Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information: Spectroscopic and structural characterization of three silaisocyanides: Exploring an elusive class of reactive molecules at high-resolution

Sven Thorwirth,*,† Ralf I. Kaiser,‡ Kyle N. Crabtree,¶,§ and Michael C. McCarthy¶

I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany, Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States, and Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, United States

E-mail: sthorwirth@ph1.uni-koeln.de

*To whom correspondence should be addressed

†I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

‡Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, United States

¶Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, United States

§Present address: Department of Chemistry, University of California-Davis, Davis, CA 95616, United States

Quantum chemical calculations

The FTMW spectroscopic searches for HCCNSi and NCNSi reported here were guided by high-level quantum-chemical calculations performed at the coupled-cluster (CC) level using the CC singles and doubles level augmented by a perturbative treatment of triple excitations, CCSD(T).[1] All calculations were performed using the CFOUR program package[2,3] in combination with Dunning's hierarchies of correlation consistent polarized valence and polarized core-valence sets: in the frozen-core approach, the *d*-augmented correlation consistent basis set cc-pV(T+*d*)Z was used for the silicon atom[4] along with standard basis sets cc-pVTZ for hydrogen, oxygen and carbon (denoted CCSD(T)/cc-pV(T+*d*)Z in the following). When considering all electrons in the correlation treatment, the cc-pwCV*X*Z (X = T and Q) basis sets[5] were used. The calculations follow the general strategies outlined recently in Ref.[6]

The best equilibrium structures of HCCNSi, HC_4NSi and NCNSi have been calculated at the CCSD(T)/cc-pwCVQZ level of theory (Tables S1 and S2), which has been shown on several occasions to yield equilibrium structures of very high quality for molecules harboring second-row elements[7,8] and has supported high-resolution spectroscopic detection of a sizable number of new molecules recently in this laboratory.[9–11] Nuclear quadrupole coupling constants $eQq(N)$ were obtained at the same level of theory. Harmonic and anharmonic force fields were calculated in the frozen-core approximation at the CCSD(T)/cc-pV(T+*d*)Z level of theory using analytic second-derivative techniques[12,13] followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force fields.[13,14] Theoretical ground state rotational constants are then obtained from the relation $B_0 = B_e - \Delta B_0$. Here, the equilibrium rotational constants B_e are obtained from the CCSD(T)/cc-pwCVQZ equilibrium structures and corrected for the effects of zero-point vibration calculated at the CCSD(T)/cc-pV(T+*d*)Z level of theory. In addition, the CCSD(T)/cc-pV(T+*d*)Z force field calculation yields the quartic centrifugal distortion parameters. The calculated spectroscopic parameters are summarized in Tables S3, S4 and S5. Harmonic and anharmonic vibrational frequencies are collected in Tables S6 and S7.

Table S1: Equilibrium structural parameters of HCCNSi and NCNSi (in Å).

	HCCNSi			
Method	$r_{\mathrm{H-C}}$	$r_{\mathrm{C-C}}$	$r_{\mathrm{C-N}}$	$r_{\mathrm{N-Si}}$
B3LYP/6-311G**, Ref.[15]	1.071	1.221	1.786	1.588
B3LYP/6-31G(d), Ref.[16]	1.0645	1.2181	1.2996	1.5846
QCISD/6-311G(d,p), Ref.[16]	1.0644	1.2160	1.3183	1.5733
fc-CCSD(T)/cc-pV(T+d)Z	1.0621	1.2182	1.3107	1.5765
fc-CCSD(T)/cc-pV(Q+d)Z	1.0619	1.2151	1.3088	1.5732
CCSD(T)/cc-pwCVTZ	1.0615	1.2142	1.3080	1.5688
CCSD(T)/cc-pwCVQZ	1.0606	1.2120	1.3065	1.5659
r_e^{emp}, fc-CCSD(T)/cc-pV(T+d)Z	1.0605(1)	1.2117(1)	1.3049(2)	1.5663(2)
		NCNSi		
	—	$r_{\mathrm{N-C}}$	$r_{\mathrm{C-N}}$	$r_{\mathrm{N-Si}}$
HF/DZP, Ref.[17]	—	1.144	1.307	1.543
B3LYP/DZP, Ref.[17]	—	1.178	1.304	1.579
MP2/DZP, Ref.[17]	—	1.196	1.318	1.584
CCSD/DZP, Ref.[17]	—	1.180	1.322	1.572
B3LYP/6-311G(d), Ref.[18]	—	1.1646	1.2969	1.5796
fc-CCSD(T)/cc-pV(T+d)Z	—	1.1720	1.3099	1.5741
fc-CCSD(T)/cc-pV(Q+d)Z	—	1.1686	1.3078	1.5710
CCSD(T)/cc-pwCVTZ	—	1.1677	1.3072	1.5665
CCSD(T)/cc-pwCVQZ	—	1.1655	1.3054	1.5638
r_e^{emp}, fc-CCSD(T)/cc-pV(T+d)Z	—	1.1656(1)	1.3037(2)	1.5640(2)

Table S2: Equilibrium structures of HCCCCNSi (in Å).

Method	$r_{\mathrm{H-C}}$	$r_{\mathrm{C-C}}$	$r_{\mathrm{C-C}}$	$r_{\mathrm{C-C}}$	$r_{\mathrm{C-N}}$	$r_{\mathrm{N-Si}}$
fc-CCSD(T)/cc-pV(T+d)Z	1.0635	1.2180	1.3702	1.2253	1.3009	1.5813
fc-CCSD(T)/cc-pV(Q+d)Z	1.0630	1.2151	1.3681	1.2222	1.2991	1.5779
CCSD(T)/cc-pwCVTZ	1.0627	1.2142	1.3676	1.2213	1.2984	1.5735
CCSD(T)/cc-pwCVQZ	1.0617	1.2120	1.3655	1.2191	1.2970	1.5705

Table S3: Spectroscopic parameters of HCCNSi and its isotopologs (in MHz).

Parameter	HCCNSi		$HCCN^{29}Si$	$HCCN^{30}Si$	
	Calc.	Exp.			
B	2842.735[a]	2844.82943(14)	2802.48249(22)	2762.64147(35)	
$D \times 10^3$	0.190[b]	0.2013(33)	0.1916(19)	0.1893(141)	
$eQq(N)$	0.907[c]	0.8895(20)	0.8905(61)	0.8987(360)	
ΔB_0[b]	2.451	...	2.399	2.350	
μ	1.44[c]	...	...	...	...
Parameter	$H^{13}CCNSi$	$HC^{13}CNSi$	$HCC^{15}NSi$	DCCNSi	
B	2754.02718(15)	2821.46479(16)	2844.68517(24)	2664.15573(12)	
$D \times 10^3$	0.1926(923)	0.2018(36)	0.2046(39)	0.1744(31)	
$eQq(N)$	0.8953(55)	0.8985(31)	...	0.9011(18)	
$eQq(D)$	...	...	...	0.2265(33)	
ΔB_0[b]	2.426	2.385	2.477	1.478	

[a] Calculated value, see text.
[b] Calculated value, fc-CCSD(T)/cc-pV(T+d)Z.
[c] Calculated value, CCSD(T)/cc-pwCVQZ.

Table S4: Spectroscopic parameters of NCNSi and its isotopologs (in MHz).

Parameter	N_oCN_iSi			$N^{13}CNSi$	$N^{13}C^{15}NSi$
	Calc.	Scaled	Exp.		
B	2907.141[a]	2909.283[b]	2909.422841(91)	2885.45388 (18)	2885.17079(17)
$D \times 10^3$	0.208[c]	0.220[b]	0.2283(26)	0.219(16)	0.228[d]
$eQq(N_o)$	−3.222[e]	...	−3.2928(12)	−3.2911(12)	−3.241(37)
$eQq(N_i)$	1.324[e]	...	1.3387(16)	1.3363(15)	...
ΔB_0[b]	1.776	...	...	1.723	1.790
μ	5.41[e]	...	...	...	...
Parameter	$^{15}N^{13}CNSi$	$^{15}NC^{15}NSi$	$^{15}NC^{15}N^{29}Si$	$^{15}NC^{15}N^{30}Si$	
B	2798.24467(25)	2819.17542(12)	2775.51184(15)	2734.43050(22)	
$D \times 10^3$	0.228[c]	0.2117(47)	0.1956(73)	0.191(14)	
$eQq(N_o)$	...	...	...	...	
$eQq(N_i)$	1.324[c]	...	...	...	
ΔB_0[b]	1.626	1.743	1.693	1.646	

[a] Calculated value, see text.
[b] Empirically scaled value $X_{scaled,\mathrm{NCNSi}} = \frac{X_{exp,\mathrm{HCCNSi}}}{X_{calc,\mathrm{HCCNSi}}} \times X_{calc,\mathrm{NCNSi}}$ $(X = B, D)$.
[c] Calculated value, fc-CCSD(T)/cc-pV(T+d)Z.
[d] Constrained to value of the normal isotopic species.
[e] Calculated value, CCSD(T)/cc-pwCVQZ.

