A Thermodynamic Landscape of Hydrogen Cyanide-Derived Molecules and Polymers

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ABSTRACT. Hydrogen cyanide (HCN)-derived molecules and polymers feature in several hypotheses on the origin of life. Over half-a-century of investigations into HCN self-reactions have led to many suggestions regarding the structural nature of the products, and an even greater number of proposed polymerization pathways. A comprehensive overview of possible reactions and structures is missing. In this work, we use quantum chemical calculations to map the relative free energy of most HCN-derived molecules and polymers that have been discussed in the literature. Our computed free energies indicate that several previously considered polymerization pathways are not spontaneous and should be discarded from future consideration. Among the most thermodynamically favored products are polyaminoimidazole and adenine.

INTRODUCTION
Polymers such as DNA, RNA and polypeptides are essential for information storage, replication, and catalysis, and fundamental to life as we know it. We can assume that earlier, or other, forms of life also require some form of polymers to perform these vital functions. Two of several unknowns in prebiotic chemistry are how 1) information-storing polymers can develop through abiotic chemical processes, and 2) under which chemical conditions (i.e., where in the Universe) such processes may occur. The first biomolecular building blocks may have originated through chemical processes native to the early Earth, or they may have been exogenously delivered, e.g., via asteroids and comets. Both scenarios imply that precursor molecules or polymers are subsequently able to transform into biologically relevant structures. In this work, we use quantum chemistry to map the thermodynamics of one such family of proposed precursors: hydrogen cyanide (HCN) and HCN-derived molecules and polymers.

HCN is a common molecule in the Universe, having been identified on various planets, dwarf planets, Saturn’s moon Titan, comets and in the interstellar medium. HCN was likely present on the early Earth. The molecule is also quite reactive. In experiments, biologically relevant molecules such as amino acids, nucleobases and pterins have all been extracted from the products of HCN polymerization experiments (see ref. for a review).

The prevalence of HCN in many astrochemical environments, and its reactive nature, places the molecule, and its possible reaction products, center stage of prebiotic chemistry and astrobiology. However, a clear picture of HCN reactivity, both in laboratory and in astrochemical environments, remains elusive.

HCN-derived polymers are complex materials that can form under a variety of laboratory conditions. These product mixtures are typically heterogeneous and insoluble in most common solvents. Various forms of characterization have been attempted to elucidate which chemical
structures can form from HCN. For example, mass spectrometry, infrared and nuclear magnetic resonance (NMR) spectroscopy have been used to infer a wide variety of functional groups in polymerization product mixtures.\textsuperscript{14–17} A plethora of different polymerization pathways have been proposed to explain this complexity (see ref. \textsuperscript{12} for a review). Due to their diverse nature, some HCN-derived polymers are functional materials with proposed uses in catalysis,\textsuperscript{11, 18} as adhesives and as coatings.\textsuperscript{19}

The complex space of HCN-derived chemistry. For this analysis, we have collected HCN-based materials that appear as suggestions, hypotheses, or confirmed detections, in literature. The limitations to our selection are motivated by practicality. The full structural space of possible HCN-derived polymers and molecules is immense. For example, one automated search for reactions that result in HCN tetramers identified 678 compounds.\textsuperscript{20} Several other structures have also been computationally predicted.\textsuperscript{21} We consider here consider a selection of pure HCN-based materials, i.e., structures where the stoichiometry of H, C and N are 1:1:1 (and no additional elements). Other HCN-based materials can incorporate oxygen,\textsuperscript{12} additional nitrogen and hydrogen\textsuperscript{22} or form through condensation reactions, e.g., through the formation of NH\textsubscript{3}.\textsuperscript{12, 18, 23, 24} Such materials, which may also be important, are beyond the scope of this work. In what follows, we will first introduce the materials we study, and then proceed to evaluate their relative thermodynamic stability.

