

Hydrogen cyanide polymers connect cosmochemistry and biochemistry

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Abstract. To understand the origin of protein/nucleic acid based life as we know it on Earth, we must “follow” the nitrogen. Because of its unique hydrogen bonding characteristics, nitrogen is the key element in catalytic and/or informational proteins and nucleic acids essential to cell function and reproduction. We present evidence that HCN is the original source of prebiotic protein and nucleobase nitrogen. We also present chemically rational models supporting the radical hypothesis that the polymerization of HCN yields *ab initio mundi* prebiotic protein and polynucleobase macromolecules of sufficient size and complexity to allow the spontaneous generation of pre-RNA World biopolymers capable of catalysis and information transfer.

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The idea that the unidentified IR bands (UIBs) from diffuse atomic and molecular clouds are attributable to polycyclic aromatic hydrocarbons (PAHs) has gained considerable popularity since their discovery in 1973 (Bernstein *et al.* 1999). However, PAHs are not the only possible explanation for these strong IR emissions and they could arise from other forms of carbonaceous material containing *sp*² hybridized carbon (such as C=N) or from organic nanoparticles (Thaddeus 2006). Since unfunctionalized PAHs have no role in biochemistry today, their involvement in prebiotic chemistry is speculative (Platts 2004, Ehrenfreund *et al.* 2006).

In contrast to PAHs, the presence of HCN in comets, protostellar, planetary and lunar atmospheres is unequivocal. It is also well known that this HCN can polymerize spontaneously to HCN polymers under a wide variety of conditions. A much more credible link from cosmochemistry to biochemistry involves HCN polymers that may be part of organic nanoparticles, including PAHs, responsible for the UIBs. There is also evidence for the presence of these polymers in meteorites, on comets and Titan.

The polymerization of HCN is a spontaneous, exothermic reaction initiated by bases such as ammonia or free radicals from ionizing radiation and occurring over a wide range of temperature and pressure in both polar (H₂O) or non-polar (hydrocarbon) phases and on surfaces (Matthews *et al.* 2006). For example, a toluene solution of 1M HCN with 1 mol% of triethylamine as a base catalyst changes from yellow to orange to brown to black over a few days with almost all the HCN ultimately being converted to a solid black precipitate consisting of roughly 1 micron polymeric particles.

Incredibly, regardless of the conditions under which it is produced, when black HCN polymer is stirred with water, it partially dissolves to yield solutions containing small but

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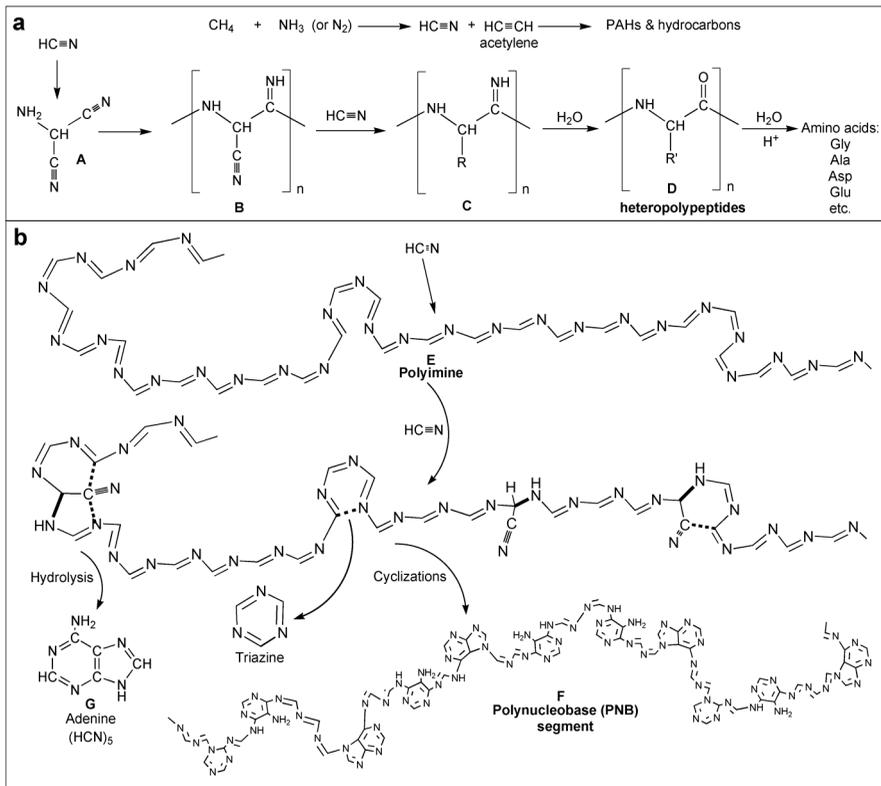


