



## SYSTEMATIC THEORETICAL STUDY ON THE INTERSTELLAR CARBON CHAIN MOLECULES

EMMANUEL E. ETIM<sup>1,2</sup>, PRASANTA GORAI<sup>3</sup>, ANKAN DAS<sup>3</sup>, SANDIP K. CHAKRABARTI<sup>2,4</sup>, AND ELANGANNAN ARUNAN<sup>1</sup>

<sup>1</sup>Inorganic and Physical Chemistry Department, Indian Institute of Science Bangalore, 560012, India

<sup>2</sup>Department of Chemical Sciences, Federal University Wukari, Katsina-Ala Road, P.M.B. 1020 Wukari, Taraba State, Nigeria

<sup>3</sup>Indian Centre for Space Physics, 43 Chalanika, Garia Station Road, Kolkata 700 084, India; [ankan.das@gmail.com](mailto:ankan.das@gmail.com)

<sup>4</sup>S. N. Bose National Centre for Basic Sciences, Salt Lake, Kolkata 700098, India

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### ABSTRACT

In an effort to further our interest in understanding the basic chemistry of interstellar molecules, here we carry out an extensive investigation of the stabilities of interstellar carbon chains;  $C_n$ ,  $H_2C_n$ ,  $HC_nN$  and  $C_nX$  ( $X = N, O, Si, S, H, P, H^-, N^-$ ). These sets of molecules account for about 20% of all the known interstellar and circumstellar molecules. Their high abundances, therefore, demand serious attention. High-level ab initio quantum chemical calculations are employed to accurately estimate the enthalpy of formation, chemical reactivity indices, global hardness and softness, and other chemical parameters of these molecules. Chemical modeling of the abundances of these molecular species has also been performed. Of the 89 molecules considered from these groups, 47 have been astronomically observed, and these observed molecules are found to be more stable with respect to other members of the group. Of the 47 observed molecules, 60% are odd-numbered carbon chains. Interstellar chemistry is not actually driven by thermodynamics, but it is primarily dependent on various kinetic parameters. However, we found that the detectability of the odd-numbered carbon chains could be correlated due to the fact that they are more stable than the corresponding even-numbered carbon chains. Based on this aspect, the next possible carbon chain molecule for astronomical observation in each group is proposed. The effect of kinetics in the formation of some of these carbon chain molecules is also discussed.

*Key words:* dust, extinction – evolution – ISM: abundances – ISM: molecules – methods: numerical – stars: formation

### 1. INTRODUCTION

As more and more interstellar and circumstellar molecules are observed, our understanding of the chemistry of these molecules is either strengthened or challenged depending on whether the new molecules fall within or outside the boundaries of their expected basic chemistry. These observations also put a constraint on the different chemical models. The fields of astronomy, astrophysics, astrochemistry and astrobiology have witnessed dramatic changes in the last few decades as a result of the advances in science and technology. In addressing the chemical origin of life and for the proper understanding of the solar system, there has been a constant and consistent searching for molecules in the interstellar and circumstellar media, resulting in the unique observation of about 200 different molecular species to date. The year 2014 has seen unparalleled observations of nine new interstellar and circumstellar molecules, including the first branched chain molecule in space, namely, isopropyl cyanide, an important biological molecule; urea, the sulfur analog (ethyl mercaptan) of the well known interstellar alcohol; ethanol, among others and the confirmation of many others (Agúndez et al. 2014; Anderson & Ziurys 2014; Belloche et al. 2014; Cernicharo et al. 2014; Kolesniková et al. 2014; Remijan et al. 2014).

Almost on a regular basis, carbon chain molecules such as  $C_n$ ,  $H_2C_n$ ,  $HC_nN$ , and  $C_nX$  ( $X = N, O, Si, S, H, P, H^-, N^-$ ) are being astronomically observed. To date, the largest claimed straight-chain interstellar molecule is the cyanopolyne,  $HC_{11}N$ , a linear carbon chain molecule. Among the carbon chains, there seems to be no easily understood trend or pattern within the observed molecules. In the  $C_nN$  and  $C_nN^-$  chains, with the exception of  $C_2N$ , only the odd-numbered carbon chains are observed from  $n = 1$  to  $n = 6$  (Jefferts et al. 1970; Friberg

et al. 1980; Guélin et al. 1998; Cernicharo et al. 2008; Thaddeus et al. 2008; Agúndez et al. 2010; Anderson & Ziurys 2014). Whereas in the  $C_nH$  chains, both odd- and even-numbered chains are observed between 1 and 8, but in the  $C_nH^-$ , only even-numbered chains are observed (Swings & Rosenfeld 1937; Tucker et al. 1974; Guélin et al. 1978; Thaddeus et al. 1985a; Cernicharo et al. 1986, 2007; Suzuki et al. 1986; Cernicharo & Guélin 1996; Guélin et al. 1997; McCarthy et al. 2006; Brünken et al. 2007a). Among the cyanopolyne chains, between 6 and 12 carbon atoms, only odd-numbered chains are observed (Snyder & Buhl 1971; Turner 1971; Avery et al. 1976; Broten et al. 1978; Kroto et al. 1978; Guélin & Cernicharo 1991; Bell et al. 1997; Cernicharo et al. 2004), while in the  $C_nSi$  group, all the molecules between carbon 1 and 4 have been observed (Thaddeus et al. 1984; Cernicharo et al. 1989; Ohishi et al. 1989; Apponi et al. 1999). This type of confusing trend is observed among the different groups of linear interstellar carbon chains.

As part of our interest in understanding the basic chemistry of interstellar and circumstellar molecules, the present work focuses on the interstellar and circumstellar carbon chains;  $C_n$ ,  $H_2C_n$ ,  $HC_nN$  and  $C_nX$  ( $X = N, O, Si, S, H, P, H^-, N^-$ ). High-level quantum chemical calculations are applied to accurately determine the enthalpies of formation, chemical reactivity indices, global hardness and softness, and other chemical parameters of these molecules. Chemical modeling of the abundances of these molecular species has also been performed, and the results are used in accounting for the general observation of more odd carbon chains than even carbon chains, and the dominance of the even carbon chains in a few cases. The possible candidates for astronomical

observation among the carbon chain molecules are also considered.

## 2. COMPUTATIONAL DETAILS

The results of the quantum chemical calculations reported in this work were obtained using the Gaussian 09 suite of programs (Frisch et al. 2009). In order to estimate accurate enthalpies of formation, which are in good agreement with the experimental values (where available) for the different carbon chains considered in this work, the G4 composite method was employed. The choice of this method is borne out of experience, as it has been shown to compute enthalpies of formation to chemical accuracy (Curtiss et al. 1998, 2007a, 2007b). The geometries of these molecules were optimized at the G4 level, and harmonic vibrational frequency calculations were used to characterize the stationary nature of all the structures with equilibrium species possessing only real frequencies. The reported zero-point corrected standard enthalpies of formation of the carbon chains were calculated from the optimized geometries. The enthalpies of formation were calculated from atomization energies. With the G4 computational method and accurate experimental values of the standard enthalpy of formation of the constituent elements involved, very high accurate enthalpies of formation can be estimated for different sets of molecular systems. Atomization energies (sometimes referred to as the total dissociation energies) were evaluated using the calculated values of the energies (sum of electronic and zero-point energy corrections). In calculating the enthalpy of formation ( $\Delta_f H$ ) at 0 K for all the molecules reported in this study, the experimental values of the standard enthalpy of formation of elements C, H, O, N, P, Si and S reported in the literature were used (Ochterski 2000). Chemical reactivity indices such as global hardness ( $\eta$ ) and softness ( $S$ ) have been calculated for different carbon chains, which were examined in this study. For the computation of  $S$  and  $\eta$ , we use the DFT method with the B3LYP/6-311g++(d, p) basis set of the Gaussian 09 program. First, we calculate the ionization potential (I) of the desired species by computing the energy (ground-state optimized energy) difference between the cation and neutral and electron affinity (A) by computing the energy difference between the neutral and anion. Chemical hardness is calculated by  $\eta = (I - A)$  (Parr & Pearson 1983) and softness is calculated by  $1/\eta$ . The chemical modeling of the abundances of these carbon chain species is described, together with the obtained results, in the discussion section.

## 3. RESULTS AND DISCUSSION

The results of the quantum chemical calculations at the G4 level of theory, which were obtained for all the carbon chain molecules, are presented and discussed in this section (3.1–3.11). In all the cases, the reported zero-point corrected standard enthalpies of formation ( $\Delta_f H^\circ$ ) are in kcal/mol. Section 3.12 examines the effect of kinetics on the formation processes of these carbon chains. In Section 3.13, chemical reactivity indices and chemical modeling supporting the observed results in the previous sections are presented and discussed before the final conclusion.

**Table 1**  
 $\Delta_f H^\circ$  for  $C_n$  Chains and Current Astronomical Status

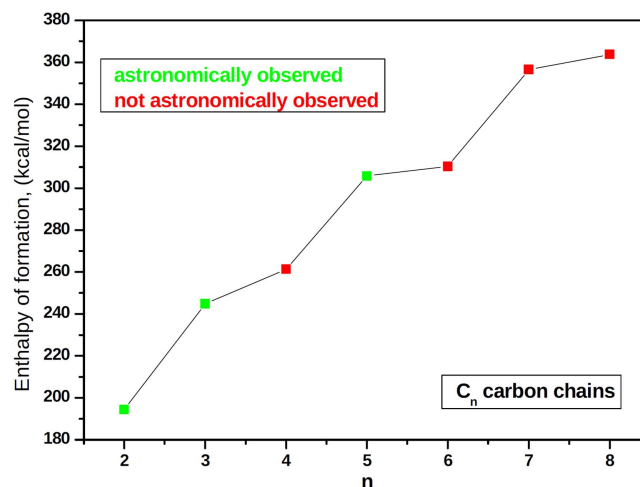
$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
2	194.432	<sup>a</sup> Observed
3	244.785	<sup>b</sup> Observed
4	261.328	Not observed
5	305.822	<sup>c</sup> Observed
6	310.379	Not observed
7	356.501	Not observed
8	363.736	Not observed

### Notes.

<sup>a</sup> Souza & Lutz (1977).

