Detection of HC$_5$N and HC$_7$N Isotopologues in TMC-1 with the Green Bank Telescope

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ABSTRACT

We report the first interstellar detection of DC$_7$N and six $^{13}$C-bearing isotopologues of HC$_7$N towards the dark cloud TMC-1 through observations with the Green Bank Telescope, and confirm the recent detection of HC$_5^{15}$N. For the average of the $^{13}$C isotopomers, DC$_7$N, and HC$_7^{15}$N, we derive column densities of $1.9(2) \times 10^{11}$, $2.5(9) \times 10^{11}$, and $1.5(4) \times 10^{11}$ cm$^{-2}$, respectively. The resulting isotopic ratios are consistent with previous values derived from similar species in the source, and we discuss the implications for the formation chemistry of the observed cyanopolyynes. Within our uncertainties, no significant $^{13}$C isotopomer variation is found for HC$_5$N, limiting the significance CN could have in its production. The results further show that, for all observed isotopes, HC$_5$N may be isotopically depleted relative to HC$_5$N and HC$_7$N, suggesting that reactions starting from smaller cyanopolyynes may not be efficient to form HC$_7$N. This leads to the conclusion that the dominant production route may be the reaction between hydrocarbon ions and nitrogen atoms.

Key words: astrochemistry – methods: observational – techniques: spectroscopic – ISM: individual objects (TMC-1) – ISM: molecules.

1 INTRODUCTION

Carbon-chain molecules are a critically important family within the interstellar medium (ISM); they represent ~40 per cent of all detected species and play a major role in the formation of more complex chemistry. Carbon chains with interstellar detections include carbenes (McCarthy et al. 1997), polyynes (Irvine et al. 1981; Bell et al. 1997; Remijan et al. 2006; Snyder et al. 2006), unsaturated hydrocarbons (Cernicharo et al. 2001), and the newly detected HC$_5$O family (McGuire et al. 2017). Furthermore, it has been suggested that they may be important precursors to the formation of polycyclic aromatic hydrocarbons (PAHs) (Guzman-Ramirez et al. 2011), which are likely to be routine targets of observations when the James Webb Space Telescope is launched in 2019 (Kirkpatrick et al. 2017).

Reactions of unsaturated carbon-chain molecules (i.e. species whose available carbon valence electrons are not all bonded to atoms so that the chain contains more double and triple carbon–carbon bonds) are often efficient in the ISM, but have many product channels for which branching ratios are not known. Because of the lack of available laboratory measurements of the dominant reaction mechanisms and rate coefficients for these branching fractions, the ability to directly investigate these pathways through interstellar observations is therefore appealing. One way to probe the underlying chemistry is through the study of the isotopologues (molecules that differ only in isotopic composition; e.g. HCCCCN versus H$_{13}$CCCCN) and isotopomers (molecules that contain the same isotopic composition, but differ in the isotope positions; e.g. H$_{13}$CCCCN versus HCC$_{13}$CN) of a species. For many molecules, specific relative isotopic fractions or isotopomer configurations can possibly constrain the dominant production method or precursors.

TMC-1, one of the prototypical dark cloud cold cores, has been the subject of intense astrochemical study. Observationally, it has been the source of many new molecular detections, including a large fraction of the known unsaturated carbon chains (Kaifu et al. 2004; McCarthy et al. 2006; Remijan et al. 2006; Snyder et al. 2006; McGuire et al. 2017). Furthermore, TMC-1 is dynamically stable, characterized by narrow-line widths ($\sim$0.3 km s$^{-1}$), cold excitation temperatures (5–10 K), and a low line density ($\sim$1 line per 200 km s$^{-1}$ for reasonable integration times with the GBT), making it ideal for the unambiguous detection of new molecules. Finally, because of its simple physical history, it is an ideal source...
to test chemical network models (Hasegawa, Herbst & Leung 1992; Herbst & Millar 2008; Ruad, Wakelam & Hersant 2016; Majumdar et al. 2017).

