

DETECTION OF THE LINEAR RADICAL HC₄N IN IRC +10216

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ABSTRACT

We report the detection of the linear radical HC₄N in the C-rich envelope of IRC +10216. After HCCN, HC₄N is the second member of the allenic chain family HC_{2n}N observed in space. The column density of HC₄N is found to be $1.5 \times 10^{12} \text{ cm}^{-2}$. The abundance ratio HC_{2n}N/HC₄N is 9, a factor of 2 larger than the decrement observed for the cyanopolyynes (HC_{2n+1}N/HC_{2n+3}N). Linear HC₄N has a ³Σ electronic ground state and is one of the three low-energy isomeric forms of this molecule. We have searched for the bent and ringed HC₄N isomers but could only derive an upper limit to their column densities: $\leq 3 \times 10^{12} \text{ cm}^{-2}$ (at 3 σ).

Subject headings: astrochemistry — ISM: molecules — line: identification — stars: AGB and post-AGB — stars: individual (IRC +10216)

Online material: color figure

1. INTRODUCTION

The detection of long linear carbon chain molecules in interstellar and circumstellar clouds has come as a surprise. Ab initio calculations show that long linear species are usually more energetic than their ring or ring-chain isomers and are observed to be less stable in the earthbound environment. Yet many linear chains, such as the cyanopolyynes HC_{2n+1}N, are found to be widespread and abundant in the cold circumstellar and interstellar clouds. This abundance of long chains and the scarcity of rings in the cold UV-shielded clouds yield keys to the formation of large molecules in interstellar space and, maybe, can help us to understand to the origin of the diffuse interstellar bands (Tulej et al. 1998; Maier et al. 2004).

Carbon chain molecules can be classified into several families, depending on the structure of their linear backbone (acetylenic backbone with alternating single and triple carbon-carbon bonds or cumulenic backbone with double bonds), on their electronic ground state (open shell or closed shell), and on their end groups (H, CN, CH₂, or CH₃). The two most widespread families are the polyynes (HC_{2n+1}N and CH₃C_{2n+1}H) and the polyacetylenic radicals (C_nH). The most abundant is presumably the family of polyacetylenes (HC_{2n}H), which, unfortunately, are nonpolar, hence not detectable at radio wavelengths. Note, however, that these species have been detected in the mid-infrared with the *Infrared Space Observatory* (Cernicharo et al. 2001a, 2001b).

It has been proposed that the polyynes and carbon chain radicals form directly in the gas phase through reactions of CCH with polyynes, polyacetylenes, and/or polyacetylenic ions (e.g., HC_{2n+1}N + CCH → HC_{2n+3}N + H; Herbst 1989; Cherchneff et al. 1993; Millar et al. 2000). Such reactions tend to insert two triply bonded carbon atoms into the carbon backbone, uncoupling the formation of chains with an odd number of C atoms from those with an even number, which could explain the alternation between high and low abundances observed as the length of the C backbone increases. For example, in the molecular shell around IRC +10216 and in the dark cloud TMC1, the two main astronomical sources of carbon chain molecules, the abundance of the C_nH radicals with an

even number of C atoms is ≈30 times larger than that of radicals of similar size with an odd number of carbon atoms. In contrast, the abundance decrement between successive species within the even (or odd) number of C atom families, C_nH/C_{n+2}H, is found to be only 4–6 (Cernicharo et al. 1987; Guélin & Cernicharo 1991; Cernicharo & Guélin 1996).

The same seems to apply to the chains terminated by CN: the abundance decrement between cyanopolyynes, HC_{2n+1}N/HC_{2n+3}N, is between 3 and 5 (for n = 1–4), whereas HCCN, the first member of the “even” chain family, is found to be ≈200 times less abundant than HC₃N (Guélin & Cernicharo 1991). So far, this similarity between polyynes and carbon chains could not be further explored as no other member of the HC_{2n}N was observed in space. In this Letter, we report the detection in IRC +10216 of the next member of this family, HC₄N, and show that the HCCN/HC₄N abundance ratio is 20 times smaller than the HC₃N/HCCN ratio.

2. OBSERVATIONS

Contrary to cyanopolyynes, which are linear and have ¹Σ electronic ground states, the lowest energy form of HCCN is a quasi-linear triplet (Saito et al. 1984; Rice & Schaefer 1987). Similarly, ab initio calculations (Ikuta et al. 2000; Aoki & Ikuta 1993; Aoki et al. 1994) predict that one of the three low-energy isomers of HC₄N is a linear triplet with a ³Σ ground state (hereafter HC₄N; see Fig. 1), the other two being a c₃ ring (c₃-HC₄N) and a bent carbene structure (b-HC₄N). The three isomers have been recently observed in the laboratory (Tang et al. 1999; McCarthy et al. 1999a, 1999b); their microwave spectra are now fully characterized, opening the way to unambiguous identification in astronomical sources.

