

LABORATORY DETECTION OF HC₆N, A CARBON CHAIN WITH A TRIPLET ELECTRONIC GROUND STATE

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ABSTRACT

A linear triplet isomer of HC₆N has been detected by Fourier transform microwave spectroscopy in a supersonic molecular beam. A total of 85 hyperfine components from six rotational transitions between 8 and 18 GHz were measured to an uncertainty of 5 kHz; a similar set of transitions were detected for the ¹⁵N isotopic species, produced using an isotopically enriched precursor gas sample. The spectroscopic constants for both species, including the fine and hyperfine coupling constants, were determined to very high accuracy, and these allow calculation of the radio spectrum to a fraction of 1 km s⁻¹ in equivalent radial velocity. Triplet HC₆N is a highly polar, low-lying isomer; measurements show it to be about 10 times more abundant than a ring-chain isomer recently detected with the same spectrometer.

Subject headings: ISM: molecules — line: identification — methods: laboratory — molecular data — molecular processes — radio lines: ISM

1. INTRODUCTION

Astronomical detection of many acetylenic free radicals, cyanopolyynes, and cumulene carbenes demonstrates that unsaturated linear carbon chains are important constituents of the interstellar gas (Herbst 1995). One of the simplest of these chains is the triplet radical HCCN (cyanomethylene), which has been detected in several astronomical sources, including IRC +10216 (Guélin & Cernicharo 1991) following laboratory characterization by Saito and coworkers (Saito, Endo, & Hirota 1984; Brown, Saito, & Yamamoto 1990). By extension, the longer triplet chains HC₄N and HC₆N are good candidates for astronomical observation since they too are calculated to be highly polar (Aoki, Ikuta, & Murakami 1993; Aoki & Ikuta 1994) and are closely related to the cyanopolyynes which, up to HC₁₁N, have been observed astronomically.

The cyclic (ring chain) isomers of HC₄N and HC₆N (McCarthy et al. 1999) and linear triplet HC₄N (Tang, Sumiyoshi, & Endo 1999) have recently been detected by Fourier transform microwave (FTM) spectroscopy. Ab initio calculations indicate that the three isomers shown in Figure 1, a triplet chain and two singlet ring chains derived from C₃H₂, are the most stable forms of HC₆N (Aoki & Ikuta 1994). The triplet chain is calculated at the SDCI+Q level of theory to lie 4.7 kcal (0.22 eV) mol⁻¹ higher in energy than the ground-state ring chain, while the two cyclic isomers differ by only a nominal 1.0 kcal mol⁻¹. The dipole moment of the triplet chain is calculated to be 4.8 D.

Here we describe the laboratory detection of linear triplet HC₆N, shown in Figure 1a, and determination of its microwave spectrum and that of the ¹⁵N isotopic species. The strength of the laboratory lines suggests that the abundance of the triplet chain in our discharge source is approximately a factor of 10 greater than that of the ring-chain isomer, suggesting that the triplet chain may be the isomeric ground state.

2. EXPERIMENT

The same FTM spectrometer recently used to detect the rotational transitions of a number of new carbon chains

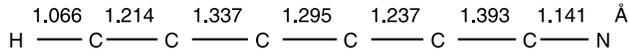
and other reactive molecules (McCarthy et al. 1997) was used in the present investigation. This instrument was designed specifically to study rotationally cold reactive molecules in a supersonic molecular beam; recent upgrades have improved its sensitivity and extended the upper frequency limit of its operating range to 43 GHz. Because the nozzle and discharge source must frequently be serviced, a gate valve assembly that allows the nozzle to be removed and cleaned without breaking vacuum in the main chamber has also been added.

