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N- AND *O*-HETEROCYCLES PRODUCED FROM THE IRRADIATION OF BENZENE AND NAPHTHALENE IN H_2O/NH_3-CONTAINING ICES

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ABSTRACT

Aromatic heterocyclic molecules are an important class of molecules of astrophysical and biological significance that include pyridine, pyrimidine, and their derivatives. Such compounds are believed to exist in interstellar and circumstellar environments, though they have never been observed in the gas phase. Regardless of their presence in the gas phase in space, numerous heterocycles have been reported in carbonaceous meteorites, which indicates that they are formed under astrophysical conditions. The experimental work described here shows that *N*- and *O*-heterocyclic molecules can form from the ultraviolet (UV) irradiation of the homocyclic aromatic molecules benzene (C_6H_6) or naphthalene ($C_{10}H_8$) mixed in ices containing H_2O and NH_3. This represents an alternative way to generate aromatic heterocycles to those considered before and may have important implications for astrochemistry and astrobiology.

Key words: astrobiology – astrochemistry – molecular data – molecular processes – solid state: refractory

1. INTRODUCTION

Aromatic compounds are an important class of molecules of astrophysical and astrobiological interest. In particular, polycyclic aromatic hydrocarbons (PAHs) are abundant in interstellar and circumstellar environments (Allamandola et al. 1989; Puget & Léger 1989; Galliano et al. 2008) and account for a significant fraction of the universe's molecular carbon. They are believed to be produced in the gas phase, in the outflows of late-type carbon (AGB) stars via a chemical pathway involving the polymerization of acetylene (e.g., Cherchneff et al. 1992).

Heterocyclic aromatic compounds are a related class of molecules in which one or more of the carbon atoms in the aromatic ring is/are replaced with an alternative heteroatom such as N or O (see Figure 1 for examples). Ricca et al. (2001) demonstrated in a computational study that if HCN is also present in the gas phase during the acetylene polymerization that produces PAH molecules, then nitrogen heterocycles (*N*-heterocycles) can also be produced. Such a mechanism was confirmed in a recent combined experimental and theoretical study in which pyrimidine cations were formed from HCN and acetylene in the gas phase (Hamid et al. 2014).

Although several plausible mechanisms for their formation have been proposed, no *N*-heterocycles have been unequivocally detected in astronomical environments to date via the detection of their rotation lines, and only upper limits have been placed on their abundances in the gas phase (Simon & Simon 1973; Kuan et al. 2004; Charnley et al. 2005; Brünken et al. 2006). Peeters et al. (2005) showed that small *N*-heterocyles are much more susceptible to photodestruction than their homocyclic counterparts, which could explain a lower abundance of these molecules in astrophysical environments. However, larger polycyclic aromatic nitrogen heterocycles (PANHs) are expected to be more stable against radiation (Mattioda et al. 2003, 2005), and it has been proposed that the presence of PANHs in interstellar space could explain aspects of the infrared (IR) emission features thought to be associated with PAHs and related aromatic materials. In particular, the position of the observed 6.2 μm band is difficult to match using only PAHs or their ions, but might be accounted for by PANHs (Peeters et al. 2002; Hudgins et al. 2005).

Despite their apparent susceptibility to photodestruction in the gas phase, small heterocycles have been detected in carbonaceous meteorites. For example, benzofurans, a type of *O*-heterocycle, have been detected in the Yamato-791198 meteorite (Komiya et al. 1993), while *N*-heterocycles such as pyridines, pyrimidines, quinolines, and isoquinolines have been detected in carbonaceous chondrites, including Orgueil, Murchison, Murray, and LON 94102 (Hayatsu 1964; Folsome et al. 1971, 1973; Hayatsu et al. 1975; van der Velden & Schwartz, 1977; Stoks & Schwartz, 1979, 1981, 1982; Callahan et al. 2011). The extraterrestrial origins of some of these compounds have been confirmed by isotopic studies (Martins et al. 2008). Although small heterocycles represent a minor fraction of the total carbon present in the meteoritic samples, their existence demonstrates that they are produced under astrophysical conditions, even though their origin remains unknown.