The astronomical observations were carried out between 1995 and 2003 using the 30 m IRAM radio telescope at Pico Veleta, Sierra Nevada (Spain). Most of the data were taken during a sensitive 3 mm wavelength (80–115 GHz) line survey of IRC +10216, which has an rms noise of few mK per 1 MHz wide channel. These data were complemented in 2003 August with more sensitive observations at the frequencies of SiNC (Guélin et al. 2004).

We detected a number of U lines, nine of which could be grouped into three close triplets with similar line intensities. The center frequencies of the triplets were harmonically related, implying a common linear carrier with a rotation constant

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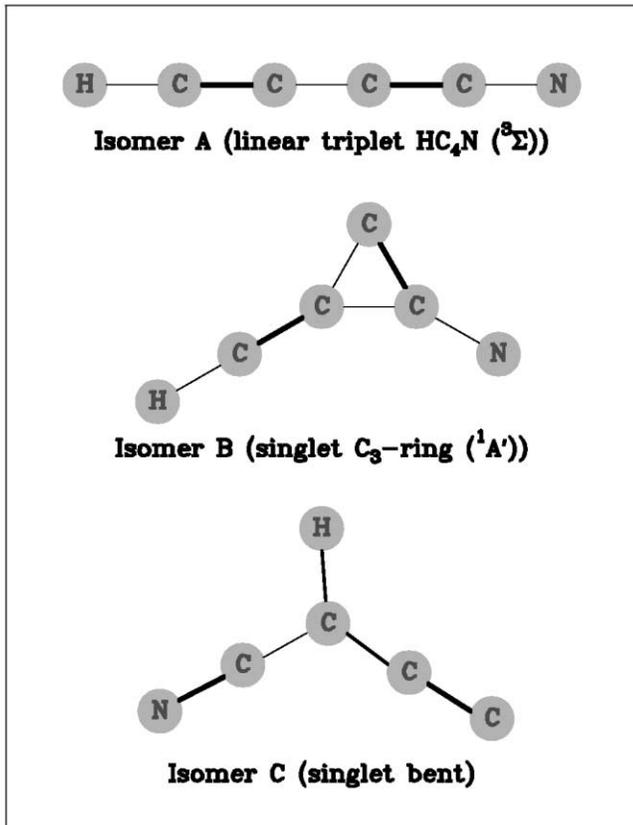


FIG. 1.—Three isomers of HC₄N considered in this Letter. The structures are taken from McCarthy et al. (1999b) and Ikuta et al. (2000). Isomer A is linear triplet HC₄N (HC₄N), isomer B corresponds to the c₃ ring structure (c₃-HC₄N), and isomer C is the singlet bent HC₄N (b-HC₄N). [See the electronic edition of the Journal for a color version of this figure.]

$B_0 = 2302$ MHz. The rotation constant suggested a molecule similar to C₃H ($B_0 = 2287$ MHz) and the triplet structure an even number of electrons. This pointed out to HC₄N, and we could quickly check that the frequencies of our nine U lines agreed with those predicted from the spectroscopic constants of Tang et al. (1999). That HC₄N was the carrier of our new lines was definitely confirmed when we succeeded in detecting a fourth line triplet (see Fig. 2e and Table 1) during a dedicated search made in 2003 October.

The observations were made in the wobbling mode, with the secondary nutating at a rate of 0.5 Hz, in order to achieve very flat baselines (see Fig. 2 and below). Only a zero-order baseline with an offset of ≈ 40 mK, corresponding to the thermal dust emission of the circumstellar envelope, has been removed from the spectra. Two SIS 3 mm receivers, with orthogonal polarizations and system temperatures of 100–130 K, were used in parallel with two 1.3 mm receivers. The 3 mm data were co-added, thus increasing the effective integration time and decreasing the rms noise. In the case of our best spectrum (Fig. 2a), the effective integration time and noise temperature were equal to 52 hr and 0.5 mK per 1 MHz wide channel, respectively.

