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# Paving the way to the synthesis of adenine in the ISM: abundant Z-cyanomethanimine

V. M. Rivilla[1], J. Martín-Pintado[2], I. Jiménez-Serra[2], S. Zeng[3], S. Martín[4,5], J. Armijos-Abendaño[6], M. A. Requena-Torres[7], R. Aladro[8], and D. Riquelme[8]

[1] INAF-Osservatorio Astrofisico di Arcetri, Largo Enrico Fermi 5, I-50125, Florence, Italy
e-mail: `rivilla@arcetri.astro.it`
[2] Centro de Astrobiología (CSIC−INTA). Ctra de Ajalvir, km. 4, Torrejón de Ardoz, 28850 Madrid, Spain
[3] School of Physics and Astronomy, Queen Mary University of London, Mile End Road, E1 4NS London, United Kingdom
[4] European Southern Observatory (ESO), Alonso de Córdova 3107, Vitacura, Santiago, Chile
[5] Joint ALMA Observatory, Alonso de Córdova 3107, Vitacura, Santiago, Chile
[6] Observatorio Astronómico de Quito, Escuela Politécnica Nacional, Av. Gran Colombia S/N, Interior del Parque La Alameda, 170136, Quito, Ecuador
[7] University of Maryland, College Park, ND 20742-2421, USA
[8] Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, 53121 Bonn, Germany

**Abstract.** We report the first detection in the interstellar medium of the Z-isomer of cyanomethanimine (HNCHCN), an HCN dimer proposed as precursor of adenine. We identified six transitions of Z-cyanomethanimine, along with five transitions of E-cyanomethanimine, using IRAM 30m observations towards the Galactic Center quiescent molecular cloud G+0.693. The Z-isomer has a column density of $(2.0\pm0.6)\times10^{14}$ cm$^{-2}$ and an abundance of $1.5\times10^{-9}$. The relative abundance ratio between the isomers is [Z/E]~6. This value cannot be explained by the two chemical formation routes previously proposed (gas-phase and grain surface), which predict abundances ratios between 0.9 and 1.5. The observed [Z/E] ratio is in good agreement with thermodynamic equilibrium at the gas kinetic temperature (130−210 K). Since isomerization is not possible in the ISM, the two species may be formed at high temperature. New chemical models, including surface chemistry on dust grains and gas-phase reactions, should be explored to explain our findings. Whatever the formation mechanism, the high abundance of Z-HNCHCN shows that precursors of adenine are efficiently formed in the ISM.

**Key words.** Galaxy: centre – ISM: molecules – ISM: abundances –ISM: clouds

## 1. Introduction

Understanding the origin of life on Earth is one of the most challenging problems in astrophysics in the framework of astrobiology. To shed light on this complex topic, it is absolutely needed a comprehensive study of the chemical complexity of the interstellar medium (ISM) that feeds the formation of stars and planets. In this sense, the chemical family of nitriles can give important clues. Nitriles, organic compounds with a $-C{\equiv}N$ functional group, play a crucial role in prebiotic chemistry since they are key intermediates in the formation of amino acids, peptides, nucleic acids and nucleobases (e.g. Balucani 2009). Adenine ($H_5C_5N_5$), one of the nucleobases of DNA and RNA, is a basic ingredient in the RNA-world scenario for the origin of life on Earth (e.g., Bernstein et al. 2004). Oró (1961) reported the synthesis of adenine from a solution of HCN and $NH_3$ under conditions similar to those thought to have existed on the primitive Earth. Chakrabarti & Chakrabarti (2000) proposed that adenine might be formed during the chemical evolution of a star-forming molecular cloud through the oligomerization of HCN in the gas phase in four simple steps.

However, by performing theoretical calculations, Smith et al. (2001) and Yim & Choe (2012) showed that the first step, the formation of an HCN dimer from two HCN molecules, does not occur efficiently in the conditions of the ISM. Therefore, the question of how HCN dimers can be formed remains open. Since they are precursors of adenine, understanding their formation mechanisms is of crucial importance from an astrobiological point of view.

The most stable dimer of HCN is C-cyanomethanimine (HNCHCN hereafter), which presents two different isomers: the Z-isomer and the E-isomer. These species are stereoisomers about the double bond N=C (see e.g. Fig. 1 of Takano et al. 1990) and the conversion from the Z- to the E-isomer requires an energy of 15.95 kK. The laboratory experiments and chemical calculations by Takano et al. (1990) and Zaleski et al. (2013), respectively, indicate that the Z-isomer is more stable and lower in energy than the E-isomer, with an estimated energy difference in the range 238−382 K. HNCHCN has been proposed as one of the most interesting prebiotic species to be studied in star-forming regions with current and the next generation astronomical facilities (Beltrán & Rivilla 2018). Nevertheless, only the high-energy E-isomer has been detected in the ISM so far. Several lines were reported in absorption towards the bright continuum of the cluster of hot cores located in the SgrB2N complex (Zaleski et al. 2013), while the Z-conformer was elusive.