HCN-derived molecules. All HCN-derived molecules that we investigate are shown in Figure 1. In addition to HCN (1), several of these molecules have been proposed to act as monomers in polymerization:\textsuperscript{12, 14, 16, 25–33} the HCN dimers iminoacetonitrile (2) and aminocyanocarbene (3), the trimer aminomalononitrile (4) and the tetramer diaminomaleonitrile (5) (Fig. 1). Out of these molecules only 5 has been directly observed during polymerization of
Speculations that 2 and 4 might form are based on indirect evidence. The proposed formation of 3 is controversial, as we will return to discuss. Aminoimidazole carbonitrile (6) and adenine (7) (Fig. 1) are less likely to take part in polymerization but are included in our study because of their relevance to prebiotic chemistry.

In what follows, we outline a collection of pathways, which connect some of the molecules in Figure 1 to different proposed polymer structures. Sometimes, these pathways will be mentioned in the context of mechanistic details (e.g., base- or radical catalyzed). However, we mostly use pathways to refer to the casual connections between reactant, intermediates, and products.

**Suggested products of HCN polymerization.** Two of the simplest HCN-derived polymers are polyimine (8) (Fig. 2, pathway 1) and the head-to-tail polymer (9) (Fig. 2, pathway 2). Structures 8 and 9 have been suggested to form through different mechanisms. He et al., have suggested that the formation of 8 is base-catalyzed, proceeding through the successive additions of cyanide anions. Mozhaev et al., who studied radiation-induced HCN polymerization, and Mamajanov and Herzfeld, who studied polymerization in the presence of radical-initiators have both suggested 9 as a plausible product. Mamajanov and Herzfeld have further proposed that 9 can subsequently transform into two-dimensional polytriazine sheets (10, Fig. 2). Both structures 9

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**Figure 1.** Different molecules linked to HCN-derived polymers.
and 10 have been computationally predicted to form when solid HCN is subjected to pressures above 72 GPa.\textsuperscript{35}

*Pathway 1*

\[
\begin{align*}
1 \xrightarrow{\text{CN}^-} & \quad \left[\begin{array}{c} \text{NH} \\
& \n\end{array}\right]_n \\
& \quad 8
\end{align*}
\]

*Pathway 2*

\[
\begin{align*}
1 \xrightarrow{\text{radical or pressure}} & \quad \left[\begin{array}{c} \text{N} \\
& \n\end{array}\right]_n \\
& \quad 9 \quad \rightarrow \\
& \quad 10
\end{align*}
\]

**Figure 2.** Examples of HCN polymerization pathways catalyzed in different ways. Top: base-catalyzed formation of polyimine (8).\textsuperscript{16} Bottom: radical-catalyzed\textsuperscript{31,32,35} and/or pressure-induced\textsuperscript{41} formation of one- and two-dimensional materials.

Figure 3 shows 11, the only three-dimensionally connected polymer in this study. This material can be viewed as an NN↔HCN substituted analogue of cubic gauche nitrogen – a metastable allotrope of nitrogen synthesized above 42 GPa.\textsuperscript{36} Structure 11 has been predicted to be dynamically stable (a minimum on the potential energy surface).\textsuperscript{37}
Figure 3. A three-dimensional HCN-derived polymer (11). Left: color representations: carbon - brown, hydrogen - pink and nitrogen - grey.

Polymerization of iminoacetonitrile (2). Several polymers have been proposed to form from the polymerization of 2. One such structure is Völker’s ladder polymer polyaminocyanomethylene (12) (Fig. 4, pathway 3a). In Völker’s model, 12 converts to a cyclic ‘ladder’ structure (13). Umemoto and colleagues have suggested an alternative ‘single-ladder’ structure (14) (pathway 3b). Ruiz-Bermejo and colleagues have suggested that 2 may react to form structures 16 and 17 (pathways 4a and 4b).

![Pathway 3 and Pathway 4 Diagrams]

Figure 4. Products of iminoacetonitrile (2) polymerization proposed by Völker and Umemoto (pathway 3a and 3b), and Ruiz-Bermejo and colleagues (pathway 4a and 4b).

Polymerization of diaminomaleonitrile (5). The molecule 5 features prominently in HCN reaction hypotheses because it is readily produced in polymerization experiments. One suggested role of 5 is as an intermediate in the hypothesized formation of 7.
known to undergo photochemical isomerization to 6. The cis- and trans-forms of 5 are also possible starting points for the Völker and Umemoto models (12, 13 and 14) shown in Figure 4. Mamajenov and Herzfeld have furthermore suggested that polymerization of 5 results in polyaminoimidazole (18 or 19) via an intermediate such as 20 (Fig. 5, pathway 5). Other structures proposed to form from 5 include the linear polymers 21 and 22 (Fig. 5, pathway 6).

