Detection of the linear radical HC$_4$N in IRC+10216

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ABSTRACT

We report the detection of the linear radical HC$_4$N in the C-rich envelope of IRC+10216. After HCCN (Guélin and Cernicharo 1991), HC$_4$N is the second member of the allenic chain family HC$_{2n}$N observed in space. The column density of HC$_4$N is found to be 1.5 10^{12} cm^{-2}. The abundance ratio HC$_2$N/HC$_4$N is 9, a factor of two larger than the decrement observed for the cyanopolyynes (HC$_{2n+1}$N/HC$_{2n+3}$N). Linear HC$_4$N has a $^3\Sigma$ electronic ground state and is one of the 3 low-energy isomeric forms of this molecule. We have searched for the bent and ringed HC$_4$N isomers, but could only derive an upper limit to their column densities $\leq$ 3 10^{12} cm^{-2} (at 3-σ).

Subject headings: Astrochemistry —line: identification— ISM: molecules— radio lines: ISM, star— circumstellar matter — stars: AGB and post-AGB, individual (IRC+10216)

1. Introduction

The detection of long linear carbon-chain molecules in interstellar and circumstellar clouds has come as a surprise. Ab initio calculation 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, may be, can help us to understand to the origin of the diffuse interstellar bands (Tulej et al. 1998; Maier, Walker and Bohlender 2004).

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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, CH_2 or CH_3). The two most widespread families are the polyynes ($HC_{2n+1}N$ and $CH_3C_{2n+1}H$) and the polyacetylenic radicals (C_nH). The most abundant is presumably the family of polyacetylenes ($HC_{2n}H$), which, unfortunately are non-polar, 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,b).

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. $HC_{2n+1}N + CCH \rightarrow HC_{2n+3}N + H$) (Herbst 1989; Cherchneff, Glassglod and Mamon 1993; Millar, Herbst and Bettens 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 alternance 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 $\simeq 30$ 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-atoms families, $C_nH/C_{n+2}H$, is found to be only 4-6 (Cernicharo et al. 1987; Guélin and Cernicharo 1991).

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 $\simeq 200$ times less abundant than HC_3N (Guélin and 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, HC_4N, and show that the $HCCN/HC_4N$ abundance ratio is 20 times smaller than the $HC_3N/HCCN$ ratio.

2. Observations

Contrary to cyanopolyynes which are linear and have $^1\Sigma$ electronic ground states, the lowest energy form of HCCN is a quasi-linear triplet (Saito et al. 1984, Rice and Schaeffer 1987). Similarly, ab initio calculations (Ikuta, Tsuboi and Aoki 2000; Aoki and Ikuta

1993; Aoki, Ikuta and Murakami 1993) predict that one of the 3 low-energy isomers of HC_4N is a linear triplet with a $^3\Sigma$ ground state (hereafter HC_4N, see Fig. 1), the other two being a C_3-ring (c_3-HC_4N) and a bent carbene structure (b-HC_4N). The 3 isomers have been recently observed in the laboratory (Tang, Sumiyoshi and Endo 1999; McCarthy et al. 1999a,b); 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 radiotelescope 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 r.m.s. noise of few mK per 1 MHz-wide channel. These data were complemented in August 2003 with more sensitive observations at the frequencies of SiNC (Guélin et al. 2004).

We detected a number of U-lines, 9 of which could be grouped into 3 close triplets with similar line intensities. The center frequencies of the triplets were harmonically related, implying a common linear carrier with a rotation constant $B_\circ = 2302$ MHz. The rotation constant suggested a molecule similar to C_5H ($B_\circ = 2287$ MHz) and the triplet structure an even number of electrons. This pointed out to HC_4N, and we could quickly check that the frequencies of our 9 U-lines agreed with those predicted from the spectroscopic constants of Tang, Sumiyoshi and Endo (1999). That HC_4N 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 October 2003.

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 $\simeq 40$ 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, so increasing the effective integration time and decreasing the r.m.s. noise. In the case of our best spectrum (Fig. 2a), the effective integration time and noise temperature were equal to 52 h 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 on-line calibration software (see also Pardo, Cernicharo and Serabyn 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 crit-

ically 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 4 triplets, which correspond to 4 successive rotational transitions of HC_4N (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 HCCN, is shown twice in this figure: full scale, i.e. from 82650 MHz to 83150 MHz (Fig. 2a) and half-scale, around the HC_4N N=18$\rightarrow$17 triplet (Fig. 2b). The r.m.s. noise in this 1 MHz resolution spectrum is only 0.5 mK, which makes it one of the the most sensitive spectra ever obtained with the 30-m telescope.