The strongest lines of triplet HC₆N were observed using a precursor of 0.5% cyanoacetylene (HCCCN) in Ne, a 1400 V low-current discharge, gas pulses 130–230 μs long at a repetition rate of 6 Hz, and a nozzle backing pressure of 2.5 ktorr—conditions similar to those that optimize lines of linear HC₄N in our spectrometer. A mixture of about 0.5% diacetylene (HC₄H) and 5% N₂ in Ne with a 1700 V discharge yielded HC₆N signals about one-third as strong as those produced using cyanoacetylene alone. This production method proved an inexpensive and convenient way to obtain the ¹⁵N isotopic species, which provided an important confirmation of the assignment. ¹⁵N has a nuclear spin of ½, so this substitution yields significantly simpler hyperfine structure (hfs), systemically reducing the number of hyperfine components of each rotational transition by ½, with a corresponding increase in line strength.

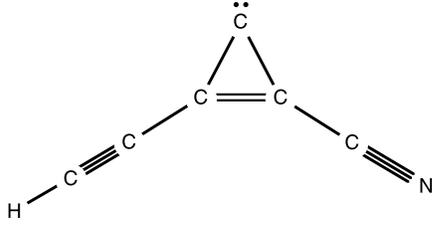
3. RESULTS AND ANALYSIS

Owing to hfs from the nitrogen and hydrogen nuclei and the triplet fine structure from the two unpaired electrons, each rotational transition of HC₆N exhibits a complex pattern of lines. For most rotational transitions, $N \rightarrow N - 1$, 18 strong lines are observed, six for each of the three fine-structure components. Instrumentally produced Doppler doubling (from the two traveling waves that constitute the resonant mode of the Fabry-Perot cavity) in the absence of blending further doubles the number of lines. At low- J the dominant interaction is nitrogen quadrupole hfs which splits each transition into three lines; each of these in turn is then split by the hydrogen hfs for a total of six lines.

(a)



(b)



(c)

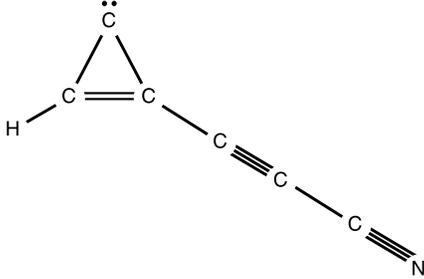


FIG. 1.—Isomers of HC_6N . (a) Theoretical geometry of the HC_6N linear triplet isomer (Aoki & Ikuta 1994), with bonds in angstroms. An explicit valence structure is not shown because the bonds are not readily classified as either acetylenic (triple and single bonds) or cumulenic (double bonds only). (b) Geometry of an undetected ring-chain isomer of HC_6N , with chains on each foot of the C_3 ring. (c) Geometry of a detected ring-chain isomer (McCarthy et al. 1999).

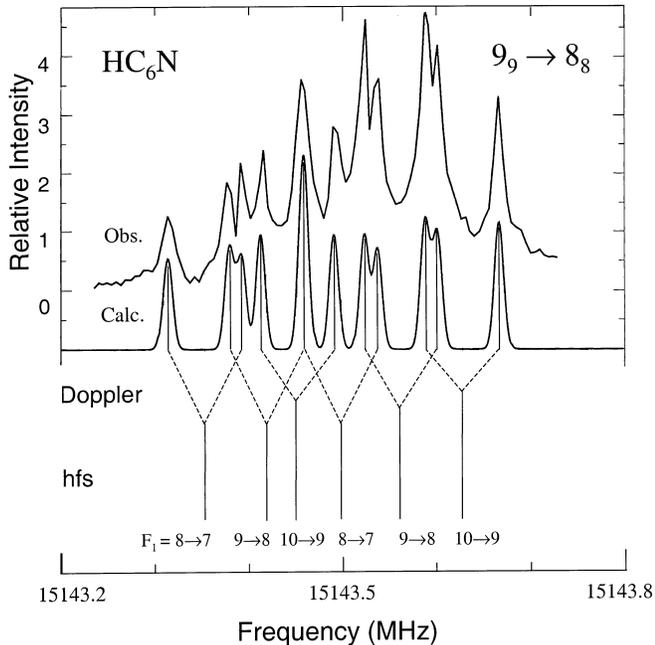


FIG. 2.—Observed (top) and calculated (bottom) spectra of a central ($N = J$) transition of HC_6N , not included in the fit. The six strongest hyperfine transitions are shown, and the appropriate instrumental Doppler splitting is indicated.

