient at this atom. Table 2 summarizes the $eQq(N)$ values for several small isocyanides, and their corresponding silicon variants. It is clear from this comparison that substitution of the carbon atom in the -NC group with silicon changes this constant little, implying that the electronic structure and bonding remains largely unaltered

Table 2 Nuclear quadrupole coupling constants $eQq(N)$ of several small isocyanides and their Si-variants (in MHz)

Molecule	$eQq(N)$	Molecule	$eQq(N)$
HNC	+0.264(1) ^a	HNSi	+0.376(5) ^b
HCCNC	+0.945(1) ^c	HCCNSi	+0.890(2) ^d
NCNC _{inner}	+1.3215(5) ^e	NCNSi _{inner}	+1.339(2) ^d
NCNC _{outer}	-3.7811(3) ^e	NCNSi _{outer}	-3.293(1) ^d
HC ₄ NC	+0.96(2) ^f	HC ₄ NSi	+0.865(83) ^d

^a Ref. 27. ^b Ref. 7a. ^c Ref. 28. ^d This study. ^e Ref. 29. ^f Ref. 30.

at the end of the chain. For HCCNC and HCCNSi, for example, the value of $eQq(N)$ is indicative of a nitrogen which is intermediate between triply and quadruply bound. Because SiN and CN have the same electronic ground state and chemical bonding, and because their spectral properties are similar when bound to different substituents, the present work supports the view that NSi, like isocyanide, can be thought of as a functional group.

A more complete picture of the chemical bonding in the silaisocyanides is possible by examining the empirical equilibrium (r_e^{emp}) structures of both HCCNSi and NCNSi. Such highly accurate structures can be derived from the present data set because rotational constants of many isotopic species are available, and zero-point vibrational corrections have been calculated quantum-chemically (Table 1). Fig. 1 summarizes the best-fit bond lengths derived using a standard least-squares fitting procedure. The empirical equilibrium lengths are in very good agreement with structures calculated at the CCSD(T)/cc-pwCVQZ level of theory. Relative to HNSi,^{7a} the N-Si bond lengths increase only very slightly ($\sim 0.02-0.03$ Å), and are nearly identical in HCCNSi and NCNSi, further evidence that the NSi unit is little perturbed by the substituent.

The present work suggests that other *R*-NSi species might be found by the same detection method. Possible candidates include longer members of the H(C≡C)_{*n*}NSi and NC(C≡C)_{*n*}NSi series, as well as the Si-variants of well known, stable nitriles such as CH₃CN, vinyl cyanide (C₂H₃CN), and ethyl cyanide (C₂H₅CN). To guide laboratory searches, structural and spectroscopic parameters of the corresponding silaisocyanide compounds, calculated at the CCSD(T) level of theory, are given in the ESI[†].

Owing to the widespread distribution and high abundance of many nitrile species in astronomical sources, it would be disappointing if molecules containing the silaisocyanide group are not eventually detected in space. The SiN radical was found more than 20 years ago towards a circumstellar envelope,³¹ and more recently towards the galactic center source Sgr B2(M).³² HCCNSi and NCNSi are particularly attractive targets for dedicated astronomical searches for many reasons: highly precise rest frequencies are now available; they possess sizable dipole moments and small rotational partition functions; they are isovalent to known (HC₃N)³³ or likely (NCCN)³⁴ astronomical molecules; and reactions involving the SiN radical have no or very low entrance barriers (*e.g.*, ~ 2.4 kcal mol⁻¹),¹³ suggesting that enough free energy may be available in shock regions where other Si-containing molecules are readily observed.

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