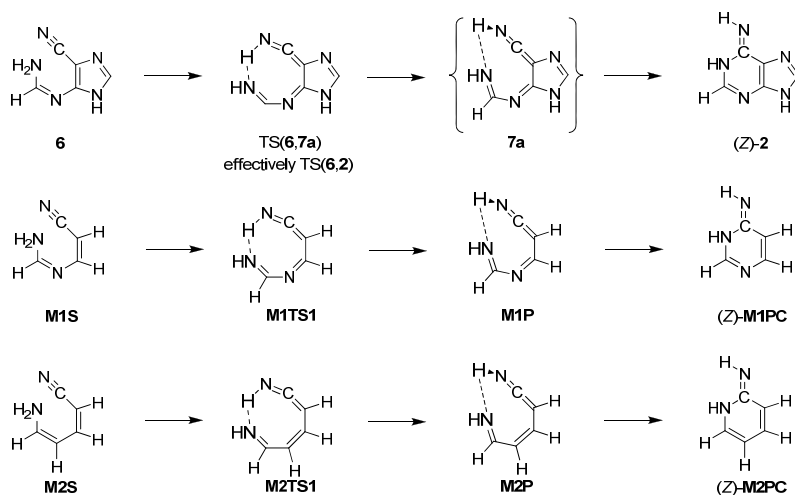


# Prebiotic Synthesis of Adenine. Hydrogen Atom Tunneling in the Virtual [1,7]-Sigmatropic Rearrangement of Monocyclic HCN-Pentamer

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Adenine can be formed by HCN pentamerization and an “adenine synthesis” is any reaction that leads to adenine itself, **1**, or any of its tautomers, (*Z*)-**2** and (*E*)-**2**, or to any of the respective *7H*-tautomers. All mechanistic proposals essentially agree with regard to the formation of the HCN tetramers diaminomaleonitrile (DAMN) and diaminofumaronitrile (DAFN) and the subsequent photochemical formation of the isomeric imidazoles **3** and **4** of AICN. The addition of HCN to AICN is a known route to adenine and presumably involves HCN pentamer **5**, the initial product of HCN aminolysis by **4**, and adenine formation after tautomerization of **5** to **6** or **7**. The tautomerizations **5**  $\rightleftharpoons$  **6** and **5**  $\rightleftharpoons$  **7** can be accomplished by one (or several) hydrogen migration(s) along skeletal bonds, and these paths provide for an indirect tautomerization **6**  $\rightleftharpoons$  **5**  $\rightleftharpoons$  **7**. There also exist possibilities for the tautomerization **6**  $\rightleftharpoons$  **7** without going through **5**, and these include the one-step [1,7]-sigmatropic H-shift from the amino group to the nitrile-N.



In this presentation, the results are reported of a study of the [1,7]-sigmatropic rearrangement of the monocyclic HCN-pentamers **6** to **7**. The related model systems **M1S** and **M2S** also were studied. The rearrangement is virtual in that structures in the PES region of **7a**, the putative product of H-migration, collapse to the (*Z*)-imino form of *9H*-adenine, (*Z*)-**2**. The transition state structure TS(**6,7a**) therefore effectively represents that transition state structure for the reaction of **6** to (*Z*)-**2**. The reaction has been studied with QCI theory and DFT methods. The M06 suite of density functionals was employed in the DFT studies and reaction rates have been computed via variational transition state theory with multidimensional tunneling.