<sup>b</sup> Hinkle et al. (1988), Cernicharo et al. (2000).

<sup>c</sup> Bernath et al. (1989).



**Figure 1.** Plot showing the  $\Delta_f H^\circ$  for  $C_n$  chain molecules.

### 3.1. $C_n$ Chains

Apart from their importance in astrophysics, astrochemistry, and astrobiology, pure carbon chain molecules such as  $C_2$ ,  $C_3$ , and  $C_5$  are of great interest to the combustion chemistry, particularly for application in flames and propellants. Table 1 shows the enthalpy of formation and the current astronomical status of the carbon chain ( $C_n$ ) molecules considered in this study. Rotational spectroscopy has been the dominant tool in the chemical examination of interstellar and circumstellar media with about 90% of all known interstellar and circumstellar molecules observed via their rotational transitions. However, the application of rotational spectroscopy in this field is hampered by the fact that it is limited to molecules with a permanent dipole moment (Etim & Arunan 2015). The  $C_n$  chain molecules have no permanent dipole moment; hence, their pure rotational transitions cannot be measured. All the known interstellar  $C_n$  chain molecules have been observed in the infrared region through their vibrational transitions.

As can be seen from Table 1, there is a steady increase in the enthalpy of formation of the  $C_n$  chains as the chain length increases.  $C_4$  is the exception, as it is yet to be observed. All the lower members of the chains with lower enthalpies of formation have been detected (Souza & Lutz 1977; Hinkle et al. 1988; Bernath et al. 1989; Cernicharo et al. 2000). With respect to the effect of thermodynamics, the lower members of the chains with lower enthalpies of formation are more stable than the higher members of the chains with higher enthalpies of

**Table 2**  
 $\Delta_f H^\circ$  for  $C_nO$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	-23.127	<sup>a</sup> Observed
2	91.369	<sup>b</sup> Observed
3	75.328	<sup>c</sup> Observed
4	148.640	Not observed
5	133.782	Not observed
6	204.526	Not observed

**Notes.**

<sup>a</sup> Smith & Stecher (1971).

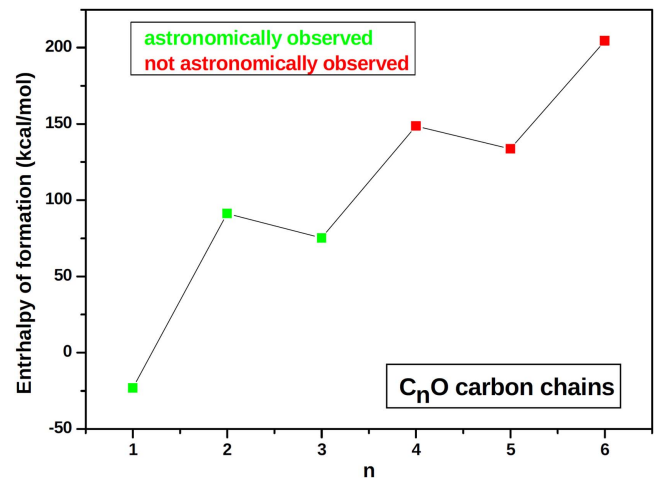
<sup>b</sup> Ohishi et al. (1991).

<sup>c</sup> Matthews et al. (1984).

formation. Figure 1 shows the plot of the enthalpy of formation of the  $C_n$  chain molecules estimated at the G4 level. The lower members of the chains remain the most likely candidates for astronomical observation compared to the higher members of the chains. As  $C_4$  is yet to be observed and  $C_5$  has already been observed, it is likely that  $C_7$ , which has a larger enthalpy of formation, may be observed before  $C_6$ , which has a lower enthalpy of formation.

### 3.2. $C_nO$ Chains

The  $C_nO$  group presents an interesting set of carbon chain molecules containing two (carbon and oxygen) of the four most important biological elements. Unlike the  $C_n$  chains, which lack a permanent dipole moment, the  $C_nO$  chains all possess a permanent dipole moment. Hence, all the known interstellar/circumstellar  $C_nO$  molecules have been observed via their rotational transition spectra. The enthalpy of formation and current astronomical status for all the  $C_nO$  molecules considered in this study are presented in Table 2, while Figure 2 depicts the plot of the enthalpy of formation for these molecules. Of the six molecules considered in the  $C_nO$  group, the first three ( $n = 1-3$ ) have been astronomically observed (Smith & Stecher 1971; Matthews et al. 1984; Ohishi et al. 1991). The trend of the enthalpy of formation is the same as in the case of the  $C_n$  chain molecules. The odd-numbered carbon chain molecules are found to be more stable (lower enthalpy of formation value) than their corresponding even-numbered ones. The interstellar chemistry of oxygen and sulfur is well coupled, with over 80% of all the known S-containing interstellar molecules having their corresponding O-containing molecules as known interstellar molecules. Also, in most of the cases, the abundance of the S-compound relative to its O-analog is approximately equal to the cosmic S/O ratio (Frerking et al. 1979; Linke et al. 1979). The high probability of  $C_5O$  as an interstellar molecule stems from two important facts;  $C_5O$  has lower enthalpy of formation compared with  $C_4O$  and  $C_6O$ , and consequently, it is more stable in interstellar medium (ISM), and can thus possibly be observed. Second,  $C_5S$ , the sulfur analog of  $C_5O$ , has recently been observed (Agúndez et al. 2014) and the O-containing molecules are known to be more abundant in ISM than in their corresponding S-analog. Hence, astronomical observation of  $C_5S$  is a clear indication of the presence of  $C_5O$  in detectable abundance in ISM.



**Figure 2.** Plot showing the  $\Delta_f H^\circ$  for  $C_nO$  chain molecules.

**Table 3**  
 $\Delta_f H^\circ$  for  $C_nS$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	72.404	<sup>a</sup> Observed
2	141.307	<sup>b</sup> Observed
3	136.292	<sup>c</sup> Observed
4	196.958	Not observed
5	190.684	<sup>d</sup> Observed
6	254.207	Not observed
7	243.688	Not observed
8	313.195	Not observed

**Notes.**

<sup>a</sup> Penzias et al. (1971).

<sup>b</sup> Saito et al. (1987).

<sup>c</sup> Yamamoto et al. (1987).

<sup>d</sup> Cernicharo et al. (1987).

<sup>e</sup> Agúndez et al. (2014).

### 3.3. $C_nS$ Chains

IRC+10216, the carbon-star envelope, has emerged as one of the richest sources of molecules, with over eighty different molecular species so far observed in it. Alongside other molecular clouds, all the known  $C_nS$  molecules were observed in IRC+10216. As discussed in the previous section, the interstellar chemistry of oxygen and sulfur is very similar in many ways. Of the four ( $CS$ ,  $C_2S$ ,  $C_3S$ ,  $C_5S$ ) observed molecules in the  $C_nS$  group (Penzias et al. 1971; Cernicharo et al. 1987; Saito et al. 1987; Yamamoto et al. 1987; Agúndez et al. 2014), 3 ( $CS$ ,  $C_2S$ ,  $C_3S$ ), three have the corresponding O-analogs known as interstellar molecules. However,  $C_5S$  has been astronomically observed, but not  $C_4S$  and  $C_6S$ . This could be correlated with its enthalpy of formation value (Table 3) compared to those of  $C_4S$  and  $C_6S$ . As shown in Table 3 and Figure 3, all the odd-numbered  $C_nS$  chains have lower enthalpy of formation than their corresponding even-numbered  $C_nS$  chains. Hence they are more stable and likely more abundant, and can thus be more easily observed than their even-numbered counterparts.

### 3.4. $C_nN$ Chains

The long carbon chain radicals like  $C_nN$  have long been thought to be present in the interstellar and circumstellar media

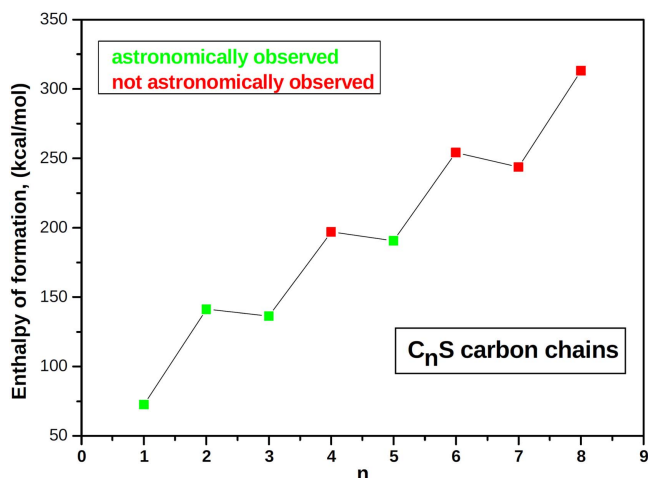


Figure 3. Plot showing the  $\Delta_f H^\circ$  for  $C_nS$  chain molecules.

in detectable abundance and supposed to play an important role in astrophysics. A number of fundamental interstellar molecules were first detected in space before being observed in the gas phase in the terrestrial laboratory. These include  $HCO^+$ ,  $C_2H$ ,  $HNC$ , and  $HN_2^+$  (Guélin & Thaddeus 1977) among others, and thus most of them were termed “non-terrestrial.” The cyanoethynyl radical,  $C_3N$ , is one such molecule whose identification was guided by the electron spin resonance spectrum of a related species,  $C_4H$  (butadienyl radical). The astronomical observations of  $C_2N$  and  $C_5N$  were hindered by the lack of accurate spectroscopic data. Their astronomical observations became possible immediately after their laboratory microwave spectra were measured (Jefferts et al. 1970; Friberg et al. 1980; Guélin et al. 1998; Anderson & Ziurys 2014). Table 4 and Figure 4 indicate a constant gradual increase in the enthalpy of formation of the  $C_nN$  chain molecules. A good correlation between the observations of the lower chains (except for  $C_4N$ ) with the enthalpy of formation can be seen.

