Thermodynamics of HCN-derived Polymers: A Quantum Chemical Study

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Abstract

Hydrogen cyanide (HCN) is a widely available molecule in planetary and interplanetary environments. It has been observed that the polymerization of HCN can lead to the formation of nucleobases and proteins (Matthews & Minard 2006). Thus, HCN and its reactivity are considered to be very important for prebiotic chemistry. Our evaluation covers several molecules and oligomers, most of which have been discussed in the literature (Ruiz-Bermejo et al., 2021), and ranks them based on thermodynamic preference. In our study, we compute the relative energies of a series of HCN-derived materials relative to HCN in liquid water. We perform an automated search with semi-empirical methods to extract the lowest energy conformers for each compound. Our work relies on density functional theory (DFT) calculations with thermal corrections coupled to an implicit solvation model to better emulate the polymerization environments. These methodologies allow us to discuss the impact of our results at relevant environments such as that of Saturn's Moon Titan or the early Earth conditions. The most stable HCN-derived material in our set is the nucleobase adenine, computed to lie ˜26 kcal mol-1 below HCN in a water solution. Our enumeration of thermodynamically plausible reaction products and the reaction routes for the abiotic formation of organic macromolecules starting from simple units of HCN offers extensive insights into the chemical and the physical limitations of suspected key prebiotic processes (Sandström & Rahm 2021). 1. C. N. Matthews, R. D. Minard, Faraday Discuss. 2006, 133, 393. 2. M. Ruiz-Bermejo, J. L. de la Fuente, C. Pérez-Fernández, E. Mateo-Martí, Processes 2021, 9, 597. 3. H. Sandström, M. Rahm, ACS Earth Space Chem. 2021, 5, 2152–2159.

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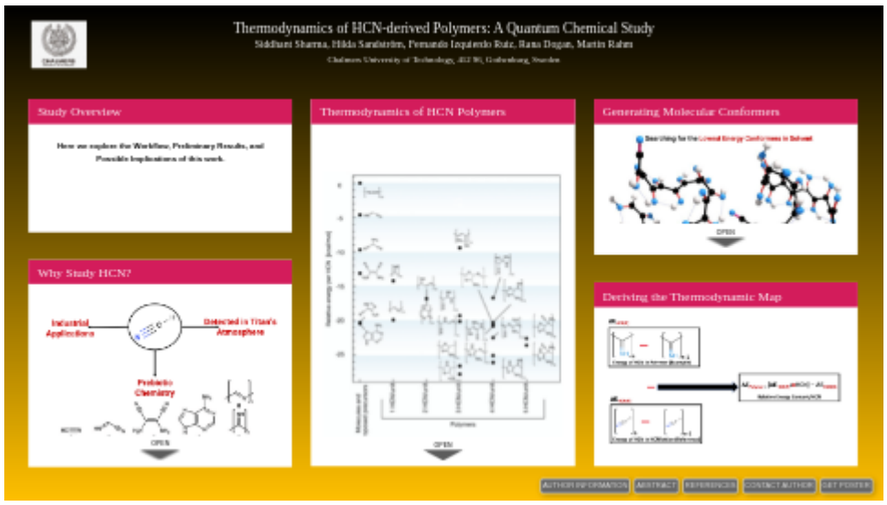

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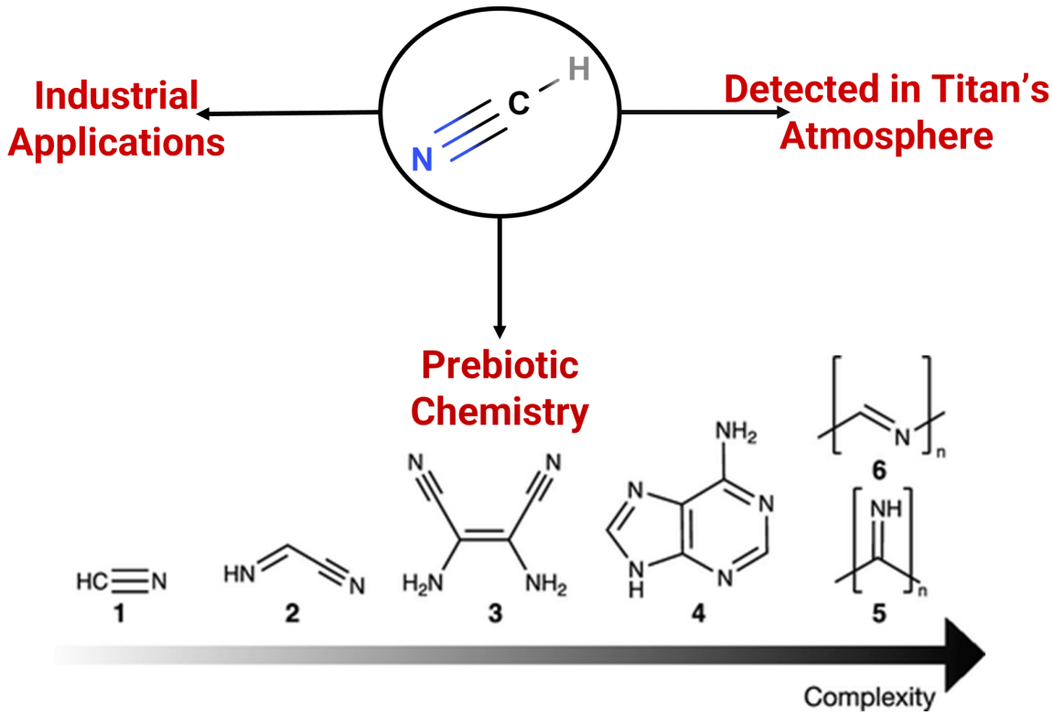
PRESENTED AT:

STUDY OVERVIEW

Here we explore the Workflow, Preliminary Results, and Possible Implications of this work.

WHY STUDY HCN?



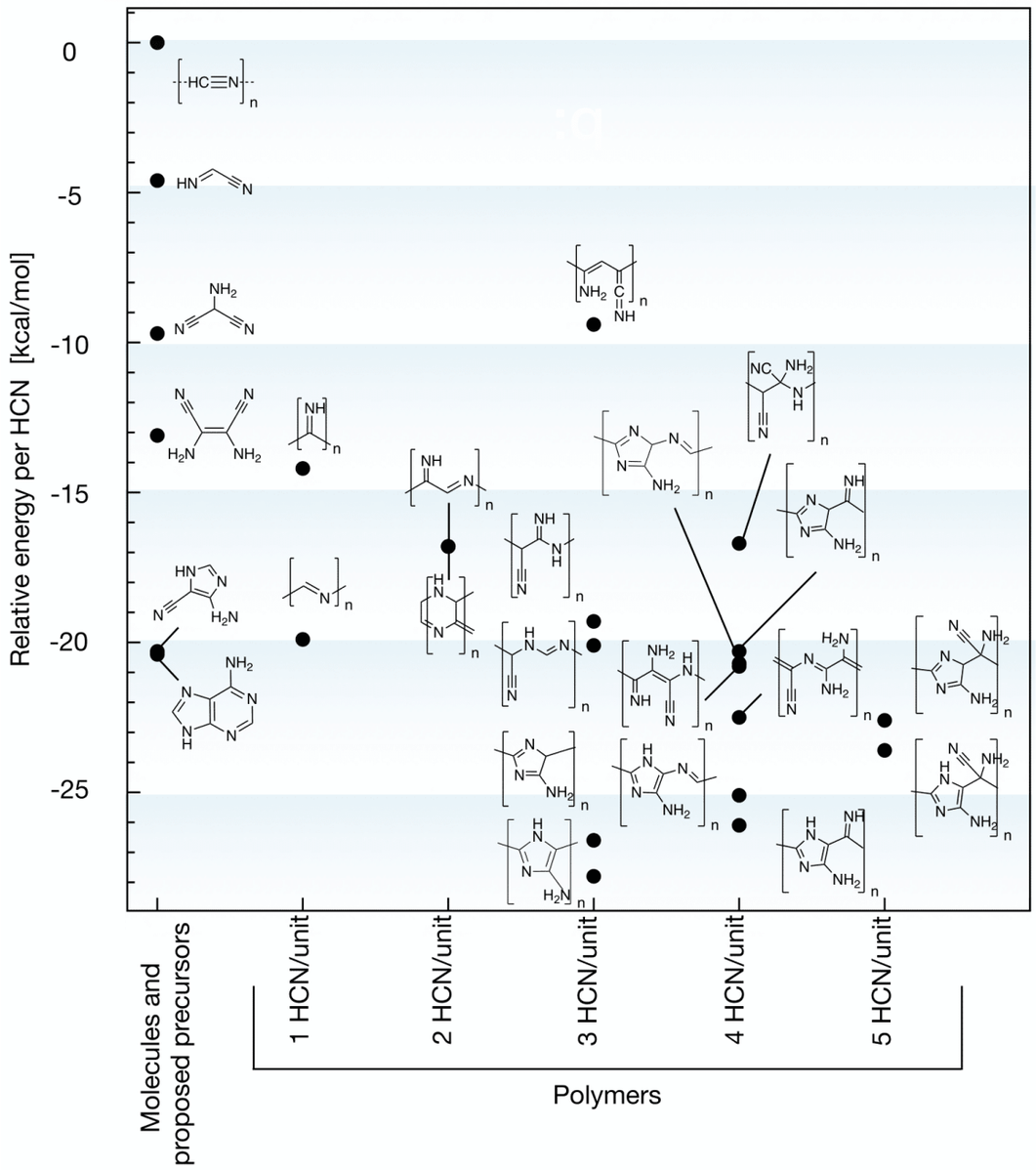
HCN oligomerization can lead to formation of Adenine (nucleobase) shown by Orgel's and Oro's seminal experiments in 1960's.