Cyanopolyynes, a family of linear molecules of the form HCₙN (where n = 3, 5, 7, etc., henceforth) with alternating single- and triple-bonded carbon atoms, have been detected in cold dark clouds (Broten et al. 1978), the expanding envelopes of evolved stars (Bell et al. 1992), and even external galaxies (Mauersberger, Henkel & Sage 1990). It has been shown that, unlike many carbon chains, the $^{12}$C/$^{13}$C ratio for HCₙN is constant even into subsequent stages of star formation through observations of warm carbon-chain chemistry in the low-mass star-forming region L1527 (Araki et al. 2016; Taniguchi, Saito & Ozeki 2016b). This finding implies that the formation of cyanopolyynes may occur primarily under dark cloud conditions. These species then remain as relics in subsequent stages of star formation, and have a unique underlying chemistry compared with other carbon-chain molecules. However, recent observations of a more evolved core, L134N, suggest that other formation pathways may dominate at later times (Taniguchi, Ozeki & Saito 2017).

Of particular interest, Loomis et al. (2016) recently discussed the non-detection of HC₁₁N, which deviates from the log-linear abundance versus molecular size trend seen for smaller cyanopolyynes (Bujarrabal et al. 1981; Bell et al. 1997; Ohishi & Kaifu 1998; Remijan et al. 2006). Although this trend was previously thought to arise from a consistent set of gas-phase reactions that add carbons directly to smaller HCₙN species (Winnewisser & Walmsley 1979; Bujarrabal et al. 1981; Fukuzawa, Osamura & Schaefer 1998; Remijan et al. 2005), it was proposed by Loomis et al. (2016) that cyclization processes may need to be considered to accurately explain this deviation. It is clear, therefore, that the chemistry of this family of species is not fully understood, especially at larger molecular sizes, and further study is needed.

For the cyanopolyne family, Takano et al. (1998) and Taniguchi et al. (2016a) discussed the potential prominence of three formation routes, among others, for a given molecule (HCₙN), which could each result in different $^{12}$C/$^{13}$C fractions. Each of these numbered mechanisms is discussed below, and, for clarity, sources of carbon atoms which could result in $^{13}$C fractionation are traced from reactants to products in example reactions in red.

**Mechanism 1 – The reaction between hydrocarbon molecules and the CN radical, including**

\[ C_{n-1}H_2 + CN \rightarrow HC_{n-1}CN + H. \]  

(1)

Here, the difference between the isotopic fractions of the CN carbon atom and the carbene C₂H₂ carbon atoms results in asymmetric fractionation along the chain (Herbst & Leung 1990; Fukuzawa et al. 1998).

**Mechanism 2 – Reactions of the next-smallest cyanopolyne (e.g. HC₃N versus HC₅N) with hydrocarbons, such as**

\[ C_2H + HC_{n-2}N \rightarrow HC_2C_{n-2}N + H. \]  

(2)

For this case, many of the isotopomers would have similar $^{12}$C/$^{13}$C ratios to their corresponding isotopomer of the precursor cyanopolyne, with potentially some small variations depending on the precursor hydrocarbon (Huntress 1977; Schiff & Bohme 1979).

**Mechanism 3 – Reactions of nitrogen atoms and hydrocarbon ions containing the same number of carbon atoms.** One such example is

\[ C_2H^+_2 + N \rightarrow H_2C_2N^+ + H \]

\[ H_2C_2N^+ + e^- \rightarrow HC_2N + H. \]  

(3)

In this scenario, $^{12}$C/$^{13}$C fractionation would be set by this precursor ion. Assuming that the ion’s carbon atoms are sufficiently scrambled, this manifests as no significant variations among the isotopomers’ ratios (Herbst 1983; Herbst, Adams & Smith 1984; Knight et al. 1986).

Previously, the $^{12}$C/$^{13}$C fractionation had only been studied for cyanocetylene (HC₅N) and cyanodietylene (HC₇N). For HC₅N, Takano et al. (1998) found that towards TMC-1 there was an $\sim$40 per cent abundance enhancement of the isotopomer with the $^{13}$C residing next to the nitrogen atom (HC₅N) relative to the other two species, suggesting that the primary formation route could be the neutral reactions between the abundant CN and C₂H₂ (Mechanism 1). This enhancement in $^{13}$CN is thought to result from the exothermic reaction exchange given by

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

(4)

Because the reaction is exothermic, only the forward process is efficient at the cold temperatures within dark clouds, which results in an enhanced $^{13}$C fractionation in CN compared with the carbene precursors whose exchange reactions are much less efficient (Watson, Anichich & Huntress 1976; Benson & Myers 1989). This enhancement of $^{13}$C in CN relative to measured Solar system isotopic fractions has been ubiquitously observed in Galactic molecular clouds (Milam et al. 2005).