### 3.5. $C_nSi$ Chains

Every unique astronomical observation of molecule(s) in the interstellar or circumstellar medium has always been a concerted effort between the laboratory spectroscopists and the astrophysicists. The successful detection (after a number of failed attempts) of  $SiC$  in IRC+10216 (Cernicharo et al. 1989), came immediately after the successful measurements of its laboratory spectrum. Whether cyclic molecules are chemically less abundant than their related linear species in the interstellar or circumstellar medium has been the question for decades, due to the fact that of about 200 known interstellar and circumstellar molecules, only about ten are cyclic. However, of the four known  $C_nSi$  molecules, two are cyclic. The ground-state geometry of  $SiC_2$  is shown to have a compact symmetric ( $C_{2v}$ ) ring, in contrast to the earlier belief that  $SiC_2$  is linear. The proper elucidation of its ground-state geometry became instrumental for its astronomical observation (Thaddeus et al. 1984). Figure 5 shows the most stable geometry for the  $SiC_3$  molecule, which is the rhomboidal isomer. The experimentally determined bond lengths of  $c-SiC_3$  through isotopic substitution measurement (Apponi et al. 1999) and the theoretically calculated bond lengths at the G4 level are in good agreement, as shown in Figures 5(A) and (B), respectively.

Table 4  
 $\Delta_f H^\circ$  for  $C_nN$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	106.413	<sup>a</sup> Observed
2	163.544	<sup>b</sup> Observed
3	173.701	<sup>c</sup> Observed
4	210.486	Not observed
5	231.723	<sup>d</sup> Observed
6	263.488	Not observed
7	287.663	Not observed
8	319.404	Not observed

#### Notes.

- <sup>a</sup> Jefferts et al. (1970).  
<sup>b</sup> Anderson & Ziurys (2014).  
<sup>c</sup> Friberg et al. (1980).  
<sup>d</sup> Guélin et al. (1998).

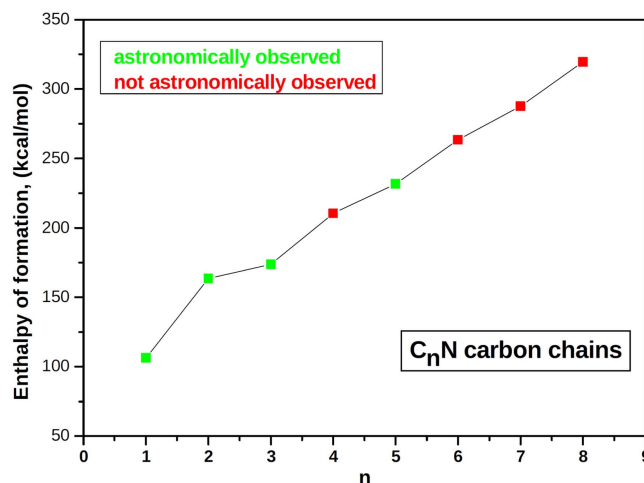


Figure 4. Plot showing the  $\Delta_f H^\circ$  for  $C_nN$  chain molecules.

Table 5 and Figure 6 show the enthalpies of formation for all the  $C_nSi$  molecules considered in this study. There is a steady increase in the enthalpy of formation value as the carbon chain increases, except for  $c-C_2Si$ . The observed molecules are also the most stable molecules (Thaddeus et al. 1984; Cernicharo et al. 1989; Ohishi et al. 1989; Apponi et al. 1999). The enthalpy of formation for the linear  $C_3Si$  molecule, 221.687 kcal/mol, is about 10 kcal/mol higher than the most stable isomer, which is cyclic in structure. The detection of more silicon-carbon molecules in IRC+10216 in particular (where all  $C_nSi$  chains have been observed) and other astronomical sources await laboratory spectra of such molecules.

### 3.6. $HC_nN$ Chains

The largest claimed interstellar linear molecule, the cyanopolyne  $HC_{11}N$ , belongs to the  $HC_nN$  chains. The enthalpies of formation of these molecules follow a unique trend, with the odd-numbered carbon chains being more stable than their preceding and the next even-numbered carbon chains, as shown in Table 6. For instance,  $HC_3N$  is more stable than both  $HC_2N$  and  $HC_4N$ ;  $HC_5N$  is more stable than both  $HC_4N$  and  $HC_6N$ , etc. Figure 7 depicts the zigzag pattern of the enthalpies of formation of the  $HC_nN$  chains. Of the eight molecules belonging to the  $HC_nN$  carbon chain, which have been detected

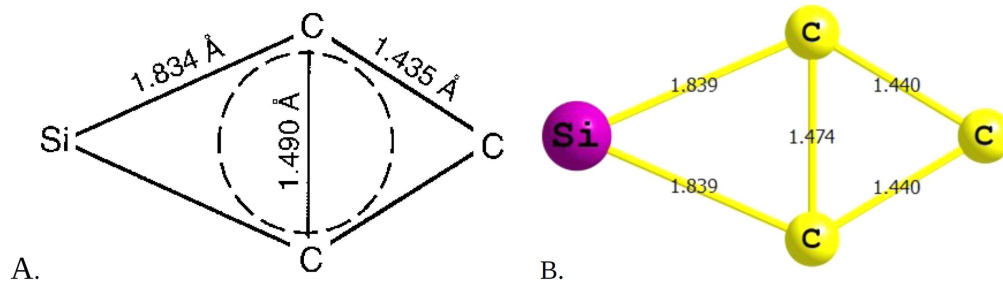


Figure 5. Experimental (A) and theoretical geometry (B) of the  $c\text{-SiC}_3$  molecule.

**Table 5**  
 $\Delta_f H^\circ$  for  $C_n\text{Si}$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	177.113	Observed (IRC+10216)
$c\text{-C}_2\text{Si}$	151.989	Observed (IRC+10216)
$c\text{-C}_3\text{Si}$	228.773	Observed (IRC+10216)
4	216.930	Observed (IRC+10216)
5	269.727	Not observed
6	277.600	Not observed

**Notes.**

- <sup>a</sup> Cernicharo et al. (1989).  
<sup>b</sup> Thaddeus et al. (1984).  
<sup>c</sup> Apponi et al. (1999).  
<sup>d</sup> Ohishi et al. (1989).

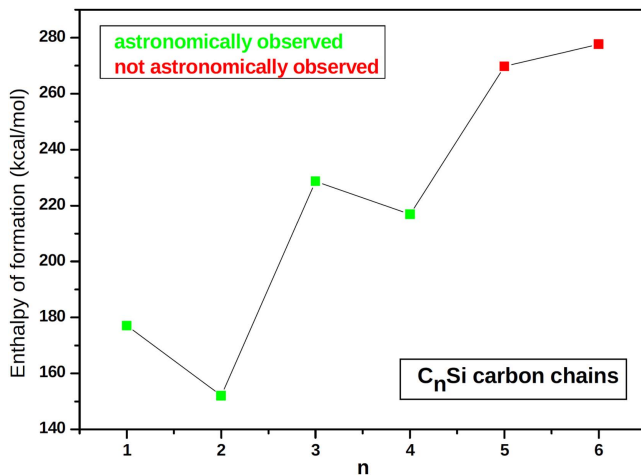


Figure 6. Plot showing the  $\Delta_f H^\circ$  for  $C_n\text{Si}$  chain molecules.

in interstellar and circumstellar media (Snyder & Buhl 1971; Turner 1971; Avery et al. 1976; Broten et al. 1978; Kroto et al. 1978; Guélin & Cernicharo 1991; Bell et al. 1997; Cernicharo et al. 2004), only two ( $\text{HC}_2\text{N}$  and  $\text{HC}_4\text{N}$ ) are even-numbered carbon chains, while the remaining six are odd-numbered ( $\text{HCN}$ ,  $\text{HC}_3\text{N}$ ,  $\text{HC}_5\text{N}$ ,  $\text{HC}_7\text{N}$ ,  $\text{HC}_9\text{N}$ , and  $\text{HC}_{11}\text{N}$ ). A very good correlation between the observations of more odd-numbered  $\text{HC}_n\text{N}$  chains and their enthalpy of formation values, in comparison to the even-numbered  $\text{HC}_n\text{N}$  chains, can be seen. The odd-numbered  $\text{HC}_n\text{N}$  chains are found to be more stable, and thus may be more easily observed compared to the even-numbered  $\text{HC}_n\text{N}$  chains. From this analogy,  $\text{HC}_{13}\text{N}$  is a more probable candidate for astronomical observation than both  $\text{HC}_{12}\text{N}$  and  $\text{HC}_{14}\text{N}$ . Accurate laboratory rest frequencies of  $\text{HC}_{13}\text{N}$  will be crucial for its astronomical searches and possible detection.

**Table 6**  
 $\Delta_f H^\circ$  for  $\text{HC}_n\text{N}$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	32.192	<sup>a</sup> Observed
2	116.586	<sup>b</sup> Observed
3	88.738	<sup>c</sup> Observed
4	161.602	<sup>d</sup> Observed
5	140.566	<sup>e</sup> Observed
6	211.115	Not observed
7	191.824	<sup>f</sup> Observed
8	263.903	Not observed
9	242.928	<sup>g</sup> Observed
10	317.217	Not observed
11	292.191	<sup>h</sup> Observed
12	372.551	Not observed
13	342.655	Not observed
14	428.028	Not observed

**Notes.**

- <sup>a</sup> Snyder & Buhl (1971).  
<sup>b</sup> Guélin & Cernicharo (1991).  
<sup>c</sup> Turner (1971).  
<sup>d</sup> Cernicharo et al. (2004).  
<sup>e</sup> Avery et al. (1976).  
<sup>f</sup> Kroto et al. (1978).  
<sup>g</sup> Broten et al. (1978).  
<sup>h</sup> Bell et al. (1997).

