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LABORATORY DETECTION OF THE CARBON CHAINS $HC_{15}N$ AND $HC_{17}N$

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ABSTRACT

The linear cyanopolyynes $HC_{15}N$ and $HC_{17}N$ were detected in the laboratory by Fourier transform microwave spectroscopy. Enough rotational lines of each species were measured in the 5–11 GHz frequency range so that precise values for the rotational and centrifugal distortion constants can be determined and the entire rotational spectra of both molecules predicted to better than 1 km s^{-1} in equivalent radial velocity over the range of interest to radio astronomy. Although there is a nearly constant decrement in line intensity from HC_3N to HC_9N of about seven, the decrement decreases by at least a factor of 2 on reaching $HC_{17}N$, and as a result the lines of $HC_{17}N$ are nearly an order of magnitude stronger than predicted by extrapolation from the shorter cyanopolyynes. With a molecular weight of 219 amu and a rotational constant of slightly more than 50 MHz, $HC_{17}N$ is the longest carbon chain identified to date by high-resolution spectroscopy.

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

A surprising property of molecular clouds is the prevalence of highly unsaturated carbon compounds in a regime dominated by hydrogen. In rich interstellar and circumstellar sources, most of the polyatomic molecules to date are carbon chains with alternating single and triple bonds, including 11 of the 19 with more than six atoms, and many more can probably be found if rest frequencies can be measured in the laboratory. Detection, however, is difficult because all but the shortest chains are highly unstable at terrestrial densities, tending to polymerize explosively to more stable compounds with a planar or graphitic structure. Recently, the application of Fourier transform microwave (FTM) spectroscopy to supersonic molecular beams has partly overcome this obstacle, yielding in this laboratory alone 27 new carbon chains of astronomical interest, including the largest interstellar molecule $HC_{11}N$ (Travers et al. 1996a; Bell et al. 1997) and the next larger cyanopolyyne $HC_{13}N$ (Travers et al. 1996b). Here we describe the detection of the next two, $HC_{15}N$ and $HC_{17}N$, shown in Figure 1. For many years laboratory spectroscopy lagged behind radio astronomy in the detection of reactive molecules of this kind, but it is now ahead, and astronomical searches—as they should to be efficient—can now be based on very precise data.

After improvements in sensitivity, our two new chains were detected with the same FTM spectrometer used previously. The observed rotational transitions, all closely harmonic as expected for a linear molecule, are shown in Figure 2, and the measured laboratory frequencies between 5 and 11 GHz are given in Table 1. Typical lines are shown in Figure 3. As for the shorter cyanopolyynes, the rotational and the leading centrifugal distortion constants were determined by fitting the standard expression for the rotational frequencies of a closed-shell linear molecule, $\nu(J) = 2B_0J - 4D_0J^3$, to the data, where J is the rotational angular momentum quantum number of the upper level of the transition. The identifications of both $HC_{15}N$ and $HC_{17}N$ are extremely secure. For both new chains, the best-fit constants (Table 2) are in excellent agreement with those expected: to a few parts in 10^5, the rotational constants B_0 are those predicted by extrapolation from the shorter cyanopolyynes, and, to the expected accuracy, the centrifugal distortion constants D_0 are those calculated on the assumption that D_0/B_0 scales as the inverse fourth power of the chain length, the scaling law found for all chains so far measured, and readily explained on the simple assumption that carbon chains behave as classical elastic rods with a Young's modulus independent of length (Travers et al. 1996a).

In the frequency range measured, the next term in the centrifugal expansion H_0 is expected to make a negligible contribution (of order 1 Hz or less). It is probably not until very high rotational transitions are reached in the vicinity of 100 GHz, with $J \sim 1000$, that this term will contribute as much as 0.3 MHz to centrifugal distortion (i.e., 1 km s^{-1} in equivalent radial velocity). To excite such high transitions, a rotational temperature in excess of 150 K is required, which is much higher than any yet observed in a carbon chain source.

