The Formation of *N*- and *O*-heterocycles from the Irradiation of Benzene and Naphthalene in H_2O/NH_3-containing Ices.

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Introduction: Aromatic hydrocarbons are an important class of molecules for both astrochemistry and astrobiology (Fig. 1). Within this class of molecules, polycyclic aromatic hydrocarbons (PAHs) are known to be ubiquitous in many astrophysical environments, and are likely present in interstellar clouds and protostellar disks [1]. In dense clouds, PAHs are expected to condense onto grains as part of mixed molecular ice mantles dominated by small molecules like H_2O, CH_3OH, NH_3, CO, and CO_2 [2]. These ices are exposed to ionizing radiation in the form of cosmic rays and ambient high-energy X-ray and UV photons.

Past laboratory studies have shown that irradiation of PAHs in mixed molecular ices leads to chemical functionalization of the PAHs' edges. Depending on the composition of the ice, this can include the addition of groups like –OH, $–CH_3$, $–NH_2$, –C≡N, extra H atoms, etc. [3]. Similar functionalization of the periphery occurs when the simple aromatic species are replaced with heterocyclic aromatic molecules (Fig. 1) [4-7]. Aromatic heterocycles differ from normal aromatic molecules in that one or more carbon atoms in the aromatic rings are replaced with a heteroatom such as N or O. Polycyclic aromatic nitrogen heterocycles (PANHs) are thought to be present in space, are seen in meteoritic organics, and can have biological importance. Indeed, functionalization of the heterocyclic molecules pyrimidine and purine can lead to the nucleobases that make up RNA and DNA, some of which have been identified in meteorites [5-8].

Although small heterocycles have been detected in meteorites [8], their origins have not been definitively established. Recent experiments conducted in our lab [9] have shown that the irradiation of the aromatic molecules benzene (C_6H_6) and naphthalene ($C_{10}H_8$) in mixed molecular ices leads to the formation of *O*- and *N*-heterocyclic molecules.

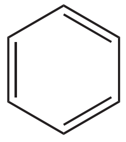
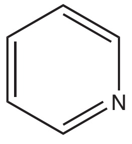
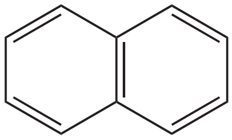
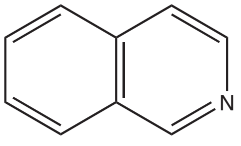
Aromatic hydrocarbon	*N-Heterocyclic aromatic hydrocarbon*
 Benzene	 Pyridine
 Naphthelene	 Isoquinoline

Fig. 1. *Examples of several simple aromatic molecules and related heterocyclic molecules.*

Methods: Several gas samples consisting of either benzene (C_6H_6) or naphthalene ($C_{10}H_8$) mixed with H_2O and/or NH_3 were prepared with relative compositions of $H_2O:C_6H_6$ (40:1), $H_2O:NH_3:C_6H_6$ (40:10:1), $H_2O:C_{10}H_8$ (200:1), or $H_2O:NH_3:C_{10}H_8$ (200:50:1). These mixtures were then each individually deposited on a cold substrate (<20 K) to form an ice layer that was simultaneously irradiated with an H_2-discharge UV lamp. After irradiation, the samples were warmed in vacuum until the original volatiles sublimed away. Any remaining residues were removed from the sample chamber and analyzed with gas chromatography–mass spectrometry (GC-MS). Identifications of compounds in these residues was accomplished by matching both the retention times and mass spectra of individual peaks with known standards. All experiments were repeated with isotopically labeled ^{18}O and ^{15}N to further confirm the results.

Results: UV irradiation of all of our mixed molecular ices resulted in the production of refractory residues that remained present on the sample head at room temperature after the original ices had sublimed away. Consistent with previous studies of the irradiation of PAHs in mixed-molecular ices [3], the majority of the new photoproducts were aromatic molecules with functionalization of their peripheral edges. However, analysis of these residues also showed evidence for the production of new heterocyclic molecules that contained either O or N atoms in their rings. New heterocycles identified included one-ringed pyridine (C_5H_5N) (Fig. 2), quinoline, and (possibly) isoquinoline (C_9H_7N), and two-ringed phthalide ($C_8H_6O_2$), coumarin ($C_9H_6O_2$), and isocoumarin ($C_9H_6O_2$). Experiments in which ^{18}O- and ^{15}N-labeled starting ice components were used yielded photoproducts having mass offsets consistent with the initial identifications obtained from the unlabeled ice residues (Fig. 2).

Interestingly, experiments in which we used isotopically normal pyridine (C_5H_5N) in place of benzene in initial ice mixtures containing $^{15}NH_3$ demonstrated that the N in the pyridine ring is highly exchangeable with N from NH_3 in the surrounding ice when exposed to UV radiation, i.e., C_5H_5N was readily converted to

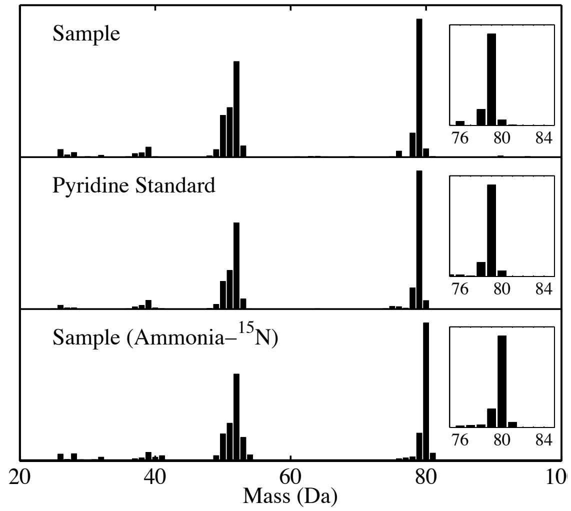


Fig. 2. *(Top) Mass spectrum of the retention peak corresponding to pyridine detected in the residue of a UV irradiated* $H_2O:NH_3:C_6H_6$ *(40:10:1) sample. (Middle) Mass spectrum of a pyridine standard. (Bottom) Mass sectrum of the peak corresponding to pyridine detected in the residue of a UV irradiated* $H_2O:{}^{15}NH_3:C_6H_6$ *(40:10:1) sample. The insets show the expected 1 amu off-set to higher mass when the isotopically normal* NH_3 *in the ice is replaced with* $^{15}NH_3$*.*

$C_5H_5{}^{15}N$. This N<-->N exchange appears to occur far more readily than when N replaces a carbon atom.

These experiments demonstrate that heterocyclic molecules can be made from PAHs in astrophysical environments via ice photoprocessing. The results demonstrate a means for the in-situ production of small heterocycles in icy grains without requiring that they be formed in or condense from the gas phase. If these grains are incorporated into larger parent bodies, this work could suggest a possible explanation for the presence of some of heterocyclic molecules detected in meteorites and mat be an important source of abiotically produced nucleobases.

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* (in press).