Because of their biological significance, the detection of *N*-heterocycles in astrophysical environments and an understanding of their formation under relevant astrophysical conditions are of great interest. The nucleobases that carry the genetic information in RNA and DNA are based on pyrimidine ($C_4H_4N_2$) and purine ($C_5H_4N_4$), both of which are *N*-heterocycles. Several experimental studies have demonstrated that pyrimidine-based nucleobases can form from the irradiation of simple ices of astrophysical relevance containing small amounts of pyrimidine (Nuevo et al. 2009, 2012, 2014; Materese et al. 2013). In these experiments, the inclusion of pyrimidine in the starting ice mixtures was justified by its presence in meteoritic samples, but the work described below shows further evidence for the plausibility of their inclusion in astrophysical ices.

Laboratory experiments have shown that UV photo-irradiation and energetic particle bombardment of ices can drive organic chemistry even at extremely low temperatures (Allamandola et al. 1988; Moore & Hudson 1998; Bernstein et al. 1999, 2001, 2002; Sandford et al. 2000; Meierhenrich et al. 2005; Bennett & Kaiser 2007; Nuevo et al. 2008). Such processes can occur in dense molecular clouds where ionizing

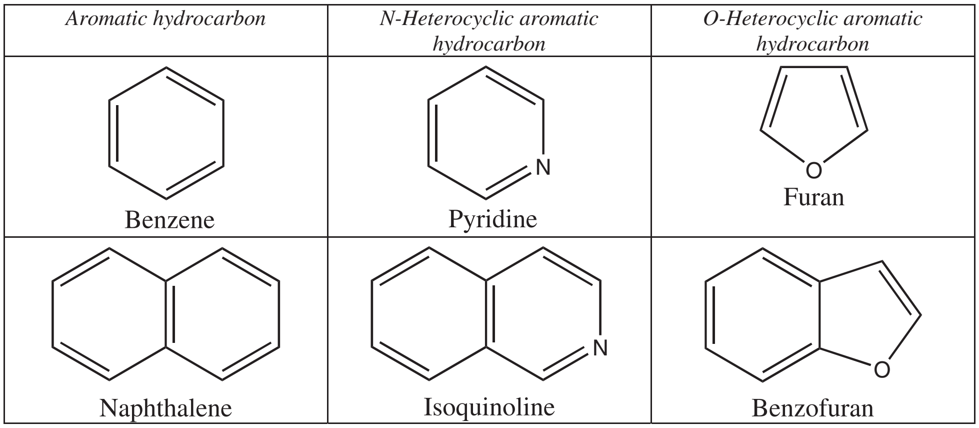


Figure 1. Examples of cyclic aromatic hydrocarbons and heterocyclic *N*- and *O*-heterocyclic aromatic molecules.

radiation in the form of UV photons and cosmic rays are expected to interact with mixed molecular ices. Recently, Ciesla & Sandford (2012) demonstrated that these types of laboratory experiments are also relevant for the conditions present in the solar nebula, and that many of the organics found in comets and meteorites may be a natural by-product of energetic processing of ices during protosolar disk evolution.

Since PAHs are ubiquitous in space, they are expected to also condense onto icy grains, the same way as other volatile and semi-volatile compounds do (Bernstein et al. 2005). Heretofore, experiments involving the irradiation of ices containing PAHs have not reported the production of heterocycles, but have shown that aromatic rings can be functionalized by moieties released from the surrounding ice, indicating that a peripheral hydrogen atom from the ring can be replaced with a chemical group such as OH, NH_2, CH_3, C≡N, COOH, etc. (Bernstein et al. 1999, 2001, 2002; Sandford et al. 2000; Callahan et al. 2013). These experiments have also shown that aromatic rings can be ruptured or fragmented and the resulting fragments can lead to the formation of non-cyclic products (e.g., Chen et al. 2008; Nuevo et al. 2012; Materese et al. 2013).

In the present experimental study, we demonstrate that both *N*- and *O*-heterocycles can form from the ultraviolet (UV) irradiation of benzene (C_6H_6) and naphthalene ($C_{10}H_8$) in H_2O ice and H_2O:NH_3 ice mixtures. Similarly, we demonstrate that the nitrogen in pyridine (C_5H_5N) is readily exchangeable with other nitrogen atoms from molecules in the surrounding ice. Our work suggests that *N*- and *O*-heterocycles can form in astrophysical environments such as interstellar clouds and protostellar disks, where PAHs may be condensed into mixed molecular ices on cold grains that are subjected to ionizing radiation. This provides an alternative pathway for the formation of heterocycles, and may in part explain the presence of these molecules in meteorites regardless of whether or not they could form and survive in the gas phase in space.