The conditions for optimal production of the two new cyanopolyynes are similar to those of the shorter members (Winnewisser, Creswell, & Winnewisser 1978): a mixture of 0.5% of cyanoacetylene (HC_3N) and 0.5% diacetylene (HC_4H) in neon, a discharge in the throat of our supersonic nozzle of about 1900 V and 50 mA, a gas pulse 300 μs in length at a repetition rate of 6 Hz, and a total gas pressure behind the nozzle of 2.5 atm. The strongest lines were obtained when the cathode was 2 cm from the free expansion and the anode was 1 cm farther upstream. The 2 cm reaction channel results in higher yields of long cyanopolyynes, presumably because the increased number of collisions in the nozzle prior to the free expansion allows time for chains with many atoms to build up.

Since the initial detection of $HC_{13}N$, the sensitivity of our spectrometer (McCarthy et al. 1997b) has been improved by about a factor of 5 by (1) better coupling between the Fabry-Perot cavity and the first stage of amplifier of the receiver, (2) cooling the cavity mirrors of the Fabry-Perot and first-stage amplifier to 77 K (Grabow et al. 1997), and (3) increasing the duty cycle of the pulsed supersonic jet source from 2 to 6 Hz by improving the pumping speed of the system. Careful optimization of the production conditions and precursor concentrations has yielded an additional factor of about 1.5 in sensitivity.

In Figure 4 the intensity of the strongest lines and the relative abundances of the cyanopolyynes are shown as a function of

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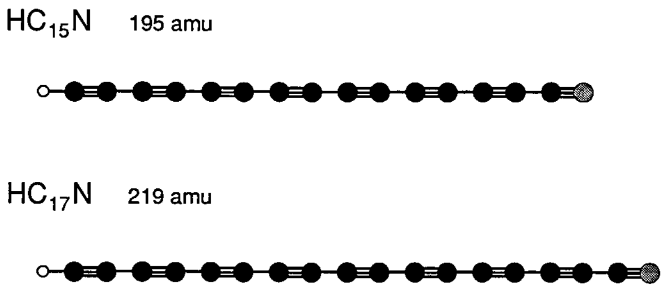

FIG. 1.—Geometrical structures of $HC_{15}N$ and $HC_{17}N$ showing the characteristic alternating single and triple carbon-carbon bonds.

the number of carbon atoms. At longer chain lengths there is a considerably flatter decrement of line intensity with length than expected from HC_3N through HC_9N, and the abundance decrement has almost vanished! The lines of $HC_{17}N$ in particular are nearly an order of magnitude stronger than predicted by the nearly constant decrement in intensity observed for the shorter chains in the series. Indeed, as is readily inferred from the detection limit in Figure 4, $HC_{17}N$ would not have been observed at all with the present instrument if this steeper decrement continued beyond HC_9N. Our new cyanopolyynes are evidently more abundant and more easily detected than might have been expected, and even longer ones are probably within reach with a fairly modest improvement in sensitivity.

Laboratory detection of long carbon chains such as $HC_{15}N$ and $HC_{17}N$ provides definitive evidence for linear structures in the size range where ring isomers are believed to be more stable than chains (von Helden, Gotts, & Bowers 1993; Wang, Rittby, & Graham 1997). With nearly 20 atoms, however, there are a large number of other isomeric forms that are worth considering as possible laboratory and astronomical molecules, including for the particular chains here heterocyclic rings containing nitrogen. A molecule with half as many atoms, C_7H_2, for example, has many more stable isomers with nonlinear heavy atom backbones than with linear or nearly linear ones (McCarthy et al. 1997a). To our knowledge only linear isomers (e.g., HCCNC, HNCCC, HC_4NC, etc.) have been considered for the shortest polyynes (HC_3N and HC_5N); other structures either have not been calculated or at such small sizes are not particularly stable. In the size range of 15–20 atoms an unexplored chemical architecture of considerable richness and diversity may be present, giving rise to a number of observable species in the transition region from the one-dimensional lattice to planar and cyclic carbon.