**Pathway 5**

\[
5 \rightarrow \begin{array}{c}
\text{NH}_2 \text{C}_n \\
\text{N} \\
\text{NH}
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{N} \\
\text{NH}_2
\end{array} \equiv \begin{array}{c}
\text{NH} \\
\text{N} \\
\text{NH}_2
\end{array}
\]

**Pathway 6**

\[
5 \rightarrow \begin{array}{c}
\text{NH}_2 \text{H}_n \\
\text{N} \\
\text{NH}_2
\end{array} \equiv \begin{array}{c}
\text{NH}_2 \\
\text{N} \\
\text{NH}_2
\end{array}
\]

**Figure 5.** Two pathways for polymerization of diaminomaleonitrile (5) proposed in literature.

**Polyaminomalnonitrile (23).** Figure 6 shows the two last pathways that we consider. Interest in polyaminomalnonitrile (23) is motivated by a suggestion by Matthews and Moser: that 23 may be a precursor to polypeptides. This proposal has been criticized for lack of experimental evidence. Both 3, 4 and 5 have been proposed as precursors to 23 (Fig 6, pathway 7).

**Pathway 7**

\[
4 \text{ or } 5 \rightarrow 3 \rightarrow \begin{array}{c}
\text{N} \\
\text{N} \\
\text{CN}_n
\end{array}
\]

**Pathway 8**

\[
5 \rightarrow \begin{array}{c}
\text{H}_2 \text{N} \\
\text{CN} \\
\text{CN}
\end{array} \rightarrow \begin{array}{c}
\text{NH}_2 \text{C}_n \\
\text{N} \\
\text{NH}
\end{array} \equiv \begin{array}{c}
\text{NH} \\
\text{N} \\
\text{NH}_2
\end{array}
\]
Figure 6. Proposed pathways to form polyaminomalononitrile (23).\textsuperscript{12, 27–29}

RESULTS & DISCUSSION

In this work, we compute the free energy of all the above-mentioned structures, as well as a few additional ones. Our study makes use of a sampling algorithm to identify candidates to the lowest energy ground states in the vast configurational space of the HCN-derived molecules and polymers (see Methods for details).\textsuperscript{43} To limit computational costs, polymers have been represented as oligomers of approximately 60 atoms. Figure 7 exemplifies predicted stable conformers for three such structures evaluated with implicit consideration of water solvation. Most experimental literature studies have been performed in aqueous solution (see ref. \textsuperscript{12} for a review) or in neat liquid HCN.\textsuperscript{16, 31, 32} HCN and water are both polar and hydrogen bonding solvents and can be expected to cause comparable trends in relative solvation energies.
Figure 7. Examples of predicted HCN oligomer structures (A) Head-to-tail polymer (9) (B) Cyclic polymer (16) (C) Copolymer (26) of repeating units belonging to 19 and 8. Color representations: carbon - brown, hydrogen - pink and nitrogen - grey.

Figure 8 summarizes our best estimates for the relative Gibbs free energy of all considered structures. Corresponding relative energies in the absence of solvation are available in the Supporting Information. The energies in Figure 8 include corrections for enthalpic and entropic contributions at 298 K. Relevant polymerization experiments have been studied in a wide range of temperatures: HCN (195-363 K), $^17$ 2 ($>233$ K), $^{44}$ 4 (298-273 K)$^{19,45}$ and 5 (298-483 K)$^{17,24}$. Lower temperatures are particularly relevant when considering processes occurring in
environments such as Saturn’s moon Titan. We address some effects of temperature on our conclusions in the Supporting information.