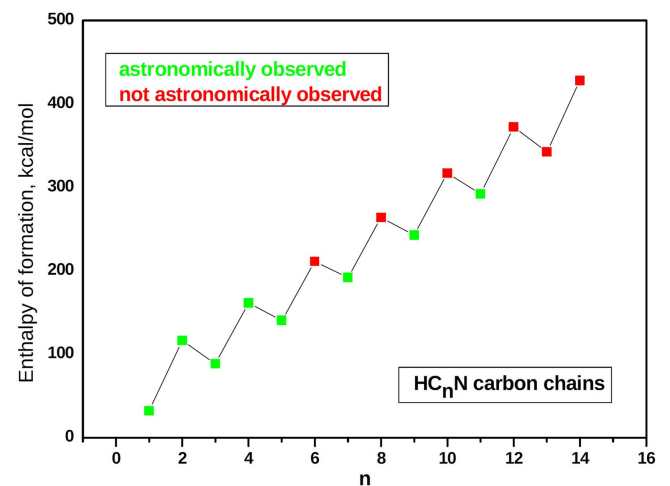


Figure 7. Plot showing the  $\Delta_f H^\circ$  for  $\text{HC}_n\text{N}$  chain molecules.

### 3.7. $C_n\text{H}$ Chains

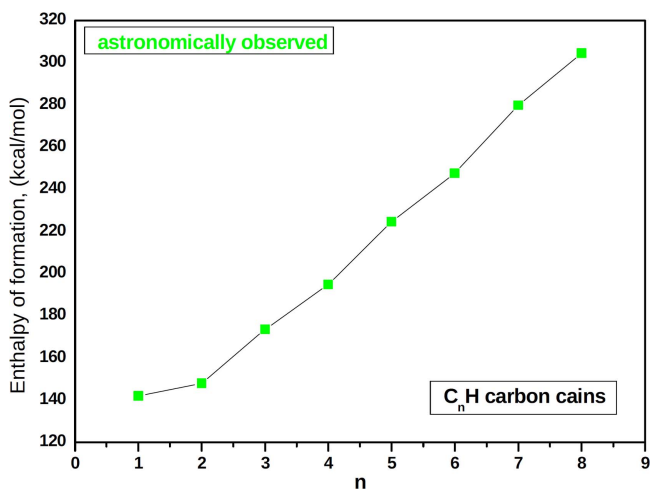
Discoveries of cyanopolynes set the pace for the recognition of long chain molecules in space, such as  $C_n\text{H}$ ,  $C_n\text{H}^-$ , etc. The acetylenic chain ( $C_n\text{H}$ ) radicals from  $n = 1$  to  $n = 8$  have all

**Table 7**  
 $\Delta_f H^\circ$  for  $C_nH$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	142.025	<sup>a</sup> Observed
2	148.023	<sup>b</sup> Observed
3	173.615	<sup>c</sup> Observed
4	194.790	<sup>d</sup> Observed
5	224.678	<sup>c</sup> Observed
6	247.560	<sup>f</sup> Observed
7	279.702	<sup>g</sup> Observed
8	304.480	<sup>h</sup> Observed

#### Notes.

- <sup>a</sup> Swings & Rosenfeld (1937).  
<sup>b</sup> Tucker et al. (1974).  
<sup>c</sup> Thaddeus et al. (1985a).  
<sup>d</sup> Guélin et al. (1978).  
<sup>e</sup> Cernicharo et al. (1986).  
<sup>f</sup> Suzuki et al. (1986).  
<sup>g</sup> Guélin et al. (1997).  
<sup>h</sup> Cernicharo & Guélin (1996).



**Figure 8.** Plot showing the  $\Delta_f H^\circ$  for  $C_nH$  chain molecules.

been observed in space, (Swings & Rosenfeld 1937; Tucker et al. 1974; Guélin et al. 1978; Thaddeus et al. 1985a; Cernicharo et al. 1986; Suzuki et al. 1986; Cernicharo & Guélin 1996; Guélin et al. 1997). The steady increase in the enthalpy of formation of these chains, as the carbon chain increases, is shown in Table 7 and Figure 8. Most of the  $C_nH$  radicals could be termed “non-terrestrial”, as they were first observed in space using the results from quantum chemical calculations prior to being studied in the laboratory. They are believed to grow steadily in the recombination phase of the interstellar medium (Suzuki 1983). In the carbon-rich astronomical sources, such as TMC and IRC+10216, where all the known  $C_nH$  chain radicals have been detected, successive members of the  $C_nH$  chains ( $n > 8$ ) are more likely to exist.

### 3.8. $C_nP$ Chains

Just like sulfur and oxygen, phosphorus (the 18th most cosmically abundant element) and nitrogen are in the same group in the periodic table. Whereas the similarity between the interstellar molecules of sulfur and oxygen is well established with almost all S-containing interstellar molecules having the O-analog as a known interstellar molecule, this is not the case

**Table 8**  
 $\Delta_f H^\circ$  for  $C_nP$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	125.335	<sup>a</sup> Observed
2	153.136	<sup>b</sup> Observed
3	174.674	Not observed
4	199.132	Not observed
5	221.889	Not observed
6	247.577	Not observed

#### Notes.

- <sup>a</sup> Guélin et al. (1990).  
<sup>b</sup> Halfen et al. (2008).

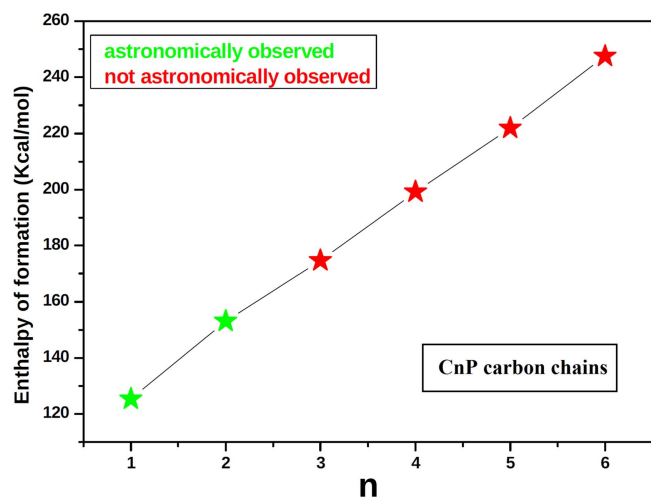
in terms of the interstellar chemistry of N-containing molecules and the P-analog, with only very few known P-containing molecules compared with the large number of N-containing interstellar/circumstellar molecules. This is due to the cosmic ratio of phosphorus and nitrogen compared with the cosmic ratio of sulfur and oxygen. Table 8 and Figure 9 display the enthalpy of formation for all the  $C_nP$  chains considered in this study. The only two astronomically observed molecules in this group, CP and  $C_2P$  (Guélin et al. 1990; Halfen et al. 2008), are also the most stable, and thus they may be detectable. As with the  $C_nH$  chains, there is a corresponding increase in the enthalpy of formation value for every successive increase in the carbon chain.

### 3.9. $H_2C_n$ Chains

Interstellar acetylene is a well known starting material in the formation processes of many interstellar and circumstellar species (Ridgway et al. 1976; Lacy et al. 1989). For the molecules with the empirical formula,  $H_2C_3$ , both the linear and the cyclic isomers have been observed in the Taurus molecular cloud, i.e., TMC-1 (Thaddeus et al. 1985b; Cernicharo et al. 1991). The cyclic isomer is now recognized as a common feature of many molecular clouds/astronomical sources. The polyacetylenic chains,  $C_4H_2$  and  $C_6H_2$ , have been observed in the proto-planetary nebula CRL 618 (Cernicharo et al. 2001) via their infrared vibrational spectra. The first three carbon chains in the  $H_2C_n$  group have been astronomically observed, as shown in Table 9 and Figure 10. The next most likely observable member of this group is neither  $H_2C_5$  nor  $H_2C_7$ , but rather  $H_2C_6$ . The even-numbered carbon chains in  $H_2C_n$  are more stable than their corresponding odd-numbered carbon counterparts, thus probably accounting for the astronomical observation of more even-numbered than odd-numbered carbon chains in this group.

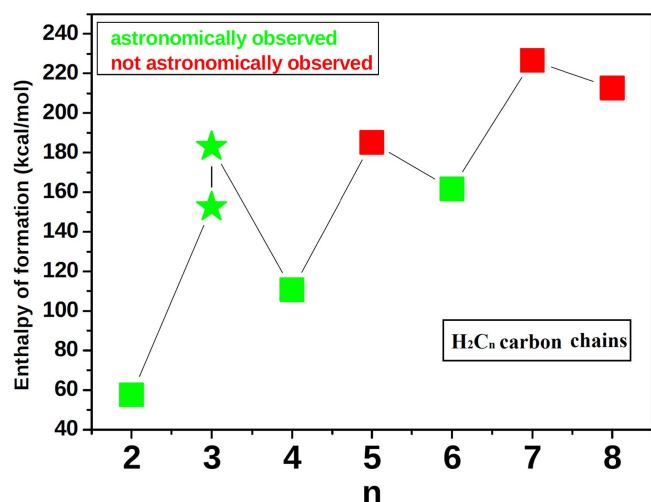
### 3.10. $C_nN^-$ Chains

Among the ion molecules in interstellar and circumstellar media, the positive ions have long been known and observed, while the negative ions have only been known for less than a decade. Of the eight  $C_nN^-$  chains considered here, only three have been astronomically observed;  $CN^-$ ,  $C_3N^-$ , and  $C_5N^-$  (Cernicharo et al. 2008; Thaddeus et al. 2008; Agúndez et al. 2010). The observed molecules (odd-numbered carbon chains) are found to be more stable than the others.  $CN^-$  is more stable than  $C_2N^-$ ;  $C_3N^-$  is more stable than both  $C_2N^-$  and  $C_4N^-$ ; and  $C_5N^-$  is more stable than both  $C_4N^-$  and  $C_6N^-$  (Table 10). Figure 11 depicts the plot of the enthalpy of

Figure 9. Plot showing the  $\Delta_f H^\circ$  for  $C_n P$  chain molecules.