We summarize here the results of an interstellar search for the Z-conformer of HNCHCN (Z-HNCHCN hereafter), already presented in more detail in Rivilla et al. (2019). Using an IRAM 30m spectral survey, we searched for this species in the G+0.693-0.027 giant molecular cloud (G+0.693 hereafter) in the Galactic Center. This region exhibits high gas kinetic temperatures ranging from $\sim$50 K to $\sim$150 K (Zeng et al. 2018), low dust temperatures of $\leq$30 K (Rodríguez-Fernández et al. 2004), and relatively low $H_2$ gas densities ($\sim$$10^4$ cm$^{-3}$; Rodríguez-Fernández et al. 2000). Due to the low $H_2$ densities, the molecules are sub-thermally excited and hence the excitation temperatures are low ($\sim$5-20 K; Requena-Torres et al. 2006; Rivilla et al. 2018; Zeng et al. 2018). G+0.693 is one of the most chemically rich reservoirs in our Galaxy. Many molecular species have been identified in this cloud, including some of prebiotic relevance such as complex organic molecules (COMs; Requena-Torres et al. 2006, 2008; Zeng et al. 2018) and phosphorus-bearing species (Rivilla et al. 2018). In particular, numerous nitrile molecules have been already detected in the source such as $C_3N$, $HC_3N$, $HC_5N$, $HC_7N$, $CH_2CN$, $CH_3CN$, $CH_3C_3N$, $NH_2CN$ and HOCN (Zeng et al. 2018). This rich nitrile chemistry makes this source an excellent target to search for more complex nitriles, and in particular Z-HNCHCN.

## 2. Detection of both isomers of cyanomethanimine

The identification of the lines was performed using the SLIM (Spectral Line Identification and Modeling) tool of the MADCUBA package[1]. We generated with SLIM-MADCUBA a synthetic spectrum assuming local thermody-

[1] Madrid Data Cube Analysis on ImageJ is a software developed at the Center of Astrobiology (CAB) in Madrid; see Rivilla et al. (2016, 2017a); Rivilla et al. (2017b).

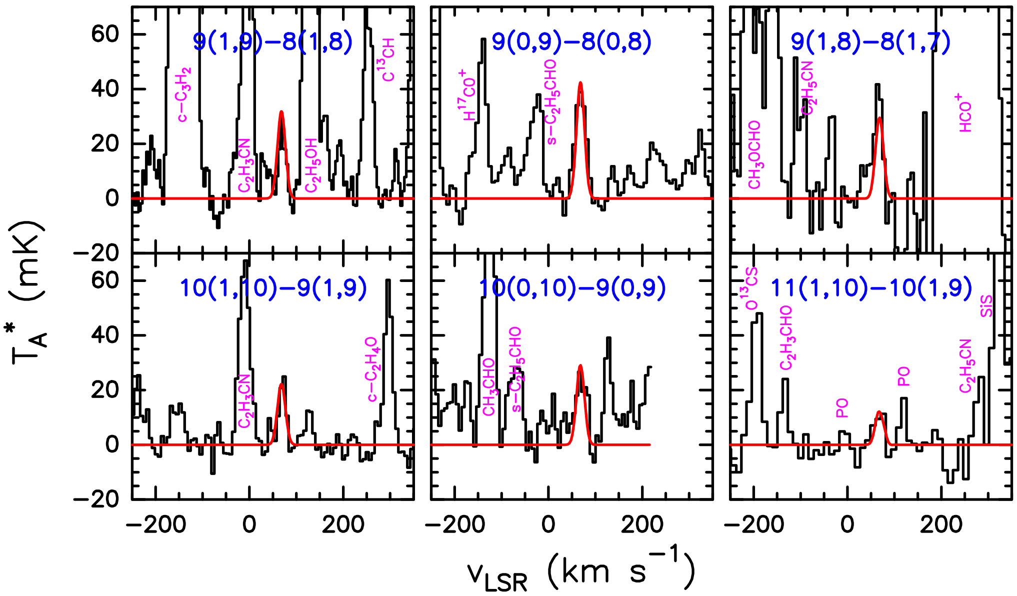


**Fig. 1.** IRAM 30m spectra of Z-HNCHCN towards the Galactic Center quiescent giant molecular cloud G+0.693. The red curves correspond to the LTE best fit obtained with MADCUBA−AUTOFIT. The quantum numbers of each transition are shown in blue in each panel. Other molecular species identified in the spectra are indicated with magenta labels.

