Supporting information to accompany:

A highly flexible molecule: The peculiar case of ethynyl isothiocyanate HCCNCS

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Table S1. Assigned transitions for HCCNCS-parent

J'-J''	*F'-F''*	υ_{obs}/MHz	o-c (kHz)
2-1	1-1	6085.9132	0.0
	3-2	6087.0431	0.4
	2-1	6087.0936	0.4
	1-0	6087.6833	0.0
	2-2	6087.8010	-0.2
3-2	2-2	9129.5720	0.0
	4-3	9130.6064	0.5
	3-2	9130.6343	0.3
	2-1	9130.7520	0.1
	3-3	9131.3924	-0.2
4-3	3-3	12173.1559	-0.5
	5-4	12174.1505	0.5
	4-3	12174.1676	-0.2
	3-2	12174.2185	0.1
	4-4	12174.9539	-0.6
5-4	4-4	15216.7091	0.0
	6-5	15217.6801	0.0
	5-4	15217.6938	1.3
	4-3	15217.7199	-0.6
	5-5	15218.4963	-0.7
6-5	5-5	18260.2384	-1.7
	7-6	18261.1955	-0.9
	6-5	18261.2060	0.4
	5-4	18261.2257	2.2
	6-6	18262.0214	-1.0
7-8	8-7	21304.6963	-1.5
	7-6	21304.7043	-0.4
	6-5	21304.7202	3.0
8-7	9-8	24348.1813	-1.0
	7-6	24348.1976	0.7

Table S2. Assigned transitions for HCCNC^{34}S

J'-J''	*F'-F''*	υ_{obs}/MHz	o-c (kHz)
3-2	4-3	8898.1278	0.8

	3-2	8898.1554	0.3
	2-1	8898.2726	-0.4
4-3	5-4	11864.1797	0.9
	4-3	11864.1951	-1.5
	3-2	11864.2466	-0.5
5-4	6-5	14830.2146	-2.6
	5-4	14830.2314	1.8
	4-3	14830.2564	-1.2
6-5	7-6	17796.2397	-2.9
	6-5	17796.2537	1.9
	5-4	17796.2720	2.4
7-6	8-7	20762.2547	0.6
	6-5	20762.2750	1.6
8-7	9-8	23728.2473	-2.4
	7-6	23728.2651	0.8

Table S3. Assigned transitions for $H^{13}CCNCS$

J'-J''	*F'-F''*	υ_{obs}/MHz	o-c (kHz)
4-3	5-4	11826.8148	0.7
	4-3	11826.8292	-2.8
6-5	7-6	17740.1919	-3.0
	6-5	17740.2058	1.7
	5-4	17740.2256	3.6
8-7	6-5	23653.5180	0.0
	9-8	23653.5317	-0.7

Table S4. Assigned transitions for $HC^{13}CNCS$

J'-J''	*F'-F''*	υ_{obs}/MHz	o-c (kHz)
4-3	5-4	12040.2099	1.5
	4-3	12040.2247	-1.5
6-5	7-6	18060.2835	-2.1
	6-5	18060.2942	-0.4
	5-4	18060.3151	2.5

Table S5. Assigned transitions for $HCCN^{13}CS$

J'-J''	*F'-F''*	υ_{obs}/MHz	o-c (kHz)
4-3	5-4	12163.5573	2.7
	4-3	12163.5716	-0.8
	3-2	12163.6202	-2.8
6-5	7-6	18245.3020	-1.9
	6-5	18245.3132	0.2
	5-4	18245.3337	2.8
8-7	6-5	24326.9923	-0.7
	9-8	24327.0081	0.4