**Table 9**  
 $\Delta_f H^\circ$  for  $H_2 C_n$  Chains and Current Astronomical Status

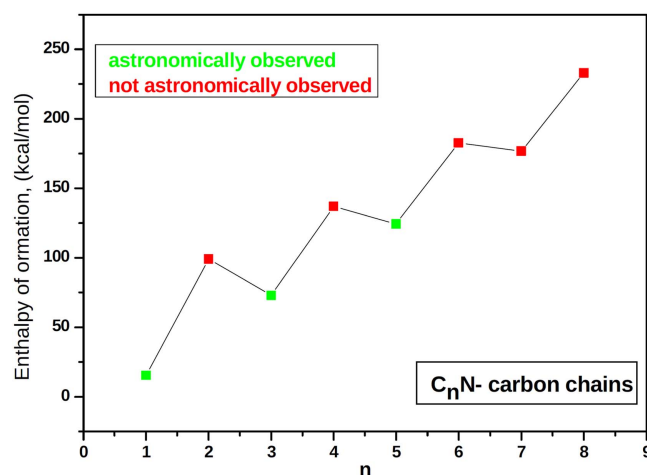
$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
2	57.612	<sup>a</sup> Observed
3 (linear)	152.590	<sup>b</sup> Observed
3 (cyclic)	183.036	<sup>c</sup> Observed
4	110.685	<sup>d</sup> Observed
5	185.283	Not observed
6	161.678	<sup>d</sup> Observed
7	226.691	Not observed
8	212.684	Not observed

**Notes.**<sup>a</sup> Ridgway et al. (1976), Lacy et al. (1989).<sup>b</sup> Cernicharo et al. (1991).<sup>c</sup> Thaddeus et al. (1985b).<sup>d</sup> Cernicharo et al. (2001).Figure 10. Plot showing the  $\Delta_f H^\circ$  for  $H_2 C_n$  chain molecules.

formation of these molecules, which shows a zigzag pattern as noted in the case of the  $HC_n N$  chains. Following the order of their astronomical observations,  $C_7 N$  can be considered as the next probable candidate as it is more stable than both  $C_6 N^-$  and  $C_8 N^-$ .

**Table 10**  
 $\Delta_f H^\circ$  for  $C_n N^-$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	15.459	<sup>a</sup> Observed
2	99.183	Not observed
3	72.910	<sup>b</sup> Observed
4	137.056	Not observed
5	124.358	<sup>c</sup> Observed
6	182.629	Not observed
7	176.752	Not observed
8	232.983	Not observed

**Notes.**<sup>a</sup> Agúndez et al. (2010).<sup>b</sup> Thaddeus et al. (2008).<sup>c</sup> Cernicharo et al. (2008).Figure 11. Plot showing the  $\Delta_f H^\circ$  for  $C_n N^-$  chain molecules.3.11.  $C_n H^-$  Chains

Molecular anions have long been predicted to be detectable in astronomical sources, and are currently estimated by chemical formation models to be in higher abundance than their neutral counterparts. The first known interstellar molecular anion,  $C_6 H^-$ , was shown to be the carrier of the unidentified series of lines of IRC+10216 via laboratory measurements of its rotational spectrum. The astronomical observations of  $C_4 H^-$  and  $C_8 H^-$  came immediately after the successful measurements of their rotational spectra (McCarthy et al. 2006; Brünken et al. 2007a; Cernicharo et al. 2007). Theoretically estimated enthalpy of formation for the  $C_n H^-$  ( $n = 1-10$ ) chains using the G4 composite method is presented in Table 11. The same is also displayed in Figure 12. The even-numbered carbons chains are more stable than the preceding and the next odd-numbered carbon chains;  $C_2 H^-$  is more stable than  $CH^-$  and  $C_3 H$ ,  $C_4 H^-$  is more stable than  $C_3 H^-$  and  $C_5 H^-$ , and so on. The rotational spectrum of  $C_2 H^-$  is known (Brünken et al. 2007b), and its astronomical observation is a function of time. The three astronomically detected  $C_n H^-$  carbon chains are all even-numbered. These are the most stable, which might account for their observation, rather than the preceding and the next odd-numbered chain in each case, which have not been observed.

**Table 11**  
 $\Delta_f H^\circ$  for  $C_n H^-$  Chains and Current Astronomical Status

$n$	$\Delta_f H^\circ$ (kcal/mol)	Astronomical Status
1	135.131	Not observed
2	92.858	<sup>a</sup> Tentatively observed
3	196.282	Not observed
4	188.822	<sup>b</sup> Observed
5	268.466	Not observed
6	227.126	<sup>c</sup> Observed
7	270.745	Not observed
8	267.406	<sup>d</sup> Observed
9	279.286	not observed
10	256.98	not observed

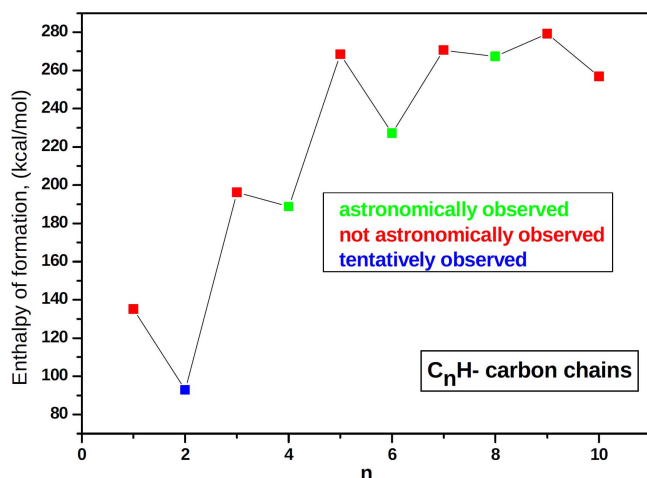
**Notes.**

<sup>a</sup> Agúndez et al. (2010) and references therein.

<sup>b</sup> Cernicharo et al. (2007).

<sup>c</sup> McCarthy et al. (2006).

<sup>d</sup> Brünken et al. (2007a).

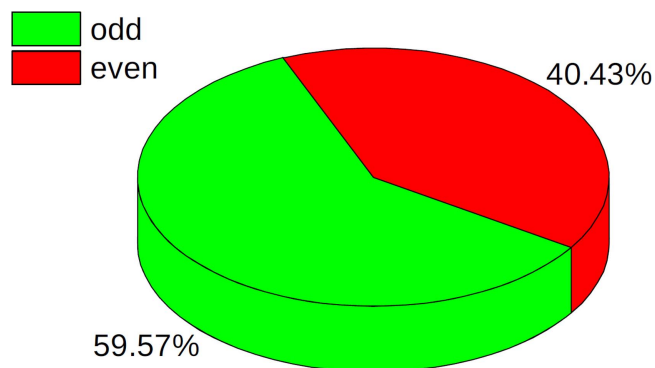


**Figure 12.** Plot showing the  $\Delta_f H^\circ$  for  $C_n H^-$  chain molecules.

**Table 12**  
 Carbon Chains which have been Considered in this Study

Chain	Total Number Considered	Odd Observed	Even Observed
$C_n$	7	2	1
$C_n O$	6	2	1
$C_n S$	8	3	1
$C_n N$	8	3	1
$C_n Si$	6	2	2
$HC_n N$	14	6	2
$C_n H$	8	4	4
$C_n P$	6	1	1
$C_n N^-$	8	3	0
$C_n H^-$	10	0	3
$H_2 C_n N$	8	2	3
Total	89	28	19

Table 12 gives the summary of all the different carbon chains, which have been considered in this study. It is obvious from the table, that in each group the number of odd- and even-numbered carbon chains observed depends on the trend of the enthalpy of formation of the molecules in that group. The odd-numbered carbon chains are found to be more stable than their



**Figure 13.** Percentage of detected odd- and even-numbered carbon chains.

corresponding even-numbered carbon chains in most of the group (Figure 13). This might have resulted in the observation of more interstellar odd-numbered (60%) than the even-numbered carbon chains.

### 3.12. Effect of Kinetics on the Formation of Carbon Chains

The effect of kinetics on the formation of carbon chain species both in the terrestrial laboratory and in the interstellar medium cannot be overemphasized. Although there is hardly consensus as to how any molecule (especially the complex ones with six atoms and above) is formed in the interstellar medium,  $C_2$  addition is the widely acclaimed route for the formation of the linear carbon chains. In the terrestrial laboratory, unsaturated molecules like acetylene, diacetylene, etc., are used as the source of the  $C_2$  in producing the carbon chains, while in the interstellar medium, acetylene, which produces the  $C_2$  is generally accepted as the starting material for the formation of these carbon chains (Cherchneff et al. 1993; Cherchneff & Glassgold 1993; McCarthy et al. 1997; Thaddeus et al. 1998). With respect to the carbon chains discussed here, a good correlation between the enthalpy of formation and observed abundances has been seen. For instance, in the  $C_n O$  chains, where the odd-numbered carbon chains are more stable than their progressive even-numbered chains,  $C_2$  addition to the lower chains to form the higher chains, clearly favors the odd-numbered chains compared to their corresponding even-numbered chains. A  $C_2$  addition to  $CO$  to form  $C_3 O$  is likely to have a lower barrier compared to  $C_2$  addition to  $C_2 O$  to form  $C_4 O$ , which could account for the delayed observation of  $C_4 O$ . This is also applicable to the  $C_n S$  chains, where a  $C_2$  addition to  $C_3 S$  to form  $C_5 S$  (astronomically observed) is more favorable than a  $C_2$  addition to  $C_2 S$  to form  $C_4 S$  (yet to be observed). And this continues to the higher members of the chains. Also, in the  $HC_n N$  and  $C_n N^-$  chains,  $C_2$  addition to form higher members of the chains is likely to favor the odd-numbered carbon chains compared to the even-numbered ones, which explains the trends in the astronomical observation of these species. In the case of  $C_n Si$ ,  $H_2 C_n$ , and  $C_n H^-$  chains, where the even-numbered are more stable than their corresponding odd-numbered chains, it is crystal clear that  $C_2$  addition to the lower members of the chains is more likely to favor the even-numbered carbon chains compared to their odd-numbered counterparts. For instance, a  $C_2$  addition to  $HC_5 N$  to form  $HC_7 N$  is could be more favorable than  $C_2$  addition to  $HC_4 N$  to form  $HC_6 N$ , which has not been detected. Correlation between the effects of kinetics on the formation of these species can be seen even for the chains with a linear