**Figure 8.** The thermodynamic landscape of HCN-derived structures. Gibbs free energy content ($\Delta G_{298K}^\circ$) is provided per mol HCN and is relative a reference chain of HCN molecules. Polymeric materials are organized by the number of HCN molecules in their monomer unit.
The energy content per HCN in the studied structures varies between +7.5 and -16.1 kcal/mol (Fig. 8). In other words, note that to arrive at a reaction energy, the values shown in Figure 8 needs to be multiplied with the number of HCN in each structure. For example, for adenine, this multiplication factor is 5, whilst for a polymer it is \( n \). Most investigated structures are clearly thermodynamically downhill from HCN in aqueous solution at 298 K. The overall thermodynamic favorability of HCN-self reactions is thus one part of the explanation for the commonly observed chemical complexity of reaction mixtures. The only materials predicted to be unstable relative to HCN are 3, 9, 12 and 14, effectively ruling these out as plausible reaction products under the studied conditions.

Our calculations infer new insight into the viability of Völker’s suggestion, that 2 is the monomer unit of 12 and 13 (Fig. 4, pathway 3a). Our data predicts that formation of 13 from 2 is thermodynamically favored. At the same time, we can rule out 12 as a major product since it is unstable relative to 2, as well as 8 + 1 (and most other structures). We can also rule out Umemoto’s single ladder model (14) (Fig. 4, pathway 3b) as a plausible polymerization product on the grounds of unfavorable thermodynamics.

Figure 8 shows that 5 is more stable than most considered structures. This prediction has several important consequences. For example, structures 12, 13, 14 are unlikely to be the products of polymerization of 5, because such transformations are predicted to be thermodynamically unfavored. Other similar examples include structures 23 and 20, predicted to lie ~1.7 and 5.8 kcal/mol HCN above 5, respectively. Establishing that formation of 23 from 5 is not thermodynamically spontaneous is important as the former is a proposed precursor to heteropolypeptides.\(^27, 40\) However, we note that our predictions do not exclude the possibility of
23 forming through other higher energy intermediates, such as the HCN trimer 4 ($\Delta G_{298}^o = -1.7$ kcal/mol HCN).

We have found only a limited number of HCN-derived polymers and molecules to be thermodynamically downhill relative to 5. For example, and in agreement with previous theoretical studies,46 the formation of 7 from 5 is thermodynamically allowed. The linear polymer 21 is another example that could feasibly form from 5. Structures 19 and 33 are predicted to be the most stable polymers out of those considered, with only the molecule 7 being more stable. Formation of 19 and 33 from 5 is predicted to be spontaneous by -6.0 and -6.3 kcal/mol HCN, respectively. The corresponding polymerization enthalpy ($\Delta H_{298}^o$) calculates as -9.9 and -9.7 kcal/mol HCN (Supporting Information, Table S3). These energies are in fair agreement with estimates derived from differential scanning calorimetry thermograms of solid-state and melt-polymerization of 5.18 That study, by Ruiz-Bermejo and colleagues, estimated heat releases of 3-5 kcal/mol HCN at 423-463 K.18

We furthermore predict that the HCN dimer 3 have an energy content of +7.5 kcal/mol HCN, i.e., its formation from HCN is uphill by 15 kcal/mol. This value is 8.5 kcal/mol lower than the corresponding value in gas phase (Supporting Information, Table S1), in turn comparable to other computational results.44, 47 We note that 3 has a similar energy content as hydrogen isocyanide in solution.48 Nevertheless, 3 is high in energy, and can be ruled out as a major component of reaction mixtures.

The energy of two- and three-dimensional materials. Our methodology for calculating the data shown in Figure 8 is limited to molecules and one-dimensional polymers. For polymers with higher dimensional connectivity, we have relied on DFT calculations with periodic boundary conditions (see Methods). Figure 9 shows our stability estimates for the 2D- and 3D polymers 10
and 11. Both systems are composed by tetrahedrally coordinated C and N atoms in a graphane-like configuration (Fig. 9). Phonon band structures of 10 (including the isomers 10A and 10B) and 11, provided in the Supporting Information, confirm that these materials are dynamically stable. In other words, these structures all constitute local minima on the potential energy surface, which allows us to account for temperature effects in our relative stability estimates. Whereas structures 10A, 10B calculates as only slightly thermodynamically favored (−1.9−0.4) relative to our reference of an infinite chain of HCN molecules at ambient conditions, 11 is instead predicted to be unstable by +0.5 kcal/mol.