2. MATERIALS AND METHODS

Descriptions of our apparatus and procedures have been published elsewhere (Materese et al. 2013). Briefly, samples are prepared in a vacuum cryogenic chamber evacuated by a diffusion pump to a pressure of a few 10^{-8} mbar. Premixed gas mixtures are vapor deposited onto a prebaked (500°C) ultra-high vacuum grade aluminum foil attached to a cold finger cooled to 15–25 K. During deposition, the growing ice film is simultaneously irradiated with UV photons from a microwave-powered H_2-discharge lamp. This lamp primarily emits photons at 121.6 nm (Lyα) and a continuum centered around 160 nm, with an estimated total flux of $\sim 2 \times 10^{15}$ photons cm^{-2} s^{-1} (Warnek 1962). Control experiments in which the deposited ice received no UV irradiation were also run under the same conditions.

Gas mixtures were prepared in 3 L glass bulbs using a glass line evacuated to a background pressure of $\sim 5 \times 10^{-6}$ mbar. The ratios between components were determined according to their partial pressures with an accuracy of 0.05 mbar. The following compounds were used as starting materials in these experiments: H_2O (liquid, purified to 18.2 MΩ cm by a Millipore Direct-Q UV 3 device), $H_2{}^{18}O$ (liquid, Cambridge Isotope Laboratory, 97% ^{18}O), NH_3 (gas, Matheson, anhydrous, 99.99%), $^{15}NH_3$ (gas, Aldrich, 98% ^{15}N), benzene (C_6H_6; liquid, Sigma–Aldrich, Chromasolv Plus HPLC grade, 99.9%), naphthalene ($C_{10}H_8$; solid, Aldrich, scintillation grade, $\geqslant$99%), and pyridine (C_5H_5N; liquid, Sigma–Aldrich, biotech grade, $\geqslant$99.9%). All liquids were freeze–pump–thawed at least four times to remove excess dissolved gases. In this work, H_2O:C_6H_6 (40:1), H_2O:NH_3:C_6H_6 (40:10:1), $H_2{}^{18}O$:NH_3:C_6H_6 (40:10:1), H_2O:$C_{10}H_8$ (40:0.2) $H_2{}^{18}O$:$C_{10}H_8$ (40:0.2), H_2O:NH_3:$C_{10}H_8$ (40:10:0.2), $H_2{}^{18}O$:NH_3:$C_{10}H_8$ (40:10:0.2), H_2O:NH_3:C_5H_5N (40:10:1), and H_2O:$^{15}NH_3$:C_5H_5N (40:10:1) mixtures were prepared. It should be noted that the lower relative abundances of naphthalene compared to benzene in these mixes was the result of constraints on its lower vapor pressure.

In a typical experiment, 15–18 mbar of each gas mixture (~1.7–2.0 mmol) was deposited onto the aluminum foil substrate while being simultaneously UV irradiated for 20–24 hr. After irradiation, each sample was warmed to 150 K under static vacuum at a rate of 1 K min^{-1}. At 150 K, the cryocooler was turned off and the chamber was flooded with argon gas (Airgas, 99.6%) to restore atmospheric pressure and assist with the retention of semi-volatile species. At 280 K, the aluminum foil substrate was extracted from the vacuum chamber, and any remaining residue was dissolved from the foil using 50 μL of methanol (liquid, Aldrich, HPLC grade, 99.9%).