Meanwhile, Taniguchi et al. (2016a) found that there was no significant difference in the abundance of the $^{15}$C-isotopomers of HC₅N towards TMC-1, suggesting that the primary formation route could be from reactions of N with hydrocarbon ions (such as C₂H₂, C₂H₂^+, and C₂H₂^++).

It is also important to compare these results to the dominant formation routes within chemical network models. Significant work has been done for this molecular family by Loomis et al. (2016) and McGuire et al. (2017), who adapted the KIDA network within NAUTILUS (Ruaud et al. 2016). At the model’s time of best agreement, multiple formation routes significantly contributed (>30 per cent) to the formation of cyanopolyynes, many of which do not necessarily agree with the observational constraints.

We have recently performed deep observations of TMC-1, which have resulted in the interstellar detection of several new molecules (McGuire et al. 2017). Here, we present the detection of six of the seven possible $^{15}$C-bearing isotopomers of HC₅N, as well as DC₅N verifying the two $^{15}$C-isotopologues detected by Cordiner et al. (2017). In addition, we confirm the recent detection of HC₇N. The observations are presented in Section 2, a review of the laboratory spectroscopy is given in Section 3, the results and analysis are discussed in Section 4, and a discussion of the astrochemical implications is given in Section 5.

### 2 OBSERVATIONS

Observations, described previously by McGuire et al. (2017), towards TMC-1 were performed on the 100 m Robert C. Byrd Green Bank Telescope (GBT) in Green Bank, WV with the K-band Focal Plane Array (KFPA) along with the Versatile GBT Astronomical Spectrometer (VEGAS) spectrometer backend. The beam size varied from 32 to 40 arcsec across the observed frequency range, with a beam efficiency of $\sim$0.92. The VEGAS backend was configured for 187.5 MHz bandwidth and 1.4 kHz (0.02 km s$^{-1}$) spectral resolution. In two separate frequency set-ups, a total of 10 individual passbands were observed for a total of 1875 MHz of spectral coverage between 18 and 24 GHz. The observations were centred on $\nu(J2000) = 04^h41^m42.5^s$, $\delta(J2000) = 25^\circ41'27''$, with...
pointing corrections performed hourly with an estimated uncertainty of ~2 arcsec. The system temperatures ranged between 40 and 80 K during the observations.

Position-switching mode was used with a 120 s ON-OFF cadence and a position 1 arcmin from the target. In total, each of the 10 frequency windows was observed between ~7.5 and 15 h on source. Data reduction was performed using the GBTIDL package. The data were placed on the atmosphere-corrected $T_A^*$ scale (Ulrich & Haas 1976) and averaged. A polynomial fit was used to remove the baseline. Subsequent smoothing to a spectral resolution of 5.7 kHz (~0.08 km s$^{-1}$) improved the signal-to-noise ratio (SNR) in the weaker features while maintaining at least three-channel sampling across the narrowest spectral feature observed. This resulted in final RMS noise of 3–5 mK (Table 1).

### 3 SPECTROSCOPY

For the new species detected here, McCarthy et al. (2000) measured the pure rotational spectra of the isotopologues of several cyanopolyynes, including HC$_3$N, between 6 and 17 GHz, and resolved the nitrogen hyperfine splitting. The rotational spectrum for HC$_5^{15}$N was measured by Bizzocchi, Degli Esposti & Botschwina (2004). The corresponding quantum transitions, frequencies (MHz), line strengths (D$^7$) and upper-level energies (K) for transitions falling within our observational coverage are shown in Table 1.