Table S6. Assigned transitions for HCCNCS in vibrationally excited state

J'-J''	*F'-F''*	*e/f*	υ_{obs}/MHz	o-c (kHz)
4-3	5-4	(-1)-(1)	12181.0831	1.1
	3-2	(-1)-(1)	12181.1087	-3.6
	4-3	(-1)-(1)	12181.1766	1.5
	5-4	(1)-(-1)	12183.5974	0.8
	3-2	(1)-(-1)	12183.6255	-1.4
	4-3	(1)-(-1)	12183.6886	-1.0
5-4	6-5	(1)-(-1)	15226.3589	0.6
	4-3	(1)-(-1)	15226.3832	-0.8
	5-4	(1)-(-1)	15226.4093	0.1
	6-5	(-1)-(1)	15229.5022	0.1
	4-3	(-1)-(1)	15229.5284	0.4
	5-4	(-1)-(1)	15229.5526	-0.4
6-5	7-6	(-1)-(1)	18271.6181	0.0
	5-4	(-1)-(1)	18271.6358	-2.3
	6-5	(-1)-(1)	18271.6498	0.2
	7-6	(1)-(-1)	18275.3933	1.7
	5-4	(1)-(-1)	18275.4104	-1.1
	6-5	(1)-(-1)	18275.4251	2.0
7-6	8-7	(1)-(-1)	21316.8626	0.1
	7-6	(1)-(-1)	21316.8883	4.6
	8-7	(-1)-(1)	21321.2659	-0.1
	7-6	(-1)-(1)	21321.2858	-1.3
8-7	9-8	(-1)-(1)	24362.0888	-2.0
	8-7	(-1)-(1)	24362.1050	-0.8
	9-8	(1)-(-1)	24367.1249	0.0
	8-7	(1)-(-1)	24367.1403	0.3