Forty spectral lines are detected in Fig. 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 (JC) and described in Cernicharo, Guélin and Kahane (2000). The catalog contains the mm transitions of some 1200 different molecular species. Of the remaining 40% unidentified lines, at least half could be tentatively assigned to some heavy species (see below). The carriers of the unambiguously identified lines are mostly ^{12}C and ^{13}C isotopomers of long carbon chain molecules (C_4H, C_7H, C_8H, H_2C_3, H_2C_4, and HC_5N), as well as silicon compounds, such as SiC_4, SiCN, and SiNC. For the first time, we detect a doubly-substituted ^{13}C isotopomer of cyanoacetylene: $H^{13}C^{13}CCN$ (see Fig2e, 96623 MHz; several lines of the three doubly-substituted ^{13}C isotopomers of HC_3N have been detected in our 3mm line survey of IRC+10216).

The number of unidentified lines at the 3 mK level detected in the 4 frequency bands is $\simeq$15 lines/GHz. Several of these lines probably arise from vibrationally excited C_5H and C_6H and their ^{13}C 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 $^2\Pi_{1/2}$ $CCCCC^{13}CH$; U82677, U82737, U92034 and U92045 could correspond to different Σ and Π vibronic states of the lowest energy bending mode of C_6H). Others probably come from ^{13}C and ^{29}Si isotopomers of of SiC_4 (for example the J=29-28 and J=32-31 lines of $^{29}SiC_4$ at 87588 and 96648 MHz respectively and the J=27-26 line of $SiC^{13}CCC$ at 82704 MHz). Finally, some unidentified lines are close to transition frequencies predicted for SiC_5 (U82746, U82876 and U82995), C_5S (U83038) and KCN (for which we have detected several

additional lines that will be published elsewhere), and C_9H (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 mm spectrum, on the basis of just one, two, or even three weak lines.

The HC_4N lines shown in Fig. 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 15"-radius hollow shell where mos t of the free radicals and carbon chains are found (Guélin, Lucas and Cernicharo 1993). From the intensities of the four triplets we derive a rotational temperature of 25 ± 4 K, close to that derived for HC_3N.

The permanent dipole moment of HC_4N has been calculated by Ikuta, Tsuboi and Aoki (2000) to be 4.3 D. Using this value and assuming thermal equilibrium at 25 K, we derive a column density for HC_4N of $1.5 \ 10^{12}$ cm^{-2}.

We have re-calculated the rotation temperature and the abundance of HCCN by adding to the 2-mm lines reported by Guélin and 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 and Cernicharo 1991), is $1.4 \ 10^{13}$ cm^{-2}. We note that the increase in rotation temperature between HCCN and HC_4N is not surprising as a similar increase is observed between the cyanopolyynes HC_3N and HC_5N.

The HCCN/HC_4N abundance ratio is found equal to 9. This is about twice the decrement observed between the successive members of the cyanopolyynes family, HC_3N/HC_5N, but $20-40$ times less than the HC_3N/HCCN ($\simeq 200$) and HC_5N/HC_4N (400) abundance ratios, which confirms that, like the carbon chain radicals, the even and odd HC_nN families have parallel, but distinct formation paths. We have also searched in our 3mm 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 $1 \ 10^{13}$ cm^{-2}, not low enough to constrain significantly the HC_4N/HC_6N 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, Glassglod and Mamon 1993; Millar, Herbst and Bettens 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., $C_3H + HCN \rightarrow HC_4N + H$, or may be $C_3N + CH_2 \rightarrow HC_4N + H$. 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 $H_3C_nN^+$ or $H_2C_nN^+$, followed by the dissociative recombination of these ions (Glassgold, Lucas and Omont 1986; Howe and Millar 1990). The low abundance of ions in IRC+10216 makes this path relatively slow (Cherchneff, Glassglod and Mamon 1993). Moreover, in the case of HCCN and HC_4N, the reaction of HCN with CH_3^+, leading to $H_2C_2N^+ + H_2$ (or $H_3C_2N^+ + H$), does not proceed (Guélin and 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, Lucas and Cernicharo 1993). Such a mechanism may well produce HCCN, HC_4N, and the cyanopolyynes observed in the outer shell, but would provide no simple explanation to 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: 2.96D (μ_a=2.9 D, μ_b=0.5 D) and 3.48 D (μ_a=3.15 D, μ_b=1.49 D), respectively, versus 4.3 D for linear HC_4N (McCarthy et al. 1999a,b; Ikuta, Tsuboi and Aoki 2000). The upper limits to the column density of these species are $\simeq 3 \ 10^{12} \ cm^{-2}$, assuming the same rotational temperature than 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 below the linear triplet isomer (Ikuta, Tsuboi and Aoki 2000). If this result is confirmed, the non-detection 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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Table 1: Observed HC$_4$N line parameters