### 4 RESULTS AND ANALYSIS

We detected, for the first time, emission from DC$_2$N and six $^{13}$C-bearing isotopologues of HC$_3$N. In addition, we confirmed the recent detection of HC$_5^{15}$N (Taniguchi & Saito 2017) with the observation of the $J = 8 \rightarrow 7$ transition, which was not reported in that work. For the $^{13}$C-isotopomers, at least one $\Delta J$ transition between $17 \rightarrow 16$ and $20 \rightarrow 19$ was detected for six of the seven isotopomers. In addition, two transitions of DC$_2$N, two transitions of HC$_3$N, and a set of five hyperfine components of a single $\Delta J$ for HC$_3$N were also detected. Spectra for these species are shown in Figs 1 and 2. The lines were seen at a $v_{\text{LSR}}$ ~5.8 km s$^{-1}$, typical of molecules in this source (Kaifu et al. 2004). For the one non-detected isotopomer, H$^{13}$CC$_4$N, an upper limit on the column density was derived whose value is consistent with the other detected isotopomers.
Detection of HC$_3$N and HC$_5$N Isotopologues

In TMC-1, the molecular emission can be well described by a single excitation temperature between $T_{\text{ex}} \sim 5$–10 K (Remijan et al. 2006; Loomis et al. 2016). To calculate the column density, we use the formalism described in Hollis et al. (2004) and given by

$$N_T = \frac{Qe^{E_u/T_{\text{ex}}}}{\kappa^2 v S} \frac{\Delta T^*_A \Delta V}{\nu^2} \frac{1}{1 - \frac{\Delta T^*_A \Delta V}{\nu^2}} \frac{1}{\eta B} \frac{1}{\Delta V} \frac{1}{T_{\text{bg}}}$$  \hspace{1cm} (5)

Here $N_T$ is the column density (cm$^{-2}$), $Q$ is the partition function (see below), $E_u$ is the upper state energy of a given transition (K), $T_{\text{ex}}$ is the excitation temperature (K), $v$ is the transition rest frequency (Hz), $S$ is the intrinsic line strength, $\kappa^2$ is the transition dipole moment squared (J cm$^{-2}$), $\Delta T^*_A$ is the peak intensity (K), $\Delta V$ is the fitted FWHM linewidth (cm s$^{-1}$), $\eta B$ is the beam efficiency ($\sim 0.92$ at 20 GHz for the GBT), and $T_{\text{bg}}$ is the continuum background temperature (2.73 K). Because of the narrow range of upper level energies of the observed transitions, we assume that $T_{\text{ex}} = 7$ K for all species.

The total partition function $Q$ accounts for both the rotational and vibrational contributions, as described by

$$Q = Q_{\text{vib}} \times Q_{\text{rot}}.$$  \hspace{1cm} (6)

While the rotational component dominates at interstellar conditions, cyanopolyynes can have $Q$ values that can be affected by the vibrational component at even modest excitation temperatures. We utilized the calculated harmonic stretching vibrational wavenumbers ($\omega$) for HC$_3$N by Botschwina et al. (1997), with the assumption that the partition function will not be significantly impacted by the presence or location of $^{13}$C or D in the molecule. The lowest three energy levels for HC$_3$N are 62, 163, and 280 cm$^{-1}$ (92, 241, and 415 K, respectively). At 7 K, the change from the vibrational contribution is negligible ($\Delta Q/Q_{7K} \sim 10^{-6}$); this correction becomes $\gtrsim 1$ per cent at $T_{\text{ex}} \gtrsim 20$ K. Similar behaviour is seen for HC$_5$N isotopologues.

Values of $\Delta T^*_A$ and $\Delta V$ were determined by Gaussian fits to the lines (see Table 1). For species with more than one transition, a single-column density was obtained based on a least-squares fit to reproduce the integrated line intensities, with a weighting based on the SNR of the lines. The calculated column densities are summarized in Table 2.

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**Figure 1.** Detected transitions of HC$_3$N isotopologues, organized by isotope-location and corresponding quantum numbers for each transition (labelled in the top left of each spectra). Velocities are given with respect to $V_{\text{lsr}}$ of the transition rest frequency, with the listed transition centred at 0 km s$^{-1}$.