Table S7: Input file (.par) and output file (.fit) for SPFIT program used for fitting the vibrationally excited state of HCCNCS.

```
hccncs                          Tue Fri SWed AuMon Mar 26 20:48:10 2018
  8  26   7   0    0.0000E+000    1.0000E+003    1.0000E+000 1.0000000000
 l  -3   1   1   1   0   1   1   1      0   -1
       100  1.522799301449558E+003 2.92471429E+023 / B
      -1000 -1.522799301449558E+003 1.00000000E-037 /correction
    110010000  3.510622799695828E+000 1.00000000E+023 /  (1 N-14)
       200 -8.579040358665501E-005 3.77299045E+023 /-DJ
      -1100  1.715808071817292E-004 1.00000000E-037 /correction
      -2000 -8.579040358665501E-005 1.00000000E-037 /correction
      40000  1.571074540143065E-001 1.00000000E+023 /qv/2
      40100  1.710332355715090E-006 1.00000000E+023 /qvJ/2
```

```
hccncs                          Tue Fri SWed AuMon Mar 26 20:48:10 2018
LINES REQUESTED=   26 NUMBER OF PARAMETERS=  8 NUMBER OF ITERATIONS=  7
 MARQUARDT PARAMETER =0.0000E+000 max (OBS-CALC)/ERROR =1.0000E+003
                    PARAMETERS - A.PRIORI ERROR
   1     1         100  1.5227992971617E+003   2.924714E+023  B
   2     1        -1000 -1.5227992971617E+003       -1.000000 correction
   3     2    110010000  3.5115927907113E+000   1.000000E+023   (1 N-14)
   4     3         200 -8.5718047358913E-005   3.772990E+023 -DJ
   5     3        -1100  1.7143609472624E-004       -2.000000 correction
   6     3        -2000 -8.5718047358913E-005        1.000000 correction
   7     4        40000  1.5711656277593E-001   1.000000E+023 qv/2
   8     5        40100  1.5580984866012E-006   1.000000E+023 qvJ/2
8 parameters read, 5 independent parameters
ENERGY SORT OF WANG SUB-BLOCKS
PROLATE ROTOR
SYMMETRIC TOP QUANTA
   V KMIN KMAX WTPL WTMN ESYMWT NSYM SPINS
   0    1    1    1    1    999    2  1.0
BLOCK - WT - SYM - V - TSP - N  -  other quanta  (rel. to F=0 )
   1    1    c    0    0  -1.0
   1    1    c    0    1   0.0
   1    1    c    0    2   1.0
   2    1    b    0    0  -1.0
   2    1    b    0    1   0.0
   2    1    b    0    2   1.0
Maximum Dimension for Hamiltonian = 3
                                EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG.
CALC.FREQ. -  DIFF. - WT.
   1:   4 -1  5  3  1  4              12181.08309   12181.08196    0.00113    0.00200   0.00098
   2:   4 -1  3  3  1  2              12181.10866   12181.11232   -0.00366    0.00200   0.00073
   3:   4 -1  4  3  1  3              12181.17657   12181.17504    0.00153    0.00200   0.00117
   4:   4  1  5  3 -1  4              12183.59736   12183.59655    0.00081    0.00200   0.00098
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  5:  4  1  3  3 -1  2          12183.62551  12183.62692  -0.00141   0.00200   0.00073
  6:  4  1  4  3 -1  3          12183.68860  12183.68963  -0.00103   0.00200   0.00117
  7:  5  1  6  4 -1  5          15226.35887  15226.35822   0.00065   0.00200   0.00082
  8:  5  1  4  4 -1  3          15226.38324  15226.38407  -0.00083   0.00200   0.00069
  9:  5  1  5  4 -1  4          15226.40930  15226.40916   0.00014   0.00200   0.00081
 10:  5 -1  6  4  1  5          15229.50218  15229.50208   0.00010   0.00200   0.00082
 11:  5 -1  4  4  1  3          15229.52843  15229.52793   0.00050   0.00200   0.00069
 12:  5 -1  5  4  1  4          15229.55263  15229.55302  -0.00039   0.00200   0.00081
 13:  6 -1  7  5  1  6          18271.61806  18271.61800   0.00006   0.00200   0.00068
 14:  6 -1  5  5  1  4          18271.63578  18271.63810  -0.00232   0.00200   0.00061
 15:  6 -1  6  5  1  5          18271.64982  18271.64950   0.00032   0.00200   0.00065
 16:  6  1  7  5 -1  6          18275.39330  18275.39154   0.00176   0.00200   0.00068
 17:  6  1  5  5 -1  4          18275.41045  18275.41163  -0.00118   0.00200   0.00061
 18:  6  1  6  5 -1  5          18275.42508  18275.42304   0.00204   0.00200   0.00065
