

LABORATORY DETECTION OF A NEW CARBON CHAIN RADICAL: H_2CCCCN

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ABSTRACT

The cyanopropynyl radical, H_2CCCCN , was detected in a supersonic molecular beam by Fourier transform microwave spectroscopy. For the normal and ^{15}N species, 89 and 40 hyperfine components, respectively, from four successive rotational transitions ($N = 2 \rightarrow 1$ to $5 \rightarrow 4$) in the lowest energy ($K_a = 0$) rotational ladder were measured between 8 and 22 GHz to an uncertainty of 5 kHz. With this data, the microwave constants of cyanopropynyl, including the fine and hyperfine coupling constants, are determined to very high accuracy, and the most interesting lines in the radio spectrum from an astronomical standpoint can now be calculated to a fraction of 1 km s^{-1} in equivalent radial velocity.

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

The cyanomethyl radical, H_2CCN , obtained by removing one hydrogen atom from the familiar stable compound methylcyanide, CH_3CN , was first encountered in the interstellar sources Sgr B2 and TMC-1 as harmonically related unidentified lines (Thaddeus, Vrtilek, & Gottlieb 1985), which were subsequently identified first by assigning hyperfine structure (hfs) in the lowest two rotational transitions in TMC-1 (Irvine et al. 1988) and then by direct detection in a laboratory discharge (Saito et al. 1988). Because carbon chains are the most prominent polyatomic constituents of the interstellar gas and circumstellar shells and one with 12 heavy atoms (HC_{11}N) has now been identified (Bell et al. 1997), the next member of the sequence of carbon chain radicals that includes cyanomethyl, the cyanopropynyl radical, H_2CCCCN , shown in Figure 1a, is a good candidate for astronomical detection. Here we describe the first laboratory detection of this molecule and determine to high precision its microwave spectrum and hfs.

Cyanopropynyl was detected in a supersonic molecular beam with two similar Fourier transform microwave (FTM) spectrometers, first at Wesleyan, then at Harvard (Hight Walker et al. 1995; McCarthy et al. 1997a). The radicals were produced by a low-current 900 V DC gas discharge synchronized with a gas pulse 300 μs long at a backing pressure of approximately 2 atm. Owing to the high yield of the H_2CCN radical in a discharge through CH_3CN (Saito et al. 1988), a methylcyanoacetylene (CH_3CCCN) sample was obtained with the aim of producing cyanopropynyl in sufficient concentration to detect its rotational spectrum. A 1% mixture of CH_3CCCN in Ar produced the strongest cyanopropynyl signals, possibly because the radical is produced primarily by cleavage of a C—H bond. In addition, other gas mixtures were used to aid the determination of the spectral carrier. Specifically, CH_3CN and diacetylene (HC_4H) (1% each) in Ar and nitrogen (N_2) and acetylene (HCCH) in Ne produced line intensities lower by factors of 3 and 6, respectively, than CH_3CCCN in Ar. Detection of $\text{H}_2\text{CCCC}^{15}\text{N}$ required ^{15}N -enriched CH_3CN , which is a fairly inexpensive and readily available isotopic species. The

lines of cyanopropynyl disappeared when a large permanent magnet was brought near the molecular beam, which indicates that the carrier was indeed a radical.

Cyanopropynyl is a nearly prolate symmetric top with a linear, heavy atom backbone (Fig. 1a) and rotational transitions that in frequency are closely harmonic. By analogy with H_2CCN , it has a 2B_1 electronic ground state and quite complex hfs, owing to the interaction of the unpaired electron with the hydrogen and nitrogen nuclei. Because the ground-state electronic wave function changes sign on interchange of the two equivalent hydrogens, the rotational levels are ortho with a total spin of 1 for the hydrogen nuclei when K_a is even. As a result, at low rotational temperature (e.g., in our supersonic beam and in TMC-1) the population in the two metastable $K_a = 1$ para ladders is significantly lower than in the ground $K_a = 0$ ortho ladder: by a factor of about 6 when hfs is not resolved (Townes & Schawlow 1955) and by a factor of 2–3 when, as in the present case, it largely is. Although the lines we detect are fairly intense, as illustrated by the spectrum of one of the observed hyperfine components of the $2_{0,2} \rightarrow 1_{0,1}$ transition shown in Figure 1b, only the $K_a = 0$ ladder has been observed to date. In an FTM spectrometer, line intensities in the power spectrum scale as the square of the populations, so the $K_a = 1$ lines are expected to be quite weak. An additional difficulty is the very large spin-doubling expected in the lower rotational transitions in the $K_a = 1$ ladder, probably of order several 100 MHz (see H_2CCN ; Saito et al. 1988), which makes the search for $K_a = 1$ lines fairly difficult. Moreover, characterization of the rotational spectrum in the $K_a = 0$ ladder is all that is required for an astronomical search for H_2CCCCN .

Four rotational transitions in the $K_a = 0$ ladder of both isotopic species of cyanopropynyl were measured in the frequency range of 8–22 GHz. We first assigned the simpler ^{15}N species, devoid of nitrogen quadrupole hfs, with 12 strong hyperfine components (versus 18 for the normal species). Qualitatively, it was observed that the frequency range of the complex hyperfine pattern of roughly 2 MHz is comparable to the magnitude of the spin-rotation splitting estimated by simple scaling from H_2CCN . The assignments were made with an interactive computer program that plotted the predicted and observed spectra and allowed the spectroscopic constants that have the largest effect on the complex pattern of lines to be distinguished. We assumed

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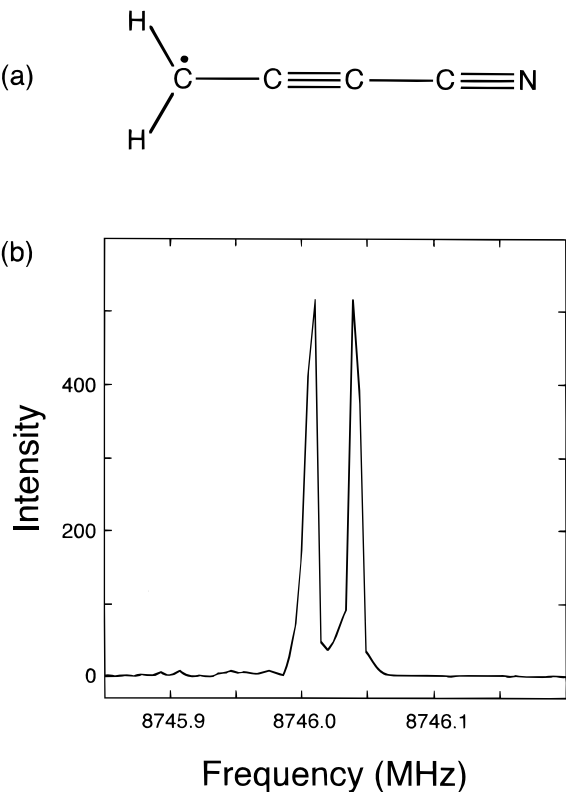


FIG. 1.—(a) Geometry of the H₂CCCCN radical; the dot indicates schematically the position of the unpaired electron. (b) A well-resolved hyperfine component (F_1 , F_2 , $F = 1/2$, $5/2$, $7/2 \rightarrow 3/2$, $3/2$, $5/2$) of the $2_{0,2} \rightarrow 1_{0,1}$ transition, observed with an integration time of 10 minutes. The double-peaked line profile results from the Doppler shift of the supersonic molecular beam with respect to the two traveling waves composing the confocal mode of the Fabry-Perot microwave cavity.

the Fermi contact interaction for hydrogen, $b_F(\text{H})$, to mainly result from spin polarization and to be comparable to that in other molecules, including cyanomethyl (Saito et al. 1988). Comparing the measured and predicted spectra, it was noted that several lines in the less congested (outer) portion of the observed spectra at 17 and 21 GHz are split into tight doublets, which we attributed to ^{15}N hfs. Varying the dipole-dipole and Fermi contact hyperfine coupling constants for ^{15}N , approximate values for these two terms were estimated. By iteratively determining one or two spectroscopic constants via least-squares fits and then using the graphics program to estimate other constants, we arrived at a final set of constants for the ^{15}N species that fully accounted for the observed hfs.

The spectroscopic constants for H₂CCCC¹⁵N were then scaled to the corresponding values for the ¹⁴N species—except for the quadrupole coupling constant, which was assumed to be the same as in cyanomethyl. We were able to assign this more complex spectrum almost immediately using the same process; in the final stage of the analysis, the spectroscopic constants for the ¹⁴N species were least-squares fitted to the measured frequencies. Although the observed intensities are in fairly good agreement with those predicted, the spectral assignment is based largely on line frequencies, since intensities in FTM spectrometers are a fairly complex function of instrumental parameters.

A total of 89 hyperfine components for H₂CCCCN (Table 1) and 40 for H₂CCCC¹⁵N (Table 2) were analyzed with an effective Hamiltonian for a linear molecule in a $^2\Sigma$

TABLE 1				
MEASURED MICROWAVE TRANSITIONS OF H ₂ CCCCN				
Frequency ^a (MHz)	O – C ^b (kHz)	$F'_1 - F_1$	$F'_2 - F_2$	$F' - F$
$2_{0,2} - 1_{0,1}$				
8742.859	–3	3/2–3/2	3/2–1/2	3/2–1/2
8743.535	–4	3/2–3/2	3/2–1/2	1/2–1/2
8743.547	–4	3/2–3/2	5/2–5/2	3/2–3/2
8743.608	2	3/2–3/2	7/2–5/2	5/2–5/2
8743.840	7	1/2–3/2	3/2–3/2	3/2–3/2
8744.367	2	3/2–3/2	1/2–1/2	3/2–3/2
8745.204	–5	3/2–1/2	5/2–3/2	5/2–3/2
8745.204	7	3/2–3/2	7/2–5/2	7/2–5/2
8745.290	7	3/2–3/2	7/2–5/2	5/2–3/2
8745.408	–9	1/2–3/2	5/2–3/2	5/2–3/2
8745.546	6	3/2–3/2	7/2–5/2	9/2–7/2
8745.546	10	1/2–1/2	3/2–1/2	5/2–3/2
8745.572	11	1/2–1/2	5/2–3/2	3/2–1/2
8745.777	–6	3/2–3/2	5/2–3/2	3/2–1/2
8746.016	–5	1/2–3/2	5/2–3/2	7/2–5/2
8746.224	–5	1/2–1/2	3/2–1/2	3/2–1/2
8746.721	–2	3/2–1/2	5/2–3/2	7/2–5/2
8747.415	1	1/2–1/2	3/2–1/2	1/2–1/2
8749.714	0	1/2–3/2	5/2–3/2	3/2–3/2
8750.083	0	3/2–3/2	1/2–1/2	1/2–3/2
8751.850	–7	3/2–1/2	3/2–3/2	5/2–5/2
$3_{0,3} - 2_{0,2}$				
13112.123	–7	3/2–3/2	7/2–7/2	9/2–9/2
13115.670	1	3/2–3/2	3/2–1/2	3/2–1/2
13116.395	8	3/2–3/2	7/2–7/2	7/2–7/2
13116.424	1	3/2–3/2	3/2–1/2	5/2–3/2
13117.335	2	3/2–3/2	5/2–3/2	7/2–5/2
13117.564	5	3/2–3/2	9/2–7/2	9/2–7/2
13117.824	0	3/2–3/2	5/2–3/2	5/2–3/2
13117.951	–2	3/2–3/2	9/2–7/2	11/2–9/2
13118.001	11	3/2–3/2	7/2–7/2	7/2–5/2
13118.001	–10	3/2–3/2	9/2–5/2	7/2–5/2
13118.132	4	3/2–3/2	5/2–3/2	3/2–1/2
13118.182	3	3/2–3/2	7/2–7/2	9/2–7/2
13118.350	–2	3/2–3/2	7/2–5/2	5/2–3/2
13118.431	–3	1/2–1/2	5/2–3/2	5/2–3/2
13118.480	–1	1/2–1/2	5/2–3/2	3/2–1/2
13118.530	3	1/2–1/2	7/2–3/2	7/2–5/2
13118.569	2	3/2–3/2	9/2–5/2	9/2–7/2
13118.605	–2	1/2–1/2	5/2–5/2	7/2–5/2
13118.886	3	1/2–1/2	7/2–5/2	9/2–7/2
13118.910	–9	1/2–1/2	7/2–5/2	5/2–3/2
13119.185	–2	3/2–3/2	7/2–5/2	9/2–7/2
13119.745	0	3/2–3/2	3/2–1/2	1/2–1/2
13121.390	4	3/2–3/2	3/2–1/2	3/2–3/2
13122.473	5	3/2–3/2	5/2–5/2	7/2–7/2
13124.283	–2	3/2–3/2	3/2–3/2	5/2–5/2
$4_{0,4} - 3_{0,3}$				
17485.533	–5	3/2–3/2	9/2–9/2	11/2–11/2
17489.032	–7	3/2–3/2	9/2–7/2	9/2–9/2
17489.492	0	1/2–1/2	7/2–7/2	9/2–7/2
17489.702	0	3/2–3/2	9/2–7/2	7/2–7/2
17490.028	4	3/2–3/2	11/2–7/2	11/2–9/2
17490.595	1	3/2–3/2	11/2–9/2	13/2–11/2
17490.640	–4	3/2–3/2	11/2–9/2	11/2–9/2
17490.702	–2	3/2–3/2	11/2–9/2	9/2–7/2
17490.828	–4	3/2–3/2	9/2–7/2	9/2–7/2
17491.038	11	3/2–3/2	7/2–5/2	7/2–5/2
17491.073	2	3/2–3/2	9/2–7/2	7/2–5/2
17491.123	–6	3/2–3/2	7/2–5/2	9/2–7/2
17491.208	2	3/2–3/2	7/2–5/2	5/2–3/2
17491.255	–4	1/2–1/2	7/2–5/2	7/2–5/2
17491.338	2	3/2–3/2	5/2–3/2	7/2–5/2
17491.338	–3	1/2–1/2	7/2–5/2	5/2–3/2
17491.370	9	3/2–3/2	9/2–7/2	11/2–9/2
17491.385	–3	1/2–1/2	7/2–5/2	9/2–7/2
17491.523	–2	1/2–1/2	9/2–7/2	9/2–7/2

TABLE 1—Continued

Frequency ^a (MHz)	O — C ^b (kHz)	F ₁ '-F ₁	F ₂ '-F ₂	F'-F
17491.746.....	0	1/2-1/2	9/2-7/2	11/2-9/2
17491.871.....	-2	1/2-1/2	9/2-7/2	7/2-5/2
17491.975.....	-6	3/2-3/2	9/2-9/2	11/2-9/2
17492.568.....	-5	1/2-1/2	7/2-5/2	5/2-5/2
17492.717.....	0	3/2-3/2	9/2-9/2	9/2-7/2
17495.824.....	-4	3/2-3/2	5/2-3/2	5/2-5/2
5_{0,5}-4_{0,4}				
21863.311.....	-2	3/2-3/2	13/2-11/2	13/2-11/2
21863.311.....	-2	3/2-3/2	13/2-11/2	15/2-13/2
21863.392.....	-1	3/2-3/2	13/2-11/2	11/2-9/2
21863.700.....	10	3/2-3/2	11/2-9/2	11/2-9/2
21863.810.....	-6	3/2-3/2	11/2-9/2	9/2-7/2
21864.012.....	-2	3/2-3/2	9/2-7/2	9/2-7/2
21864.087.....	-3	3/2-3/2	9/2-7/2	7/2-5/2
21864.102.....	-1	1/2-1/2	9/2-7/2	9/2-7/2
21864.102.....	-1	3/2-3/2	11/2-9/2	13/2-11/2
21864.137.....	-2	1/2-1/2	9/2-7/2	11/2-9/2
21864.210.....	6	1/2-1/2	9/2-7/2	7/2-5/2
21864.210.....	-4	3/2-3/2	9/2-7/2	11/2-9/2
21864.467.....	0	3/2-3/2	7/2-5/2	7/2-5/2
21864.502.....	6	1/2-1/2	11/2-9/2	11/2-9/2
21864.602.....	3	1/2-1/2	11/2-9/2	13/2-11/2
21864.762.....	6	1/2-1/2	11/2-9/2	9/2-7/2
21864.770.....	-4	3/2-3/2	7/2-5/2	9/2-7/2
21864.850.....	6	3/2-3/2	7/2-5/2	5/2-3/2

^a Experimental uncertainties (1 σ) are 5 kHz.^b Observed frequency minus that calculate from the least-squares fit (see text). Best fit constants are given in Table 3.

electronic state. Eight spectroscopic constants for the normal species and seven for the ¹⁵N species, including the fine structure and hydrogen and nitrogen hyperfine coupling constants, were determined to high accuracy (see Table 3) using a program that includes all off-diagonal terms in the Hamiltonian matrix (Pickett 1991). As shown in Table 4, the effective constants in the linear molecule Hamiltonian are simply related to those of the asymmetric top. The rms of the fits (~ 5 kHz) are comparable to the measurement uncertainties. Because the Fermi contact interaction for the hydrogen is the largest interaction in the four rotational levels observed here, the coupling scheme used in labeling the energy levels (Fig. 2) and the observed transitions is

$$I(H) + S = F_1, \quad N + F_1 = F_2, \quad F_2 + I(N) = F.$$

On purely spectroscopic grounds, there can be almost no doubt that we are observing cyanopropynyl, and there is additional evidence as well. The lines we observe are absent in a HC₄H/Ar discharge and in a DCCD/N₂/Ar discharge, as expected, which confirms that the carrier contains nitrogen and hydrogen. No ab initio calculation has been reported for H₂CCCCN, but as shown in Tables 3 and 4, the effective rotational constant, $B_{\text{eff}} = (B + C)/2$, agrees to within 1% with an estimate based on the C—C and C—H bond lengths, the H—C—H angle in H₂CCCH, and the C—N bond length in HCCCN (Botschwina et al. 1993, 1995). The spin-rotation constant is within 20% of the value predicted by simple scaling from H₂CCN; the magnetic hyperfine coupling constants for both the hydrogen and the nitrogen are in good agreement with those of H₂CCN; the Fermi contact constant for hydrogen, $b_F(H)$, only 20% less than in H₂CCN, is well within the range of values for similar molecules; and the quadrupole coupling constant in

TABLE 2

MEASURED MICROWAVE TRANSITIONS OF H₂CCCC¹⁵N

Frequency ^a	O — C ^b	F ₁ '-F ₁	F ₂ '-F ₂	F'-F
2_{0,2}-1_{0,1}				
8512.720.....	2	3/2-3/2	7/2-5/2	4-3
8513.045.....	2	3/2-3/2	7/2-5/2	3-2
8513.240.....	-2	3/2-1/2	5/2-3/2	3-2
8513.345.....	5	1/2-1/2	3/2-1/2	2-1
8513.747.....	-3	1/2-3/2	5/2-3/2	2-1
8514.081.....	3	1/2-3/2	5/2-3/2	3-2
8514.860.....	1	3/2-1/2	5/2-3/2	2-1
3_{0,3}-2_{0,2}				
12769.335.....	-4	3/2-3/2	5/2-3/2	3-2
12769.359.....	5	3/2-3/2	9/2-7/2	5-4
12769.520.....	1	3/2-3/2	9/2-7/2	4-3
12769.810.....	0	1/2-1/2	5/2-3/2	2-1
12769.926.....	-7	3/2-3/2	7/2-5/2	4-3
12770.224.....	0	1/2-1/2	5/2-3/2	3-2
12770.584.....	0	1/2-1/2	7/2-5/2	3-2
12770.600.....	1	3/2-3/2	3/2-1/2	2-1
12770.600.....	-4	3/2-3/2	7/2-5/2	3-2
12770.841.....	-1	1/2-1/2	7/2-5/2	4-3
4_{0,4}-3_{0,3}				
17026.052.....	-1	3/2-3/2	11/2-9/2	6-5
17026.149.....	-5	3/2-3/2	11/2-9/2	5-4
17026.635.....	0	3/2-3/2	9/2-7/2	5-4
17026.655.....	4	3/2-3/2	7/2-5/2	4-3
17026.717.....	6	1/2-1/2	7/2-5/2	3-2
17027.011.....	1	1/2-1/2	7/2-5/2	4-3
17027.011.....	-7	3/2-3/2	7/2-5/2	3-2
17027.060.....	-5	3/2-3/2	9/2-7/2	4-3
17027.397.....	5	1/2-1/2	9/2-7/2	4-3
17027.611.....	0	1/2-1/2	9/2-7/2	5-4
17027.795.....	2	3/2-3/2	5/2-3/2	3-2
5_{0,5}-4_{0,4}				
21282.770.....	3	3/2-3/2	13/2-11/2	7-6
21282.837.....	1	3/2-3/2	13/2-11/2	6-5
21283.334.....	-2	3/2-3/2	11/2-9/2	6-5
21283.523.....	-1	1/2-1/2	9/2-7/2	4-3
21283.574.....	1	3/2-3/2	9/2-7/2	5-4
21283.670.....	3	3/2-3/2	11/2-9/2	5-4
21283.780.....	-2	1/2-1/2	9/2-7/2	5-4
21283.903.....	3	3/2-3/2	9/2-7/2	4-3
21284.179.....	1	1/2-1/2	11/2-9/2	5-4
21284.365.....	-8	1/2-1/2	11/2-9/2	6-5
21284.710.....	1	3/2-3/2	7/2-5/2	4-3
21284.790.....	2	3/2-3/2	7/2-5/2	3-2

^a Experimental uncertainties (1 σ) are 5 kHz.^b Observed frequency minus that calculated from the least-squares fit (see text). Best-fit constants are given in Table 3.

the ¹⁴N species differs by only 4% from H₂CCN. Conclusive confirmation of the identification is provided by detection of the ¹⁵N species at the predicted isotopic shift, with hyperfine coupling constants that are in excellent agreement with those scaled from the ¹⁴N isotopic species.

Four rotational transitions of cyanopropynyl corresponding to those observed in the laboratory and a predicted transition at higher frequency are plotted in Figure 3. In the rotational transitions we detect there is no regular pattern in the observed hfs; it is not until $N \geq 8$ (i.e., at ~ 35 GHz) that the spectra calculated from our constants exhibit a clear six-line pattern corresponding to the three hyperfine-split components of the two spin-doublets. Above about 100 GHz ($N > 20$; see Fig. 3), hfs has largely collapsed, and only the 2.3 MHz spin-doubling remains. Despite the

TABLE 3
SPECTROSCOPIC CONSTANTS OF CYANOPROPYNYL (IN MHz)

CONSTANT	H ₂ CCCN		H ₂ CCCC ¹⁵ N	
	Measured	Expected	Measured	Expected ^a
B_{eff}	2186.4301(2)	2168 ^b	2128.3888(2)	2128.79
$D_{\text{eff}} \times 10^6$	139(5)	150 ^c	130(5)	132
γ	-2.316(1)	-2.8 ^d	-2.258(3)	-2.255
$b_F(\text{H})$	-50.6(1)	-61 ^e	-50.7(3)	-50.6
$c(\text{H})$	-18.897(6)	-24 ^e	-18.95(5)	-18.90
$b_F(\text{N})$	5.162(3)	7 ^e	-7.21(5)	-7.24
$c(\text{N})$	-12.322(7)	-23 ^e	17.23(4)	17.16
$eqQ(\text{N})$	-4.148(4)	-4.3 ^e		

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

^a Derived from H₂CCCC¹⁴N (this work).

^b Calculated from estimated structure (see text).

^c Effective centrifugal distortion constant in the $K_a = 0$ rotational ladder of H₂C₅ (McCarthy et al. 1997b).

^d Scaled from H₂CCN assuming that γ is proportional to B_{eff} (Brown & Watson 1977).

^e From H₂CCN (Saito et al. 1988).

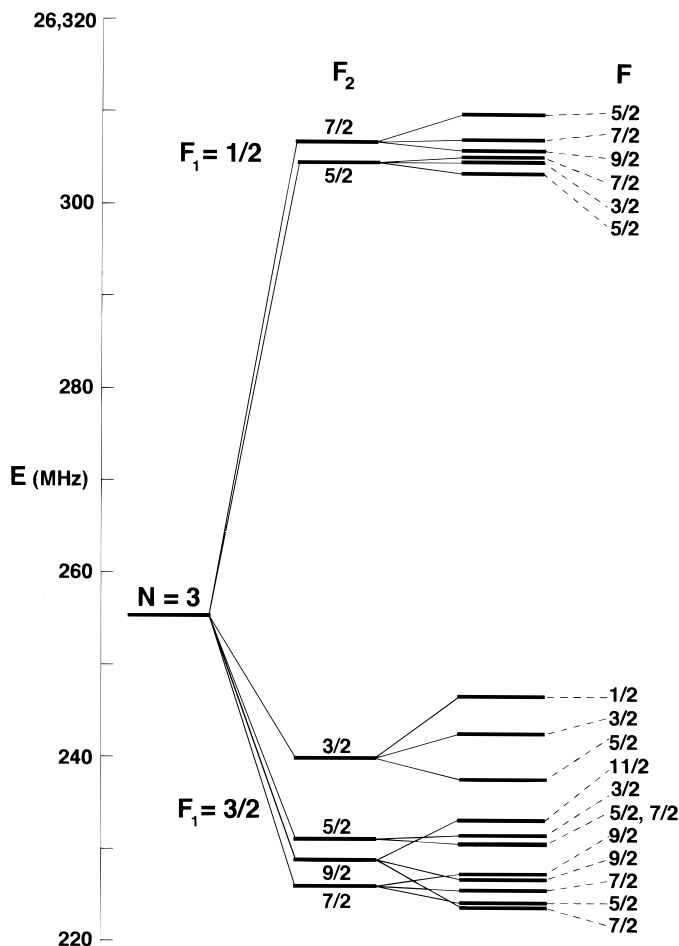


FIG. 2.—The $3_{0,3}$ rotational level of H₂CCCN showing the fine and hyperfine splittings in the coupling scheme in which the two hydrogen nuclear spins are first coupled to the electron spin, the resulting angular momentum is coupled next to the rotation, and finally to the nitrogen nuclear spin.

TABLE 4
RELATION BETWEEN THE SPECTROSCOPIC CONSTANTS OF A LINEAR MOLECULE AND THOSE OF AN ASYMMETRIC TOP^a

Spectroscopic Constant	Linear Molecule	Asymmetric Top ($K_a = 0$)
Rotation	B_{eff}	$(B + C)/2$
Centrifugal distortion	D_{eff} ^b	D_J
Spin-rotation	γ	$(\epsilon_{bb} + \epsilon_{cc})/2$
Hyperfine interactions:		
Fermi contact	b_F	a_F
Dipole-dipole	c	$(3/2)T_{aa}$
Electric quadrupole	eQq	χ_{aa}

^a Hirota et al. 1994.