Long carbon chains are difficult to stretch but easy to bend, and the lowest frequency bends of the present two are probably

TABLE 1

MEASURED ROTATIONAL TRANSITIONS OF $HC_{15}N$ AND $HC_{17}N$

	FREQUENCIES[a]	
$J' \rightarrow J$	$HC_{15}N$ (MHz)	$HC_{17}N$ (MHz)
38 → 37	5468.202	...
39 → 38	5612.102	...
40 → 39	5756.001	...
41 → 40	5899.901	...
42 → 41	6043.800	...
43 → 42	6187.700	...
44 → 43	6331.599	...
45 → 44	6475.499	...
46 → 45	6619.398	...
48 → 47	6907.196	...
49 → 48	7051.096	...
50 → 49	7194.995	...
51 → 50	7338.894	...
55 → 54	...	5577.339
59 → 58	...	5982.960
60 → 59	...	6084.366
61 → 60	...	6185.770
62 → 61	...	6287.178
63 → 62	...	6388.582
64 → 63	9209.578	6489.984
65 → 64	9353.477	6591.391
66 → 65	9497.375	6692.800
70 → 69	10072.968	...
71 → 70	10216.866	...

[a] Experimental uncertainties (1 σ) are 1–2 kHz. Observed minus calculated frequencies are in the range 0–2 kHz; the rms of both fits is about 1.5 kHz.

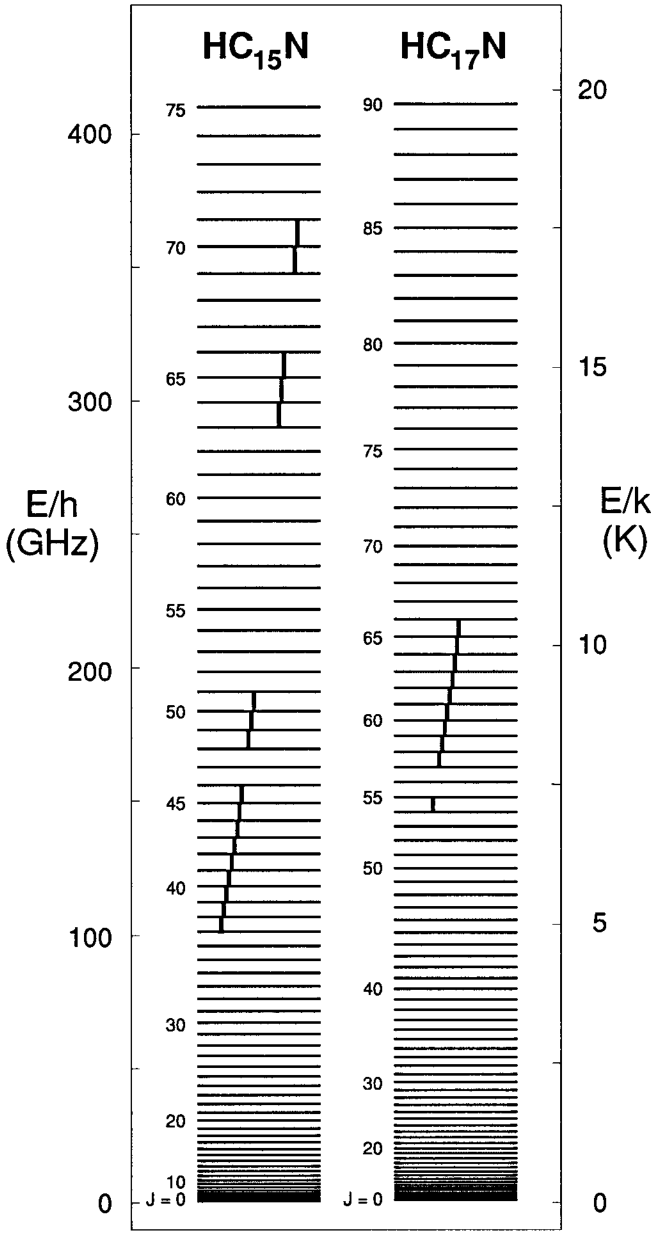

FIG. 2.—Lower rotational levels of $HC_{15}N$ and $HC_{17}N$, with observed transitions indicated (*vertical bars*).