 19:  7  1  8  6 -1  7          21316.86263  21316.86238   0.00025   0.00200   0.00073
 20:  7  1  7  6 -1  6          21316.88828  21316.88352   0.00476   0.00200   0.00072
 21:  7 -1  8  6  1  7          21321.26588  21321.26608  -0.00020   0.00200   0.00073
 22:  7 -1  7  6  1  6          21321.28582  21321.28722  -0.00140   0.00200   0.00072
 23:  8 -1  9  7  1  8          24362.08879  24362.09057  -0.00178   0.00200   0.00123
 24:  8 -1  8  7  1  7          24362.10499  24362.10561  -0.00062   0.00200   0.00123
 25:  8  1  9  7 -1  8          24367.12490  24367.12502  -0.00012   0.00200   0.00123
 26:  8  1  8  7 -1  7          24367.14029  24367.14006   0.00023   0.00200   0.00123
NORMALIZED DIAGONAL:
  1  1.00000E+000   2  9.95341E-001   3  3.64981E-001   4  1.00000E+000   5  3.60399E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                        NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
  1        100        B     1522.799301( 91)        0.000000
  2    110010000   (1 N-14)         3.511( 61)         -0.000
  3        200       -DJ       -0.08579(101)E-03    -0.00000E-03
  4      40000      qv/2        0.157107( 92)        0.000000
  5      40100     qvJ/2           1.71(100)E-06       -0.00E-06
 MICROWAVE AVG =      -0.000025 MHz, IR AVG =       0.00000
 MICROWAVE RMS =       0.001580 MHz, IR RMS =       0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=       0.78975       0.78975
  1  2 -0.151571  1  3 -0.930878  1  4  0.000000  1  5 -0.000000  2  1 -0.151571  2  3  0.125286  2  4 -
0.000000  2  5  0.000000
  3  1 -0.930878  3  2  0.125286  3  4 -0.000000  3  5  0.000000  4  1  0.000000  4  2 -0.000000  4  3 -
0.000000  4  5 -0.932798
  5  1 -0.000000  5  2  0.000000  5  3  0.000000  5  4 -0.932798
hccncs                          Tue Fri SWed AuMon Mar 26 20:48:10 2018
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Table S8: Computed structural parameters (distances *r* in Å, angles α in °) for HCCNCS at the CCSD(T) level employing various basis sets. Structures, which do not represent a local minimum, are indicated in italics. All Structures are either linear or planar.

Method	**Basis**	r_1(H-C$_1$)[1]	r_2(C$_1$-C$_2$)[1]	r_3(C$_2$-N)[1]	r_4(N-C$_3$)[1]	r_5(C$_3$-S)[1]	α_1(C$_2$C$_1$H)[1]	α_2(NC$_2$C$_1$)[1]	α_3(C$_3$NC$_2$)[1]	α_4(SC$_3$N)[1]
fc-CCSD(T)	ANO0	1.0704	1.2251	1.3183	1.2074	1.5862	177.88	183.64	156.10	184.46
fc-CCSD(T)	ANO1	1.0627	1.2124	1.3047	1.1941	1.5780	179.07	181.88	166.85	181.52
fc-CCSD(T)	ANO2	1.0623	1.2097	1.3025	1.1901	1.5757	179.49	181.14	171.97	181.54
fc-CCSD(T)	*cc-pV(T+d)Z*	*1.0582*	*1.2085*	*1.2982*	*1.1890*	*1.5738*	*180.00*	*180.00*	*180.00*	*180.00*
fc-CCSD(T)	cc-pwCVTZ	1.0632	1.2115	1.3032	1.1910	1.5759	179.57	180.79	174.95	181.00
fc-CCSD(T)	*cc-pwCVTZ*	*1.0632*	*1.2115*	*1.3028*	*1.1906*	*1.5761*	*180.00*	*180.00*	*180.00*	*180.00*
fc-CCSD(T)	*cc-pwCVQZ*	*1.0625*	*1.2096*	*1.3013*	*1.1892*	*1.5739*	*180.00*	*180.00*	*180.00*	*180.00*
fc-CCSD(T)	*cc-pwCV5Z*	*1.0619*	*1.2093*	*1.3009*	*1.1892*	*1.5724*	*180.00*	*180.00*	*180.00*	*180.00*
fc-CCSD(T)	cc-pCVTZ	1.0634	1.2122	1.3040	1.1917	1.5784	179.58	180.78	174.91	181.01
ae-CCSD(T)	cc-pCVTZ	1.0624	1.2103	1.3017	1.1896	1.5755	180.00	180.00	180.00	180.00
ae-CCSD(T)	cc-pCVQZ	1.0613	1.2072	1.2993	1.1872	1.5704	180.00	180.00	180.00	180.00
ae-CCSD(T)	cc-pCV5Z	1.0611	1.2065	1.2990	1.1867	1.5694	180.00	180.00	180.00	180.00
ae-CCSD(T)	cc-pwCVTZ	1.0621	1.2093	1.3009	1.1888	1.5726	180.00	180.00	180.00	180.00
ae-CCSD(T)	cc-pwCVQZ	1.0612	1.2070	1.2991	1.1870	1.5698	180.00	180.00	180.00	180.00
ae-CCSD(T)	cc-pwCV5Z	1.0610	1.2063	1.2988	1.1866	1.5690	180.00	180.00	180.00	180.00
ae-CCSD(T)	*aug-cc-pwCVTZ*	*1.0626*	*1.2100*	*1.3010*	*1.8931*	*1.5733*	*180.00*	*180.00*	*180.00*	*180.00*

[1]Definition of structural parameters: