IMPLICATION OF FORMATION MECHANISMS OF HC₅N IN TMC-1 AS STUDIED BY ¹³C ISOTOPIC FRACTIONATION

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ABSTRACT

We observed the J = 9 − 8 and 16 − 15 rotational transitions of the normal species and five ¹³C isotopologues of HC₅N to study its formation mechanisms toward the cyanopolyne peak in Taurus Molecular Cloud-1, with the 45-m radio telescope of the Nobeyama Radio Observatory. We detected the five ¹³C isotopologues with high signal-to-noise ratios between 12 and 20, as well as the normal species. The abundance ratios of the five ¹³C isotopologues of HC₅N are found to be 1.00:0.97:1.03:1.05:1.16 (±0.09) (1σ) for [H¹³CCCN];[H¹³CCCN]:[HCC¹³CCCN];[HCC¹³CCCN];[HCC₁₃CCCN]. We do not find any significant differences among the five ¹³C isotopologues. The averaged [HC₅N]/[¹³C isotopologue] abundance ratio is determined to be 94 ± 6 (1σ), which is slightly higher than the local interstellar elemental ¹²C/¹³C ratio of 60–70. Possible formation pathways are discussed on the basis of these results.

Key words: astrochemistry – ISM: individual objects (TMC-1) – ISM: molecular

1. INTRODUCTION

More than 180 molecules have been detected in the interstellar medium and circumstellar shells of evolved stars, and approximately 40% of them are classified into carbon-chain molecules. It is therefore of fundamental importance for astrochemistry to study their formation processes. However, these molecules are so reactive due to unsaturated chemical bonds and/or unpaired electrons that laboratory measurements of their reaction rates are not routine experiments. Although formation mechanisms of the carbon-chain molecules have mainly been studied by chemical model calculations (e.g., McElroy et al. 2013; Wakelam et al. 2015), it is still difficult to reproduce molecular abundances derived by observations and to determine formation mechanisms of carbon-chain molecules because of uncertain rate coefficients and of poor knowledge of elementary reactions involving carbon-chain molecules.

Another method to study major formation pathways of molecules is based mainly on observations. Recent developments of radio astronomical instruments allow us to detect low-abundance species, including rare isotopologues, with a reasonable observation time. Formation mechanisms of some representative carbon-chain molecules have been investigated by observing their ¹³C isotopic fractionation, such as HC₃N (Takano et al. 1998), CCH (Sakai et al. 2010), CCS (Sakai et al. 2007), C₂S, and C₂H (Sakai et al. 2013), toward the cyanopolyne peak in Taurus Molecular Cloud-1 (TMC-1 CP; d = 140 pc, and cyclic-C₃H₂ (Yoshida et al. 2015) toward the low-mass star-forming region L1527. TMC-1 CP is a representative cold dark cloud where various carbon-chain molecules are abundant. For instance, Kaifu et al. (2004) carried out spectral line survey observations in the 8.8–50 GHz region toward TMC-1 CP with the 45-m radio telescope of the Nobeyama Radio Observatory (NRO), and demonstrated that this source is rich in carbon-chain molecules.

Cyanoacetylene, HC₃N, is a very abundant carbon-chain molecule in TMC-1 CP. Takano et al. (1998) observed three ¹³C isotopologues of HC₃N toward TMC-1 CP, and the relative abundance of HCC¹³CN is significantly higher than that of the other isotopologues: [H¹³CCCN];[H¹³CCCN];[HCC¹³CN] is 1:0:1:0:1.4. These results imply that HC₃N is mainly formed by the reaction between a hydrocarbon molecule with two equivalent carbon atoms and a molecule with one carbon atom, whose ¹²C/¹³C ratios are different from each other. According to ab initio calculations, the reaction of C₂H₂ + CN is exothermic, and has no significant energy barrier (Woon & Herbst 1997; Fukuzawa et al. 1998). The laboratory experiments show that the rate coefficient for this reaction is sufficiently large (k ≳ 4 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) at low temperatures (Sims et al. 1993). Considering these results, Takano et al. (1998) suggested that HC₅N is formed by the reaction between C₂H₂ and CN.

It can naturally be predicted that HC₅N is formed by the similar mechanism of HC₃N, the reaction of C₄H₂ + CN. Fukuzawa et al. (1998) conducted ab initio calculations on the reactions of C₂n+₁ H₂ + CN (n = 1 − 4), which form HC₂n+₁ N, and found that these reactions are all exothermic and have no energy barriers. In addition, Seki et al. (1996) measured the rate constant for the reaction C₂H₂ + CN to be (4.2 ± 0.2) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at room temperature. These results suggest that HC₂n+₁ N can be formed by the reaction of C₂H₂ and CN. If so, we would be able to observe different abundances of the five ¹³C isotopologues of HC₅N. Observations of the ¹³C isotopologues of HC₅N were carried out toward TMC-1 CP by Takano et al. (1990). Although they
detected the five $^{13}$C isotopologues of HC$_3$N, they could not determine their relative abundances well due to low signal-to-noise ratios ($3-6$). Takano et al. (1998) also reported the spectra of the two $^{13}$C isotopologues, HC$_{13}$CCCN and HCCC$^{13}$CN, with slightly higher signal-to-noise ratios ($\approx 8$). However, they could not discuss its main formation pathway, because of the lack of data for the other three $^{13}$C isotopologues.

In the present paper, we observed the five $^{13}$C isotopologues of HC$_3$N toward TMC-1 CP with the NRO 45-m telescope with high enough signal-to-noise ratios to constrain mechanisms responsible for the formation of HC$_3$N.

### 2. OBSERVATIONS

We carried out observations of the normal species and the five $^{13}$C isotopologues of HC$_3$N with the NRO 45-m radio telescope in 2014 March, April (2013–2014 season), December, and 2015 January (2014–2015 season). The observed position was $(\alpha_{2000}, \delta_{2000}) = (04^h41^m42^s49, 25^\circ41^\prime27^\prime00)$ for TMC-1 CP. The Z45 receiver (Nakamura et al. 2015) and the high electron mobility transistor (HEMT) amplifier receiver (H22), both of which can obtain dual-polarization data simultaneously, were used for the observations of the $J = 16 - 15$ and $J = 9 - 8$ transitions at 42 GHz and 23 GHz, respectively. The exact frequencies of the observed lines are given in Table 1. The system temperatures of the Z45 and the H22 receivers were from 100 to 130 K, and from 90 to 110 K, respectively. The beam sizes and the main beam efficiencies ($\eta_B$) were 37$''$ and 0.72 for 42 GHz (Nakamura et al. 2015), and 72$''$ and 0.8 for 23 GHz. The telescope pointing was checked every 1.5 hr by observing the SiO maser line ($J = 1 - 0$) from NML Tau and GL 5134, and the pointing error was less than 3$''$. We used the SAM45 FX-type digital correlator in frequency settings whose bandwidths and resolutions are 125 MHz and 30.52 kHz, respectively, for observations at 42 GHz, and 63 MHz and 15.26 kHz, respectively, for those at 23 GHz. These frequency resolutions correspond to the velocity resolution of about 0.2 km s$^{-1}$.

We employed the position-switching mode, where the off-source position was set to be $+30\arcmin$ away in the right ascension. The smoothed bandpass calibration method (Yamaki et al. 2012) was adopted in the analysis, which allows us to greatly improve the signal-to-noise ratios, compared with the standard position-switch observations. In fact, the scan pattern of this method was a set of 20 and 5 s for on-source and off-source positions, respectively. We applied 60 and 32 channel-smoothing for the off-source spectra at 23 GHz and 42 GHz, respectively.

### 3. RESULTS AND ANALYSIS

#### 3.1. Results

The spectra of the five $^{13}$C isotopologues of HC$_3$N were taken with signal-to-noise ratios of 12–20, as shown in Figure 1. We also obtained high quality data for the normal species. Since the spectra show a symmetric single peak structure, we fitted the spectra with a Gaussian profile and obtained the spectral line parameters, as summarized in Table 1. The line widths ($\Delta \nu$ [km s$^{-1}$]) in the 23 GHz region $\approx 0.8$ km s$^{-1}$) are broader than those in the 42 GHz region $\approx 0.5$ km s$^{-1}$). Although the origin of their difference is unclear, the following possibility can be considered. It is well known that the TMC-1 CP region has a complex velocity structure (Langer et al. 1995; Dickens et al. 2001). Since the telescope beam samples a wider area at 23 GHz than at 42 GHz, the line width could be larger at 23 GHz. However, this difference does not affect our discussion on the relative abundance ratios among the five $^{13}$C isotopologues seriously, and hence, we do not discuss the line width further. The values of $V_{\text{LSR}}$ are consistent with one another, and are in good agreement with the $V_{\text{LSR}}$ value reported for this source (5.85 km s$^{-1}$, Kaifu et al. 2004).

The ratio of the integrated intensities ($T'^{\text{a}}_{\text{AV}}$ [K km s$^{-1}$]) of the five $^{13}$C isotopologues is derived to be 1.00:0.95:0.97:1.01:1.16 $\pm 0.16$ ($1\sigma$) and 1.00:1.01:1.12:1.13:1.17 $\pm 0.19$ ($1\sigma$) for [H$^{13}$C]CCCN:[H$^{13}$C]CCCN:[H$^{13}$C]CCCN:[HCC$^{13}$CCN]:[HCCC$^{13}$CN] for the $J = 9 - 8$ and

### Table 1: Spectral Line Parameters of HC$_5$N and Its Five $^{13}$C Isotopologues

| Species         | Transition | Frequency* (GHz) | $T^b_{\Lambda}$ (mK) | $\Delta\nu$ (km s$^{-1}$) | $V_{\text{LSR}}$ (km s$^{-1}$) | $T'^{\text{a}}_{\text{AV}}$ (K km s$^{-1}$) | rms$^d$ (mK) |
|-----------------|------------|------------------|----------------------|------------------------|-----------------------------|---------------------------------------------|-------------|
| HC$_5$N         | 9 – 8      | 23.9639007 (1)   | 1600 (20)            | 0.88 (1)               | 5.90 (9)                    | 1.50 (3)                                    | 2.6         |
|                 | 16 – 15    | 42.6021529 (2)   | 1874 (57)            | 0.46 (2)               | 5.9 (2)                     | 0.93 (4)                                    | 3.3         |
| H$^{13}$CCCCCN  | 9 – 8      | 23.3400887 (5)   | 44 (2)               | 0.57 (3)               | 6.0 (3)                     | 0.027 (2)                                   | 2.2         |
|                 | 16 – 15    | 41.4931720 (9)   | 31 (3)               | 0.44 (4)               | 5.8 (5)                     | 0.0147 (19)                                 | 3.2         |
| HC$^{13}$CCCCN  | 9 – 8      | 23.7183241 (5)   | 35 (2)               | 0.67 (4)               | 5.8 (3)                     | 0.025 (2)                                   | 2.4         |
|                 | 16 – 15    | 42.1655778 (9)   | 31 (3)               | 0.44 (4)               | 5.8 (4)                     | 0.0148 (16)                                 | 3.0         |
| HCC$^{13}$CCN   | 9 – 8      | 23.9390819 (6)   | 25 (1)               | 0.97 (6)               | 5.8 (3)                     | 0.026 (2)                                   | 2.1         |
|                 | 16 – 15    | 42.5580316 (9)   | 31 (3)               | 0.49 (4)               | 5.8 (4)                     | 0.0165 (16)                                 | 3.1         |
| HCCC$^{13}$CN   | 9 – 8      | 23.9419794 (5)   | 31 (2)               | 0.81 (5)               | 5.8 (3)                     | 0.027 (2)                                   | 2.1         |
|                 | 16 – 15    | 42.5632150 (9)   | 35 (3)               | 0.45 (4)               | 5.9 (4)                     | 0.0166 (19)                                 | 3.1         |
| HCC$^{13}$CCN   | 9 – 8      | 23.7271659 (6)   | 43 (2)               | 0.69 (4)               | 5.9 (3)                     | 0.031 (2)                                   | 2.4         |
|                 | 16 – 15    | 42.1812962 (10)  | 35 (3)               | 0.47 (4)               | 5.8 (5)                     | 0.0172 (18)                                 | 3.0         |

Notes. The numbers in parenthesis represent one standard deviation in the Gaussian fit except for frequency.

* Taken from the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2005).

$^b$ We calibrated the peak intensities of the $J = 16 - 15$ rotational transitions. We divided the results of Gaussian fit by 1.3, which was obtained by comparing Suzuki et al. (1992) and Nakamura et al. (2015).

$^c$ We calculated the integrated intensities and their errors using $T^a_{\Lambda}$ and $\Delta \nu$, which are determined by the Gaussian fit, where the errors are estimated from those of $T^a_{\Lambda}$ and $\Delta \nu$.

$^d$ The rms noises in emission-free regions.
Although HCCCC13CN is slightly brighter than the other species, there are no significant differences in intensities among the five 13C isotopologues. The result contrasts with that for HC5N, which shows clear differences in intensities of the three 13C isotopologues (Takano et al. 1998).
Table 2

| Species          | Column Density$^b$ (×10$^{11}$ cm$^{-2}$) | 12C/13C$^a$ Ratio | Column Density$^b$ (×10$^{11}$ cm$^{-2}$) | 12C/13C$^a$ Ratio |
|------------------|------------------------------------------|-------------------|------------------------------------------|-------------------|
| HC$_3$N          | (6.2 ± 0.3) × 10$^2$                     | ...               | ...                                      | ...               |
| H$^{13}$CCCCCN   | 6.4 ± 0.9                                | 98 ± 14           | 7.0 ± 1.0                                | 89 ± 13           |
| H$^{13}$CCCCCN   | 6.2 ± 0.8                                | 101 ± 14          | 6.8 ± 0.9                                | 91 ± 12           |
| HCC$^{13}$CCCN   | 6.6 ± 0.8                                | 95 ± 12           | 6.8 ± 0.9                                | 91 ± 12           |
| HCCC$^{13}$CCN   | 6.7 ± 0.9                                | 93 ± 13           | 6.9 ± 1.0                                | 90 ± 13           |
| HCCCC$^{13}$CN   | 7.4 ± 0.9                                | 85 ± 11           | 7.5 ± 1.0                                | 83 ± 11           |

Notes. The error corresponds to one standard deviation.

$^a$ The values of 13C isotopologues were calculated by using $T_{ex}$ = 6.5 K obtained from the normal species.

$^b$ The values were calculated by using the $T_{ex}$ derived for each isotopologue.

3.2. Analysis

The rotational population of HC$_3$N is not completely thermalized to the gas kinetic temperature, because the H$_2$ density of TMC-1 CP (4 × 10$^4$ cm$^{-3}$ (Hirahara et al. 1992)) is equal to or lower than the critical densities of the HC$_3$N lines. However, Takano et al. (1990) showed that the observed brightness temperatures of the HC$_3$N lines are well approximated by the rotation temperature of 6.5 K. Then, we calculated the column densities of the normal species and the five 13C isotopologues of HC$_3$N using the local thermodynamic equilibrium (LTE) as shown in the following formulae (Takano et al. 1998):

$$\tau = -\ln \left[ 1 - \frac{T_*}{f \eta_B \{ J(T_{ex}) - J(T_{bg}) \} } \right]$$

(1)

where

$$J(T) = \frac{h \nu}{k} \left\{ \exp \left( \frac{h \nu}{kT} \right) - 1 \right\}^{-1} ,$$

(2)

and

$$N = \frac{3h\Delta \nu}{8\pi^2} \left( \sqrt{\frac{\pi}{4 \ln 2 \mu^2} J_{\text{lower}} + 1} \right) \exp \left( \frac{E_{\text{lower}}}{kT_{ex}} \right) \times \left\{ 1 - \exp \left( -\frac{h \nu}{kT_{ex}} \right) \right\}^{-1} .$$

(3)

In Equation (1), $T_*$ denotes the antenna temperature, $f$ the beam filling factor, $\eta_B$ the main beam efficiency (see Section 2), and $\tau$ the optical depth. We used 0.8 and 1 for $f$ in the 23 GHz and 42 GHz band data, respectively. We employed these $f$ values, because a size of the emitting region of carbon-chain molecules in TMC-1 CP is approximately 2/5 according to the mapping observations by Hirahara et al. (1992). $T_{ex}$ is the excitation temperature, $T_{bg}$ is the cosmic microwave background temperature ($\approx$2.7 K), and $J(T)$ in Equation (2) is the Planck function. We derived $T_{ex}$ and $\tau$ simultaneously from the observed intensities of the 23 and 42 GHz lines by using formula (1). In Equation (3), $N$ is the column density, $\Delta \nu$ is the line width (FWHM), $Q$ is the partition function, $\mu$ is the permanent electric dipole moment of HC$_3$N (4.33 × 10$^{-18}$ [esu cm]) (Alexander et al. 1976), and $E_{\text{lower}}$ is the energy of the lower rotational energy level. In the energy level calculations, we used the rotational constants of the normal species and the 13C isotopologues (Alexander et al. 1976; Sanz et al. 2005).

The calculated column densities and the 12C/13C ratios are summarized in Table 2. For the normal species, the excitation temperature and the column density are determined to be 6.5 ± 0.2 K and (6.2 ± 0.3) × 10$^{13}$ cm$^{-2}$, respectively, where the errors are estimated from the Gaussian fits and represent the confidence level of one standard deviation. The optical depths for the $J = 9 - 8$ and 16 − 15 lines are 1.084 ± 0.014 and 1.19 ± 0.03 (1σ), respectively. The obtained excitation temperature and column density of the normal species are consistent with the previous result (6.5 ± 0.2 K and (6.3 ± 0.6) × 10$^{13}$ cm$^{-2}$) (Takano et al. 1990) within the error ranges.

We calculated the column densities of the five 13C isotopologues using Equation (3) and the excitation temperature derived for the normal species (6.5 K). The calculated column densities of the normal species and the five 13C isotopologues, and the 12C/13C ratios are summarized in Table 2. For the five 13C isotopologues, the column densities were derived to be (6.4 ± 0.9) × 10$^{11}$, (6.2 ± 0.8) × 10$^{11}$, (6.6 ± 0.8) × 10$^{11}$, (6.7 ± 0.9) × 10$^{11}$, and (7.4 ± 0.9) × 10$^{11}$ cm$^{-2}$, for H$_{13}$CCCCCN, H$^{13}$CCCCCN, HCC$^{13}$CCCN, HCCC$^{13}$CCN, and HCCCC$^{13}$CN, respectively. The abundance ratio of the 13C isotopologues of HC$_3$N is then 1.00:0.97:1.03:1.05:1.16 (±0.19) (1σ) for [H$_{13}$CCCCCN]/[H$^{13}$CCCCCN]; [HCC$^{13}$CCCN]/[HCCC$^{13}$CCN]; [HCCC$^{13}$CCN]/[HCCCC$^{13}$CN]. This result agrees with those obtained from integrated intensities. The averaged 12C/13C ratio of HC$_3$N is 94 ± 6 (1σ), which is slightly higher than the elemental ratio of 60−70 in the local interstellar medium (e.g., Langer & Penzias 1990, 1993; Savage et al. 2002; Milam et al. 2005). The intensities are also affected by the calibration errors (main beam efficiency and filling factor). However, we obtained the data of the normal species and the five 13C isotopologues simultaneously. Then, these calibration errors do not affect the 12C/13C ratios. We discuss these ratios in Section 4.2.

We investigated the sensitivities of the assumed $T_{ex}$ values on the column densities and the 12C/13C ratios. We calculated the column densities of the normal species and the five 13C isotopologues using $T_{ex}$ of 5.9 and 7.1 K, which are the lowest and highest values in the 3σ error range of the excitation temperature. We derived the column densities of the normal species to be (7.0 ± 0.5) × 10$^{13}$ cm$^{-2}$ and (4.7 ± 0.2) × 10$^{13}$ cm$^{-2}$ for 5.9 K and 7.1 K, respectively. The column densities of the 13C isotopologues were not significantly affected by the change of the excitation temperature. The 12C/13C ratios averaged for the five isotopologues are 125 ± 6 (1σ) and 89 ± 5 (1σ) for 5.9 K and 7.1 K, respectively. Although the 12C/13C ratios slightly depend on the excitation...
temperature, the $^{12}$C/$^{13}$C ratio of HC$_3$N is still higher than that of the elemental ratio in the local interstellar medium.