![Figure 9. Structure and predicted energies of 10 and 11. Shown Gibbs free energies (ΔG^0_{298K}) are in kcal/mol are relative to an infinite chain of HCN molecules in vacuum. Color representations: carbon - brown, hydrogen - pink and nitrogen - grey.](https://doi.org/10.26434/chemrxiv-2024-ln735)
**Approximate Stability Prediction of HCN-based Polymers.** The repeating units of several structures in Figure 8 can be considered combinations of simpler monomer units. For example, structure 23 can be viewed as a combination of 8 and 15 (Fig. 8). Figure 10 illustrates how our calculated energies of smaller polymer units can be used to estimate the relative energies of more complex HCN-based structures through a weighted averaging approach (see the Methods for details). Such linear extrapolation is approximate and can be expected to fail e.g., in the presence of extensive conjugation. Nonetheless this approach constitutes a rapid route to exploring the thermodynamics of a larger structural space of HCN-derived materials.
Figure 10. Quantum mechanically calculated stability (c.f. Figure 8) plotted against a weighted average extrapolation of known energies of smaller sub-units (see Methods). The mean absolute error is 3.0 kcal/mol.

CONCLUSIONS

Our study shows that several hypotheses regarding HCN’s reactions to molecules and polymers can be ruled out on the grounds of thermodynamics. For example, diaminomaleonitrile (5), a prominently suggested reaction intermediate in HCN-based prebiotic chemistry, is predicted to be lower in energy compared to many proposed polymer products. Our study also infers a new perspective on adenine (7), a nucleobase, present in all life as we currently know it (Fig. 8). Formation of 7 is predicted to be thermodynamically downhill from all herein considered structures at ambient conditions. The low experimental yields (<0.01 %) of 7 from HCN in typical condensed phase experiments therefore means such reactions must be kinetically controlled.

The presented thermodynamic landscape of HCN-derived materials has several consequences for interpreting HCN’s reactivity in various astrochemical environments, in and beyond the solar system. Most (but not all) previously proposed HCN-derived polymers and molecules can form spontaneously ($\Delta G_r < 0$) at close to Earth ambient conditions. In low-temperature environments, like those on Titan, the entropic penalty for making larger molecules and polymers ($-T\Delta S$) naturally decreases. In other words, the chances for thermodynamic spontaneity of macromolecular formation increases in cold environments.

At the same time as more structures can become thermodynamically viable at lower temperature, such chemistry will naturally be more limited by reaction kinetics. Enhanced kinetic control of
HCN-based prebiotic chemistry means a greater ability of colder environments to generate specific metastable products out of an increased pool of thermodynamically allowed options. We can therefore speculate on the potential of colder worlds, such as Titan, in generating kinetically selected products that may otherwise not form at higher temperatures. Some such materials could, hypothetically, be crucial templates for the origin of life.11

METHODS

Conformational search. The Conformer-Rotamer Ensemble Sampling Tool (CREST)43 was used in automated searches of lowest lying conformers of molecules and oligomers. The energy evaluations in CREST make use of the semi-empirical xtb program.50 Conformational structure searches in aqueous solution were performed with the analytical linearized Poisson-Boltzmann (ALPB) model. 51 Structural differences between predicted larger and smaller oligomers risk influencing the computed energy content, e.g., through different end-effects. We therefore additionally relied on visual inspection to ensure models of oligomers of different length were similar in appearance/folding.

Electronic Structure Calculations. With the exception for two and three-dimensional networks, all structures were optimized using the B3LYP52 functional, as implemented in Gaussian 16, revision B.01.53 Missing treatment of dispersion effects in B3LYP was corrected for using Grimme’s method combined with Becke-Johnson damping (D3BJ).54 The standard polarizable continuum (PCM) model of Gaussian was used to model interactions with water solvent.55 Our best estimate to total Gibbs free energies, $G_f$, were calculated as

$$G_f = E_f + G_{corr},$$  

(1)
where \( G_{\text{corr}} \) denote thermal corrections obtained following optimization and frequency analyses using the cc-pVDZ basis set. Final electronic energies, \( E_f \) in Eq. (1) were calculated as single point calculations at the B3LYP-D3BJ/aug-cc-pVTZ level of theory. Method validation were performed against the M06-2X\(^{56}\) meta-GGA functional, and close agreement was found (Supporting Information, Table S4). The average absolute deviation between B3LYP-D3 and M06-2X results are 0.65 kcal/mol, with a maximum of 3.2 kcal/mol for compound 9. The corresponding average deviation is \(-0.01 \pm 0.85\) kcal/mol.