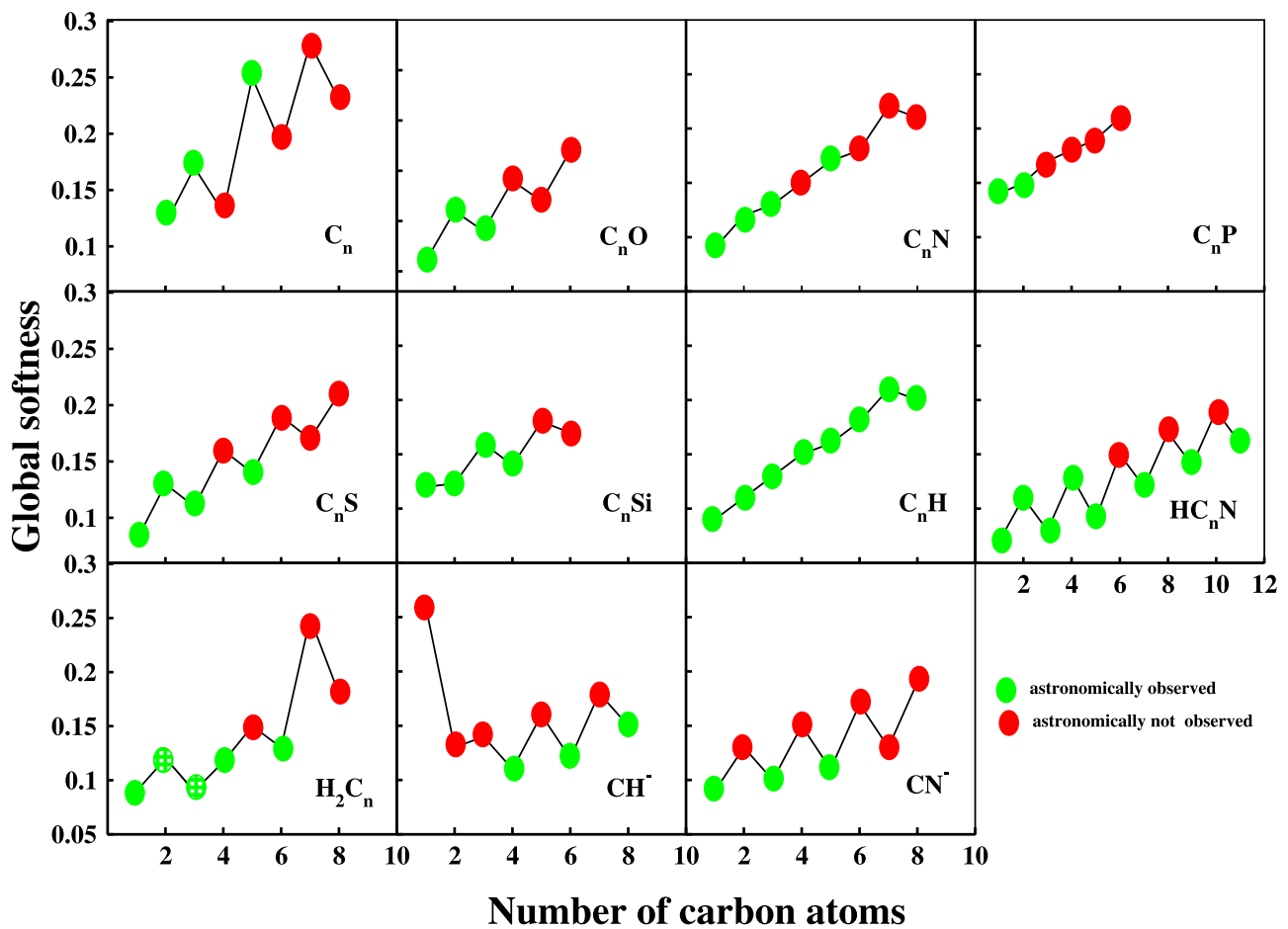


**Table 13**  
Global Reactivity Indices for the Carbon Chain Molecules

Carbon Chains	Electron Affinity (ev)	Ionization Potential (ev)	Global Hardness ( $\eta$ )	Global Softness (S)	Electrophilicity Index ( $\omega$ )
C <sub>2</sub>	4.315589604	12.38118018	8.06559057	0.12398348	4.320547246
C <sub>3</sub>	4.299943058	10.03321861	5.73327555	0.17442036	4.479104517
C <sub>4</sub>	3.223841626	10.48334934	7.25950771	0.13775039	3.23518983
C <sub>5</sub>	5.061235976	8.983784335	3.92254836	0.25493631	6.286174748
C <sub>6</sub>	4.573961705	9.574978885	5.00101718	0.19995932	5.003795043
C <sub>7</sub>	5.054541975	8.581572853	3.52703088	0.28352459	6.589948956
C <sub>8</sub>	4.638425476	8.973879391	4.33545392	0.23065636	5.342429173
CO	-1.15085110	14.19743128	15.3482824	0.06515387	1.386256536
C <sub>2</sub> O	2.34194785	11.3391474	8.99719955	0.1111457	2.600425363
C <sub>3</sub> O	1.07569326	11.91692674	10.8412335	0.09224043	1.946367251
C <sub>4</sub> O	2.9618232	10.00853788	7.04671468	0.1419101	2.984196789
C <sub>5</sub> O	2.124637729	10.36919758	8.24455985	0.1212921	2.366650306
C <sub>6</sub> O	3.324768653	9.175651811	5.85088316	0.17091437	3.338395837
CH	0.120138265	11.00240651	10.8822682	0.09189261	1.421015815
C <sub>2</sub> H	3.111703509	11.56853937	8.45683586	0.11824754	3.185433869
C <sub>3</sub> H	1.926647692	9.361641627	7.43499393	0.1344991	2.142326491
C <sub>4</sub> H	3.47244484	10.36144233	6.88899749	0.145159	3.472501523
C <sub>5</sub> H	2.593898064	8.655995991	6.06209793	0.16495939	2.609660009
C <sub>6</sub> H	3.647169143	9.20098561	5.55381647	0.18005636	3.715352351
C <sub>7</sub> H	2.975782641	7.758237977	4.78245534	0.20909761	3.01150744
C <sub>8</sub> H	3.823907089	8.65754704	4.83363995	0.20688343	4.028710732
CN	4.962404226	15.61593357	10.6535293	0.09386561	4.968634956
C <sub>2</sub> N	2.940870434	11.09087072	8.15000029	0.12269938	3.019781486
C <sub>3</sub> N	4.493470428	12.46142655	7.96795612	0.1255027	4.509759578
C <sub>4</sub> N	3.312577953	9.828969953	6.516392	0.15345915	3.312804873
C <sub>5</sub> N	4.888198779	10.5489832	5.66078442	0.17665396	5.262225376
C <sub>6</sub> N	3.605127553	9.117174544	5.51204699	0.1814208	3.67052773
C <sub>7</sub> N	4.971356771	9.555305054	4.58394828	0.21815255	5.7544253
C <sub>8</sub> N	3.803988355	8.626553273	4.82256492	0.20735854	4.005087743
CP	3.624420425	10.72087752	7.09645709	0.14091539	3.624829446
C <sub>2</sub> P	2.731533249	9.229122182	6.49758893	0.15390324	2.752122361
C <sub>3</sub> P	3.658761193	9.590434952	5.93167376	0.16858648	3.699234095
C <sub>4</sub> P	3.154316538	8.617627938	5.4633114	0.18303917	3.170665797
C <sub>5</sub> P	3.821539698	8.940409387	5.11886969	0.19535563	3.977131533
C <sub>6</sub> P	3.431410071	8.207797269	4.7763872	0.20936326	3.545335153
HCN	-0.70335987	13.50925535	14.2126152	0.07036003	1.442301049
HC <sub>2</sub> N	1.977478559	10.69984312	8.72236456	0.11464781	2.303195479
HC <sub>3</sub> N	-0.05679016	11.341542	11.3983322	0.08773213	1.396537913
HC <sub>4</sub> N	2.023765125	9.568992381	7.54522726	0.13253411	2.226441001
HC <sub>5</sub> N	0.9548475	11.55373638	10.5988889	0.09434951	1.845295677
HC <sub>6</sub> N	2.439038072	8.919565466	6.48052739	0.15430843	2.488568184
HC <sub>7</sub> N	1.592246982	9.470487167	7.87824019	0.1269319	1.941805593
HC <sub>8</sub> N	2.732295168	8.471257899	5.73896273	0.17424752	2.733934842
HC <sub>9</sub> N	2.030105378	8.964491463	6.93438609	0.14420887	2.179016971
HC <sub>10</sub> N	2.90070643	8.139006888	5.23830046	0.19090161	2.908273187
HC <sub>11</sub> N	2.433160413	8.604403205	6.17124279	0.16204191	2.467651466
H <sub>2</sub> C <sub>2</sub>	0.677808389	11.27155432	10.5937459	0.09439532	1.684806183
l-H <sub>2</sub> C <sub>3</sub>	1.945042588	10.29523704	8.35019445	0.11975769	2.242828688
c-H <sub>2</sub> C <sub>3</sub>	-1.08125684	9.15234512	10.2336010	0.0977517	0.79575879
H <sub>2</sub> C <sub>4</sub>	1.859653262	10.34897952	8.48932626	0.11779498	2.194678204
H <sub>2</sub> C <sub>5</sub>	2.618905327	9.231217459	6.61231213	0.15123303	2.654620033
H <sub>2</sub> C <sub>6</sub>	2.548155726	10.02097349	7.47281776	0.13381833	2.642627825
H <sub>2</sub> C <sub>7</sub>	3.056083438	6.991176246	3.93509281	0.25412361	3.206640608
H <sub>2</sub> C <sub>8</sub>	2.988626415	8.396290533	5.40766412	0.18492273	2.996125755
CSi	2.293974178	10.54732331	8.25334913	0.12116293	2.497454647
C <sub>2</sub> Si	1.678207747	9.765921174	8.08771343	0.12364434	2.024182854
C <sub>3</sub> Si	2.66475651	9.066534157	6.40177765	0.15620661	2.687206357
C <sub>4</sub> Si	2.343199574	9.39489394	7.05169437	0.14180989	2.442371155
C <sub>5</sub> Si	3.048681941	8.506959236	5.45827729	0.18320799	3.058035434
C <sub>6</sub> Si	2.784622661	8.774501573	5.98987891	0.16694828	2.788314986
CS	0.299352446	11.50772193	11.2083695	0.08921904	1.554719952
C <sub>2</sub> S	2.689736562	10.40672208	7.71698552	0.12958428	2.778242044
C <sub>3</sub> S	1.702779628	10.75483733	9.0520577	0.11047212	2.143051687
C <sub>4</sub> S	3.159758815	9.441370985	6.28161217	0.1591948	3.159787407