Table S5: Spectroscopic parameters of HC_4NSi (in MHz and D).

Parameter	HC_4NSi	
	Calc.	Exp.
B	922.3[a]	923.10380(13)
$D \times 10^3$	0.0123[b]	0.0137(12)
$eQq(N)$	0.874[c]	0.865(83)
ΔB_0	−0.553[b]	···
μ	2.12[c]	···

[a] Calculated value, see text.
[b] Calculated value, fc-CCSD(T)/cc-pV(T+d)Z.
[c] Calculated value, CCSD(T)/cc-pwCVQZ.

Table S6: Vibrational fundamental frequencies (fc-CCSD(T)/cc-pV(T+d)Z) of HCCNSi (in cm^{-1}) and IR intensities (km/mol).

Vib. Mode	Fundamental		IR Intensity
	Harmonic	Anharmonic	
$\nu_1(\sigma)$	3472	3336	73
$\nu_2(\sigma)$	2140	2066	1
$\nu_3(\sigma)$	1453	1429	17
$\nu_4(\sigma)$	714	699	0.1
$\nu_5(\pi)$	545	551	35
$\nu_6(\pi)$	460	471	17
$\nu_7(\pi)$	176	175	9

Table S7: Vibrational fundamental frequencies (fc-CCSD(T)/cc-pV(T+d)Z) of NCNSi (in cm^{-1}) and IR intensities (km/mol).

Vib. Mode	Fundamental		IR Intensity
	Harmonic	Anharmonic	
$\nu_1(\sigma)$	2239	2211	42
$\nu_2(\sigma)$	1480	1458	82
$\nu_3(\sigma)$	708	704	5
$\nu_4(\pi)$	521	516	17
$\nu_5(\pi)$	166	165	1

Experiment

A sensitive FT microwave spectrometer was used to detect rotational lines of the new silaisocyanides. It operates between 5 and 43 GHz, and is described in detail elsewhere.[19,20] Using a low-repetition rate pulsed nozzle source (6 Hz), molecules adiabatically expand from a small hole in one of the cavity mirrors into a large vacuum chamber; as they traverse the center of the Fabry-Perot cavity, their rotational temperature has dropped to only a few Kelvin ($T_{rot} \sim 3$ K), and they are excited by a short microwave pulse. Following excitation, radiation from the coherently rotating molecules is detected with a sensitive heterodyne receiver. Owing to a narrow instantaneous bandwidth (1 MHz), wide searches in frequency are accomplished by extensive computer-control and automation, in which the mirror separation and the applied frequency are synchronously changed.

The source conditions used to detect all three molecules were similar to those used to produce other transient molecules, in which a rich combination of familiar and exotic molecules are produced by applying an electrical discharge to a mixture of stable precursors heavily diluted in an inert buffer gas. Here, HCCNSi was observed through a discharge consisting of methyl cyanide, CH_3CN (formally carrying the HCCN structural motif), and silane, SiH_4 (serving as the source of silicon), both diluted to 1% in Ne. A number of rare isotopic species of HCCNSi were then observed using commercially available, isotopically-enriched samples of CH_3CN (Aldrich): $^{13}CH_3CN$, $CH_3{}^{13}CN$, $CH_3C^{15}N$, and CD_3CN, while $HCCN^{29}Si$ and $HCCN^{30}Si$ were observed in natural abundance (^{29}Si: 4.7% and ^{30}Si: 3.1%). NCNSi was first detected using a three-component mixture of HC_3N, SiH_4, and N_2 in Ne, but a mixture CH_3CN, SiH_4, and N_2 also produced strong lines of this species, enabling extensive isotopic spectroscopy to subsequently be undertaken. Lines of HC_4NSi were only observed with a mixture of HC_3N and SiH_4 in Ne. For all three molecules, the discharge potential was typically in the 1000-1200 V range, and the stagnation pressure behind the nozzle was 2.5 kTorr (3.2 atm).

Measurements, Analysis, and Structural Determinations

Both HCCNSi and NCNSi are expected to exhibit fair simple pure rotational spectra characteristic of linear molecules with compact fine structure at low-J owing to the presence of one or two nitrogen nuclei ($I_{\mathrm{N}} = 1$, see, e.g., Figure S1). The SPFIT/SPCAT suite of programs[21] was used to predict frequencies of rotational lines and to determine best-fit spectroscopic parameters from frequency measurements; the STRFIT program was used for structural determinations.[22] In the latter procedure, empirical equilibrium rotational constants were calculated according to $B_e^{emp} = B_0^{exp} + \Delta B_0^{calc}$ (see Table 1 in the main manuscript), and the equilibrium structural parameters were determined through a least-squares fit to the empirical moments of inertia I_e^{emp} (see, e.g., Ref.[6]). As can be seen from the numbers given in Figure 1 in the main manuscript, statistical uncertainties from this procedure are of order $1 - 2 \times 10^{-4}$ Å.

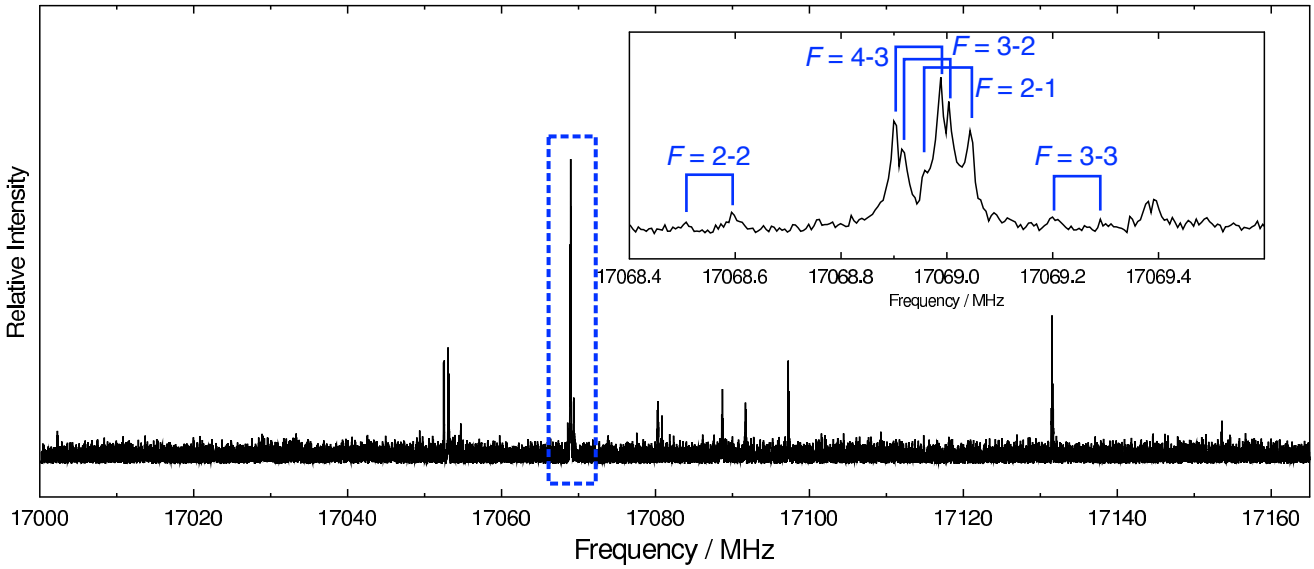

Figure S1: Original survey scan in search for the $J = 3 - 2$ rotational transition of HCCNSi at 17 GHz and spectroscopic assignment under consideration of hyperfine structure from the nitrogen nucleus.

Calculations of other *R*-NSi species

To support future microwave studies, four selected (and more complex) silaisocyandes were calculated at the same level of theory used for guiding the spectroscopic searches for HCCNSi, NCNSi and HC_4NSi here. Structural and spectroscopic parameters are collected in Figure S2 and Table S8.