TABLE 1

MEASURED MICROWAVE TRANSITIONS OF LINEAR TRIPLET HC_6N

Frequency ^a (MHz)	O-C ^b (kHz)	$J'-J$	F'_1-F_1	$F'-F$
$N'-N = 5-4$				
8412.555.....	6	5-4	4-3	7/2-5/2
8412.600.....	-1		5-4	9/2-7/2
8412.863.....	0		6-5	11/2-9/2
8413.145.....	-2		4-3	9/2-7/2
8413.195.....	-3		5-4	11/2-9/2
8413.448.....	-1		6-5	13/2-11/2
$N'-N = 6-5$				
9503.209.....	0	5-4	6-5	11/2-9/2
9503.623.....	-7		5-4	9/2-7/2
9504.379.....	-6		4-3	7/2-5/2
9506.289.....	6		6-5	13/2-11/2
9506.737.....	-1		5-4	11/2-9/2
9507.470.....	4		4-3	9/2-7/2
10,095.330.....	1	6-5	5-4	9/2-7/2
10,095.403.....	-2		6-5	11/2-9/2
10,095.548.....	-2		7-6	13/2-11/2
10,095.715.....	3		5-4	11/2-9/2
10,095.788.....	2		6-5	13/2-11/2
10,095.950.....	1		7-6	15/2-13/2
10,486.196.....	0	7-6	6-5	13/2-11/2
10,486.694.....	0		7-6	15/2-13/2
10,487.118.....	-1		8-7	17/2-15/2
10,487.667.....	-3		6-5	11/2-9/2
10,488.185.....	0		7-6	13/2-11/2
10,488.603.....	0		8-7	15/2-13/2
$N'-N = 7-6$				
11,298.231.....	1	6-5	7-6	13/2-11/2
11,298.580.....	-3		6-5	11/2-9/2
11,299.165.....	-1		5-4	9/2-7/2
11,300.552.....	0		7-6	15/2-13/2
11,300.925.....	-1		6-5	13/2-11/2
11,301.486.....	-4		5-4	11/2-9/2
11,777.785.....	1	7-6	7-6	13/2-11/2
11,778.035.....	-2		6-5	11/2-9/2
11,778.146.....	-2		6-6	13/2-11/2
11,778.200.....	1		8-7	15/2-13/2
11,778.268.....	1		7-5	13/2-11/2
11,778.375.....	-1		7-6	15/2-13/2
11,778.490.....	-1		8-7	17/2-15/2
12,101.714.....	0	8-7	7-6	15/2-13/2
12,102.109.....	1		8-7	17/2-15/2
12,102.437.....	1		9-8	19/2-17/2
12,102.860.....	0		7-6	13/2-11/2
12,103.266.....	1		8-7	15/2-13/2
12,103.588.....	1		9-8	17/2-15/2
$N'-N = 8-7$				
13,067.894.....	1	7-6	8-7	15/2-13/2
13,068.175.....	0		7-6	13/2-11/2
13,068.625.....	-3		6-5	11/2-9/2
13,069.668.....	1		8-7	17/2-15/2
13,069.961.....	-2		7-6	15/2-13/2
13,070.403.....	0		6-5	13/2-11/2
13,460.708.....	2	8-7	7-6	13/2-11/2
13,460.823.....	-3		8-7	15/2-13/2
13,460.833.....	2		9-8	17/2-15/2
13,460.853.....	3		7-6	15/2-13/2