**Table 13**  
(Continued)

Carbon Chains	Electron Affinity (ev)	Ionization Potential (ev)	Global Hardness ( $\eta$ )	Global Softness (S)	Electrophilicity Index ( $\omega$ )
C <sub>5</sub> S	2.481569466	9.63361942	7.15204995	0.13982005	2.565309993
C <sub>6</sub> S	3.452934277	8.804488519	5.35155424	0.1868616	3.509363981
C <sub>7</sub> S	2.959483021	9.001607792	6.04212477	0.16550469	2.95979682
C <sub>8</sub> S	3.693210806	8.368290018	4.67507921	0.21390012	3.889768375
CN <sup>-</sup>	-6.72932108	4.962404226	11.6917253	0.08553058	0.033378256
C <sub>2</sub> N <sup>-</sup>	-4.94071675	2.940870434	7.88158719	0.126878	0.06342925
C <sub>3</sub> N <sup>-</sup>	-5.60834808	4.493470428	10.1018185	0.09899208	0.015380302
C <sub>4</sub> N <sup>-</sup>	-3.36525919	3.312577953	6.67783715	0.14974908	5.19501E-05
C <sub>5</sub> N <sup>-</sup>	-3.91196313	4.888198779	8.80016191	0.11363427	0.013537195
C <sub>6</sub> N <sup>-</sup>	-2.21244886	3.605127553	5.81757642	0.17189289	0.04167444
C <sub>7</sub> N <sup>-</sup>	-2.62399385	4.971356771	7.59535063	0.13165949	0.090682329
C <sub>8</sub> N <sup>-</sup>	-1.34579346	3.803988355	5.14978182	0.19418298	0.146674226
CH <sup>-</sup>	-3.69620405	0.120138265	3.81634232	0.262031	0.418864631
C <sub>2</sub> H <sup>-</sup>	-4.15879760	3.111703509	7.27050111	0.1375421	0.018850249
C <sub>3</sub> H <sup>-</sup>	-5.00950713	1.926647692	6.93615483	0.1441721	0.171276856
C <sub>4</sub> H <sup>-</sup>	-5.56902763	3.47244484	9.04147247	0.11060145	0.06077079
C <sub>5</sub> H <sup>-</sup>	-3.65484275	2.593898064	6.24874082	0.16003224	0.022516609
C <sub>6</sub> H <sup>-</sup>	-4.06075498	3.647169143	7.70792413	0.12973662	0.002773984
C <sub>7</sub> H <sup>-</sup>	-2.53308061	2.975782641	5.50886326	0.18152565	0.00444704
C <sub>8</sub> H <sup>-</sup>	-2.99548368	3.823907089	6.81939077	0.14664067	0.012579667



**Figure 14.** Variation of global softness with the number of carbon atoms present in carbon chains.

**Table 14**  
Initial Abundances

Species	Abundance w.r.t. total H
H <sub>2</sub>	$5.00 \times 10^{-01}$
He	$1.00 \times 10^{-01}$
N	$2.14 \times 10^{-05}$
O	$1.76 \times 10^{-04}$
H3+	$1.00 \times 10^{-11}$
C+	$7.30 \times 10^{-05}$
S+	$8.00 \times 10^{-08}$
Si+	$8.00 \times 10^{-09}$
Fe+	$3.00 \times 10^{-09}$
Na+	$2.00 \times 10^{-09}$
Mg+	$7.00 \times 10^{-09}$
P+	$3.00 \times 10^{-09}$
Cl+	$4.00 \times 10^{-09}$
e-	$7.31 \times 10^{-05}$
HD	$1.60 \times 10^{-05}$

increase in the enthalpy of formation such as in the C<sub>n</sub>H, C<sub>n</sub>P, C<sub>n</sub>N and C<sub>n</sub> chains.

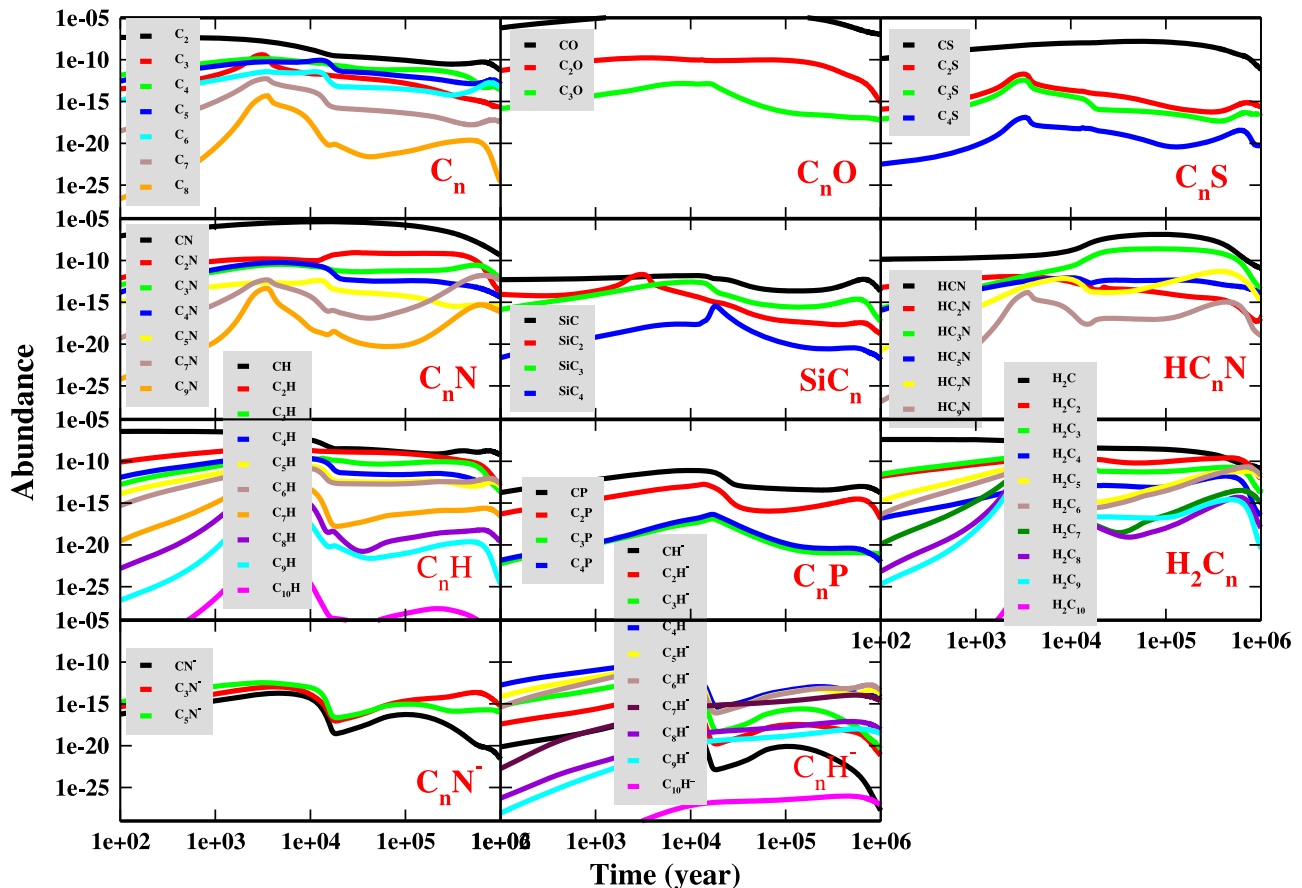
### 3.13. Other Studies Supporting the Above Results

The correlation between the thermodynamics and observation of the linear interstellar carbon chains has been discussed in the previous sections. Here, it is also correlated with the chemical reactivity indices such as global hardness ( $\eta$ ) and softness (S). Soft species are more reactive and unstable in

comparison to the hard species. Larger values of S indicate that the species are more unstable, and larger values of  $\eta$  indicate that the species are more stable. All the parameters are pointed out in Table 13. For the sake of simplicity, in Figure 14, we have shown the softness values for the carbon chain species.

#### 3.13.1. Chemical Modeling

The need for chemical modeling is ever increasing, because of the recent development of various sensitive ground-based and space-borne facilities as well as the vast data produced by the low-temperature laboratory experiments. Chemical modeling plays a very important role in the understanding of the empirical outcome of the observational results. We use our large gas-grain chemical network (Das et al. 2013, 2015a, 2015b; Majumdar et al. 2014a, 2014b) for the purpose of chemical modeling. We assume that gas and grains are coupled through accretion and thermal/non-thermal/cosmic ray evaporation processes. Details of these processes and chemical network were already presented in Das et al. (2015a, 2015b). The gas-phase chemical network is principally adopted from the UMIST 2006 (Woodall et al. 2007) database. Since the UMIST 2006 database does not consider some of the carbon chain molecules, we include their reactions from the UMIST 2012 network (McElroy et al. 2013). These databases contain different assorted reaction pathways and rate coefficients from the literature and, therefore, our calculated thermodynamical parameters do not seem to play any role in this modeling.