**Calculations of Extended Structures.** Periodic DFT calculations were carried out using the Vienna Ab Initio Software Package (VASP)\(^{57}\) version 5.4.4. The B3LYP-D3BJ level of theory was used both for structure optimizations and calculations of phonon spectra. These calculations relied on projected augmented wave (PAW) potentials\(^{58}\) used together with a plane wave kinetic energy cutoff of 800 eV. \( \Gamma \)-centered \( k \)-point mesh with a resolution \(< 2\pi 0.066\) Å\(^{-1}\) were used for integration over reciprocal space. Two-dimensional polymers were separated by 30 Å vacuum layers. Energies and forces were converged to less than 1 meV/atom and 1 meV/(Å×atom), respectively. Thermal corrections were obtained with the code PHONOPY\(^{59}\) version 2.11.0. The supercell dimensions were \(2 \times 2 \times 2\), \(2 \times 2 \times 1\), and \(4 \times 1 \times 2\) for the 11, 10A, and 10B polymers, respectively.

**Estimating Stability of Molecules:** The average energy per unit of HCN is here used when comparing different materials:

\[
\Delta G_{298K}^0 = \frac{G_{f, \text{material}}}{k} - G_{f, \text{HCN}}
\] (2)
where $G_{f,\text{material}}$ is the total free energy of the molecule and $k$ is the number of HCN in the molecule, while $G_{f,\text{HCN}}$ is the average energy of HCN inside a one-dimensional H-bonded chain.

**Estimating Stability of Polymers.** The average Gibbs energy per unit of HCN inside polymeric materials are here evaluated as:

$$G_{298K}^0 = \frac{G_{f,\text{Long}} - G_{f,\text{Short}}}{k},$$

(3)

where $G_{f,\text{Long}}$ and $G_{f,\text{Short}}$ are the total free energies of the ($n$)-long and ($n - k$)-short polymer models, respectively. In Eq. (3) $n$ is the number of HCN in the long oligomer model, and $k$ is the number of HCN in a monomer unit. The sizes of our oligomer models were chosen to have at least 4 repeating polymer units, and $n$ is always near 20. Each polymer model was capped by a cyanide group in one end and a hydrogen atom in the other end.

**Computing the energy of 10 and 11.** The energies of HCN in 10A, 10B and 11 were calculated by dividing the total energy of the polymeric material by the number of HCN in the unit cell. To obtain relative energies we then compared to the average energy of HCN in infinite HCN chain. Our molecular and periodic calculations are of comparable levels of theory, also evidenced by the hydrogen bond distances between HCN differing by less than 0.025 Å.

**Energy Estimates of Composite Polymers.** The Gibbs free energy content of HCN in composite polymers, $G_{\text{cp}}$, can, as a first approximation, be estimated from a weighted average of our quantum mechanically computed free energies $G_{f,\text{i}}$.

$$G_{\text{cp}} = \frac{\sum_{i=1}^{l} k_i G_{f,i}}{\sum_{i=1}^{l} k_i}$$


where \( k_i \) is the number of HCN in the polymer units of polymers \( i \), and \( l \) is the number of monomer units in the combined polymer.

ASSOCIATED CONTENT

Supporting Information: Table with relative free energy, enthalpy and zero-point energies in aqueous solution. Figure of temperature dependence of the thermodynamic stability of 2 and 8. Table with relative free energy, enthalpy and zero-point energies in vacuum. Phonon bands of structures 10A, 10B and 11 (PDF).

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Notes

The authors declare that they have no competing interests.

ABBREVIATIONS

HCN, hydrogen cyanide; DFT, density functional theory; CREST, Conformer-Rotamer Ensemble Sampling Tool; ALPB, analytical linearized Poisson-Boltzmann; VASP, Vienna ab initio simulation package; PAW, projected augmented wave; B3LYP, Becke, 3-parameter, Lee–Yang–Parr

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