**Figure 2.** Detected transitions of HC$_5$N isotopologues, organized by isotope-location and corresponding quantum numbers for each transition (labelled in the top left of each spectra). Velocities are given with respect to $V_{\text{lsr}}$ of the transition rest frequency, with the listed transition centred at 0 km s$^{-1}$.
Table 2. Measured column densities and upper limits for isotopomers and isotopologues discussed here, and, when relevant, the isotopic ratio (i.e. $^{12}$C/$^{13}$C; H/D; $^{14}$N/$^{15}$N).

| Species           | $N_T$ ($\times 10^{12} \text{ cm}^{-2}$) | $N_T/N_T^{15} \text{N}$ ($\times 10^{-11}$) | Isotopic ratio$^a$ | $R^b$  |
|-------------------|-------------------------------------|------------------------------------------|-------------------|--------|
| HC$_3$N           | 139(36)                             | 139(36)                                  | –                 | –      |
| HC$_3$^{13}CN     | 1.7(6)                              | 1.7(6)                                   | 83(34)            | 85(35) |
| HC$_3$^{13}CCN    | 2.6(7)                              | 2.6(7)                                   | 52(20)            | 53(20) |
| HC$_3$^{13}CC$_2$N | 2.1(7)                              | 2.1(7)                                   | 66(27)            | 67(28) |
| HC$_3$^{13}CC$_3$N | 1.6(4)                              | 1.6(4)                                   | 88(32)            | 90(33) |
| HC$_3$^{13}CC$_4$N | 1.8(5)                              | 1.8(5)                                   | 78(31)            | 79(32) |
| HC$_3$^{13}CC$_5$N | 2.0(7)                              | 2.0(7)                                   | 71(31)            | 73(31) |
| H$^{13}$CC$_6$N   | <2.2                                | <2.2                                      | >63               | >64    |
| DC$_3$N           | 2.5(9)                              | 2.5(9)                                   | 56(24)            | 61(29) |
| Weighted $^{13}$C Average Value | 1.9(2) | 1.9(2) | 73(21) | 75(21) |
| Total $^{13}$C-isotopologue$^a$ | 13.3(1.8) | 13.3(1.8) | 9.6(2.7)%$^d$ | 9.4(2.7)%$^d$ |
| HC$_3$N           | 492(122)                            | 492(122)                                  | –                 | –      |
| HC$_3$^{15}N      | 1.5(4)                              | 1.5(4)                                   | 326(109)          | 344(114)|
| HC$_3$^{13}CN     | 4.6(9)                              | 4.6(9)                                   | 107(35)           | 108(36)|
| HC$_3$^{13}CCN    | 4.4(9)                              | 4.4(9)                                   | 111(37)           | 113(38)|
| HC$_3$^{13}CC$_2$N | 5.3(1.2)                           | 5.3(1.2)                                 | 93(31)            | 94(32) |
| HC$_3$^{13}CC$_3$N | 3.4(7)                              | 3.4(7)                                   | 144(47)           | 146(49)|
| H$^{13}$CC$_4$N   | 4.8(1.0)                            | 4.8(1.0)                                 | 102(33)           | 103(34)|
| DC$_3$N           | 5.3(1.2)                            | 5.3(1.2)                                 | 92(30)            | 96(32) |
| Weighted $^{13}$C Average Value | 4.4(4) | 4.4(4) | 111(30) | 113(31)|
| Total $^{13}$C-isotopologue$^a$ | 22(3) | 22(3) | 4.5(1.2)%$^d$ | 4.4(1.2)%$^d$ |

$^a$Column density ratio of most common isotopologue versus less common species given (e.g. $^{12}$C/$^{13}$C; H/D; $^{14}$N/$^{15}$N).

$^b$Isotopic ratio, including all other singly substituted isotopologues (see Section 4.2).

$^c$Calculated by 7 times the weighted average of $^{13}$C values.

$^d$Percent of total molecular density of HC$_3$N containing a single $^{13}$C substitution.

To calculate the uncertainties, we considered both the measurements and analysis. The absolute flux calibration procedure for the GBT is estimated to have $\sim$20 per cent uncertainty. We include 1σ uncertainties in $\Delta T_a^*$ and $\Delta V$ derived from the Gaussian fits. Due to our assumption of a single excitation temperature of $T_{ex} = 7 \text{ K}$, we find that variations of previously calculated excitation temperatures (5–10 K) result in between 15 and 20 per cent uncertainty in the resulting column densities for HC$_3$N isotopologues and $\sim$5 per cent for HC$_3$N isotopomers. We assume that the source is significantly extended beyond the GBT beam, and thus the contributions to the uncertainty from pointing are trivial, and no beam filling correction is applied. The resulting column densities, with all uncertainties added in quadrature, are given in Table 2.