**Figure 15.** Chemical evolution of carbon chains for dense cloud.



**Table 15**  
Abundances of Carbon Chain Molecules

Carbon Chains	Peak Abundance (Final Abundance) with Respect to Total H in all Forms	
	Translucent Cloud	Dense Cloud
C <sub>2</sub>	5.32E-08(4.53E-08)	4.62E-08 (4.94E-12)
C <sub>3</sub>	1.58E-13 (1.17E-13)	3.97E-10 (3.44E-16)
C <sub>4</sub>	1.51E-11 (2.03E-12)	1.32E-10 (2.31E-14)
C <sub>5</sub>	1.69E-11 (1.17E-11)	8.62E-11 (1.23E-13)
C <sub>6</sub>	1.23E-12 (7.90E-13)	3.69E-12 (4.40E-14)
C <sub>7</sub>	7.68E-15 (6.90E-15)	5.37E-13 (3.66E-18)
C <sub>8</sub>	2.40E-20 (7.91E-21)	4.86E-15 (3.29E-25)
CO	6.26E-06 (1.08E-07)	2.93E-05 (1.09E-07)
C <sub>2</sub> O	2.46E-11 (1.23E-13)	1.67E-10 (7.85E-16)
C <sub>3</sub> O	5.07E-16 (5.35E-18)	1.43E-13 (5.85E-18)
CH	2.22E-07 (5.68E-08)	3.72E-07 (5.43E-10)
C <sub>2</sub> H	1.19E-09 (2.98E-10)	2.89E-09 (1.13E-13)
C <sub>3</sub> H	2.88E-11 (1.12E-11)	2.97E-10 (2.49E-14)
C <sub>4</sub> H	2.97E-11 (5.16E-12)	3.51E-10 (1.86E-13)
C <sub>5</sub> H	4.86E-12 (1.45E-12)	2.79E-11 (9.76E-14)
C <sub>6</sub> H	3.49E-11 (3.40E-11)	1.51E-11 (1.96E-13)
C <sub>7</sub> H	9.51E-15 (5.67E-15)	1.23E-12 (2.73E-17)
C <sub>8</sub> H	2.08E-17 (6.61E-18)	1.04E-12 (2.76E-20)
CN	3.60E-07 (1.58E-09)	4.25E-06 (4.08E-10)
C <sub>2</sub> N	1.29E-11 (4.14E-14)	8.32E-10 (3.19E-14)
C <sub>3</sub> N	5.88E-13 (7.75E-15)	3.45E-11 (5.93E-13)
C <sub>4</sub> N	2.68E-13 (3.21E-16)	5.90E-11 (4.11E-15)
C <sub>5</sub> N	1.53E-14 (7.44E-16)	4.14E-13 (2.63E-16)
C <sub>6</sub> N		
C <sub>7</sub> N	4.16E-16 (1.62E-17)	1.61E-12 (4.86E-13)
C <sub>9</sub> N	1.19E-21 (2.54E-23)	4.64E-14 (7.61E-17)
CP	2.53E-12 (2.53E-12)	7.83E-12 (1.63E-14)
C <sub>2</sub> P	9.57E-16 (3.55E-16)	1.79E-13 (1.21E-17)
C <sub>3</sub> P	1.82E-20 (9.47E-21)	1.31E-17 (6.57E-22)
C <sub>4</sub> P	4.83E-20 (3.27E-20)	4.45E-17 (9.13E-23)
C <sub>5</sub> P		
C <sub>6</sub> P		
HCN	1.06E-10 (2.06E-12)	1.33E-07 (1.27E-11)
HC <sub>2</sub> N	3.06E-14 (4.14E-17)	1.21E-12 (1.23E-17)
HC <sub>3</sub> N	1.13E-14 (5.67E-17)	2.46E-09 (3.28E-14)
HC <sub>5</sub> N	1.66E-14 (2.67E-16)	8.37E-13 (1.10E-14)
HC <sub>7</sub> N	2.37E-15 (1.06E-16)	4.86E-12 (1.35E-15)
HC <sub>9</sub> N	1.17E-20 (2.36E-22)	1.53E-14 (1.03E-19)
H <sub>2</sub> C <sub>2</sub>	1.76E-11 (4.77E-12)	2.75E-10 (8.38E-13)
H <sub>2</sub> C <sub>3</sub>	2.33E-11(7.51E-11)	4.48E-10 (4.95E-14)
H <sub>2</sub> C <sub>4</sub>	1.21E-14 (2.87E-15)	1.69E-12 (3.58E-17)
H <sub>2</sub> C <sub>5</sub>	8.96E-12 (9.26E-13)	5.64E-11 (1.05E-12)
H <sub>2</sub> C <sub>6</sub>	1.90E-11 (7.85E-12)	2.11E-11 (2.05E-12)
H <sub>2</sub> C <sub>7</sub>	3.18E-14 (5.86E-15)	5.77E-12 (1.06E-15)
H <sub>2</sub> C <sub>8</sub>	8.27E-17 (1.71E-17)	1.93E-12 (1.22E-18)
H <sub>2</sub> C <sub>9</sub>	4.73E-18 (1.21E-18)	1.42E-12(5.32E-21)
CSi	1.47E-12 (1.47E-12)	1.51E-12 (1.97E-14)
C <sub>2</sub> Si	1.04E-14 (1.04E-14)	2.14E-12 (1.64E-19)
C <sub>3</sub> Si	1.48E-14 (1.07E-14)	3.57E-16 (5.17E-18)
C <sub>4</sub> Si	4.04E-19 (1.73E-19)	3.57E-16 (1.32E-22)
CS	1.79E-10 (9.97E-11)	1.58E-08 (7.11E-12)
C <sub>2</sub> S	2.32E-15 (2.32E-15)	1.93E-12 (2.46E-16)
C <sub>3</sub> S	2.24E-16 (2.19E-16)	3.53E-13 (3.98E-17)
C <sub>4</sub> S	1.07E-20 (1.04E-20)	1.27E-17 (5.04E-21)
CN <sup>-</sup>	4.71E-16 (1.82E-18)	1.85E-14 (2.52E-22)
C <sub>3</sub> N <sup>-</sup>	2.03E-15 (6.99E-18)	1.07E-13 (5.09E-16)
C <sub>5</sub> N <sup>-</sup>	2.12E-14 (2.01E-16)	3.46E-13 (1.04E-16)
CH <sup>-</sup>	6.46E-19 (8.64E-23)	1.30E-16 (1.80E-28)
C <sub>2</sub> H <sup>-</sup>	1.65E-16 (1.34E-18)	1.07E-14 (7.42E-22)
C <sub>3</sub> H <sup>-</sup>	2.24E-14 (1.49E-17)	6.53E-13 (4.20E-21)
C <sub>4</sub> H <sup>-</sup>	3.32E-12 (1.29E-13)	4.46E-11 (6.74E-15)
C <sub>5</sub> H <sup>-</sup>	1.58E-12 (1.35E-13)	1.31E-11 (1.32E-14)

**Table 15**  
(Continued)

Carbon Chains	Peak Abundance (Final Abundance) with Respect to Total H in all Forms	
	Translucent Cloud	Dense Cloud
C <sub>6</sub> H <sup>-</sup>	1.00E-11 (4.81E-12)	1.02E-11 (4.01E-14)
C <sub>7</sub> H <sup>-</sup>	1.11E-14 (2.44E-15)	2.81E-12 (1.71E-17)
C <sub>8</sub> H <sup>-</sup>	7.99E-18 (8.47E-19)	7.78E-13 (5.64E-21)
C <sub>9</sub> H <sup>-</sup>	1.01E-18 (5.61E-23)	3.05E-13 (2.93E-19)

of thermodynamics, it should be with the appropriate weighted average. The peak and final abundances of these species after 10<sup>6</sup> years are shown in Table 15. Keeping in mind all these aspects, the abundances might be correlated with the energy and stability values of several carbon chain species. Few prominent examples of these correlations could be seen from Figures 15 and 16 and Table 15. Some examples are:

- From Figure 12, it can be seen that C<sub>6</sub>H<sup>-</sup> is more stable than C<sub>5</sub>H<sup>-</sup>, C<sub>7</sub>H<sup>-</sup>, C<sub>8</sub>H<sup>-</sup>, C<sub>9</sub>H<sup>-</sup>, and C<sub>10</sub>H<sup>-</sup> and in Figures 15 and 16, and Table 15, we find that C<sub>6</sub>H<sup>-</sup> is comparatively more abundant, as expected.
- From Figure 10, it is evident that H<sub>2</sub>C<sub>6</sub> is more stable than H<sub>2</sub>C<sub>5</sub>, H<sub>2</sub>C<sub>7</sub>, and H<sub>2</sub>C<sub>8</sub>. This is also prominent from Figures 15 and 16 and Table 15.

#### 4. CONCLUSION

A comprehensive investigation of different interstellar carbon chain molecules; C<sub>n</sub>, H<sub>2</sub>C<sub>n</sub>, HC<sub>n</sub>N and C<sub>n</sub>X (X = N, O, Si, S, H, P, H<sup>-</sup>, N<sup>-</sup>) with a total of 89 species has been carried out using high-level quantum chemical simulation to determine their accurate enthalpies of formation, chemical reactivity indices, global hardness and softness, and other chemical parameters of these molecules. Chemical modeling of the abundances of these molecular species has also been performed. From the results, in all the groups considered, the most stable molecules have been astronomically observed. The next possible candidate for astronomical observations in each of the carbon chain groups considered is proposed. The effect of kinetics on the formation of some of these molecular species is shown to be correlated with our observations.

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