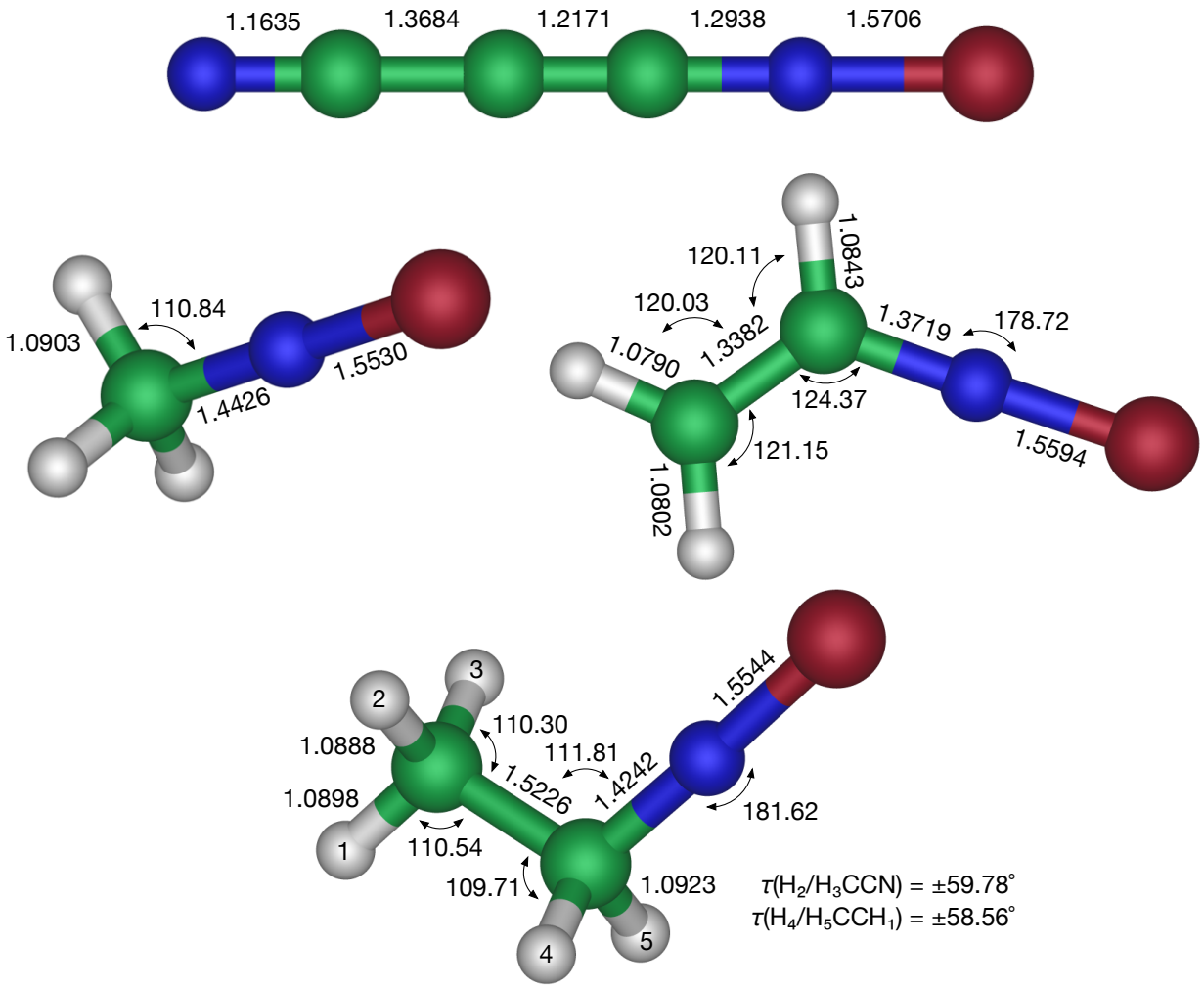

Figure S2: Four *R*-NSi species studied here at the CCSD(T)/cc-pwCVQZ level of theory: NC_3NSi (cyanosilaisocyanoacetylene, top), CH_3NSi (methylsilaisocyanide, center left), C_2H_4NSi (vinylsilaisocyanide, center right), and C_2H_5NSi (ethylsilaisocyanide, bottom).

Table S8: Spectroscopic parameters of selected R-NSi species (in MHz and D) calculated at the CCSD(T) level of theory.

Parameter	NC_3NSi	CH_3NSi	C_2H_3NSi	C_2H_5NSi
${A_e}^a$	⋯	⋯	47926.610	25224.799
${B_e}^a$	922.591	5287.692	2997.098	2913.072
${C_e}^a$	⋯	⋯	2820.705	2698.527
$\Delta {A_0}^b$	⋯	⋯	+83.270	+163.450
$\Delta {B_0}^b$	−0.413	+17.656	+8.284	+13.726
$\Delta {C_0}^b$	⋯	⋯	+10.482	+15.381
A_0	⋯	⋯	47843.340	25061.349
B_0	923.004	⋯	2988.814	2899.346
C_0	⋯	⋯	2810.223	2683.146
$D_J \times 10^{3\,b}$	0.0126	1.07	0.630	0.990
$D_{JK} \times 10^{1\,b}$	⋯	0.734	−0.553	−0.275
${D_K}^b$	⋯	⋯	3.93	0.605
$d_1 \times 10^{3\,b}$	⋯	⋯	−0.102	−0.186
$d_2 \times 10^{6\,b}$	⋯	⋯	−5.45	−9.46
${eQq_{inner}}^a$	+0.990	+0.741	⋯	⋯
${eQq_{outer}}^a$	−4.014	⋯	⋯	⋯
${\chi_{aa}}^a$	⋯	⋯	+0.409	+0.509
${\chi_{bb}}^a$	⋯	⋯	−0.489	−0.224
${\mu_a}^a$	6.77	0.44	0.46	0.42
${\mu_b}^a$	⋯	⋯	0.09	0.06

[a] Calculated value, CCSD(T)/cc-pwCVQZ.
[b] Calculated value, fc-CCSD(T)/cc-pV(T+d)Z.

Summary of experimental microwave transition frequencies

HCCNSi

In total, the lowest six rotational transitions of HCCNSi were observed between 5 and 34 GHz. In addition to the parent isotopic species $H^{12}C^{12}C^{14}N^{28}Si$, six more isotopologs were observed: $HCCN^{29}Si$ and $HCCN^{30}Si$ were detected in natural abundance, and four others using appropriate isotopically enriched precursor samples of methyl cyanide: $H^{13}CCNSi$, $HC^{13}CNSi$, $HCC^{15}Si$, and DCCNSi. The measured lines are given in Tables S9 to S15 and the best-fit constants are summarized in Table S3.

HCCNSi - truncated fit files from SPFIT (in MHz)

Table S9: HCCNSi parent species

```
                                        EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
   1:   1  0  0  1                          5689.20770    5689.20831   -0.00061    0.00200   0.00000
   2:   1  2  0  1                          5689.61400    5689.61308    0.00092    0.00200   0.00000
   3:   1  1  0  1                          5689.88270    5689.88294   -0.00024    0.00200   0.00000
   4:   2  1  1  1                         11378.86120   11378.86153   -0.00033    0.00200   0.00000
   5:   2  3  1  2                         11379.29290   11379.29200    0.00090    0.00200   0.00000
   6:   2  2  1  1                         11379.31310   11379.31128    0.00182    0.00200   0.00000
   7:   2  1  1  0                         11379.53800   11379.53616    0.00184    0.00200   0.00000
   8:   2  2  1  2                         11379.57810   11379.58113   -0.00303    0.00200   0.00000
   9:   3  2  2  2                         17068.54910   17068.55007   -0.00097    0.00200   0.00000
  10:   3  4  2  3                         17068.94360   17068.94413   -0.00053    0.00200   0.00000
  11:   3  3  2  2                         17068.95680   17068.95484    0.00196    0.00200   0.00000
  12:   3  2  2  1                         17069.00020   17068.99981    0.00039    0.00200   0.00000
  13:   3  3  2  3                         17069.24290   17069.24397   -0.00107    0.00200   0.00000
  14:   4  5  3  4                         22758.57700   22758.57710   -0.00010    0.00200   0.00000
  15:   4  4  3  3                         22758.58570   22758.58391    0.00179    0.00200   0.00000
  16:   4  3  3  2                         22758.60090   22758.60319   -0.00229    0.00200   0.00000
  17:   5  6  4  5                         28448.18850   28448.18895   -0.00045    0.00200   0.00000   28448.19106   -0.00256 0.5521
  18:   5  5  4  4                         28448.18850   28448.19367   -0.00517    0.00200   0.00000   28448.19106   -0.00256 0.4479
  19:   5  4  4  3                         28448.20670   28448.20437    0.00233    0.00200   0.00000
  20:   6  7  5  6                         34137.78010   34137.77581    0.00429    0.00200   0.00000   34137.77980    0.00030 0.3919
  21:   6  6  5  5                         34137.78010   34137.77927    0.00083    0.00200   0.00000   34137.77980    0.00030 0.3304
  22:   6  5  5  4                         34137.78010   34137.78608   -0.00598    0.00200   0.00000   34137.77980    0.00030 0.2777
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.89357E-01    3   9.99595E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                            NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2844.829429(144)        -0.000000
   2           200         -D          -0.2013( 33)E-03       0.0000E-03
   3     110010000    1.5*eQq          1.34926(296)         -0.00000
 MICROWAVE AVG =        0.000027 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001538 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        0.76896         0.76896
```