For the purposes of calculating the molecular abundances, we used the H$_2$ column density derived by Gratier et al. (2016) from observations from Kaifu et al. (2004) of $N_{H_2} = 10^{22} \text{ cm}^{-2}$, with the caveat that the beam size of the survey performed with the Nobeyama 45m dish telescope is about twice that of the GBT, and thus a non-isotopic distribution of H$_2$, or any molecular species, may result in different column densities derived between the observations. These abundances are also given in Table 2. In addition to comparing the relative column densities of the isotopomers, an average value across all detected $^{13}$C-isotopomers is also calculated. The column density for each detected species was averaged, weighted by the error of each value, and is also tabulated in Table 2. These calculated values are compared to previous observations in Table 3.

4.1 Treatment of hyperfine splitting

For HC$_3$N, the brightest detected signal is a blend of three hyperfine components. Two additional, weaker $\Delta F = 0$ hyperfine components are resolved. The central, bright feature has been shown to be slightly optically thick (Gratier et al. 2016). Our calculation of the column density was therefore derived using the two, optically thin hyperfine components, yielding a value of $5(1) \times 10^{13} \text{ cm}^{-2}$, in agreement with the previous work (MacLeod, Avery & Broten 1981; Gratier et al. 2016; Taniguchi et al. 2016a).

For all other species studied here, the hyperfine components are unresolved. As such, for the purposes of calculating column densities, the hyperfine splitting is not considered and the integrated intensity is used instead. This likely slightly overestimates the linewidths due to the blending of hyperfine components. However, this is still a reasonable assumption, as the lines are well-modelled by a single Gaussian lineshape, and thus will not significantly impact the resulting column densities, which are calculated via the integrated intensity in equation (5).

4.2 Calculation of line ratios and total values

Relative isotopic ratios calculated for H/D, $^{12}$C/$^{13}$C, and $^{14}$N/$^{15}$N are tabulated in Table 2. It should be noted that none of the uncertainties described above for determining the column densities should cancel out in the calculation of the ratios, as the uncertainty in the absolute flux calibration comes from the time and frequency variability of the calibrator source. For HC$_3$N, where we lack a
Table 3. Comparison of observed ratios to previous values of cyanopolyynes and related species in the literature.

| Source | H$_2$C$_5$N | H$_2$C$_7$N | H$_2$C$_9$N | HCN | CN$^a$ | ISM$^b$ | H/D | $^{14}$N/$^{15}$N |
|--------|-------------|-------------|-------------|------|-------|--------|-----|-------------------|
| This work | 73(21) | 111(30) | – | – | – | 56(24) | 92(30) | 326(109) |
| A | 87(19) | – | 87(19) | – | – | >59 | – | – |
| B | – | 54(22) | 130(23) | 170(30) | – | – | 52(26) | 20 | 81(82) |
| C | – | 94(6) | – | – | – | – | – | – |
| D | – | 77(7) | 55(7) | – | – | – | – | – |
| E | – | – | 56.8$^d$ | 69$^d$ | – | – | 71$^d$ | 91(38) | – | – | – | – |
| F | – | – | – | 68(15) | 88.9(6) | – | – | – | – | 424(3) |
| G | – | – | – | – | – | – | – | – |
| H | – | – | – | – | – | – | – | – |
| I | – | – | – | – | – | – | – | – |
| J | – | – | – | – | – | – | – | – |
| K | – | – | – | – | – | – | – | – |
| L | – | – | – | – | – | – | – | – |
| M | – | – | – | – | – | – | – | – |
| N | – | – | – | – | – | – | – | – |

$^a$CN values acquired from observations of Galactic diffuse molecular clouds.

$^b$ISM values acquired from Solar system measurements (i.e. local ISM).

$^c$First value is average of H$^{13}$CC$_2$N and H$^{13}$CCCN. Second value is for H$_2$C$_{13}$CN.

$^d$Uncertainties not given for most values in Turner (2001).

$^e$Value given in literature is H$^{13}$CN/H$^{15}$CN, which was scaled by the HCN/H$^{13}$CN ratio from Turner (2001).