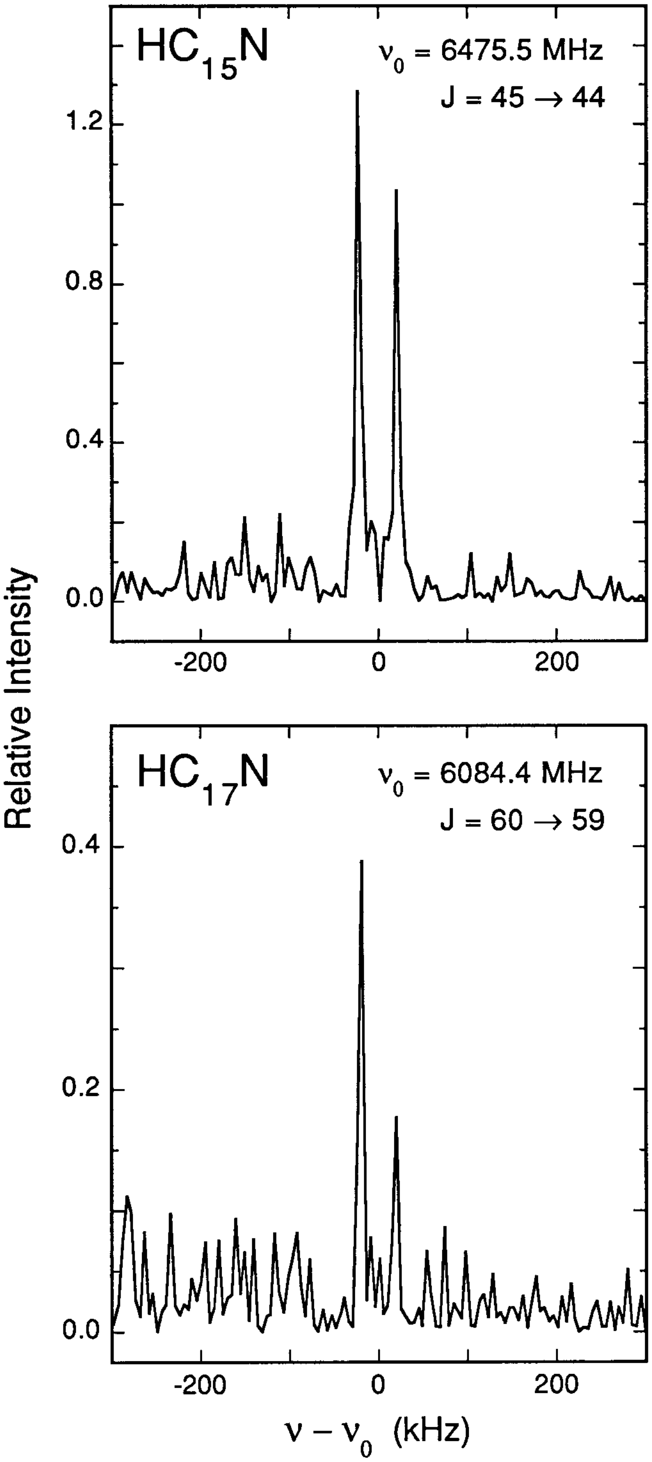

FIG. 3.—Sample lines of $HC_{15}N$ and $HC_{17}N$ obtained with integration times of 13 and 60 minutes, respectively. The double-peaked line shape is instrumental in origin—it results from the Doppler shift of the supersonic jet relative to the two traveling waves that compose the confocal mode of the Fabry-Perot cavity.

TABLE 2

ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS

	$HC_{15}N$		$HC_{17}N$	
CONSTANT	Observed[a] (MHz)	Expected[b] (MHz)	Observed[a] (MHz)	Expected[b] (MHz)
B_0	71.950133(6)	71.951	50.70323(6)	50.703
$D_0 \times 10^6$	0.0369(9)	0.032	0.025(7)	0.014

[a] Uncertainties (in parentheses) are 1 σ in the last significant digit.

[b] Extrapolated from shorter cyanopolyynes by means of a third-order polynomial fit to the rotational constants. For chains longer than HC_7N, this simple extrapolation has been found to yield an accuracy of a few parts in 10^5 when applied step by step. The rotational constants of $HC_{19}N$ and $HC_{21}N$ so estimated are 37.069 and 27.919 MHz, respectively.

within range of existing high-frequency radio telescopes, as a simple classical calculation shows. The frequencies of the bending modes of a thin elastic rod scale as the inverse square of the rod's length (Landau & Lifshitz 1959), so one expects the more "classical" of the transverse vibrations of a long chain, the lowest frequency bend especially, to scale with length in approximately that way. The low-frequency bends measured for HCN (Allen, Tidwell, & Plyler 1956) and HC_3N (Mallinson & Fayt 1976), and those calculated theoretically for the next two in the sequence, HC_5N and HC_7N (Botschwina et al. 1997a, 1997b), fit this scaling law to about 15%. Applied to the chains here, this law predicts that the lowest frequency bend of $HC_{15}N$ should be 16 times less than that of HC_3N at 222 cm^{-1}, or at about 14 cm^{-1}, and that of $HC_{17}N$ should be 20 times less than that of HC_3N, or at about 11 cm^{-1}.