Table S10: $HCCN^{29}Si$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  1  1  1                      11209.47240   11209.47399   -0.00159    0.00200   0.00000
    2:   2  3  1  2                      11209.90610   11209.90456    0.00154    0.00200   0.00000
    3:   2  2  1  1                      11209.92200   11209.92384   -0.00184    0.00200   0.00000
    4:   2  1  1  0                      11210.14690   11210.14877   -0.00187    0.00200   0.00000
    5:   2  2  1  2                      11210.19280   11210.19375   -0.00095    0.00200   0.00000
    6:   3  4  2  3                      16814.86390   16814.86355    0.00035    0.00200   0.00000
    7:   3  3  2  2                      16814.87800   16814.87426    0.00374    0.00200   0.00000
    8:   3  2  2  1                      16814.92070   16814.91924    0.00146    0.00200   0.00000
    9:   4  5  3  4                      22419.80460   22419.80407    0.00053    0.00200   0.00000
   10:   4  4  3  3                      22419.81240   22419.81089    0.00151    0.00200   0.00000
   11:   4  3  3  2                      22419.82620   22419.83017   -0.00397    0.00200   0.00000
   12:   5  6  4  5                      28024.72470   28024.72441    0.00029    0.00400   0.00000   28024.72652   -0.00182 0.5517
   13:   5  5  4  4                      28024.72470   28024.72912   -0.00442    0.00400   0.00000   28024.72652   -0.00182 0.4483
   14:   5  4  4  3                      28024.74200   28024.73983    0.00217    0.00400   0.00000
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.35234E-01    3   9.99350E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2802.482491(222)        -0.000000
   2           200         -D          -0.1916( 76)E-03       0.0000E-03
   3     110010000    1.5*eQq           1.3495( 47)          -0.0000
 MICROWAVE AVG =       -0.000056 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.002061 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        0.97283         0.97283
```

Table S11: $HCCN^{30}Si$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  3  1  2                      11050.54120   11050.54056    0.00064    0.00200   0.00132
    2:   2  2  1  1                      11050.55790   11050.55982   -0.00192    0.00200   0.00100
    3:   3  4  2  3                      16575.81750   16575.81767   -0.00017    0.00200   0.00101
    4:   3  3  2  2                      16575.82990   16575.82837    0.00153    0.00200   0.00087
    5:   3  2  2  1                      16575.87340   16575.87330    0.00010    0.00200   0.00191
    6:   4  5  3  4                      22101.07560   22101.07647   -0.00087    0.00200   0.00140
    7:   4  4  3  3                      22101.08370   22101.08328    0.00042    0.00200   0.00137
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.46126E-01    3   9.95995E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B       2762.64147( 35)         -0.00000
   2           200         -D          -0.1893(141)E-03       0.0000E-03
   3     110010000    1.5*eQq            1.348( 54)            0.000
 MICROWAVE AVG =       -0.000039 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001029 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.51464         0.51464
```

Table S12: $HCC^{15}NSi$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   1  0                             5689.36920    5689.36952   -0.00032    0.00200   0.00000
    2:   2  1                            11378.73400   11378.73413   -0.00013    0.00200   0.00000
    3:   3  2                            17068.08910   17068.08892    0.00018    0.00200   0.00000
    4:   4  3                            22757.42910   22757.42898    0.00012    0.00200   0.00000
    5:   5  4                            28446.74970   28446.74941    0.00029    0.00200   0.00000
    6:   6  5                            34136.04470   34136.04528   -0.00058    0.00200   0.00000
    7:   7  6                            39825.31260   39825.31170    0.00090    0.00400   0.00000
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.13510E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2844.685169(238)        -0.000000
   2           200         -D          -0.2046( 39)E-03       0.0000E-03
 MICROWAVE AVG =        0.000066 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000448 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        0.16823         0.16823
```

Table S13: $H^{13}CCNSi$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  3  1  2                    11016.08320   11016.08335   -0.00015    0.00200   0.00000
    2:   2  2  1  1                    11016.10570   11016.10254    0.00316    0.00200   0.00000
    3:   2  1  1  0                    11016.32770   11016.32637    0.00133    0.00200   0.00000
    4:   2  2  1  2                    11016.36990   11016.37113   -0.00123    0.00200   0.00000
    5:   3  4  2  3                    16524.13080   16524.13159   -0.00079    0.00200   0.00000
    6:   3  3  2  2                    16524.14400   16524.14225    0.00175    0.00200   0.00000
    7:   3  2  2  1                    16524.18780   16524.18701    0.00079    0.00200   0.00000
    8:   4  5  3  4                    22032.16030   22032.16131   -0.00101    0.00200   0.00000
    9:   4  4  3  3                    22032.16880   22032.16810    0.00070    0.00200   0.00000
   10:   4  3  3  2                    22032.18460   22032.18728   -0.00268    0.00200   0.00000
   11:   5  6  4  5                    27540.17030   27540.17076   -0.00046    0.00200   0.00000   27540.17286   -0.00256 0.5518
   12:   5  5  4  4                    27540.17030   27540.17545   -0.00515    0.00200   0.00000   27540.17286   -0.00256 0.4482
   13:   5  4  4  3                    27540.18710   27540.18611    0.00099    0.00200   0.00000
   14:   6  7  5  6                    33048.15720   33048.15625    0.00095    0.00200   0.00000   33048.15783   -0.00063 0.5425
   15:   6  6  5  5                    33048.15720   33048.15969   -0.00249    0.00200   0.00000   33048.15783   -0.00063 0.4575
   16:   6  5  5  4                    33048.16830   33048.16648    0.00182    0.00200   0.00000
   17:   7  8  6  7                    38556.11670   38556.11357    0.00313    0.00200   0.00000   38556.11654    0.00016 0.3830
   18:   7  7  6  6                    38556.11670   38556.11620    0.00050    0.00200   0.00000   38556.11654    0.00016 0.3311
   19:   7  6  6  5                    38556.11670   38556.12090   -0.00420    0.00200   0.00000   38556.11654    0.00016 0.2860
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.29199E-01    3   9.78911E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                             NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2754.027175(147)        -0.000000
   2           200         -D         -0.19260(230)E-03      0.00000E-03
   3     110010000    1.5*eQq          1.3430( 82)          -0.0000
 MICROWAVE AVG =        0.000111 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001583 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        0.79169         0.79169
```