A 1 μL aliquot of each sample solution was injected into a Thermo Trace gas chromatograph coupled with a DSQ II mass spectrometer (GC-MS) equipped with a Restek Rtx-200MS column. This GC-MS device utilized splitless injection, with an injector temperature of 250°C, and a carrier gas (He) flow rate of 1.0 mL min^{-1}. Initially, the temperature was held at 40°C for 4 minutes, then ramped at 6°C min^{-1} to 250°C, and finally held at 250°C for 10 minutes. Masses were recorded from 19 to 500 Daltons (Da), and data analysis was performed with the Xcalibur^{TM} software (Thermo Finnigan). Peaks in the resulting GC-MS chromatograms were compared with the NIST database of mass spectra or with the mass spectra of commercial standards (obtained with the same GC-MS device used to measure our residue samples). Measured standards included pyridine, quinoline (C_9H_7N; liquid, Aldrich, reagent grade, 98%), isoquinoline (C_9H_7N; solid, Aldrich, 97%), coumarin ($C_9H_6O_2$; solid, Sigma, HPLC grade, 99%), and phthalide ($C_8H_6O_2$; solid, Aldrich, 98%). Note that the retention times of these compounds in the residues may slightly differ from those obtained for the corresponding standards, due to the presence of other compounds in the residues that may interact with the compound of interest. However, comparison between the mass spectra of the corresponding peaks in the residues and the standards provides a robust identification of these compounds.

The amount of each identified heterocycle present in the sample residues was estimated by injecting the corresponding standard (1 μL) with a known concentration (10^{-4} M) into the GC-MS device immediately after one of the sample runs. The peak associated with a given compound in the single-ion chromatograms (SICs) of both the samples and the corresponding standard for the most intense mass peak were then integrated, and the peak integration of each standard was used as a normalization factor. It should be noted that these quantities were obtained from single experiments, and that the sensitivities of these values to parameters such as temperature, initial ice concentration, and radiation dose are not known. Additionally, given that some of the compounds in each residue and the solvent used to extract it from the aluminum foil substrate are semi-volatile, these quantities should be considered as lower-limit estimates rather than reliable yields.

3. RESULTS

UV irradiation of $H_2O:C_6H_6$ (40:1) ice mixtures (mixture 1) resulted in the production of refractory residues that were collected and analyzed with GC-MS. Numerous oxidized benzene derivatives and related compounds were tentatively identified using the NIST database and are listed in Table A1. Since these compounds were not the focus of this study, no further attempt was made to confirm their identities by comparison with standards. Unlike all the other experiments described hereafter, these experiments did not yield any identified heterocycles.

UV irradiation of $H_2O:NH_3:C_6H_6$ (40:10:1) ice mixtures (mixture 2) resulted in residues containing a complex mixture of oxidized and aminated benzene derivatives and related compounds (Table A1). In addition, the *N*-heterocycle pyridine (79 Da) was detected, with a retention time consistent with its standard (R_t = 7.2 minutes; Table 1). Chromatograms and mass spectra of the sample and standard are shown in Figure 2. Pyridine production is quite modest relative to the most abundant photoproducts, with approximately 0.5 nmol of pyridine being detected in the whole sample ($N_{C_5H_5N}/N_{C_6H_6} \sim 1 \times 10^{-5}$). Experiments using isotopically labeled $^{15}NH_3$ were performed to confirm the pyridine identification. As expected, this substitution resulted in an increase of 1 Da per nitrogen atom present in all detected nitrogen-containing photoproducts, and confirmed the original identification of pyridine (Figure 2, Table 1).