Figure 1. Pathways and structures proposed for HCN polymerization. A sample of HCN polymer may possess any or all of these structures including hybrids (multimers).

measurable quantities of a number of amino acids and nucleobases, the building blocks of both proteins and nucleic acids (Oró 1961, Oró & Kamat 1961). These solutions must also contain higher molecular weight macromolecules because on further hydrolysis by heating in acid or base (6N HCl 24 hr at 110° or pH 8 phosphate buffer, 140°, 3 days) greatly increased types and quantities of amino acids and nucleobases are detected. Glycine is the major amino acid produced (1 to 9%) with lesser amounts of alanine, aspartic acid, glutamic acid and several other amino acids (Matthews & Moser 1966, 1967). The nucleobases adenine, guanine, uracil and eight others were identified from the hydrolysis of solids produced in a dilute aqueous NH_4CN solution frozen at -78 °C for 27 years (Miyakawa *et al.* 2002). Without hydrolysis, the yields of amino acids or nucleobases were at least 10 times lower or were undetectable. Eight of twelve nucleobases were undetectable without hydrolysis.

There have been many studies showing how small molecules such as HCN, aldehydes, ammonia, or HCN tetramer can be converted into prebiotic monomers: amino acids via the Strecker synthesis or nucleobases via HCN tetramer chemistry (see below). There are two major problems with monomers: 1) they are water soluble and would be infinitely dilute in the primitive ocean; 2) condensing the amino acids or nucleobases into polymers with catalytic or informational capabilities would be virtually impossible in the watery ocean environment. Matthews & Moser (1967) showed that water is not required initially to form amino acids, as it would be if the Strecker route was involved. When methane and ammonia (or nitrogen) are sparked in the absence of water, hydrogen cyanide and acetylene are formed and both polymerize, the acetylene yielding primarily hydrocarbons and PAHs and the HCN yielding primarily HCN polymer (see Figure 1). Here, we

propose models whereby HCN polymerizes directly to form macromolecules containing polypeptide and linked nucleobase segments.

First reported by Proust (1808), HCN polymer has still not been fully characterized because of the complex heterogeneous nature of its structure. We can, however, rationalize the hydrolysis products with models that are consistent with known mechanistic organic chemistry (Figure 1). In the 1960's, Matthews proposed a mechanism (Figure 1a). Polyaminomalnonitrile, **B**, can be considered an addition polymer of the reactive trimer aminomalnonitrile, **A**. Cumulative reactions of HCN on the highly activated nitrile groups of **B** then yield the heteropolyamides **C** which are readily converted by water to heteropolypeptides, **D**, with release of ammonia and CO₂. **D** can be hydrolyzed to amino acids as shown. There are several chemical experiments consistent with this model including deuterium exchange studies (Matthews *et al.* 1977) and synthesis and modification of an analogue, poly- α -cyanoglycine (Minard *et al.* 1975).

Using solid state NMR, Mamajanov & Herzfeld (2008) have shown that black HCN polymer contains the extended polyimine structure **E** shown in Figure 1b. A mechanism has been proposed (Figure 1b) for the transformation of the polyimine structure into a polynucleobase (PNB) that can be hydrolyzed into nucleobases. Addition of HCN across -CH=N- bonds of the polyimine creates pendant cyano groups that can undergo thermal or photochemical cyclization to form triazines, purines and pyrimidines linked together in a polynucleobase macromolecule **F**. Small molecule cyclization chemistry related to that shown has been explored in reactions of HCN tetramer with HCN to form adenine (Ferris & Orgel 1966, Glaser *et al.* 2007). This new model helps to explain the sequence of carbons and nitrogens in purines and pyrimidines.