Table S14: $HC^{13}CNSi$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  1  1  1                    11285.40220   11285.40344   -0.00124    0.00200   0.00168
    2:   2  3  1  2                    11285.83390   11285.83346    0.00044    0.00200   0.00055
    3:   2  2  1  1                    11285.85420   11285.85272    0.00148    0.00200   0.00055
    4:   2  1  1  0                    11286.07640   11286.07736   -0.00096    0.00200   0.00094
    5:   2  2  1  2                    11286.12120   11286.12229   -0.00109    0.00200   0.00107
    6:   3  4  2  3                    16928.75620   16928.75627   -0.00007    0.00200   0.00065
    7:   3  3  2  2                    16928.76860   16928.76696    0.00164    0.00200   0.00065
    8:   3  2  2  1                    16928.81180   16928.81189   -0.00009    0.00200   0.00066
    9:   4  5  3  4                    22571.65980   22571.65987   -0.00007    0.00200   0.00064
   10:   4  4  3  3                    22571.66880   22571.66668    0.00212    0.00200   0.00064
   11:   4  3  3  2                    22571.68190   22571.68593   -0.00403    0.00200   0.00064
   12:   5  6  4  5                    28214.54330   28214.54230    0.00100    0.00200   0.00082   28214.54441   -0.00111 0.5518
   13:   5  5  4  4                    28214.54330   28214.54701   -0.00371    0.00200   0.00082   28214.54441   -0.00111 0.4482
   14:   5  4  4  3                    28214.56110   28214.55771    0.00339    0.00200   0.00082
   15:   6  7  5  6                    33857.40280   33857.39967    0.00313    0.00200   0.00163   33857.40367   -0.00087 0.3919
   16:   6  6  5  5                    33857.40280   33857.40313   -0.00033    0.00200   0.00163   33857.40367   -0.00087 0.3301
   17:   6  5  5  4                    33857.40280   33857.40994   -0.00714    0.00200   0.00163   33857.40367   -0.00087 0.2780
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.59913E-01    3   9.99484E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                             NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2821.464794(162)        -0.000000
   2           200         -D         -0.2018( 36)E-03       0.0000E-03
   3     110010000    1.5*eQq          1.3478( 47)          -0.0000
 MICROWAVE AVG =       -0.000032 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001752 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.87604         0.87604
```

Table S15: DCCNSi

							EXP.FREQ.	- CALC.FREQ. -	DIFF.	- EXP.ERR.-	EST.ERR.-AVG.	CALC.FREQ. -	DIFF. -	WT.
1:	2	1	2	1	1	2	10656.15110	10656.14950	0.00160	0.00200	0.00094			
2:	2	1	2	1	1	1	10656.17030	10656.17228	-0.00198	0.00200	0.00091			
3:	2	1	1	1	1	2	10656.17810	10656.17979	-0.00169	0.00200	0.00095			
4:	2	1	1	1	1	1	10656.20230	10656.20258	-0.00028	0.00200	0.00100			
5:	2	2	1	1	1	0	10656.52710	10656.53842	-0.01132	0.01000	0.00106			
6:	2	3	4	1	2	3	10656.59380	10656.59316	0.00064	0.00200	0.00041			
7:	2	2	3	1	1	2	10656.60370	10656.60219	0.00151	0.00200	0.00041	10656.60289	0.00081	0.5597
8:	2	3	2	1	2	1	10656.60370	10656.60377	-0.00007	0.00200	0.00041	10656.60289	0.00081	0.4403
9:	2	3	3	1	2	2	10656.61170	10656.60829	0.00341	0.00200	0.00047			
10:	2	2	2	1	1	1	10656.66420	10656.66432	-0.00012	0.00200	0.00074			
11:	2	1	2	1	0	1	10656.84270	10656.84161	0.00109	0.00200	0.00065			
12:	2	1	1	1	0	1	10656.87070	10656.87190	-0.00120	0.00200	0.00078			
13:	2	2	3	1	2	3	10656.89160	10656.89312	-0.00152	0.00200	0.00073			
14:	2	2	1	1	2	1	10656.91110	10656.91278	-0.00168	0.00200	0.00087			
15:	3	4	3	2	3	3	15984.82070	15984.81998	0.00072	0.00200	0.00121			
16:	3	3	2	2	2	2	15984.85060	15984.85118	-0.00058	0.00200	0.00098			
17:	3	2	1	2	1	1	15984.89180	15984.89299	-0.00119	0.00200	0.00095			
18:	3	4	5	2	3	4	15984.90370	15984.90209	0.00161	0.00200	0.00050			
19:	3	3	2	2	2	1	15984.91100	15984.90696	0.00404	0.00200	0.00051	15984.90833	0.00267	0.1447
20:	3	4	3	2	3	2	15984.91100	15984.90793	0.00307	0.00200	0.00051	15984.90833	0.00267	0.2380
21:	3	3	4	2	2	3	15984.91100	15984.90864	0.00236	0.00200	0.00051	15984.90833	0.00267	0.2960
22:	3	4	4	2	3	3	15984.91100	15984.90896	0.00204	0.00200	0.00051	15984.90833	0.00267	0.3212
23:	3	3	3	2	2	2	15984.93230	15984.92719	0.00511	0.00400	0.00055			
24:	3	2	3	2	1	2	15984.95430	15984.95437	-0.00007	0.00200	0.00052			
25:	3	2	2	2	1	1	15984.98130	15984.98045	0.00085	0.00200	0.00066			
26:	4	5	6	3	4	5	21313.19990	21313.19261	0.00729	0.00200	0.00059	21313.20324	-0.00334	0.1752
27:	4	5	4	3	4	3	21313.19990	21313.19628	0.00362	0.00200	0.00059	21313.20324	-0.00334	0.1146
28:	4	5	5	3	4	4	21313.19990	21313.19640	0.00350	0.00200	0.00059	21313.20324	-0.00334	0.1431
29:	4	4	5	3	3	4	21313.19990	21313.19735	0.00255	0.00200	0.00059	21313.20324	-0.00334	0.1381
30:	4	4	3	3	3	2	21313.19990	21313.19945	0.00045	0.00200	0.00059	21313.20324	-0.00334	0.0821
31:	4	4	4	3	3	3	21313.19990	21313.20576	-0.00586	0.00200	0.00059	21313.20324	-0.00334	0.1069
32:	4	3	4	3	2	3	21313.19990	21313.21702	-0.01712	0.00200	0.00059	21313.20324	-0.00334	0.1120
33:	4	3	2	3	2	1	21313.19990	21313.22531	-0.02541	0.00200	0.00059	21313.20324	-0.00334	0.0520
34:	4	3	3	3	2	2	21313.19990	21313.22701	-0.02711	0.00200	0.00059	21313.20324	-0.00334	0.0759
35:	5	6	7	4	5	6	26641.46980	26641.46413	0.00567	0.00200	0.00094	26641.47114	-0.00134	0.1601
36:	5	6	6	4	5	5	26641.46980	26641.46649	0.00331	0.00200	0.00094	26641.47114	-0.00134	0.1354
37:	5	6	5	4	5	4	26641.46980	26641.46665	0.00315	0.00200	0.00094	26641.47114	-0.00134	0.1132
38:	5	5	6	4	4	5	26641.46980	26641.46767	0.00213	0.00200	0.00094	26641.47114	-0.00134	0.1326
39:	5	5	4	4	4	3	26641.46980	26641.46980	-0.00000	0.00200	0.00094	26641.47114	-0.00134	0.0882
40:	5	5	5	4	4	4	26641.46980	26641.47233	-0.00253	0.00200	0.00094	26641.47114	-0.00134	0.1083
41:	5	4	5	4	3	4	26641.46980	26641.47865	-0.00885	0.00200	0.00094	26641.47114	-0.00134	0.1120
42:	5	4	3	4	3	2	26641.46980	26641.48346	-0.01366	0.00200	0.00094	26641.47114	-0.00134	0.0652
43:	5	4	4	4	3	3	26641.46980	26641.48370	-0.01390	0.00200	0.00094	26641.47114	-0.00134	0.0850
44:	6	7	8	5	6	7	31969.71980	31969.71366	0.00614	0.00200	0.00174	31969.71864	0.00116	0.1509
45:	6	7	7	5	6	6	31969.71980	31969.71527	0.00453	0.00200	0.00174	31969.71864	0.00116	0.1307
46:	6	7	6	5	6	5	31969.71980	31969.71550	0.00430	0.00200	0.00174	31969.71864	0.00116	0.1125
47:	6	6	7	5	5	6	31969.71980	31969.71640	0.00340	0.00200	0.00174	31969.71864	0.00116	0.1291
48:	6	6	5	5	5	4	31969.71980	31969.71816	0.00164	0.00200	0.00174	31969.71864	0.00116	0.0921
49:	6	6	6	5	5	5	31969.71980	31969.71930	0.00050	0.00200	0.00174	31969.71864	0.00116	0.1091
50:	6	5	6	5	4	5	31969.71980	31969.72340	-0.00360	0.00200	0.00174	31969.71864	0.00116	0.1118
51:	6	5	5	5	4	4	31969.71980	31969.72638	-0.00658	0.00200	0.00174	31969.71864	0.00116	0.0903
52:	6	5	4	5	4	3	31969.71980	31969.72654	-0.00674	0.00200	0.00174	31969.71864	0.00116	0.0734

NORMALIZED DIAGONAL:
1 1.00000E+00 2 6.01010E-01 3 9.95336E-01 4 9.68365E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00

			NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
1	100	B	2664.155725(122) 0.000000
2	200	-D	-0.17443(309)E-03 -0.00000E-03
3	110010000	1.5*eQqN	1.35168(276) -0.00000
4	220010000	1.5*eQqD	0.3397(49) 0.0000

MICROWAVE AVG = -0.000276 MHz, IR AVG = 0.00000
MICROWAVE RMS = 0.002966 MHz, IR RMS = 0.00000
END OF ITERATION 2 OLD, NEW RMS ERROR= 0.84522 0.84522

NCNSi

The five lowest rotational transitions of NCNSi fall between 5 and 30 GHz, and each was measured at high spectral resolution. Although each line has complicated, slowly-spaced hyperfine structure owing to the two nitrogen nuclei, the spectral analysis was straightforward because the experimental quadrupole coupling constants are close to those predicted: $eQq(N_{\mathrm{outer}}) = -3.2$ MHz and $eQq(N_{\mathrm{inner}}) = +1.3$ MHz. Like for HCCNSi, six additional isotopologs of NCCNSi were detected using SiH_4 along with isotopically-enriched samples of CH_3CN alone or in combination with $^{15}N_2$. The experimental data are given in Tables S16 to S22, and the best-fit constants in Table S4.

NCNSi - truncated fit files from SPFIT (in MHz)

Table S16: NCNSi parent species

							EXP.FREQ.	- CALC.FREQ.	- DIFF.	- EXP.ERR.	- EST.ERR.	-AVG. CALC.FREQ.	- DIFF.	- WT.