TABLE 1—Continued

Frequency ^a (MHz)	O-C ^b (kHz)	J'-J	F' ₁ -F ₁	F'-F
13,460.967.....	-2		8-7	17/2-15/2
13,461.054.....	1		9-8	19/2-17/2
13,731.769.....	-1	9-8	8-7	17/2-15/2
13,732.087.....	2		9-8	19/2-17/2
13,732.339.....	-1		10-9	21/2-19/2
13,732.668.....	1		8-9	15/2-13/2
13,732.992.....	1		9-8	17/2-15/2
13,733.241.....	0		10-9	19/2-17/2
N'-N = 9-8				
14,818.147.....	2	8-7	9-8	17/2-15/2
14,818.368.....	1		8-7	15/2-13/2
14,818.723.....	1		7-6	13/2-11/2
14,819.519.....	2		9-8	19/2-17/2
14,819.749.....	-1		8-7	17/2-15/2
14,820.095.....	0		7-6	15/2-13/2
15,372.806.....	0	10-9	9-8	19/2-17/2
15,373.061.....	1		10-9	21/2-19/2
15,373.262.....	1		11-10	23/2-21/2
15,373.516.....	0		9-8	17/2-15/2
15,373.778.....	0		10-9	19/2-17/2
15,373.974.....	0		11-10	21/2-19/2
N'-N = 10-9				
16,553.714.....	-2	9-8	10-9	19/2-17/2
16,553.891.....	2		9-8	17/2-15/2
16,554.170.....	0		8-7	15/2-13/2
16,554.793.....	1		10-9	21/2-19/2
16,554.973.....	1		9-8	19/2-17/2
16,555.247.....	0		8-7	17/2-15/2
17,022.172.....	0	11-10	10-9	21/2-19/2
17,022.379.....	-1		11-10	23/2-21/2
17,022.538.....	-1		12-11	25/2-23/2
17,022.739.....	-1		10-9	19/2-17/2
17,022.951.....	-2		11-10	21/2-19/2
17,023.109.....	-1		12-11	25/2-23/2

^a Estimated experimental uncertainties (1 σ) are $\lesssim 5$ kHz.

^b Observed frequency minus that calculated from the least-squares fit (see text). Best-fit constants are given in Table 3.

The coupling scheme used here to label the observed transitions is

$$N + S = J, J + I(N) = F_1, F_1 + I(H) = F.$$

Inspection of the expressions for the total energy from magnetic interactions for a linear Hund's case $b_{\beta J}$ molecule like HC₆N (Townes & Schawlow 1955, eqs. [8]–[12], p. 200) reveals that, since the hfs coupling constants $b_F = b + c/3$ and c for both the hydrogen and nitrogen nuclei are comparable, we expect the frequency spacing between the hfs-split lines to scale approximately as N^{-1} for $J = N \pm 1$ fine-structure transitions and as N^{-2} for $J = N$ fine-structure transitions. The observed splittings follow this pattern. Although many unidentified lines are detected when nitrogen-containing precursors are used in our molecular beam discharge source, the distinctive fine and hyperfine structure of HC₆N provide a readily recognized spectroscopic signature. This made identification of the molecule fairly straightforward.

The relative intensities of the hyperfine components provide a further check of the assignment. Because the

