Searching for C_4H_3N Isomers on Titan Using ALMA. P. R. Leeseberg[1,2,3], C. A. Nixon[2], A. E. Thelen[4], M. A. Cordiner[5,6] [1]Southeastern Universities Research Association, Washington, DSC 20005, USA. (paigel17@iastate.edu) [2]Planetary Systems Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA. [3]Center for Research and Exploration in Space Science & Technology II[4] Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. [5]Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA. [6]Department of Physics, Catholic University of America, Washington, DC 20064, USA.

Introduction: Photochemistry of N_2 and CH_4 in Titan's atmosphere results in the production of a large variety of molecular species, including simple and complex organics, but our knowledge of the detailed molecular inventory still needs to be completed. The Cassini Ion and Neutral Mass Spectrometer (INMS) [1] and Cassini Plasma Spectrometer (CAPS) [2] instruments detected many heavy positive and negative ionospheric species in Titan's upper atmosphere [3], but their exact identities and neutral counterparts have yet to be confirmed. Methylcyanoacetylene (CH_3C_3N) was recently discovered on Titan [4], prompting an investigation of the other structural isomers of C_4H_3N. These isomers have been observed in the interstellar medium (ISM) [5-7]; however, they have yet to be discovered in the atmosphere of any Solar System planet. The detection, or stringent upper limit, of these isomer species, would further inform our understanding of Titan's atmospheric photochemistry and molecular inventory and allow for the resolution of questions posed by measurements made by Cassini.

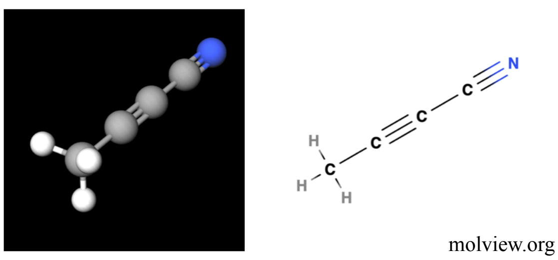

Figure 1: The structure of methylcyanoacetylene (CH_3C_3N) which has been discovered in Titan's atmosphere.

Observations: We conducted a search for propargyl cyanide ($HCCCH_2CN$) and cyanoallene ($H_2CCCHCN$) using observational data from the Atacama Large Millimeter/sub-millimeter Array (ALMA) in Band 6 (~230-272 GHz) and Band 7 (~273-373 GHz) acquired from 2014 through 2016.

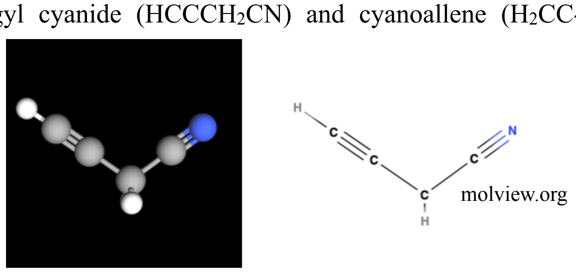

Figure 2: The structure of propargyl cyanide ($HCCCH_2CN$), one of the two isomers.

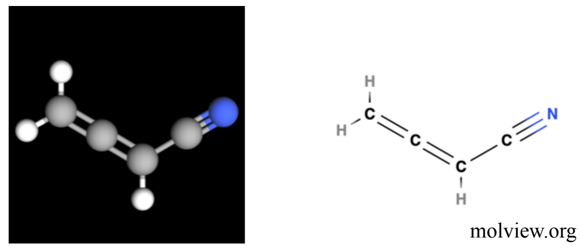

Figure 3: The structure of cyanoallene ($H_2CCCHCN$), one of the two isomers.

Analysis: We identified areas of interest by targeting our search in frequency ranges with high predicted line strengths using The Cologne Database for Molecular Spectroscopy (CDMS) [8,9]. We found five main areas of interest for each isomer and used the ALMA database to search for data in those predicted frequen-

$H_2CCCHCN$		
Frequency (GHZ)	Highest Intensity	Number of Transitions
243.09 - 243.843	-2.8557	28
258.585 - 259.561	-2.8259	38
268.883 - 269.899	-2.7085	37
284.359 - 285.449	-2.7101	34
366.407 - 367.419	-2.7418	33

Table 1: The five main areas where we targeted our search for cyanoallene.

$HCCCH_2CN$		
Frequency (GHZ)	Highest Intensity	Number of Transitions
252.898 - 253.244	-3.1223	30
254.942 - 255.043	-3.7541	31
288.562 - 288.905	-3.6274	43
322.08 - 322.487	-3.3935	66
355.705 - 356.211	-3.3598	78

Table 2: The five main areas where we targeted our search for propargyl cyanide.

cy ranges. Once the data was downloaded, we performed data calibration and interferometric deconvolution processes using the Common Astronomy Software Package 5.8 (CASA) [10]. Some notable settings were used, including specmode set to cube and outframe set to TOPO. We identified strong candidates for further analysis using the Cube Analysis and Rendering Tool for Astronomy (CARTA) and performed continuum

Figure 4: The resulting spectrum from Titan in blue using CARTA of a disk-averaged spectrum using data set 2012.1.00261.S. The predicted location of the spectral lines of propargyl cyanide and cyanoallene were superimposed onto the in green.

subtraction on those images. A retrieval model fitting using the Non-linear optimal Estimator for MultivariatE spectral analySIS (NEMESIS; [11]) radiative transfer package was performed with the goal of upper-limit calculations.

Future Work: The chemistry of these heavy nitriles is poorly understood, and the results from this study will help inform photochemical models of Titan's atmosphere and other carbon and nitrogen-rich planetary atmospheres in the galaxy. H_3C_3N has the lowest energy, is the most stable isomer, and is the most abundant. Cyanoallene ($H_2CCCHCN$) is moderately stable. Propargyl cyanide ($HCCCH_2CN$) has the highest energy, is the least stable isomer, and is the least abundant [12]. If we get upper limits on these species, it will help to constrain their ratios. Multiple observations will be combined to produce higher S/N spectra with the intent of either detecting or providing stringent upper limits for both undetected C_4H_3N isomers.

References: [1] Waite, J. H. et al., 2004, SSRv, 114, L113. [2] Young, D. T. et al., 2004, SSRv, 114, L1. [3] Waite, J. H. et al., 2007, Science, 316, L870. [4] Thelen, A. E. et al., 2020, ApJL, 903, L22. [5] Broten, N. W. et al., 1984, ApJL, 276, L25. [6] Lovas, F. J. et al., 2006, ApJL, 637, L37. [7] Mcguire, B. A. et al., 2020, ApJL, 900, L10. [8] Müller, H. S. P. et al., 2001, A&A, 370 L49. [9] Müller, H. S. P. et al., 2005, J. Mol. Struct., 743, L215. [10] The CASA Team et al., 2022, PASP, 134, L17. [11] Irwin, P. J. G. et al., 2008, JQSRT, 109, L1136. [12] Marcelino, N. et al., 2020, A&A, 646, L9.

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