References: [A] Langston & Turner (2007); [B] Gratier et al. (2016); [C] Taniguchi et al. (2016a); [D] Takano et al. (1998); [E] Turner (2001); [F] Milam et al. (2005); [G] Meibom et al. (2007); [H] MacLeod et al. (1991); [I] Schloerb et al. (1981); [J] Howe et al. (1994); [K] Taniguchi & Saito (2017); [L] Ikeda, Hirota & Yamamoto (2002); [M] Ritchey et al. (2015); [N] Marty et al. (2011).

detection of H$^{13}$CC$_2$N, we calculate a total column density of all $^{13}$C-substituted isotopomers by scaling the average column density for the isotopologue by the number of isotopomers, which is equal to the number of carbon atoms in the molecule.

As discussed in Langston & Turner (2007), the presence of isotopologues affects the observed abundances of the main isotopic species, especially for increasingly complex molecules. As the number of atoms in a species increases, so does the probability that any given molecule will contain at least a single isotope-substituted atom. This would be most apparent in fullerenes like C$_{60}$, where a Galactic $^{12}$C/$^{13}$C ratio of ~68, or 1.5 per cent (Milam et al. 2005), would result in ~60 per cent of all C$_{60}$ containing, at least one $^{13}$C substitution. Similarly, it may be important to consider the size of the molecule when comparing the total isotopologue fraction. Given the same ISM ratio and purely $^{13}$C-substitution, and no additional chemical bias, the larger cyanopolyynes would be expected to have the following total singly substituted $^{13}$C fractional abundances: H$_2$C$_5$N (7.2 per cent), H$_2$C$_7$N (10 per cent), H$_2$C$_9$N (12 per cent), and H$_2$C$_{11}$N (15 per cent).

Given the non-trival fraction of isotopologues for a given large species, as the observational capabilities improve, it will likely be important to consider their abundances when calculating isotopic ratios. For the purposes of comparing to standard ISM values, a more accurate ratio for fractionation would be (taking $^{15}$N of H$_2$C$_5$N as an example)

$$R = \frac{N_f(\text{HC}_5\text{N}) + \sum N_f(\text{H}^{13}\text{CC}_2\text{N isotopomers}) + N_f(\text{DC}_5\text{N})}{N_f(\text{HC}_5^{13}\text{N})}$$

(7)

Here, it is assumed that doubly substituted isotopologues do not contribute significantly yet to the ratio, which may not be valid for species as large as C$_{60}$. In addition to the standard column density ratio given, this additional value is also given in Table 2, even though the relative differences (~10 per cent) are still well within the observational uncertainties. As chemical models increase their molecular complexity, it will become increasingly important to consider the isotopologues of large molecules, as well as their precursor species. This is already shown by Majumdar et al. (2017) on the modelling of deuterated species towards TMC-1, where the robust inclusion of deuterated chemistry was found to alter the chemical time-scales by up to a factor of 3. This effect will also be more apparent when species contain at least one atom with a higher natural percentage in non-standard isotopes, such as S and Cl and species common in silicate grain precursors (Mg, Si, Ti, Fe). While the upper limit of this effect will likely decrease the modelled abundances by no more than roughly a factor of 2, it is certainly an important effect to consider in the future.

5 DISCUSSION

Constraining the chemistry for larger cyanopolyynes requires the consideration of both the possible formation routes, as described in Section 1, and the many precursor species, whose isotopic ratios across the literature are summarized in Table 3. The analysed isotopic ratios in this work agree reasonably well with previous observations or lower limits for the same species. The general spread in values for a given species may be attributable to the spread in excitation temperatures used (5–10 K) or inconsistent treatments of both the optical depths and hyperfine structure in the column density calculations for H$_2$C$_N$ and H$_2$C$_N$. For H$_2$C$_N$, the relative enhancement of $^{13}$C/$^{12}$C for H$_2$C$_{13}$CN and the agreement of the $^{14}$N/$^{15}$N ratio with Galactic measurements of CN both indicate that this species may be efficiently produced through the reaction containing CN, as described in Mechanism 1 (Takano et al. 1998). Taniguchi et al. (2016a) showed that H$_2$C$_N$ does not show this same trend. Through the comparison of the various isotopologues
studied here, it is further possible to differentiate among the three mechanisms described in Section 1 for both HC₅N and HC₇N.