Turning to extraterrestrial chemistry, there is a growing body of evidence for the presence of HCN polymers on bodies such as moons (Titan), meteorites, and comets. Titan's atmosphere consists primarily of a mixture of nitrogen, a few percent of methane, and traces of acetylene, HCN, CO, and CO₂. In 1980, the Voyager 1 mission passed by Titan and showed it was covered by a thick orange-colored aerosol smog. Matthews (1982) proposed this was due to the presence of HCN polymers in Titan's atmosphere. In experimental simulations of Titan atmospheric chemistry, discharge-induced reactions of the N₂ and CH₄ produce solids called tholins that are primarily non-volatile high molecular weight hydrocarbons and nitrogen heterocycles. The major gaseous product is HCN that can be trapped together with ammonia at low temperature and which polymerizes at higher temperatures (Imanaka 2004). Work in the labs of Bar-Nun *et al.* (1988) and Scatertgood *et al.* (1992) showed that, under high energy conditions, acetylene polymerizes more readily than HCN. These observations lead us to propose a new model for Titan's atmospheric chemistry. Methane and acetylene polymerize in the upper atmosphere to give aerosol droplets of colorless hydrocarbons and polyacetylene. HCN does not readily polymerize in the gas phase, but instead is absorbed by the hydrocarbon droplets where it concentrates to the point that it can undergo ammonia or radiation initiated polymerization. As this occurs, the droplet obtains the orange color of HCN polymer. The composite hydrocarbon/HCN polymer droplets gradually rain or settle out onto the surface of Titan. The recent Cassini-Huygens mission to Titan showed evidence of ammonia and hydrogen cyanide from the Aerosol Collector Pyrolyzer-Mass Spectrometer on the Huygens lander (Israel *et al.* 2005). Waite *et al.* (2007) have recorded spectra from Cassini's ion beam and electron spectrometers that indicate the presence of negative ions with molecular weights up to 8,000 consistent with complex carbon-nitrogen precursors. This Titan atmospheric chemistry is likely relevant to early Earth.

As seen for HCN polymer, amino acids and nucleobases can be released by hydrolysis from the macromolecular material found in carbonaceous meteorites. There are many

similarities in the types and relative amounts of the compounds detected from meteorites and HCN polymer hydrolysates. Hydrolysis experiments with D₂O instead of H₂O produce similar deuterium labeling patterns for glycine derived from HCN polymer and from the Murchison meteorite, but not from glycine monomer (Matthews *et al.* 1977).

In 1986, the Giotto mission to Comet Halley showed that its nucleus was very dark in color. Spectral analysis indicated the presence of C-H and C≡N species in the crust and H₂O, HCN, and CN radicals in the coma (Kissel & Krueger 1987). Impact mass spectrometry indicated that some emanating particles consisted of primarily CHON or CHN (Fomenkova 1997). Matthews & Ludicky (1986) proposed that this data was consistent with the presence of HCN polymers on Halley and other comets. The Stardust mission returned cometary matter to Earth in January 2006. The high O and N contents, lower aromatic contents, and elevated -CH₂-/CH₃- ratios are all qualitatively consistent with what is expected from radiation processing of astrophysical ices and the polymerization of simple species such as HCO, H₂CO, and HCN (Sandford *et al.* 2006).

Comets or meteorites bearing HCN polymers could have been an exogenous source of these and other organic compounds. In addition, atmospheric reactions of methane and nitrogen could have been an endogenous source. With both these possible inputs, it seems likely that HCN polymers were present on the early Earth. These polymers are the most likely starting point for the origin of protein/nucleic acid based life and therefore are the critical link connecting cosmochemistry and biochemistry.

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Discussion

SANDFORD: We have done lots of experiments where we irradiate ices that are similar to what we see in dense clouds to see what complex organics are made. Most of these ices are very rich in H₂O, CH₃OH, and CO, so there is enough oxygen around that we don't see CN polymers of exactly the type you are talking about. However, one of the more abundant products we do see even in these O-rich mixtures is hexamethylenetetramine. I am curious what you think about how this might be related to what you've talked about.

MATTHEWS: Some papers have come out from the French workers on the question of hexamethylenetetramine versus HCN polymer (Fray, N., Bénilan, H., Cottin, H., *et al.* 2004, *Meteoritics and Planetary Science*, 39, 581). They say their experiments fit the HCN polymer very well, but not the hexamethylenetetramine. That's not a very good answer, but they have studied it.

CODY: We have attempted to do some NMR on HCN polymer and we've recognized, and you've confirmed in your talk, that these polymers have a lot of free radicals in them. I am intrigued as to whether you know, on the basis of electron paramagnetic resonance spectroscopy, if these are di-radicaloid type radicals?

MATTHEWS: The polymers are free radical in character. We usually use base catalysis, but radical catalysis is just as good. One of the papers (Budil, D. E., Roebber, J. L., Liebman, S. A., & Matthews, C. N. 2003, *Astrobiology*, 3, 323) shows you have carbon and nitrogen free radicals.

KHARE: In life as we know it, we need 20 amino acids. Out of those 20, two amino acids contain sulfur. Do you have any recipe to include these sulfur-containing amino acids as well?

MATTHEWS: They will be contained if H₂S is in the HCN polymer. If you have H₂S in the HCN mixture, it will modify the polyamino structure with the active CN group in the middle and give you S-containing side chains.



Cliff and Sandra Matthews enjoying a walk at the Victoria Peak during the Wednesday tour (photo by Bill Irvine).