There is a need to explore the plausible mechanisms and thermodynamics involved in the formation of HCN-derived polymers to elucidate how likely they can occur on Earth and environments such as that of Titan [1].

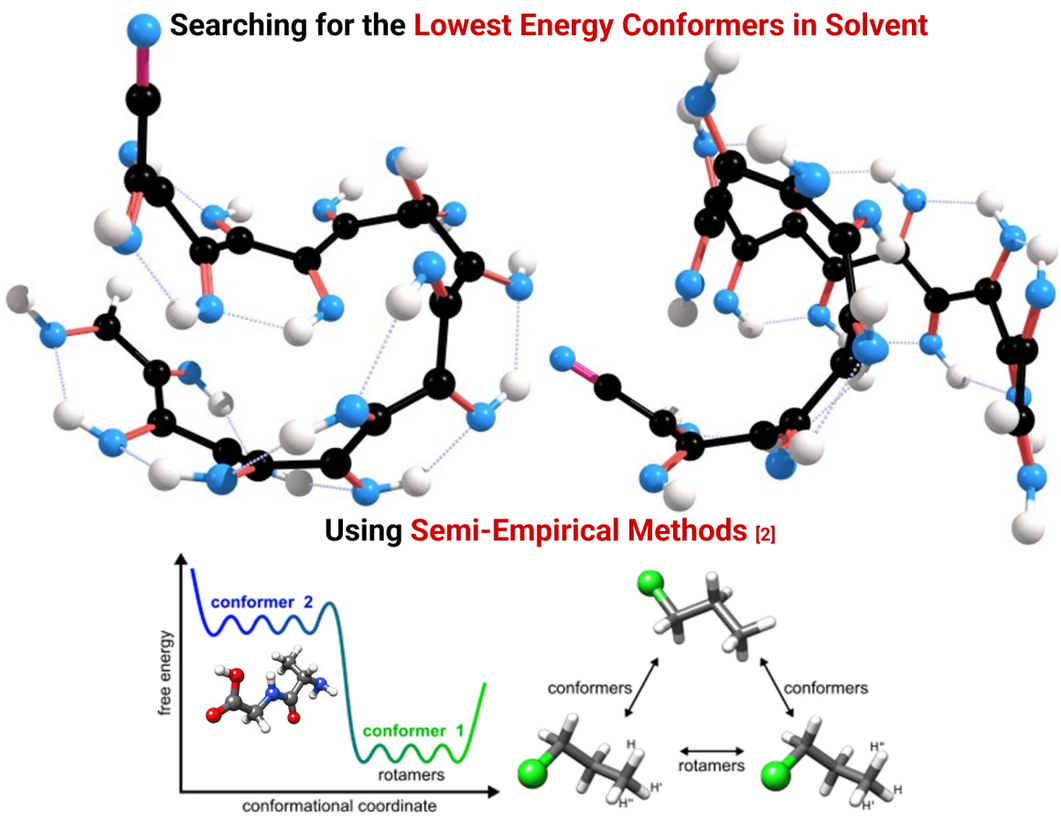
[1] Rahm, M., Lunine, J. I., Usher, D. A., & Shalloway, D. (2016). Polymorphism and electronic structure of polyimine and its potential significance for prebiotic chemistry on Titan. In Proceedings of the National Academy of Sciences (Vol. 113, Issue 29, pp. 8121–8126). Proceedings of the National Academy of Sciences. https://doi.org/10.1073/pnas.1606634113

[2] Sandström, H., & Rahm, M. (2021). The Beginning of HCN Polymerization: Iminoacetonitrile Formation and Its Implications in Astrochemical Environments. In ACS Earth and Space Chemistry (Vol. 5, Issue 8, pp. 2152–2159). American Chemical Society (ACS). https://doi.org/10.1021/acsearthspacechem.1c00195

THERMODYNAMICS OF HCN POLYMERS



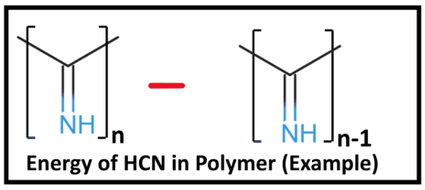
GENERATING MOLECULAR CONFORMERS



[3] Pracht, P., Bohle, F., & Grimme, S. (2020). Automated exploration of the low-energy chemical space with fast quantum chemical methods. In Physical Chemistry Chemical Physics (Vol. 22, Issue 14, pp. 7169–7192). Royal Society of Chemistry (RSC). https://doi.org/10.1039/c9cp06869d