In contrast to the ∼40% enhancement of HC₅¹⁴CN over HC₅¹³CCN and H¹³C₂CN (Takano et al. 1998), the relative isotopic ratios of all ¹³C isotopomers for both HC₅N and HC₇N were all consistent with their respective average values within our uncertainties. The ratio of column densities of the HC₅₋₁³CN isotopomers to the weighted average ¹³C-isotopologue values can be used to more explicitly test the significance of Mechanism 1 in the formation of larger cyanopolyynes. Specifically, the column densities of HC₅¹⁴CN and HC₅¹³CN agree with their respective ¹³C average values to <10% per cent. Because both HC₅N and HC₇N do not display the HC₅₋₁³CN enhancement, this provides evidence that larger cyanopolyynes are not produced from CN to the same extent as HC₅N. Even though H¹³CCCN was not detected here, the formation route from CN should not significantly alter the ¹²C/¹³C isotopic ratio of this molecule and so does not conflict with this conclusion. Thus, we can eliminate Mechanism 1 as the dominant pathway for both HC₅N and HC₇N.

As shown in Table 3, while still in agreement within the uncertainties, all isotopologues of HC₅N are found to be depleted (i.e. larger isotopic ratios) relative to HC₃N and HC₇N, showing that this isotopic depletion seen in Taniguchi et al. (2016a) does not occur for HC₅N. While the average ¹²C/¹³C ratio for HC₃N agrees very well with ratios corresponding to HC₅N, the ratios of HC₅N ¹²C/¹³C and HC₇N ¹²C/¹³C is ∼50% lower than any of these values. For HC₇N, the ¹⁴N/¹³N ratio is much larger compared to HC₃N and Galactic measurements of CN, which have been shown to have enhanced ¹⁵N isotope abundances relative to average ISM values (Hily-Blant et al. 2013; Ritchey, Federman & Lambert 2015; Roueff, Loison & Hickson 2015). Similarly, the DC₅N abundance is diminished by roughly the same percentage relative to HC₅N as the ¹³C-substituted isotopologues in our data. However, large uncertainties due to the SNR of our data and inconsistent treatment of the excitation temperature and hyperfine splitting across the literature result in a large spread of H/D for any given species, making this trend less certain than for the ¹²C/¹³C and ¹⁴N/¹³N isotopic abundance ratios. Considering all of this, the mixture of formation and destruction mechanisms for cyanopolyynes appears to not be consistent across the molecular family.

More specifically, because the ¹²C/¹³C ratio in HC₅N is not in agreement with the ratios observed for HC₃N and HC₇N, the carbon fractionation in these species does not appear to be inherited from the next-smallest cyanopolyne, as would be predicted by Mechanism 2. Given that Mechanism 2 is inefficient for HC₅N and HC₇N production, the only remaining formation pathway proposed is the reaction of hydrocarbon ions with nitrogen atoms (Mechanism 3), and thus is the best prediction for the dominant formation route for large cyanopolyynes. If the trends discussed here are found to be true, a dedicated investigation of the underlying chemistry of hydrocarbon ions and undetected C,H isotopologues may reveal a unique ¹³C distribution and provide constraints on the formation of cyanopolyynes and other carbon-chain molecules.

6 CONCLUSIONS

The interstellar detections of DC₅N, six of the seven ¹³C-bearing isotopologues of HC₅N and HC₇N are reported towards TMC-1 with observations using the GBT. Column densities for each of the detected species and an upper limit for H¹³CCCN were calculated, as well as the resulting isotopic ratios for each species. From analysis of these ratios, we find that:

(i) There are no significant ¹²C/¹³C variations among the isotopomers of both HC₃N and HC₅N, implying that CN is not an important precursor for their formation.

(ii) For all isotopologues studied in this work, while the values still agree within our uncertainties, HC₅N is found to be isotopically depleted relative to other HC₅N molecules and this trend does not continue on to HC₇N. Given also that the ¹³C and ¹⁴N ratios for HC₅N and HC₇N agree very well, there is evidence that cyanopolyynes are not efficiently formed from their next-smallest molecular family member, HC₅₋₁³N.

(iii) As a result, the only remaining significant formation route for HC₅N and HC₇N is the reaction of hydrocarbon ions and nitrogen atoms.

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