TABLE 2

MEASURED MICROWAVE TRANSITIONS OF LINEAR TRIPLET HC₆¹⁵N

Frequency ^a (MHz)	O-C ^b (kHz)	J'-J	F' ₁ -F ₁	F'-F
N'-N = 5-4				
8222.443.....	-1	5-4	11/2-9/2	5-4
8223.028.....	1		11/2-9/2	6-5
8223.211.....	3		9/2-7/2	5-4
N'-N = 6-5				
9867.155.....	4	6-5	13/2-11/2	6-5
9867.275.....	-1		11/2-9/2	5-4
9867.555.....	4		13/2-11/2	7-6
9867.678.....	2		11/2-9/2	6-5
N'-N = 7-6				
11,028.558.....	-4	6-5	11/2-9/2	5-4
11,029.286.....	1		13/2-11/2	6-5
11,030.849.....	0		11/2-9/2	6-5
11,031.567.....	-1		13/2-11/2	7-6
11,511.800.....	1	7-6	15/2-13/2	7-6
11,511.893.....	2		13/2-11/2	6-5
11,512.088.....	-4		15/2-13/2	8-7
11,512.183.....	-1		13/2-11/2	7-6
11,839.834.....	-1	8-7	17/2-15/2	9-8
11,840.985.....	-3		17/2-15/2	8-7
N'-N = 8-7				
12,759.513.....	3	7-6	13/2-11/2	6-5
12,760.077.....	0		15/2-13/2	7-6
12,761.276.....	1		13/2-11/2	7-6
12,761.836.....	-2		15/2-13/2	8-7
13,156.415.....	-2	8-7	17/2-15/2	8-7
13,156.487.....	0		15/2-13/2	7-6
13,156.641.....	1		17/2-15/2	9-8
13,156.708.....	-2		15/2-13/2	8-7
13,431.708.....	0	9-8	19/2-17/2	10-9
13,432.111.....	1		17/2-15/2	9-8
13,432.616.....	1		19/2-17/2	9-8
13,433.018.....	0		17/2-15/2	8-7
N'-N = 9-8				
14,471.555.....	1	7-6	15/2-13/2	7-6
14,471.999.....	0		17/2-15/2	8-7
14,472.929.....	1		15/2-13/2	8-7
14,473.370.....	-1		17/2-15/2	9-8
14,801.015.....	-1	9-8	19/2-17/2	9-8
14,801.070.....	-1		17/2-15/2	8-7
14,801.193.....	1		19/2-17/2	10-9
14,801.248.....	1		17/2-15/2	9-8
15,034.444.....	0	10-9	21/2-19/2	11-10
15,034.766.....	0		19/2-17/2	10-9
15,035.165.....	0		21/2-19/2	10-9
15,035.490.....	2		19/2-17/2	9-8
N'-N = 10-9				
16,169.187.....	4	9-8	17/2-15/2	8-7
16,169.533.....	-1		19/2-17/2	9-8
16,170.266.....	1		17/2-15/2	9-8
16,170.612.....	-2		19/2-17/2	10-9
16,445.604.....	0	10-9	21/2-19/2	10-9
16,445.645.....	-3		19/2-17/2	9-8
16,445.745.....	0		21/2-19/2	11-10
16,445.790.....	0		19/2-17/2	10-9
16,645.466.....	0	11-10	23/2-21/2	12-11
16,645.725.....	-1		21/2-19/2	11-10
16,646.043.....	0		23/2-21/2	11-10
16,646.306.....	1		21/2-19/2	10-9

^a Estimated experimental uncertainties (1 σ) are $\lesssim 5$ kHz.

^b Observed frequency minus that calculated from the least-squares fit (see text). Best-fit constants are given in Table 3.

intensities of FTM lines are determined by many experimental parameters, relative intensities reliable to within 15% are often difficult to achieve; care was taken to obtain reproducible HC₆N relative line intensities, and the measured intensities are in fairly good agreement with those predicted. An example of the agreement between theory and experiment is shown in Figure 2.

A total of 85 hyperfine transitions for HC₆N and 53 for HC₆¹⁵N were measured and analyzed using an effective Hamiltonian for a linear molecule in a ³Σ electronic state (Pickett 1991). Frequencies and hyperfine assignments are given in Tables 1 and 2. A total of 10 spectroscopic constants for the normal species and nine for the ¹⁵N species (Table 3) were determined by least-square fits of theoretical spectra to the data, achieving an rms of about 5 kHz, which is comparable to the measurement uncertainties. Only clearly resolved transitions were included in the fit, but the spectra of transitions with blended lines agreed well with the theoretical spectra calculated using the best-fit constants.