The temperature scale was calibrated with the help of two absorbers, respectively, at room and liquid nitrogen temperature, using the atmosphere transparency model ATM developed by Cernicharo (1985) currently installed in the 30 m telescope online calibration software (see also Pardo et al. 2001). Pointing and focus were regularly checked on planets and on the strong

nearby quasar OJ 287. Between the pointing sessions, we monitored the shapes of the strong lines that were observed in parallel with the 1.3 mm receivers. The cusped shapes and the line horn-to-center intensity ratios depend indeed critically on the accuracy of the telescope pointing and focus. Thanks to these precautions, the intensities of the lines observed several times in the 1995–2003 period were found constant within 10%.

3. RESULTS AND DISCUSSION

Figure 2 shows the spectra covering the four triplets, which correspond to four successive rotational transitions of HC₄N (from $N = 18 \rightarrow 17$ to $21 \rightarrow 20$). The spectrum centered at 82.9 GHz, which was observed while searching for SiCN (Guélin et al. 2000), SiNC (Guélin et al. 2004), and HC₄N, is shown twice in this figure: full scale, i.e., from 82,650 to 83150 MHz (Fig. 2a), and half-scale, around the HC₄N $N = 18 \rightarrow 17$ triplet (Fig. 2b). The rms noise in this 1 MHz resolution spectrum is only 0.5 mK, which makes it one of the most sensitive spectra ever obtained with the 30 m telescope.

Forty spectral lines are detected in Figure 2a. Most are weak and partly blended. The blended lines are easily resolved, thanks to their characteristic cusps, sharp edges, and constant width in velocity (this shape results from the uniform expansion of the outer circumstellar envelope). We can identify almost 60% of these lines with the help of the molecular line catalog maintained by one of us (J. C.) and described in Cernicharo et al. (2000). The catalog contains the millimeter transitions of some 1200 different molecular species. Of the remaining 40% of unidentified lines, at least half could be tentatively assigned to some heavy species (see below). The carriers of the unambiguously identified lines are mostly ¹²C and ¹³C isotopomers of long carbon chain molecules (C₄H, C₇H, C₈H, H₂C₃, H₂C₄, and HC₃N) as well as silicon compounds, such as SiC₄, SiCN, and SiNC. For the first time, we detect a doubly substituted ¹³C isotopomer of cyanoacetylene: H¹³C¹³CCN (see Fig. 2e; 96623 MHz; several lines of the three doubly substituted ¹³C isotopomers of HC₃N have been detected in our 3 mm line survey of IRC +10216).

The number of unidentified lines at the 3 mK level detected in the four frequency bands is ≈ 15 lines GHz⁻¹. Several of these lines probably arise from vibrationally excited C₃H and C₆H and their ¹³C isotopomers, species for which we have no accurate laboratory frequencies (for example, U82924 and/or U82938 and U82995 could well correspond to the $J = 61/2 \rightarrow 59/2$ lines of ²Π_{1/2} CCCCC¹³CH; U82677, U82737, U92034, and U92045 could correspond to different Σ and Π vibronic states of the lowest energy bending mode of C₆H). Others probably come from ¹³C and ²⁹Si isotopomers of SiC₄ (for example, the $J = 29-28$ and $J = 32-31$ lines of ²⁹SiC₄ at 87588 and 96648 MHz, respectively, and the $J = 27-26$ line of SiC¹³CCC at 82704 MHz). Finally, some unidentified lines are close to transition frequencies predicted for SiC₅ (U82746, U82876, and U82995), C₅S (U83038), and KCN (for which we have detected several additional lines that will be published elsewhere), and C₉H (U83011). Obviously, the U-line density is too high at present to claim the detection of any of these species, which all have a rich millimeter spectrum, on the basis of just one, two, or even three weak lines.

The HC₄N lines shown in Figure 2 are cusped (see, in particular, Fig. 2a, where the lines have the highest signal-to-noise ratio). This implies that this molecule is mostly confined into the outer part of the circumstellar envelope, presumably in the

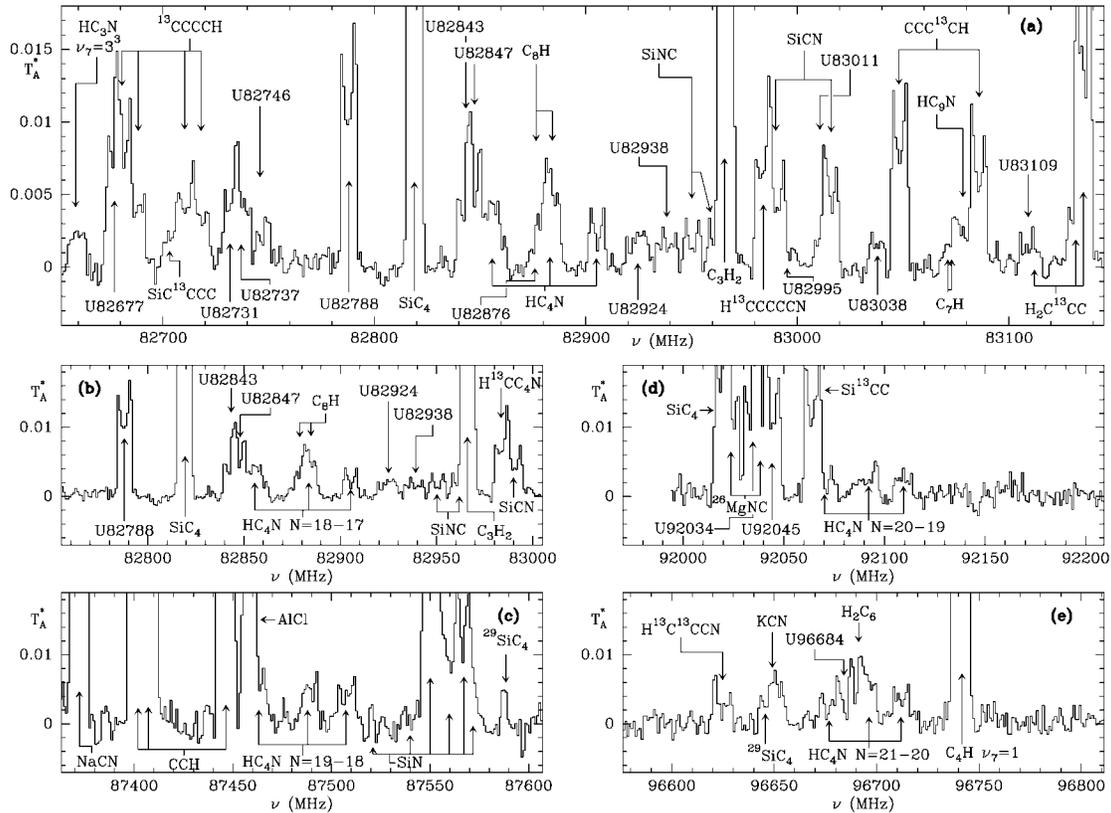


FIG. 2.—Four spectra observed toward IRC +10216 with the IRAM 30 m telescope, centered on the $N = 18-17$ through $21-20$ rotational transitions of HC₄N. The intensity scale is T_A^* , and the spectral resolution is 1 MHz. The rms noise in the upper spectrum is 0.5 mK.

15" radius hollow shell where most of the free radicals and carbon chains are found (Guélin et al. 1993). From the intensities of the four triplets, we derive a rotational temperature of 25 ± 4 K, close to that derived for HC₃N.

The permanent dipole moment of HC₄N has been calculated by Ikuta et al. (2000) to be 4.3 D. Using this value and assuming thermal equilibrium at 25 K, we derive a column density for HC₄N of 1.5×10^{12} cm⁻².

We have recalculated the rotation temperature and the abundance of HCCN by adding to the 2 mm lines reported by Guélin & Cernicharo (1991) the lines observed in our new 3 mm survey. We find a rotational temperature of 15 ± 2 K, slightly higher

than our previous estimate (12 ± 2 K). The HCCN lines are also cusped, and the HCCN column density, assuming a dipole moment of 3 D (Guélin & Cernicharo 1991), is 1.4×10^{13} cm⁻². We note that the increase in rotation temperature between HCCN and HC₄N is not surprising as a similar increase is observed between the cyanopolyynes HC₃N and HC₅N.

The HCCN/HC₄N abundance ratio is found to be equal to 9. This is about twice the decrement observed between the successive members of the cyanopolyynes family, HC₃N/HC₅N, but 20–40 times less than the HC₃N/HCCN (≈ 200) and HC₅N/HC₄N (400) abundance ratios, which confirms that, like the carbon chain radicals, the even and odd HC _{ν} N families have parallel

