

**The Formation of *N*- and *O*-heterocycles from the Irradiation of Benzene and Naphthalene in H<sub>2</sub>O- and NH<sub>3</sub>-Containing Ices.** C. K. Materese<sup>1,2</sup>, S. A. Sandford<sup>1</sup>, and M. Nuevo<sup>1,3</sup>. <sup>1</sup>NASA Ames Research Center, Moffett Field, CA. E-mail: Christopher.K.Materese@nasa.gov. <sup>2</sup>Oak Ridge Associated Universities, Oak Ridge, TN. <sup>3</sup>Bay Area Environmental Research Institute, Petaluma, CA.

**Introduction:** Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in many astrophysical environments, and are likely present in interstellar clouds and protostellar disks [1]. In dense molecular clouds, PAHs and other gas-phase species are expected to condense onto grains to form mixed molecular ice mantles dominated by small molecules like H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, CO, and CO<sub>2</sub> [2]. These icy mantles likely undergo energetic processing from ionizing radiation in the form of cosmic rays and high-energy photons.

Prior work in our laboratory designed to simulate the conditions in dense molecular clouds has shown that irradiation of PAHs in mixed molecular ices leads to chemical functionalization of their periphery. This functionalization is heavily dependent on the composition of the ice, and may include the addition of groups like -OH, -CH<sub>3</sub>, -NH<sub>2</sub>, -C≡N, extra H atoms, etc. [3].

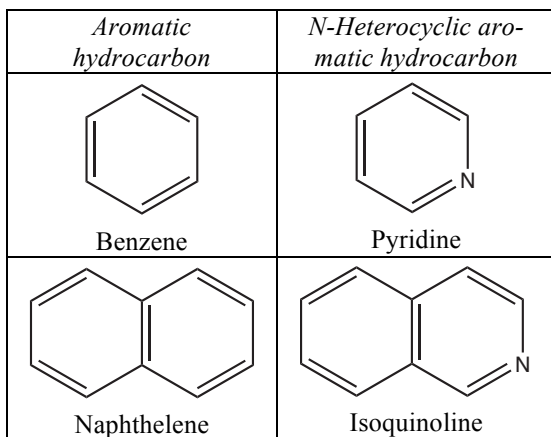
Aromatic heterocycles are a related class of molecules that differ from PAHs in that one or more carbon atoms are replaced with a heteroatom such as N or O. Large polycyclic aromatic nitrogen heterocycles (PANHs) are thought to be present in space, they are seen in meteoritic organics, and many are biologically important. Like PAHs, heterocyclic aromatic molecules that are irradiated in mixed molecular ices can gain functionalization of their peripheral rings [4-7]. Laboratory experiments have shown that, functionalization of the *N*-heterocycle pyrimidine can lead to the production of nucleobases.[5-7].

Small heterocycles have been detected in meteorites [8], but their origins have not been definitively established. Here we report on a series of recent experiments conducted in our laboratory that show that the irradiation of the aromatic molecules benzene (C<sub>6</sub>H<sub>6</sub>) and naphthalene (C<sub>10</sub>H<sub>8</sub>) in H<sub>2</sub>O and H<sub>2</sub>O+NH<sub>3</sub> ices leads to the formation of *O*- and *N*-heterocyclic molecules [9].

**Results:** Mixed molecular ices were deposited onto a cryocooled substrate and irradiated with UV photons. When the samples were warmed to room temperature, the volatile ices sublimed and left behind a refractory organic residue. The majority of the photoproducts remaining in this residue were benzene and naphthalene with functionalization of their peripheries [3]. However, they were also shown to contain heterocycles with either O or N atoms in their rings, including pyridine (C<sub>5</sub>H<sub>5</sub>N), quinoline and (possibly) isoquinoline (C<sub>9</sub>H<sub>7</sub>N), phthalide (C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>), as well as coumarin and isocoumarin (C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>). Experiments were repeated with <sup>18</sup>O- and <sup>15</sup>N-labeled starting ice components to further confirm the identification of these compounds.

These experiments show that heterocyclic aromatic molecules can form from the UV irradiation of simple aromatic molecules in mixed molecular ices. It is expected that this chemistry would also occur in the icy grains found in dense molecular clouds. If these grains subsequently become incorporated into larger parent bodies, then this work could suggest a possible explanation for the presence of heterocyclic molecules in meteorites. By extension, these processes may be important in the formation of nucleobases in astrophysical environments.

**References:** [1] Allamandola, L. J. et al. 1989. *ApJS* 71:733–775. [2] Bernstein, M. P. et al. 2005. *ApJS* 161:53–64. [3] Bernstein, M. P. et al. 2002. *ApJ* 576:1115–1120. [4] Elsila, J. E. et al. 2006. *Meteorit. Planet. Sci.* 41:785–796. [5] Nuevo M. et al. 2009. *Astrobiology* 9:683–695. [6] Nuevo M. et al. 2012. *Astrobiology* 12:295–314. [7] Materese et al. 2013. *Astrobiology* 13:948–962. [8] Callahan M. P. et al. 2011. *PNAS* 108:13995–13998. [9] Materese et al. 2015. *ApJ* 800:116



**Fig. 1.** Examples of simple aromatic molecules and *N*-heterocyclic molecules.