^b $D_{\text{eff}} \sim \{D_J + (B - C)^2/32[A - (B + C)/2]\}$ (see McCarthy et al. 1997b).

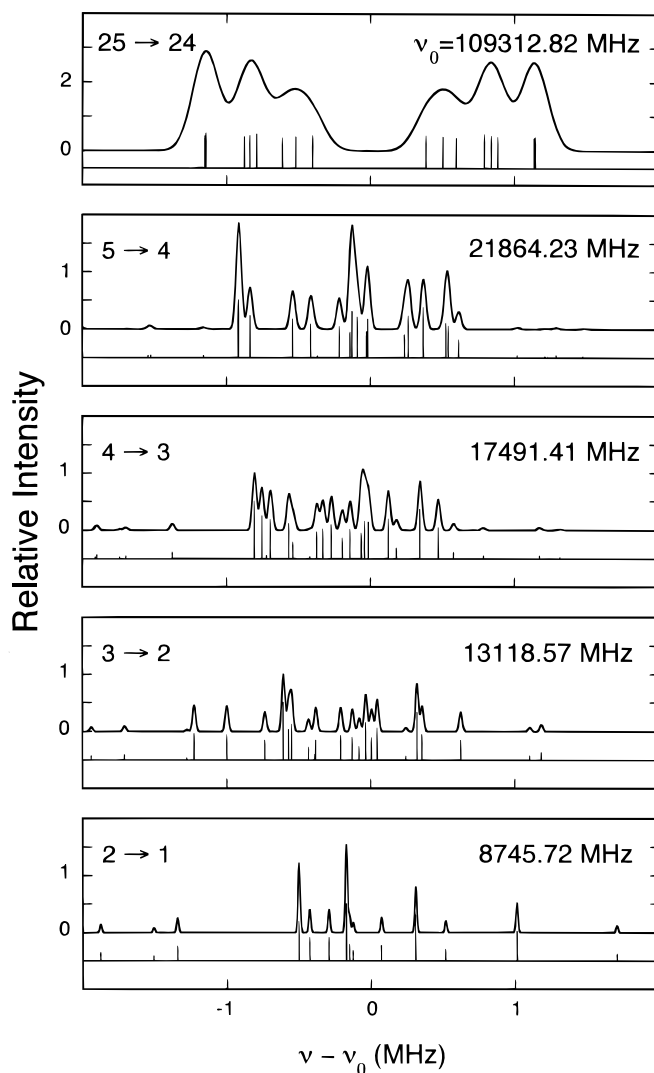


FIG. 3.—Calculated spectra of the four rotational transitions of H₂CCCN observed in the laboratory ($N = 5 \rightarrow 4$, $4 \rightarrow 3$, $3 \rightarrow 2$, and $2 \rightarrow 1$) and the predicted $N = 25 \rightarrow 24$ transition, the latter showing partially resolved hydrogen hfs in the two spin components. The spectra are plotted with an assumed Doppler line width (FWHM) of 0.5 km s^{-1} appropriate to TMC-1. The uncertainties in the rest frequencies ($\sim 5 \text{ kHz}$) are comparable to the width of the vertical lines that indicate the positions of the individual hyperfine components. The small apparent displacement of v_0 from the centroid of the hyperfine manifold in the lower rotational transitions is the result of weak hyperfine satellites up to 10 MHz away.

complex nature of the H₂CCCCN spectrum, astronomers can accurately predict the centroids of the rotational transitions in the ground $K_a = 0$ ladder from the standard expression $\nu_{N+1 \rightarrow N} = 2B_{\text{eff}}(N+1) - 4D_{\text{eff}}(N+1)^3$.

It would appear that cyanopropynyl is an excellent candidate for detection in TMC-1 if the formation mechanisms of H₂CCCCN and CH₃CCCCN are similar to those of H₂CCN and CH₃CN because the H₂CCN/CH₃CN ratio there is about 10, and the abundance of CH₃CCCCN is comparable to CH₃CN (Broten et al. 1984). The formation of H₂CCN in dense molecular clouds is not well understood, but two possible mechanisms involving ion-molecule reactions have been proposed (Saito 1989-1990). Turner et al. (1990) found that the H₂CCN/CH₃CN ratio appears to be correlated with the kinetic temperature of the molecular cloud, with a higher ratio observed in the colder sources. They concluded that H₂CCN and CH₃CN are probably not formed from the same precursor ion (e.g., CH₃CNH⁺) because the large H₂CCN/CH₃CN ratio would imply that the branching ratio of the dissociative recombination reaction is much larger than is observed in analogous reactions and that the ratio should not depend on temperature.