TABLE 1
OBSERVED HC₄N LINE PARAMETERS

Observation Frequency (MHz)	Calculated Frequency (MHz)	Transition ($N, J \rightarrow N', J'$)	$\int T_A^* dv$ (mK km s ⁻¹)
82855.6(6)	82855.52	18, 17–17, 16	110(20)
82884.1(10) ^b	82883.57	18, 18–17, 17	94(14)
82905.4(3)	82905.41	18, 19–17, 18	86(10)
87463.5(10) ^b	87463.15	19, 18–18, 17	127(35)
87487.9(10)	87487.87	19, 19–18, 18	135(35)
87507.6(5)	87507.31	19, 20–18, 19	142(20)
92070.0(10) ^b	92070.22	20, 19–19, 18	90(24)
92092.4(10)	92092.13	20, 20–19, 19	105(24)
92109.2(6)	92109.48	20, 21–19, 20	90(18)
96677.1(5)	96676.82	21, 20–20, 19	75(15)
96696.0(10) ^b	96696.32	21, 21–20, 20	100(23)
96712.1(5)	96711.88	21, 22–20, 21	75(15)

NOTES.—The numbers in parentheses are 1σ uncertainties on the last digit, derived from least-squares fits; they do not include the 5% calibration uncertainty. A superscript “b” denotes a partly blended line. The frequencies in the second column are calculated from the spectroscopic constants measured by Tang et al. (1999) in the laboratory.

but distinct formation paths. We have also searched in our 3 mm line survey for the linear triplet HC_6N but without success. The 3σ upper limit to the column density of this species, assuming a rotation temperature of 25 K, is $1 \times 10^{13} \text{ cm}^{-2}$, not low enough to constrain significantly the $\text{HC}_4\text{N}/\text{HC}_6\text{N}$ ratio but already 25 times lower than the HC_7N column density (Cernicharo et al. 1987).

As noted above, the carbon chain molecules C_{2n+1}N and HC_{2n+1}N are thought to be formed in IRC +10216 from the reaction of radicals such as CCH and CN with carbon chain molecules or radicals (Cherchneff et al. 1993; Millar et al. 2000). Similarly, we could consider that HC_4N may form through the reaction of C_3N and C_3H with HCN and CH_2 , e.g., $\text{C}_3\text{H} + \text{HCN} \rightarrow \text{HC}_4\text{N} + \text{H}$ or maybe $\text{C}_3\text{N} + \text{CH}_2 \rightarrow \text{HC}_4\text{N} + \text{H}$. All the reactants are relatively abundant in the outer layers of the circumstellar envelope, and we expect, by analogy with similar reactions studied in the laboratory, that at least one of these reactions could proceed rapidly.

Another path proposed for the formation of cyanopolyynes involves ion-molecule reactions yielding $\text{H}_3\text{C}_n\text{N}^+$ or $\text{H}_2\text{C}_n\text{N}^+$, followed by the dissociative recombination of these ions (Glassgold et al. 1986; Howe & Millar 1990). The low abundance of ions in IRC +10216 makes this path relatively slow (Cherchneff et al. 1993). Moreover, in the case of HCCN and HC_4N , the reaction of HCN with CH_3^+ , leading to $\text{H}_2\text{C}_2\text{N}^+ + \text{H}_2$ (or $\text{H}_3\text{C}_2\text{N}^+ + \text{H}$), does not proceed (Guélin & Cernicharo 1991), making the ion-molecule path even slower and less likely than in the case of cyanopolyynes.

Finally, a last process, formation on dust grains followed by photodesorption when the grains reach the outer envelope layers, has been advocated in the case of IRC +10216 (Guélin et al. 1993). Such a mechanism may well produce HCCN, HC_4N , and the cyanopolyynes observed in the outer shell but would provide no simple explanation for why the abundance decrement within each family seems to be so constant.

The HC_4N lines detected during this study belong to the linear triplet isomer. We have unsuccessfully searched for the singlet bent HC_4N isomer and for the c_3 ring cyclic isomer. Those latter have a permanent dipole moment almost as large as the linear isomer: 2.96 D ($\mu_a = 2.9$ D, $\mu_b = 0.5$ D) and 3.48 D ($\mu_a = 3.15$ D, $\mu_b = 1.49$ D), respectively, versus 4.3 D for linear HC_4N (McCarthy et al. 1999a, 1999b; Ikuta et al. 2000). The upper limits to the column density of these species are $\approx 3 \times 10^{12} \text{ cm}^{-2}$, assuming the same rotational temperature as that for linear triplet HC_4N (25 K).

The most accurate calculations of the HC_4N structure to date (level CCSD[T]/cc-pCVTZ) predict that the singlet ring isomer of HC_4N lies 4.2 kcal mol⁻¹ below the linear triplet isomer (Ikuta et al. 2000). If this result is confirmed, the nondetection of the ringed isomer (and of the bent isomer) would further stress the discrimination against ringed structures already noted in the case of carbon chain radicals.

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