The evidence that we have observed the rotational spectrum of triplet HC₆N and not that of some other molecule is extremely strong: (1) the rotational constants of the normal species are in satisfactory agreement with ab initio calculations, (2) the spin-rotation constant is close to that predicted by scaling from the shorter chains HCCN and HC₄N, and (3) the hyperfine coupling constants for both nitrogen and hydrogen agree well with those of the related molecules HCCN and H₂CCCCN. The observed shift in the rotational constant *B* on ¹⁵N substitution also agrees extremely well with that expected, and the HC₆¹⁵N hyperfine constants *b_F*(N) and *c*(N) are well predicted by scaling those of the normal species by the ratio of the nuclear magnetic moments divided by the nuclear spins of the normal and rare isotopes. Furthermore, as expected for a paramagnetic molecule the transitions here exhibit a strong Zeeman

effect when a permanent magnet is brought near the molecular beam.

4. DISCUSSION

Remarkably strong lines of the linear triplets HC₄N and HC₆N are observed in our microwave spectrometer. Figure 3 shows the molecular abundances, determined from the spectroscopic data, of the linear and ring-chain isomers of HC₄N and HC₆N as well as the similarly sized cyanopolyynes chains HC₅N and HC₇N. The abundances of the two HC₄N isomers are comparable, but triplet HC₆N is nearly 10 times more abundant than the ring-chain isomer, implying that the triplet chain may be significantly lower in energy than the ring chain. This difference in energy may explain the unexpectedly large intensity decrement found previously between the HC₄N and HC₆N ring chains (McCarthy et al. 1999). An alternative interpretation may be that the ring chain is actually comparable to or lower in energy than the triplet species, but the reaction mechanisms in our discharge source favor the formation of the triplet chain. This second explanation seems less likely because detections of many other carbon-chain isomers with our spectrometer imply that activation barriers are not a serious impediment to molecule formation in this source. The four isomers of C₅H₂ (Gottlieb et al. 1998), for example, show a fairly good correlation of abundance with relative energy. Higher level ab initio calculations are clearly needed to help clarify this apparent discrepancy between calculated relative energy and experimental abundance.

The first member of the HC_{2*n*}N series, HCCN, has been observed in IRC + 10216, as have the similarly sized carbon chains with terminal nitrile groups, HC₃N, HC₅N, and HC₇N. The closely related acetylenic radical C₇H and others in the C_{*n*}H series have also been observed in that

TABLE 3
SPECTROSCOPIC CONSTANTS OF LINEAR TRIPLET HC₆N (IN MHz)

Constant	HC ₆ N		HC ₆ ¹⁵ N	
	Measured	Expected	Measured	Expected ^a
<i>B</i>	841.30728(7)	835 ^b	822.28700(8)	725
<i>D</i> × 10 ⁶ ...	10.3(5)	11.3 ^c	10.1(5)	9.8
<i>λ</i>	10729.75(6)	13500 ^d	10729.83(8)	10730
<i>λ_D</i> × 10 ⁶ ...	-130(50)		-170(50)	
<i>γ</i>	-0.946(3)	-1.13 ^e	-0.928(4)	-0.95
<i>b_F</i> (H)	-26.27(2)	-51 ^f	-26.29(1)	-26.3
<i>c</i> (H)	18.42(4)	-19 ^f	18.41(6)	18.4
<i>b_F</i> (N)	5.448(9)	5.2 ^f	-7.65(1)	-7.8
<i>c</i> (N)	-12.97(3)	-12 ^f	18.14(6)	18.5
<i>eqQ</i> (N)	-4.09(2)	-4.1 ^f		

NOTE.—Uncertainties in parentheses are 1 σ in the units of the last significant digit.

^a Derived from HC₆N (this work).

^b From Aoki & Ikuta 1994.

^c Obtained using the relationship between carbon chain length *L* and stiffness: $\log(D/B) = (-3.98-4) \log L$ (Thaddeus et al. 1998).

^d From HCCN (McCarthy et al. 1995).