W. D. Langer & T. Velusamy (1997, private communication) of the Jet Propulsion Laboratory have undertaken a search for H₂CCCCN in TMC-1 [$\alpha(1950) = 04^{\text{h}}38^{\text{m}}41^{\text{s}}$, $\delta(1950) = 25^{\circ}35'39''$] during 1996 December and 1997 April with the NASA Deep Space Network 70 m telescope at Goldstone, California. An upper limit of $T_A \leq 5$ mK for the $N = 5 \rightarrow 4$ transition at 21,864 MHz, averaged over the 0.20

km s⁻¹ spectral resolution, was obtained in a position-switching observing mode with an on-source integration time of 6 hr. These observations allow us to estimate that the column density of H₂CCCCN in TMC-1 is $\leq 2 \times 10^{11}$ cm⁻² for an assumed dipole moment of 4.42 D (P. Botschwina 1997, private communication), a rotational temperature of 10 K, a line width of 0.5 km s⁻¹, and on the assumption that the source fills the telescope beam (45"; Langer et al. 1995).

It cannot be ruled out that H₂CCCCN and CH₃CCCCN may be produced by dissociative recombination of the same precursor ion, even though the upper limit of the H₂CCCCN column density is about 10 times less than CH₃CCCCN in TMC-1 (5×10^{12} cm⁻²; Broten et al. 1984). There are very few established cases in which more than one interstellar molecule is formed from the same molecular ion, so additional astronomical observations of H₂CCCCN and CH₃CCCCN may provide insights into the formation of complex interstellar molecules.

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REFERENCES

- Bell, M. B., Feldman, P. A., Travers, M. J., McCarthy, M. C., Gottlieb, C. A., & Thaddeus, P. 1997, *ApJ*, 483, L61
 Botschwina, P., Horn, M., Seeger, S., & Flügge, J. 1993, *Mol. Phys.*, 78, 191
 Botschwina, P., Oswald, R., Flügge, J., & Horn, M. 1995, *Z. Phys. Chem.*, 188, 29
 Broten, N. W., MacLeod, J. M., Avery, L. W., Irvine, W. M., Höglund, B., Friberg, P., & Hjalmarson, A. 1984, *ApJ*, 276, L25
 Brown, J. M., & Watson, J. K. G. 1977, *J. Mol. Spectrosc.*, 65, 65
 Hight Walker, A. R., Chen, W., Novick, S. E., Bean, B. D., & Marshall, M. D. 1995, *J. Chem. Phys.*, 102, 7298
 Hirota, E., Brown, J. M., Hougen, J. T., Shida, T., & Hirota, N. 1994, *Pure Appl. Chem.*, 66, 571
 Irvine, W. M., et al. 1988, *ApJ*, 334, L107
 Langer, W. D., Velusamy, T., Kuiper, T. B. H., Levin, S., Olsen, E., & Migenes, V. 1995, *ApJ*, 453, 293
 McCarthy, M. C., Travers, M. J., Kovács, A., Chen, W., Novick, S. E., Gottlieb, C. A., & Thaddeus, P. 1997a, *Science*, 275, 518
 McCarthy, M. C., Travers, M. J., Kovács, A., Gottlieb, C. A., & Thaddeus, P. 1997b, *ApJS*, 113, 105
 Pickett, H. M. 1991, *J. Mol. Spectrosc.*, 148, 371
 Saito, S. 1989-1990, *Appl. Spectrosc. Rev.*, 25, 261
 Saito, S., Yamamoto, S., Irvine, W. M., Ziurys, L. M., Suzuki, H., Ohishi, M., & Kaifu, N. 1988, *ApJ*, 334, L113
 Thaddeus, P., Vrtilek, J. M., & Gottlieb, C. A. 1985, *ApJ*, 299, L63
 Townes, C. H., & Schawlow, A. L. 1955, *Microwave Spectroscopy* (New York: McGraw-Hill)
 Turner, B. E., Friberg, P., Irvine, W. M., Saito, S., & Yamamoto, S. 1990, *ApJ*, 355, 546

Note added in proof.—After acceptance of this paper, we learned of an RCCSD(T) calculation of H₂CCCCN by P. Botschwina (1997, personal communication). The equilibrium rotational constant $(B_e + C_e)/2 = 2185.2$ MHz is in excellent agreement with experiment (2186.4301 ± 0.0002 MHz; Table 3), implying that the theoretical geometry is probably very accurate.