We also evaluated the ratio by using the excitation temperature derived for each $^{13}$C isotopologue. We derived $T_{ex}$ to be 6.2 ± 0.6, 6.2 ± 0.6, 6.3 ± 0.5, 6.3 ± 0.6, and 6.3 ± 0.5 K ($\sigma$) for H$^{13}$CCCCCN, HC$^{13}$CCCCN, HCC$^{13}$CCCN, HCCC$^{13}$CCCN, and HCCCC$^{13}$CN, respectively, from the intensities of the observed two rotational transitions. These results are consistent with the value obtained from the normal species (6.5 K) within the errors, which implies that we can neglect the effect of self-trapping for the normal species. We then calculated the column densities using $T_{ex}$ obtained for each $^{13}$C isotopologue. The $^{13}$C isotopic fractionation is not affected by the changes in $T_{ex}$, and the $^{12}$C/$^{13}$C ratios are also not affected within the errors. The results are also shown in Table 2.

4. DISCUSSION

4.1. Formation Mechanisms of HC$_3$N

We here consider possible reactions leading to cyanopolyynes, using the UMIST Database for Astrochemistry 2012 (McElroy et al. 2013). By focusing on the rate constants, activation energies, abundances, and formation pathways of precursors, we can sketch formation pathways of cyanopolyynes, as shown in Figure 2. Three types of formation pathways are possible as follows.

Pathway 1: the reactions of C$_{2n}$H$_2$ + CN,
Pathway 2: the growth of the cyanopolyyne carbon chains via C$_{2n}$H$_2$ + HC$_{2n+1}$N, and
Pathway 3: the reactions between hydrocarbon ions and nitrogen atoms followed by electron recombination reactions.

For HC$_3$N, Pathway 1 is suggested to play a dominant role in its production: Takano et al. (1998) reported that the main formation pathway of HC$_3$N is the reaction of C$_2$H$_2$ + CN on the basis of their observational results of $^{13}$C isotopic fractionation. Fractionation of $^{13}$C in CN proceeds through the following reaction (Kaiser et al. 1991):

\[ ^{13}\text{C}^+ + \text{CN} \rightarrow \text{C}^+ + ^{13}\text{CN} + \Delta E \ (34 \text{ K}). \]  

This reaction is exothermic with an energy of 34 K due to decreasing the zero-point vibrational energy. Hence, its backward reaction is not effective in cold dark clouds, where the typical temperature is approximately 10 K (e.g., Benson & Myers 1989). As a result, the $^{12}$C/$^{13}$C ratio for CN decreases in comparison with those for hydrocarbons such as C$_2$H$_2$ and C$_2$H$_4$, because similar fractionation processes of $^{13}$C do not occur in hydrocarbons (Watson et al. 1976).

If HC$_3$N is mainly formed by Pathways 1 and/or 2, at least one carbon atom in HC$_3$N, possibly that adjacent to the nitrogen atom, is not equivalent to the others. Assuming that HC$_3$N is mainly formed by Pathway 2, the $^{13}$C isotopic fractionation of HC$_3$N should be $x:y:1:0:1:0:1:4$, where $x$ and $y$ are arbitrary values, for [H$^{13}$CCCCCN][HC$^{13}$CCCCCN], [HCC$^{13}$CCCN][HCCC$^{13}$CCCN][HCCCC$^{13}$CN], unless scrambling of the carbon atoms is efficient. However, our observed abundances are roughly equal for all the $^{13}$C isotopologues. It is not likely that Pathway 1 and 2 are the main formation pathways of HC$_3$N.

On the basis of the above consideration, we propose that Pathway 3 should significantly contribute to the formation of HC$_3$N. In Pathway 3, all carbon atoms in HC$_3$N originate from the hydrocarbon ions. If all the carbon atoms in the mother hydrocarbon ion have the similar $^{12}$C/$^{13}$C ratio, the observational result can be explained. This seems indeed possible for a large hydrocarbon ion, because it is generally produced through various processes. This pathway is similar to the chemical model calculation by Markwick et al. (2000), where HC$_3$N can be produced through the reaction between a hydrocarbon ion (C$_2$H$_3^+$) and a nitrogen atom. Thus, we propose that Pathway 3 overwhelms Pathways 1 and 2, resulting in almost equivalent abundances of the $^{13}$C isotopologues of HC$_3$N.