^e Scaled from HCCN assuming that γ is proportional to *B*.

^f From H₂CCCCN (Chen et al. 1998).

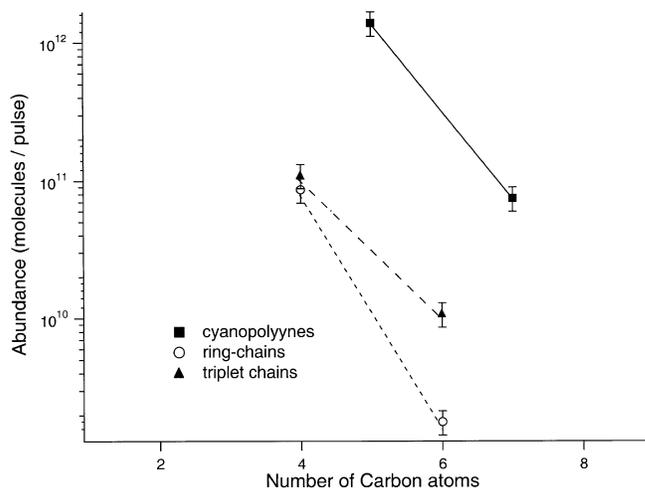


FIG. 3.—Measured abundances in the FTM spectrometer of the ring-chain and triplet linear isomers of HC₄N and HC₆N, as a function of the number of carbon atoms in the chain. The abundances of HC₅N and HC₇N are also plotted for comparison. All measurements were made at the same time to minimize production fluctuations, and production conditions were optimized for each molecule. Relative abundances are obtained from line intensities by taking into account the rotational partition functions and dipole moments. A calibrated sample of 0.937% OCS in Ne was used to convert relative to absolute abundances; error bars shown are 20% of the abundance—approximately the percent difference in abundances when O¹³C³⁴S and ¹⁸OC³⁴S were used for calibration.