namic equilibrium (LTE) conditions to compare with the observations. We confirmed the presence of ten transitions of Z-HNCHCN in the spectra towards G+0.693 with a significant detection level (>4$\sigma$). Six of these transitions are unblended, i.e., they are not contaminated by emission from other molecular species, while the other four are blended with other species. The spectra are shown in Figure 1. This is the first detection of this species in the ISM. Then, we used the MADCUBA-AUTOFIT tool that compares the observed spectra with the LTE synthetic spectra, taking into account all the transitions considered, and it provides the best non-linear least-squared fit using the Levenberg-Marquardt algorithm. The results of the fit are summarized in Table 1. We derived an excitation temperature of 8±2 K, very similar to that determined for other complex species in this region (Requena-Torres et al. 2008; Zeng et al. 2018), and a column density of $(2.0\pm0.6)\times10^{14}$ cm$^{-2}$.

We repeated the analysis for the E-isomer. We identified eight transitions above >4$\sigma$, of which five are unblended. We obtained a column density of $(0.33\pm0.03)\times10^{14}$ cm$^{-2}$. Both conformers have velocities of around ~68 km s$^{-1}$, consistently with many other molecules observed towards this region (see e.g. Zeng et al. 2018). The molecular ratio between the two conformers is [Z/E]=6.1±2.4. The total molecular abundance of C-cyanomethanimine, considering both isomers, is $1.74\times10^{-9}$.

We derived the fractional molecular abundances by dividing their column densities by the $H_2$ column density ($N_{H_2}$) measured in G+0.693. We adopted $N_{H_2}$= 1.35 $\times10^{23}$ cm$^{-2}$ as inferred by Martín et al. (2008) from $C^{18}O$ observations. The derived abundances are presented in Table 1. The Z-isomer has a relatively high abundance of $1.5\times10^{-9}$, which is comparable to those of other nitrogen-bearing species in this source such as $CH_3CN$ or $HC_5N$.

We also searched in the spectra of G+0.693 for other molecules that have been proposed as possible precursors of HNCHCN (see further discussion in Section 3): the cyanogen radical (CN), methanimine ($CH_2NH$) and cyanogen

(NCCN). The results of AUTOFIT are presented in Table 1. We obtained a CN fractional abundance of $1.5\times10^{-8}$. The results of $CH_2NH$ were previously presented in Zeng et al. (2018) and are also shown in Table 1.

Since the detection of NCCN is not possible through radio and millimeter observations due to the lack of a permanent electric dipole moment, we searched for its protonated form, $NCCNH^+$. We confirmed the presence of this species through the detection of the J=10-9 and J=11-10 rotational transitions. Our analysis yielded a fractional molecular abundance of $1.4\times10^{-11}$ for this species (Table 1). If we assume a $[NCCNH^+]/[NCCN]$ ratio of $\sim10^{-4}$ as inferred from the chemical modelling of Agúndez et al. (2015), the abundance of NCCN would be $1.4\times10^{-7}$ cm$^{-2}$.

## 3. Formation of cyanomethanimine, a precursor of adenine

Due to the lack of detections, very little is known about the formation of HNCHCN. Zaleski et al. (2013) suggested that radical chemistry on the surface of dust grains might form HNCHCN. More recently, two possible formation routes have been proposed. Vazart et al. (2015) studied the neutral-neutral gas-phase reaction between the cyanogen radical and methanimine:

$$CN + CH_2NH \rightarrow HNCHCN + H \tag{1}$$

A different chemical pathway has been proposed by Shivani & Tandon (2017) both on the surface of icy dust grains and in the gas phase:

$$NCCN + H + H \rightarrow HNCHCN \tag{2}$$

All proposed formation paths seem to be barrierless, which suggests that both gas-phase and grain surface reactions are able to form efficiently HNCHCN provided that the precursors are sufficiently abundant. Our data indicate that the reactants of the proposed reactions (CN, $CH_2NH$ and NCCN) are relatively abundant in G+0.693, with abundances ranging from $4\times10^{-9}$ to $1.4\times10^{-7}$ (Table 1). This suggests that these mechanisms might be able to explain the high abundance of HNCHCN ($1.74\times10^{-9}$) inferred in this cloud.