Both these frequencies lie comfortably within the range of existing astronomical telescopes, for example, the Caltech Submillimeter 10.4 m Telescope on Mauna Kea. A precise laboratory measurement, however, is almost certainly a prerequisite for an astronomical search. The transition dipole moments for these low-frequency bends are even more uncertain than the frequencies. Estimated transition dipoles for the $HC_{2n+1}N$ bending transitions range from less than 0.1 D (from quantum chemical calculations) to of order 1 D (from elementary bond-dipole analysis; A. L. Cooksy 1997, private communication), the uncertainty resulting from the largely unknown distribution of the dipole moment along the long conjugated chain. Quantum chemical calculations of the structures of $HC_{15}N$ and $HC_{17}N$

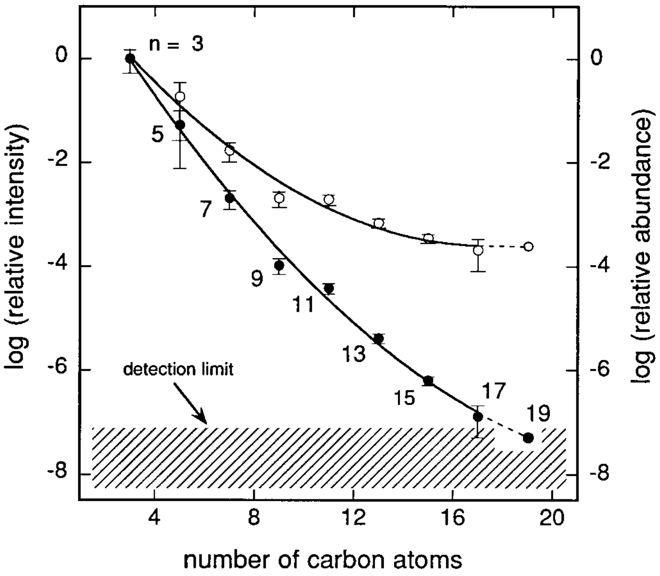

FIG. 4.—Relative intensity of the strongest rotational lines of the cyanopolyynes (*filled circles*) and their relative abundance (*open circles*) in the FTM spectrometer, as a function of the number of carbon atoms in the chain. The error bars are estimated 2 σ uncertainties. Relative abundances are obtained from line intensities by taking into account the dependence on the chain length of the rotational partition functions and dipole moments. The limit of the detection sensitivity is approximately that achieved in a total observation time of 3 hr.

might yield considerably better transition moments and are therefore highly desirable before attempting to observe these undoubtedly faint vibrational transitions in astronomical sources. On the basis of CCSD(T) calculations up to $HC_{11}N$ (Botschwina & Horn 1997), the permanent electric dipole moments of $HC_{15}N$ and $HC_{17}N$ are estimated to be 5.81 and 5.93 D, respectively, with an uncertainty of about 0.05 D (P. Botschwina 1997, private communication).

In the interstellar gas, as in our laboratory source, long chains may be more abundant than extrapolation from the short chains suggests. A solid-state physicist is inclined to describe the structures in Figure 1 as one-dimensional solid lattices, not gas-phase molecules, and chains as large as those here may, in important respects, behave in interstellar space more like grains than familiar smaller molecules. In particular, they may be relatively stable against processes like dissociative recombination and photodissociation, which rapidly destroy small molecules and ions in diffuse interstellar clouds—one of the reasons that chains comparable in size to those in Figure 1 are plausible candidates for the carriers of the diffuse interstellar bands (Thaddeus 1994). This is a compelling reason to attempt to find still longer chains in the laboratory by a refinement of the present techniques, such as the cooling of crucial components of the present spectrometer to the temperature of liquid helium.

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