1:	1	1	1	0	1	0	5817.70730	5817.70814	-0.00084	0.00200	0.00000	5817.70821	-0.00091	0.0687
2:	1	1	1	0	1	2	5817.70730	5817.70819	-0.00089	0.00200	0.00000	5817.70821	-0.00091	0.4756
3:	1	1	1	0	1	1	5817.70730	5817.70823	-0.00093	0.00200	0.00000	5817.70821	-0.00091	0.4556
4:	1	1	2	0	1	1	5818.03150	5818.03023	0.00127	0.00200	0.00000	5818.03021	0.00129	0.3837
5:	1	1	2	0	1	2	5818.03150	5818.03019	0.00131	0.00200	0.00000	5818.03021	0.00129	0.6163
6:	1	1	0	0	1	1	5818.35610	5818.35635	-0.00025	0.00200	0.00000			
7:	1	2	1	0	1	0	5818.86900	5818.86893	0.00007	0.00200	0.00000	5818.86894	0.00006	0.9000
8:	1	2	1	0	1	1	5818.86900	5818.86902	-0.00002	0.00200	0.00000	5818.86894	0.00006	0.1000
9:	1	2	3	0	1	2	5818.94330	5818.94250	0.00080	0.00200	0.00000			
10:	1	2	2	0	1	1	5819.26830	5819.26866	-0.00036	0.00200	0.00000	5819.26864	-0.00034	0.6172
11:	1	2	2	0	1	2	5819.26830	5819.26862	-0.00032	0.00200	0.00000	5819.26864	-0.00034	0.3828
12:	1	0	1	0	1	0	5820.54260	5820.54352	-0.00092	0.00200	0.00000	5820.54359	-0.00099	0.0338
13:	1	0	1	0	1	2	5820.54260	5820.54358	-0.00098	0.00200	0.00000	5820.54359	-0.00099	0.5190
14:	1	0	1	0	1	1	5820.54260	5820.54362	-0.00102	0.00200	0.00000	5820.54359	-0.00099	0.4472
15:	2	2	1	1	2	2	11636.22620	11636.22825	-0.00205	0.00200	0.00000			
16:	2	1	0	1	0	1	11636.47510	11636.47390	0.00120	0.00200	0.00000			
17:	2	2	2	1	2	2	11636.52780	11636.52806	-0.00026	0.00200	0.00000			
18:	2	2	3	1	2	3	11636.70170	11636.70239	-0.00069	0.00200	0.00000			
19:	2	1	2	1	0	1	11636.80170	11636.80147	0.00023	0.00200	0.00000			
20:	2	1	1	1	0	1	11637.01670	11637.01750	-0.00080	0.00200	0.00000			
21:	2	2	1	1	1	0	11637.14100	11637.14056	0.00044	0.00200	0.00000			
22:	2	3	2	1	2	2	11637.31710	11637.31602	0.00108	0.00200	0.00000			
23:	2	2	3	1	1	2	11637.61580	11637.61470	0.00110	0.00200	0.00000			
24:	2	3	2	1	2	1	11637.71360	11637.71566	-0.00206	0.00200	0.00000			
25:	2	3	4	1	2	3	11637.72700	11637.72595	0.00105	0.00200	0.00000			
26:	2	3	3	1	2	2	11637.79720	11637.79531	0.00189	0.00200	0.00000			
27:	2	2	2	1	1	1	11638.08910	11638.08849	0.00061	0.00200	0.00000			
28:	2	3	3	1	2	3	11638.12110	11638.12143	-0.00033	0.00200	0.00000			
29:	2	1	1	1	1	0	11639.20500	11639.20476	0.00024	0.00200	0.00000			
30:	2	1	2	1	1	2	11639.31500	11639.31486	0.00014	0.00200	0.00000			
31:	2	1	1	1	1	2	11639.53030	11639.53089	-0.00059	0.00200	0.00000			
32:	2	1	2	1	1	1	11639.63740	11639.63685	0.00055	0.00200	0.00000			
33:	3	3	3	2	3	3	17455.35770	17455.35918	-0.00148	0.00200	0.00000			
34:	3	3	2	2	3	2	17455.41270	17455.41447	-0.00177	0.00200	0.00000			
35:	3	3	4	2	3	4	17455.45890	17455.45819	0.00071	0.00200	0.00000			
36:	3	3	3	2	3	2	17455.83960	17455.83847	0.00113	0.00200	0.00000			
37:	3	2	1	2	1	1	17455.87100	17455.87111	-0.00011	0.00200	0.00000			
38:	3	4	3	2	3	3	17456.06330	17456.06126	0.00204	0.00200	0.00000			
39:	3	3	2	2	2	2	17456.20060	17456.20244	-0.00184	0.00200	0.00000			
40:	3	2	3	2	1	2	17456.29740	17456.29574	0.00166	0.00200	0.00000			
41:	3	2	1	2	1	0	17456.41030	17456.41471	-0.00441	0.00200	0.00000			
42:	3	2	2	2	1	1	17456.42260	17456.42479	-0.00219	0.00200	0.00000			
43:	3	3	4	2	2	3	17456.48280	17456.48175	0.00105	0.00200	0.00000			
44:	3	3	2	2	2	1	17456.50460	17456.50224	0.00236	0.00200	0.00000			
45:	3	4	5	2	3	4	17456.53800	17456.53567	0.00233	0.00200	0.00000			
46:	3	4	3	2	3	2	17456.54310	17456.54056	0.00254	0.00200	0.00000			
47:	3	4	4	2	3	3	17456.56680	17456.56632	0.00048	0.00200	0.00000			
48:	3	3	3	2	2	2	17456.62640	17456.62643	-0.00003	0.00200	0.00000			
49:	3	2	1	2	2	1	17457.93320	17457.93532	-0.00212	0.00200	0.00000			
50:	3	2	3	2	2	3	17457.99580	17457.99589	-0.00009	0.00200	0.00000			
51:	3	2	2	2	2	2	17458.18890	17458.18918	-0.00028	0.00200	0.00000			
52:	4	4	4	3	4	4	23274.16450	23274.16661	-0.00211	0.00200	0.00000			
53:	4	4	5	3	4	5	23274.22800	23274.22967	-0.00167	0.00200	0.00000			
54:	4	3	2	3	2	2	23274.72860	23274.72874	-0.00014	0.00200	0.00000			
55:	4	4	3	3	3	3	23274.90560	23274.90609	-0.00049	0.00200	0.00000			
56:	4	3	4	3	2	3	23275.22740	23275.22526	0.00214	0.00200	0.00000			
57:	4	3	3	3	2	2	23275.27680	23275.27662	0.00018	0.00200	0.00000			
58:	4	3	2	3	2	1	23275.28400	23275.28241	0.00159	0.00200	0.00000			
59:	4	4	5	3	3	4	23275.31010	23275.30716	0.00294	0.00200	0.00000			
60:	4	4	3	3	3	2	23275.32480	23275.33008	-0.00528	0.00200	0.00000			
61:	4	5	6	3	4	5	23275.33960	23275.33911	0.00049	0.00200	0.00000			
62:	4	5	4	3	4	3	23275.34880	23275.34681	0.00199	0.00200	0.00000			
63:	4	5	5	3	4	4	23275.35980	23275.35625	0.00355	0.00200	0.00000			
64:	4	4	4	3	3	3	23275.37160	23275.37375	-0.00215	0.00200	0.00000			
65:	4	3	2	3	3	2	23276.71310	23276.71549	-0.00239	0.00200	0.00000			
66:	4	3	4	3	3	4	23276.73900	23276.73941	-0.00041	0.00200	0.00000			
67:	5	4	5	4	3	4	29094.06090	29094.05779	0.00311	0.00200	0.00000			
68:	5	4	4	4	3	3	29094.08720	29094.08492	0.00228	0.00200	0.00000			
69:	5	4	3	4	3	2	29094.09380	29094.09102	0.00278	0.00200	0.00000			
70:	5	5	6	4	4	5	29094.09790	29094.10339	-0.00549	0.00200	0.00000			
71:	5	5	4	4	4	3	29094.11810	29094.12039	-0.00229	0.00200	0.00000			
72:	5	6	7	4	5	6	29094.12510	29094.12454	0.00056	0.00200	0.00000			
73:	5	6	5	4	5	4	29094.13360	29094.13193	0.00167	0.00200	0.00000	29094.13383	-0.00023	0.4604
74:	5	6	6	4	5	5	29094.13360	29094.13545	-0.00185	0.00200	0.00000	29094.13383	-0.00023	0.5396
75:	5	5	5	4	4	4	29094.14020	29094.14013	0.00007	0.00200	0.00000			

NORMALIZED DIAGONAL:
1 1.00000E+00 2 4.22434E-01 3 9.99827E-01 4 9.48642E-01

MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00

			NEW PARAMETER (EST. ERROR)	-- CHANGE THIS ITERATION
1	100	B	2909.422841(91)	0.000000
2	200	-D	-0.22825(264)E-03	-0.00000E-03
3	110010000	1.5*eQq	-4.93921(174)	0.00000
4	220010000	1.5*eQq	2.00798(235)	0.00000

MICROWAVE AVG = 0.000006 MHz, IR AVG = 0.00000
MICROWAVE RMS = 0.001836 MHz, IR RMS = 0.00000
END OF ITERATION 1 OLD, NEW RMS ERROR= 0.91779 0.91779

Table S17: $N^{13}CNSi$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
   1:   1  2  3  0  1  2                5771.00630    5771.00466    0.00164    0.00200   0.00000
   2:   2  1  2  1  0  1               11540.92660   11540.92651    0.00009    0.00100   0.00000
   3:   2  1  1  1  0  1               11541.14070   11541.14215   -0.00145    0.00100   0.00000
   4:   2  2  1  1  1  0               11541.26490   11541.26604   -0.00114    0.00100   0.00000
   5:   2  2  3  1  1  2               11541.74000   11541.73930    0.00070    0.00100   0.00000
   6:   2  3  2  1  2  1               11541.83850   11541.84020   -0.00170    0.00200   0.00000
   7:   2  3  4  1  2  3               11541.85320   11541.85045    0.00275    0.00100   0.00000
   8:   2  3  3  1  2  2               11541.91940   11541.91970   -0.00030    0.00100   0.00000
   9:   2  2  2  1  1  1               11542.21300   11542.21222    0.00078    0.00100   0.00000
  10:   2  3  3  1  2  3               11542.24460   11542.24522   -0.00062    0.00100   0.00000
  11:   2  1  1  1  1  0               11543.32840   11543.32857   -0.00017    0.00100   0.00000
  12:   2  1  2  1  1  2               11543.43960   11543.43845    0.00115    0.00100   0.00000
  13:   2  1  1  1  1  2               11543.65240   11543.65410   -0.00170    0.00100   0.00000
  14:   3  3  4  2  2  3               17312.67020   17312.66911    0.00109    0.00100   0.00000
  15:   3  4  5  2  3  4               17312.72530   17312.72299    0.00231    0.00200   0.00000   17312.72484    0.00046 0.6231
  16:   3  4  3  2  3  2               17312.72530   17312.72789   -0.00259    0.00200   0.00000   17312.72484    0.00046 0.3769
  17:   3  4  4  2  3  3               17312.74910   17312.75359   -0.00449    0.00200   0.00000
NORMALIZED DIAGONAL:
   1   1.00000E+00    2   3.75011E-01    3   9.52125E-01    4   9.93725E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      2885.453884(178)        -0.000000
   2          200         -D          -0.2185(157)E-03       0.0000E-03
   3    110010000    1.5*eQq         -4.93664(175)          0.00000
   4    220010000    1.5*eQq          2.00443(231)          0.00000
 MICROWAVE AVG =       -0.000182 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001658 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        1.23726         1.23726
```