Obs. Freq. MHz	Calc. Freq. MHz	Transition (N,J→N',J')	$\int T_A^* dv$ mK.kms^{-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)

Table 1: The number in parenthesis are 1σ uncertainties on the last digit, derived from least square fits; they do not include the 5% calibration uncertainty. [b] denotes a partly blended line. The frequencies in col. 2 are calculated from the spectroscopic constants measured by Tang, Sumiyoshi and Endo (1999) in the laboratory.

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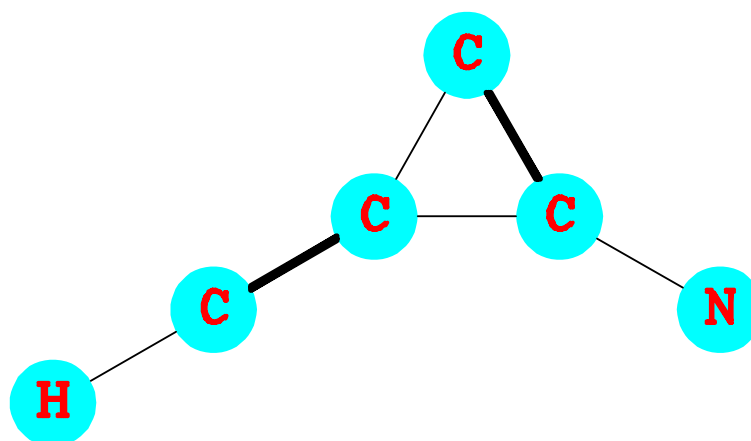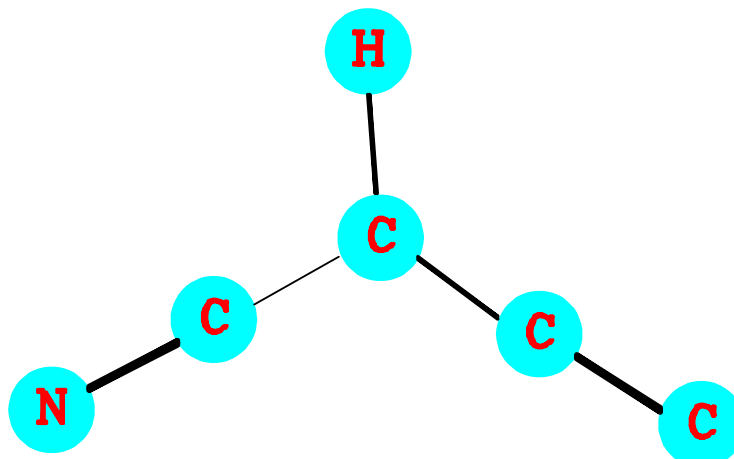
Fig. 1.— The three isomers of HC$_4$N considered in this paper. The structures are taken from McCarthy et al. (1999b) and Ikuta, Tsuboi and Aoki (2000). Isomer *A* is linear triplet HC$_4$N (HC$_4$N), isomer *B* corresponds to the C$_3$-ring structure (c$_3$-HC$_4$N), and isomer *C* is the singlet bent HC$_4$N (b-HC$_4$N).

(a)

CCC^{13}CH

U83109

H$_2$C$_3$

83100

HC$_9$N

C$_7$H

SiCN

U83011

U83038

H^{13}CCCCCN

U82995

83000

C$_3$H$_2$

SiNC

U82938

U82924

ν (MHz)

82900

(d)

SiC$_4$

Si^{13}CC

HC$_4$N N=20−19

^{26}MgNC

U92045

U92034

92000

92050

92100

92150

92200

ν (MHz)

T$_A^*$

0.01

0

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 HC$_4$N. The intensity scale is T$_A^*$, the spectral resolution 1 MHz. The r.m.s. noise in the upper spectrum is 0.5 mK.