DERIVING THE THERMODYNAMIC MAP

$\Delta E_{HCN(P)}$

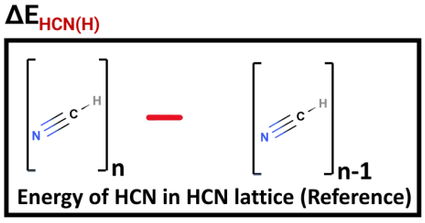


Energy of HCN in Polymer (Example)

$\Delta E_{Polymer} = [\Delta E_{HCN(P)}/n\text{HCN}] - \Delta E_{HCN(H)}$

Relative Energy Content/HCN

$\Delta E_{HCN(H)}$



Energy of HCN in HCN lattice (Reference)

AUTHOR INFORMATION

Siddhant Sharma or ‘Sid’ hails from New Delhi, India, and is a current senior undergraduate majoring in biochemistry and chemistry. He is a research associate with the Blue Marble Space Institute of Science, Seattle (BMSIS). For the summers of 2021, Siddhant joined the Chalmers University of Technology in Sweden through the Chalmers Astrophysics & Space Science Summer (CASSUM) Research Fellowships working with Dr. Martin Rahm (https://rahmlab.com/) on prebiotic macromolecular synthesis using quantum chemistry which is presented here in this poster.

[1] Siddhant's Google Scholar (https://scholar.google.co.in/citations?user=zkgwkugAAAAJ&hl=en&oi=ao)
[2] SETI Institute Announces Recipients of SETI Forward Award for Undergraduates | SETI Institute (https://www.seti.org/press-release/seti-institute-announces-recipients-seti-forward-award-undergraduates)

ABSTRACT

Hydrogen cyanide (HCN) is a widely available molecule in planetary and interplanetary environments. It has been observed that the polymerization of HCN can lead to the formation of nucleobases and proteins **[1]**. Thus, HCN and its reactivity are considered to be very important for prebiotic chemistry. Our evaluation covers several molecules and oligomers, most of which have been discussed in the literature, and ranks them based on the thermodynamic preference. In our study, we compute the relative energies of a series of HCN-derived materials relative to HCN in liquid water. We perform an automated search with semi-empirical methods to extract the lowest energy conformers for each compound. Our work relies on density functional theory (DFT) calculations with thermal corrections coupled to an implicit solvation model to better emulate the polymerization environments. These methodologies allow us to discuss the impact of our results at relevant environments such as that of Saturn's Moon Titan or the early Earth conditions. The most stable HCN-derived material in our set is the nucleobase adenine, computed to lie ~26 kcal mol^{-1} below HCN in a water solution. Our enumeration of thermodynamically plausible reaction products and the reaction routes for the abiotic formation of organic macromolecules starting from simple units of HCN offers extensive insights into the chemical and the physical limitations of suspected key prebiotic processes.

[1] Matthews, C.N., & Minard, R.D. (2006). Hydrogen cyanide polymers, comets and the origin of life. Faraday Discussions, **133,** 393.

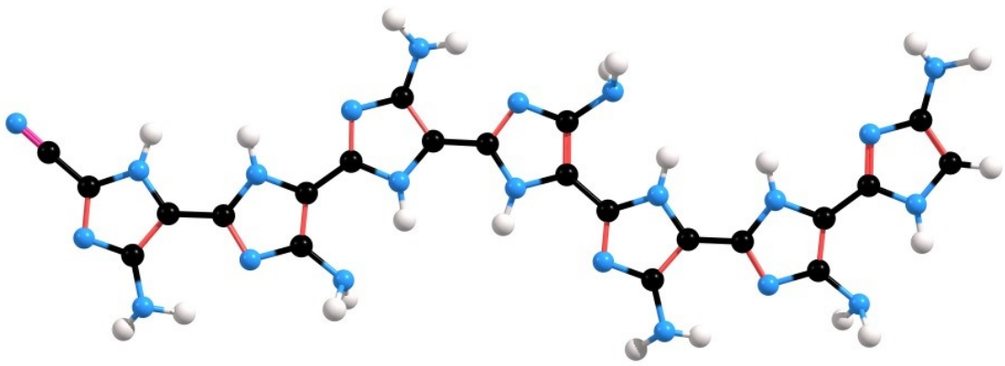


Figure: Graphical representation of polyaminoimidazole, one of the polymers simulates in our study.

(https://agu.confex.com/data/abstract/agu/fm21/2/3/Paper_929532_abstract_862456_0.jpg)