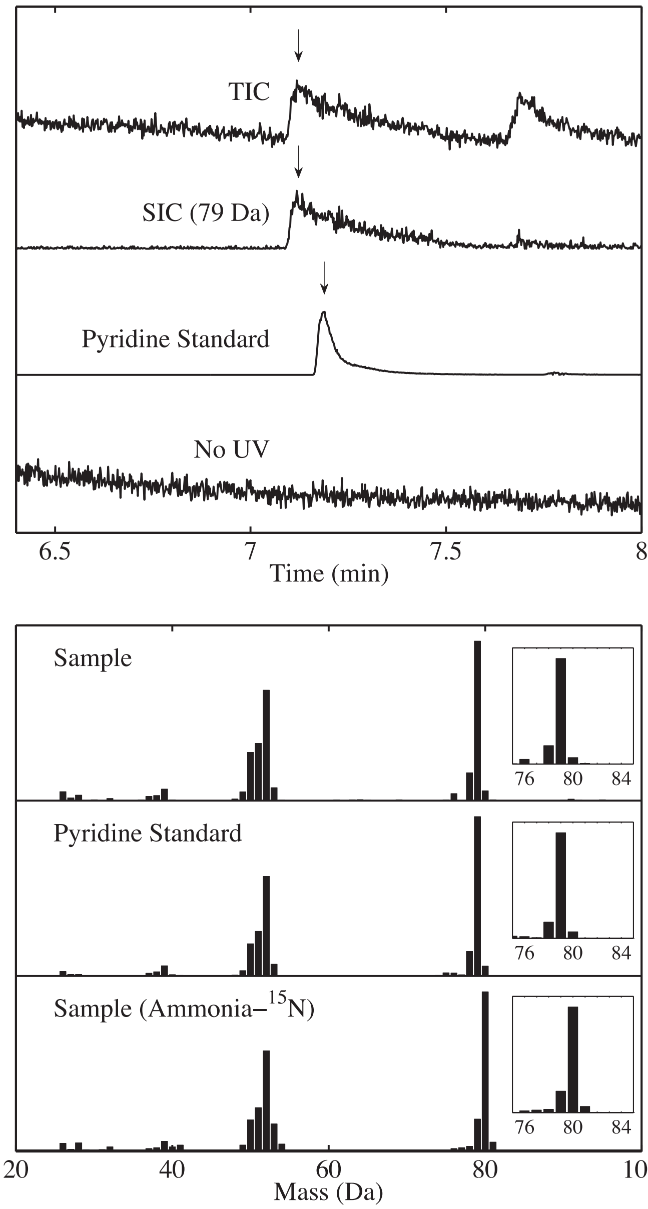
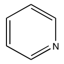
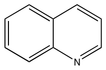
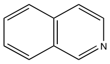
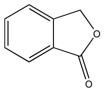
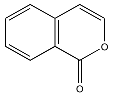
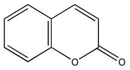


Figure 2. Top: total-ion chromatogram (TIC) of the residue produced from a UV-irradiated $H_2O:NH_3:C_6H_6$ ice (top). Upper middle: mass 79 Da single-ion chromatogram (SIC) of the same residue. Lower middle: pyridine standard. Bottom: TIC of an unirradiated $H_2O:NH_3:C_6H_6$ ice (control sample). Bottom: (top) mass spectrum of the peak identified as pyridine in the residue produced from a UV-irradiated $H_2O:NH_3:C_6H_6$ ice. Middle: mass spectrum of a pyridine standard. Bottom: mass spectrum of the peak identified as pyridine in the residue produced from a UV-irradiated $H_2O:{}^{15}NH_3:C_6H_6$ ice.

UV irradiation of $H_2O:C_{10}H_8$ (40:0.2) ice mixtures (mixture 3) produced residues that contained a complex mixture of hydrogenated and oxidized naphthalenes and related compounds (Table A1), many of which were previously observed in similar experiments (Bernstein et al. 1999, 2001, 2002; Sandford et al. 2000). In addition, several *O*-heterocycles, including phthalide (134 Da, R_t = 26.5 minutes, 0.4 nmol, $N_{C_8H_6O_2}/N_{C_{10}H_8} \sim 4 \times 10^{-5}$), coumarin (146 Da, R_t = 27.8 minutes, 0.2 nmol, $N_{C_9H_6O_2}/N_{C_{10}H_8} \sim 2 \times 10^{-5}$), and probably isocoumarin (146 Da, R_t = 26.6 minutes) were detected. The mass spectra and retention times of both phthalide (Figure 3, Table 1) and coumarin (Figure 4, Table 1) closely match their standards. We were unable to obtain a standard for isocoumarin, so its identification is entirely based on a match with the NIST database. This experiment was repeated using isotopically labeled $H_2{}^{18}O$, and the resulting products had mass spectra consistent with ^{18}O-labeled phthalide, coumarin, and isocoumarin, as the masses of their

Table 1
Complete List of Heterocyclic Compounds Detected in These Experiments

Species	Structure	R_t (GC-MS) (minutes)	Parent peak (Da)	Isotopically Labeled Parent Peak (Da)	Quantity[a] (nmol)	Ice Mixture
Pyridine (C_5H_5N)		7.1	79	80 (^{15}N)	0.5	2
Quinoline (C_9H_7N)		20.1	129	130 (^{15}N)	0.02	4
Isoquinoline (C_9H_7N)		21.1	129	130 (^{15}N)	0.1	4
Phthalide ($C_8H_6O_2$)		26.5	134	138 (^{18}O)	0.4	3, 4
Isocoumarin[b] ($C_9H_6O_2$)		26.6	146	150 (^{18}O)	…	3, 4
Coumarin ($C_9H_6O_2$)		27.8	146	150 (^{18}O)	0.2	3, 4

Notes.
[a] Quantities should be considered to be rough lower limits as material is lost while samples are warmed.
[b] No standard available.

fragments were, as expected, increased by 2 Da per oxygen atom (Figures 3 and 4, Table 1).