Based on the above discussion on HC$_3$N, we also propose that the longer cyanopolyynes may be formed by a mechanism similar to that of HC$_3$N, namely the reactions between hydrocarbon ions and nitrogen atoms. However, it is difficult to confirm our suggestion by observations of $^{13}$C isotopic fractionation at the present. Langston & Turner (2007) tentatively detected the $^{13}$C isotopologues of HC$_7$N using the $J = 11 - 10$ and $12 - 11$ transitions for the first time in the interstellar medium. They calculated the averaged $^{12}$C/$^{13}$C ratio of HC$_7$N, but they could not study its $^{13}$C isotopic fractionation as they only obtained upper limits for each of the seven $^{13}$C isotopologues. Hence, more sensitive observations are needed to confirm the flat $^{13}$C abundance over the seven $^{13}$C isotopologues of HC$_7$N. In the theoretical model by Markwick et al. (2000), the pathways leading to HC$_3$N and HC$_9$N via reactions between hydrocarbon ions (C$_5$H$_7^+$ and C$_9$H$_5^+$, respectively) and nitrogen atoms followed by the
The reaction leads to a reduction in cyanopolyynes longer than HC5N are mainly produced by the neutral reaction between hydrocarbon ions and nitrogen atoms, whereas HC3N is mainly produced by the neutral–neutral reaction between C2H2 and CN. One possible reason is the high abundance of C2H2 (Markwick et al. 2000).

4.2. Dilution of the 13C Species

We compile 12C/13C ratios of some carbon-chain molecules at TMC-1 CP in Table 3. The 12C/13C ratios of carbon-chain molecules show more or less higher than that of the local interstellar elemental ratio (60–70) (e.g., Langer & Penzias 1990, 1993; Savage et al. 2002; Milam et al. 2005). This can be explained by the following reaction, which should be effective under low-temperature conditions (e.g., Watson et al. 1976; Langer et al. 1984),

\[
^{13}\text{C}^+ + \text{CO} \rightarrow ^{13}\text{C}^+ + ^{13}\text{CO} + \Delta E \text{ (35 K).} \tag{5}
\]

The reaction leads to a reduction in 13C+. Consequently, 13C isotopologues of carbon-chain molecules are also reduced, because C is and C are important raw materials of carbon-chain molecules.

We derived the five 12C/13C ratios of HC5N, and they are slightly higher than those of HC3N (see Table 3). Langston & Turner (2007) were able to detect the 13C isotopologues only by combining the observations of all seven isotopologues of HC5N into one spectrum. They derived the averaged 12C/13C ratio of HC5N by the combination of multiple lines of the seven 13C isotopologues of HC5N. These ratios indicate that the 13C species of the cyanopolyynes are less diluted than other carbon-chain molecules. For example, for HC5N and HC5N, the 12C/13C ratios coincide among their 13C isotopologues within about 20% and 10%, respectively. On the other hand, for CCS, 12C/13C of 13CCS is about four times larger than that of C13CS. In other words, an interesting characteristic of the 12C/13C ratios of the two cyanopolyynes is that their differences appear to be small among the 13C isotopologues of each cyanopolyyne, compared to other carbon-chain molecules. The reason why the 13C species of the cyanopolyynes are not significantly diluted is unclear. Mechanisms of the dilution of the 13C species are still controversial and are left for future studies.

5. CONCLUSIONS

We carried out observations of the J = 9 – 8 and 16 – 15 rotational transitions of the normal species and the five 13C isotopologues of HC5N toward TMC-1 CP with the NRO 45-m telescope. The abundance ratios of the five 13C isotopologues are found to be 1.00:0.97:1.03:1.05:1.16 ± (0.19) (1σ) for [HC13CCCNN]:[HC13CCCN]:[HC13C3CN]:[HC313CCCN]:[HC13CCC13CN]. Based on the result, we suggest that reactions between hydrocarbon ions and nitrogen atoms play an important role in the formation of HC5N. We derived the 12C/13C ratios from the five 13C isotopologues of HC5N. The averaged value is 94 ± 6 (1σ), and the 13C species of cyanopolyynes are less diluted than other carbon-chain molecules.

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