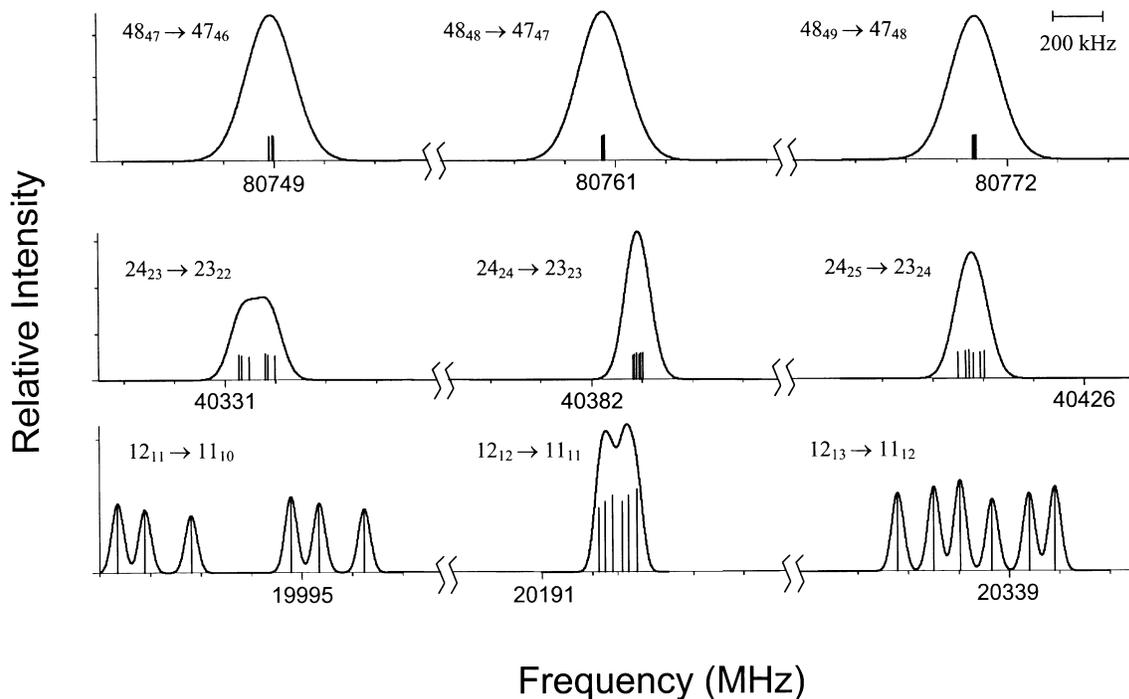


FIG. 4.—Calculated spectra of three rotational transitions of HC_6N , plotted with an assumed Doppler line width of 0.5 km s^{-1} , appropriate to TMC-1

source. Although C_5H and C_8H are more abundant than C_7H by factors of about 20 and 4, respectively (Guélin et al. 1997), the abundance decrement is shallow enough that detection of triplet HC_6N would appear feasible, especially if its formation mechanism is similar to that of these related molecules. Even if the present chain is not the most stable isomer of HC_6N , astronomical detection may nevertheless be possible because molecular abundances in the interstellar and circumstellar gas can dramatically depart from thermal equilibrium.

The identification by FTM spectroscopy of HC_4N (Tang et al. 1999) and HC_6N allows exact determination of their astronomically most interesting lines and permits radio searches for both molecules to be conducted efficiently. Figure 4 shows calculated hfs for three rotational transitions of HC_6N between 20 and 81 GHz, exhibiting the characteristic collapse of hfs with increasing N . Calculations of additional transitions at astronomically observable frequencies can be readily obtained from the spectroscopic constants in Table 3. There is no evidence for HC_6N in a recent extensive survey of IRC + 10216 at a level of 10 mK in antenna temperature (Kawaguchi et al. 1995), but this limit could be lowered significantly by deliberate searches at the specific frequencies provided by the present work.

With the recent assignment of several diffuse interstellar bands to C_7 (Tulej et al. 1998), other carbon chains of similar size and structure are worth consideration as carriers of diffuse bands. HC_6N is isoelectronic with HC_7H , a nonpolar molecule whose origin band was recently measured in the visible region at 504 nm (Ball, McCarthy, & Thaddeus 1999), so HC_6N may also have strong electronic transitions at optical wavelengths. Unlike HC_7H , HC_6N has a strong radio spectrum, owing to its large dipole

moment, so its production can be monitored in the microwave band by FTM spectroscopy. Its abundance here ($\sim 1 \times 10^{10}$ molecules pulse $^{-1}$ in our spectrometer) ought to be sufficient for laser detection.

Now that two of the three low-lying isomers of HC_6N have been identified in the laboratory, it may be possible to detect the remaining ring chain shown in Figure 1b. This isomer is calculated to have comparable dipole moments along its a and b inertial axes (S. Ikuta 1998, private communication) which will give rise to a - and b -type rotational transitions well within the frequency range of our microwave spectrometer. Unlike b -type transitions, a -type transitions are fairly insensitive to the poorly calculated angles of the side chains with respect to the ring. The a -type transitions can therefore be predicted with greater accuracy than the b -type transitions. Because the a -type transitions are also separated by nearly harmonic frequency intervals, identifying the transitions of the isomer shown in Figure 1b in the laboratory should be fairly straightforward. Owing to the terminal nitrile group, both a - and b -type transitions have quadrupole hfs that can be predicted to better than 10% and serves as a useful signature.

Note added in manuscript.—After submission of this paper, the rotational spectrum of the next longer member in the linear triplet series, HC_8N , was detected with the present instrument. Line strengths of the hyperfine components are about 20 times weaker than here. A full account of this work will be given elsewhere.

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Note added in proof.—K. Aoki (2000, private communication) has informed the authors that more recent calculations, to be published in *Theochem*, indicate that the linear isomer of HC₆N is the ground state.