Since we have detected for the first time both isomers, we can use the [Z/E] ratio to constrain the proposed formation scenarios. Vazart et al. (2015) showed that the gas-phase formation route from CN and $CH_2NH$ produces a ratio [Z/E]$\sim$1.5, regardless of the temperature. The calculations by Shivani & Tandon (2017) predict a [Z/E] ratio of 0.9 in gas-phase and of 1 on the surface of dust grains. Therefore, both pathways fail to explain the observed ratio of $\sim$6, which might indicate that we are missing key formation routes and/or destruction reactions. A complete study including all the formation and destruction channels of the involved species is needed before drawing firm conclusions. Interestingly, the [Z/E] ratio found in G+0.693 seems to indicate that the two isomers are close to thermodynamic equilibrium at the kinetic temperature $T_{\rm k}$ of the cloud. If this is the case, the abundances of the isomers are related through the expression:

$$[Z/E] = \frac{N(Z)}{N(E)} = \frac{1}{g} \times exp\left(\frac{\Delta E}{T_{\rm k}}\right), \tag{3}$$

where $\Delta E$ is the energy difference between the isomers, and $g$ accounts for the statistical weights, which in this case is 1. Takano et al. (1990) derived experimentally an energy difference of 237−382 K, which is in good agreement with the value of 370 K inferred with the quantum chemical calculations by Zaleski et al. (2013), and with the value of 307 K more recently estimated by Puzzarini (2015). Then, the observed [Z/E] ratio of 6.1 implies a $T_{\rm k}$ in the range 130−210 K, which is in good agreement with the kinetic temperature found by Zeng et al. (2018) in G+0.693. This suggests that the two isomers are in thermodynamic equilibrium at the $T_{\rm k}$ of the gas. We note that also the populations of other isomers in the ISM seem to be in thermodynamic equilibrium at $T_{\rm k}$, as e.g. the conformers of ethyl formate ($C_2H_5OCHO$) in the hot molecular cores located in the W51 and Orion KL regions (Rivilla et al. 2017b; Tercero et al. 2013). Since the isomerization barrier between the E− and Z−isomers of HNCHCN is very high

**Table 1.** Derived parameters of the HNCHCN isomers detected towards G+0.693

| Species | N ($\times10^{14}$ cm$^{-2}$) | $T_{ex}$ (K) | $v_{LSR}$ (km s$^{-1}$) | FWHM (km s$^{-1}$) | Abundance ($\times10^{-10}$) |
|---|---|---|---|---|---|
| Z−HNCHCN | 2.0±0.6 | 8±2 | 68.3±0.8 | 20$^{(a)}$ | 15 |
| E−HNCHCN | 0.33±0.03 | 8$^{(a)}$ | 68.0±0.8 | 21±2 | 2.4 |
| $^{13}$CN | 0.94±0.03 | 10$^{(a)}$ | 71.6±0.4 | 18.8±0.9 | 7.0 |
| CN | | | | | 150$^{(c)}$ |
| $CH_2NH^{(b)}$ | 5.4±0.3 | 9.7±0.4 | 69±1 | 25±1 | 40 |
| $NCCNH^+$ | 0.019±0.004 | 10$^{(a)}$ | 69±2 | 22±5 | 0.14 |
| NCCN | | | | | 1400$^{(d)}$ |

(a) Parameter fixed in the MADCUBA−AUTOFIT analysis. (b) From Zeng et al. (2018). (c) Assuming the isotopic ratio of $^{12}$C/$^{13}$C∼21 derived in G+0.693 by Armijos-Abendaño et al. (2014). (d) Assuming a [$NCCNH^+$]/[NCCN] ratio of $\sim10^{-4}$, as inferred from chemical modelling by Agúndez et al. (2015).

(15.95 kK; Zaleski et al. 2013) this process cannot occur in the ISM. This means that the $T_k$ derived from eq. 3 reflects the temperature at which the molecules were formed. Since the dust in G+0.693 is cold (≤30 K; Rodríguez-Fernández et al. 2004 ), and the gas temperatures are high (∼50 K to ∼150 K; (e.g. Zeng et al. 2018), this opens two possible chemical pathways:

i) gas-phase reactions occurring at the high kinetic temperatures of the cloud; and
ii) formation on dust triggered by non-thermal energetic events like cosmic-ray impacts, and their subsequent release by grain sputtering in moderate-velocity shock waves.

The latter scenario is plausible in the case of G+0.693 since large-scale low-velocity shocks are widespread in the region due to the encounter of two streams of molecular gas (Hasegawa et al. 1994; Henshaw et al. 2016). However, the current observations do not allow to discriminate between these two possible chemical routes.

Whatever the formation mechanism, our analysis of the first detection in the ISM of the Z-isomer of HNCHCN reveals that its abundance is higher than that of the E-conformer by a factor of 6. Given the proposed role of HNCHCN as precursor of adenine (Eschenmoser 2007; Chakrabarti & Chakrabarti 2000; Balucani 2012; Jung & Choe 2013), the relative high abundance of this species, $1.5\times10^{-9}$, argues in favor of an efficient synthesis of key precursors of adenine in space. This is a crucial step to understand how the basic ingredients of life could have been assembled in the ISM before their incorporation to the primitive Earth. The role of HNCHCN in the formation of more complex nitrile dimers, and in particular adenine, should be addressed in detail with new detections of HNCHCN in more interstellar sources and with chemical modelling.

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