Table S18: $N^{13}C^{15}NSi$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
   1:   2  2  1  1                     11540.67320   11540.67585   -0.00265    0.00200   0.00069
   2:   2  3  1  2                     11540.74740   11540.74531    0.00209    0.00200   0.00116
   3:   3  2  2  1                     17310.83880   17310.83799    0.00081    0.00200   0.00191
   4:   3  3  2  2                     17311.00000   17311.00007   -0.00007    0.00200   0.00104
   5:   3  4  2  3                     17311.03830   17311.03867   -0.00037    0.00200   0.00121
NORMALIZED DIAGONAL:
   1   1.00000E+00    2   1.00000E+00    3   9.76216E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      2885.170787(173)        -0.000000
   2          200         -D     -0.228246531(  0)E-03  0.000000000E-03
   3    110010000    1.5*eQq          -4.862( 55)            0.000
 MICROWAVE AVG =       -0.000037 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.001559 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.77959         0.77959
```

Table S19: $^{15}N^{13}CNSi$

```
                                    EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
   1:   2  3  1  2                     11192.94660   11192.94271    0.00389    0.00200   0.00000
   2:   2  2  1  1                     11192.97280   11192.97139    0.00141    0.00200   0.00000
   3:   3  4  2  3                     16789.42730   16789.42746   -0.00016    0.00300   0.00000
   4:   3  3  2  2                     16789.43560   16789.44339   -0.00779    0.00300   0.00000
NORMALIZED DIAGONAL:
   1   1.00000E+00    2   1.00000E+00    3   1.00000E+00
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                           NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1          100          B      2798.244674(250)        -0.000000
   2          200         -D     -0.228240000(  0)E-03 -0.000000000E-03
   3    110010000    1.5*eQq      2.008050000(  0)      -0.000000000
 MICROWAVE AVG =       -0.000663 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.004413 MHz, IR RMS =        0.00000
 END OF ITERATION  1 OLD, NEW RMS ERROR=        1.66090         1.66090
```

Table S20: $^{15}NC^{15}NSi$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   1  0                           5638.35010    5638.35000    0.00010    0.00050   0.00022
    2:   2  1                          11276.69490   11276.69491   -0.00001    0.00050   0.00034
    3:   3  2                          16915.02960   16915.02966   -0.00006    0.00050   0.00032
    4:   4  3                          22553.34920   22553.34917    0.00003    0.00050   0.00048
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   3.81794E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2819.175421(120)         0.000000
   2           200         -D          -0.2117( 47)E-03      -0.0000E-03
 MICROWAVE AVG =        0.000014 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000063 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.12533         0.12533
```

Table S21: $^{15}NC^{15}N^{29}Si$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  1                          11102.04170   11102.04109    0.00061    0.00050   0.00040
    2:   3  2                          16653.04920   16653.04990   -0.00070    0.00050   0.00037
    3:   4  3                          22204.04550   22204.04463    0.00087    0.00100   0.00090
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.01041E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2775.511837(151)         0.000000
   2           200         -D          -0.1956( 73)E-03      -0.0000E-03
 MICROWAVE AVG =        0.000262 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000736 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        1.18445         1.18445
```

Table S22: $^{15}NC^{15}N^{30}Si$

```
                                  EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:   2  1                          10937.71590   10937.71589    0.00001    0.00050   0.00040
    2:   3  2                          16406.56240   16406.56241   -0.00001    0.00050   0.00037
    3:   4  3                          21875.39520   21875.39519    0.00001    0.00100   0.00090
NORMALIZED DIAGONAL:
    1   1.00000E+00    2   4.01041E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                              NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1           100          B      2734.430499(151)        -0.000000
   2           200         -D          -0.1906( 73)E-03       0.0000E-03
 MICROWAVE AVG =        0.000002 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.000006 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.00983         0.00983
```

HC_4NSi

Six harmonically-related lines of HC_4NSi have been detected between 7 and 17 GHz. Table S23 lists the measured lines; predicted and best-fit constants are provided in Table S5. Owing to relative low signal-to-noise ratio of its lines, and that CH_3CN was apparently not a good precursor for this molecule, no additional isotopic spectroscopy was attempted.

Table S23: HC_4NSi - parent species

					EXP.FREQ.	- CALC.FREQ.	- DIFF.	- EXP.ERR.	- EST.ERR.	-AVG. CALC.FREQ.	- DIFF.	- WT.
1:	4	5	3	4	7384.82020	7384.82033	-0.00013	0.00200	0.00107			
2:	4	4	3	3	7384.82840	7384.82688	0.00152	0.00200	0.00074			
3:	4	3	3	2	7384.84470	7384.84540	-0.00070	0.00200	0.00179			
4:	5	6	4	5	9231.02550	9231.02660	-0.00110	0.00200	0.00096			
5:	5	5	4	4	9231.03250	9231.03114	0.00136	0.00200	0.00077			
6:	6	7	5	6	11077.23020	11077.23044	-0.00024	0.00200	0.00078	11077.23196	-0.00176	0.5427
7:	6	6	5	5	11077.23020	11077.23376	-0.00356	0.00200	0.00078	11077.23196	-0.00176	0.4573
8:	6	5	5	4	11077.24090	11077.24031	0.00059	0.00200	0.00087			
9:	7	8	6	7	12923.43550	12923.43187	0.00363	0.00200	0.00074	12923.43474	0.00076	0.3830
10:	7	7	6	6	12923.43550	12923.43442	0.00108	0.00200	0.00074	12923.43474	0.00076	0.3311
11:	7	6	6	5	12923.43550	12923.43895	-0.00345	0.00200	0.00074	12923.43474	0.00076	0.2860
12:	8	9	7	8	14769.63220	14769.63077	0.00143	0.00200	0.00101	14769.63299	-0.00079	0.3766
13:	8	8	7	7	14769.63220	14769.63278	-0.00058	0.00200	0.00101	14769.63299	-0.00079	0.3315
14:	8	7	7	6	14769.63220	14769.63610	-0.00390	0.00200	0.00101	14769.63299	-0.00079	0.2919
15:	9	10	8	9	16615.82910	16615.82689	0.00221	0.00200	0.00164	16615.82866	0.00044	0.3715
16:	9	9	8	8	16615.82910	16615.82851	0.00059	0.00200	0.00164	16615.82866	0.00044	0.3320
17:	9	8	8	7	16615.82910	16615.83106	-0.00196	0.00200	0.00164	16615.82866	0.00044	0.2965

NORMALIZED DIAGONAL:
1 1.00000E+00 2 4.21984E-01 3 9.89376E-01
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00

			NEW PARAMETER (EST. ERROR)	-- CHANGE THIS ITERATION
1	100	B	923.103797(125)	0.000000
2	200	-D	-0.01366(116)E-03	-0.00000E-03
3	110010000	1.5*eQq	1.297(124)	0.000

MICROWAVE AVG = 0.000019 MHz, IR AVG = 0.00000
MICROWAVE RMS = 0.001036 MHz, IR RMS = 0.00000
END OF ITERATION 2 OLD, NEW RMS ERROR= 0.51789 0.51789

References

(1) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A 5th-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

(2) CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

(3) Harding, M. E.; Metzroth, T.; Gauss, J.; Auer, A. A. Parallel Calculation of CCSD and CCSD(T) Analytic First and Second Derivatives. *J. Chem. Theory Comput.* **2008**, *4*, 64–74.

(4) Dunning, T. H.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys.* **2001**, *114*, 9244–9253.

(5) Peterson, K. A.; Dunning, T. H. Accurate correlation consistent basis sets for molecular core-valence correlation effects: The second row atoms Al-Ar and the first row atoms B-Ne revisited. *J. Chem. Phys.* **2002**, *117*, 10548–10560.

(6) Puzzarini, C.; Stanton, J. F.; Gauss, J. Quantum-chemical calculation of spectroscopic parameters for rotational spectroscopy. *Int. Rev. Phys. Chem.* **2010**, *29*, 273–367.

(7) Coriani, S.; Marcheson, D.; Gauss, J.; Hättig, C.; Helgaker, T.; Jørgensen, P. The accuracy of ab initio molecular geometries for systems containing second-row atoms. *J. Chem. Phys.* **2005**, *123*, 184107–1–184107–12.

(8) Thorwirth, S.; Harding, M. E. Coupled-cluster calculations of C_2H_2Si and CNHSi structural isomers. *J. Chem. Phys.* **2009**, *130*, 214303.

(9) Lattanzi, V.; Thaddeus, P.; McCarthy, M. C.; Thorwirth, S. Laboratory detection of protonated SO_2 in two isomeric forms. *J. Chem. Phys.* **2010**, *133*, 194305.

(10) Halfen, D. T.; Clouthier, D. J.; Ziurys, L. M.; Lattanzi, V.; McCarthy, M. C.; Thaddeus, P.; Thorwirth, S. The Pure Rotational Spectrum of HPS (X^1A'): Chemical Bonding in Second-Row Elements. *J. Chem. Phys.* **2011**, *134*, 134302.

(11) Crabtree, K. N.; Martinez Jr., O.; Barreau, L.; Thorwirth, S.; McCarthy, M. C. Microwave Detection of Sulfoxylic Acid (HOSOH). *J. Phys. Chem. A* **2013**, *117*, 3608–3613.

(12) Gauss, J.; Stanton, J. F. Analytic CCSD(T) second derivatives. *Chem. Phys. Lett.* **1997**, *276*, 70–77.

(13) Stanton, J. F.; Gauss, J. Analytic second derivatives in high-order many-body perturbation and coupled-cluster theories: computational considerations and applications. *Int. Rev. Phys. Chem.* **2000**, *19*, 61–95.

(14) Stanton, J. F.; Lopreore, C. L.; Gauss, J. The equilibrium structure and fundamental vibrational frequencies of dioxirane. *J. Chem. Phys.* **1998**, *108*, 7190–7196.

(15) Parker, D. S. N.; Wilson, A. V.; Kaiser, R. I.; Labrador, T.; Mebel, A. M. Synthesis of the Silaisocyanoacetylene Molecule. *J. Am. Chem. Soc.* **2012**, *134*, 13896–13901.

(16) Yang, L.-M.; Ding, Y.-H.; Wang, Q.; Sun, C.-C. Monosilicon-substituted cyanoacetylene: A computational study. *J. Comput. Chem.* **2006**, *27*, 578–595.

(17) Ignatyev, I. S.; Schaefer, H. F. Silacyanogen. *J. Chem. Phys.* **1997**, *107*, 5776.

(18) Ding, Y.-H.; Li, Z.-S.; Huang, X.-R.; Sun, C.-C. SiCNN—A New Stable Isomer with Si≡C Triple Bonding. *Chem. Eur. J.* **2001**, *7*, 1539–1545.

(19) McCarthy, M. C.; Travers, M. J.; Kovacs, A.; Gottlieb, C. A.; Thaddeus, P. Eight New Carbon Chain Molecules. *Astrophys. J. Suppl. Ser.* **1997**, *113*, 105–120.

(20) McCarthy, M. C.; Chen, W.; Travers, M. J.; Thaddeus, P. Microwave Spectra of 11 Polyyne Carbon Chains. *Astrophys. J. Suppl. Ser.* **2000**, *129*, 611–623.

(21) Pickett, H. M. The fitting and prediction of vibration-rotation spectra with spin interactions. *J. Mol. Spectrosc.* **1991**, *148*, 371–377.

(22) Kisiel, Z. Least-Squares Mass-Dependence Molecular Structures for Selected Weakly Bound Intermolecular Clusters. *J. Mol. Spectrosc.* **2003**, *218*, 58–67.