UV irradiation of H_2O:NH_3:$C_{10}H_8$ (40:10:0.2) ice mixtures (mixture 4) produced refractory residues containing oxidized and aminated naphthalene derivatives (Table A1). As with the H_2O:$C_{10}H_8$ experiments, phthalide, coumarin, and probably isocoumarin were observed. These experiments also resulted in the production of the *N*-heterocycles quinoline (129 Da, $R_t = 20.1$ minutes, 0.02 nmol, $N_{C_9H_7N}/N_{C_{10}H_8} \sim 3 \times 10^{-6}$) and possibly isoquinoline (129 Da, $R_t = 21.1$ minutes, 0.1 nmol, $N_{C_9H_7N}/N_{C_{10}H_8} \sim 1 \times 10^{-5}$). The mass spectra and retention times of both these compounds were consistent with their standards (Figures 5 and 6, Table 1). Experiments in which the starting NH_3 was replaced by isotopically labeled $^{15}NH_3$ resulted in an increase of 1 Da per nitrogen atom present in the previous products (Figures 5 and 6, Table 1). The mass spectrum of the peak assigned to quinoline in this experiment is fully consistent with ^{15}N-labeled quinoline. Isoquinoline was only tentatively identified, as its mass spectrum is consistent with ^{15}N-labeled isoquinoline, but the mass 129 peak is abnormally large, possibly due to a coelution with another unidentified compound.

UV irradiation of H_2O:NH_3:C_5H_5N (40:10:1) ice mixtures (mixture 5) was performed to test for the production of pyrimidine, a heterocycle containing 2 N atoms in its ring structure. However, the pyrimidine peak appears very quickly after the very large peak of pyridine in the chromatogram, making this potential product very difficult to resolve. As a result, these experiments did not answer the question of pyrimidine formation. However, experiments using H_2O:$^{15}NH_3$:C_5H_5N ices suggested that the nitrogen atom in the pyridine ring may be highly exchangeable with those from the surrounding NH_3 when exposed to UV radiation, as it appeared that much of the of pyridine remaining in the final residues had been converted into ^{15}N-pyridine (Figure 7). This suggests that it is much easier to exchange a nitrogen atom in an aromatic ring for another nitrogen atom than it is to replace a carbon atom in an aromatic ring with a nitrogen or oxygen atom.

4. DISCUSSION

The photo-induced rupture of small aromatic hydrocarbons and *N*-heterocycles embedded in ices has been previously reported (Chen et al. 2008; Nuevo et al. 2012, 2014; Materese et al. 2013). These experimental studies showed that such molecules can play the role of carbon sources to form new organic molecules including urea, amino acids, and carboxylic acids. The process described in our present study is different and new in the sense that it suggests that the rings of aromatic cyclic molecules such as benzene and naphthalene may open via photo-induced reactions, interact with the surrounding ices, and re-cyclize into a different aromatic compound that contains heteroatoms such as N and O.

Although we cannot definitively state the mechanisms governing these reactions, we can offer some possibilities and discuss their implications. A simple mechanism where the ring opens, a nitrogen or oxygen is added from the surrounding ice, and the ring then closes, is not sufficient to explain the results presented here because this process would yield products with rings that contain too many carbon atoms. We can envision several possible alternative mechanisms for this process: (1) Rupture of the ring, followed by the elimination of a carbon and addition of a heteroatom, followed by closure of the ring. (2) Addition of the heteroatom as a side group to the ring followed by rupture of the ring and subsequent closure of the ring with the heteroatom incorporated in the ring and an adjacent carbon moved to the periphery, followed by the elimination of the peripheral carbon, as previously observed in experiments in

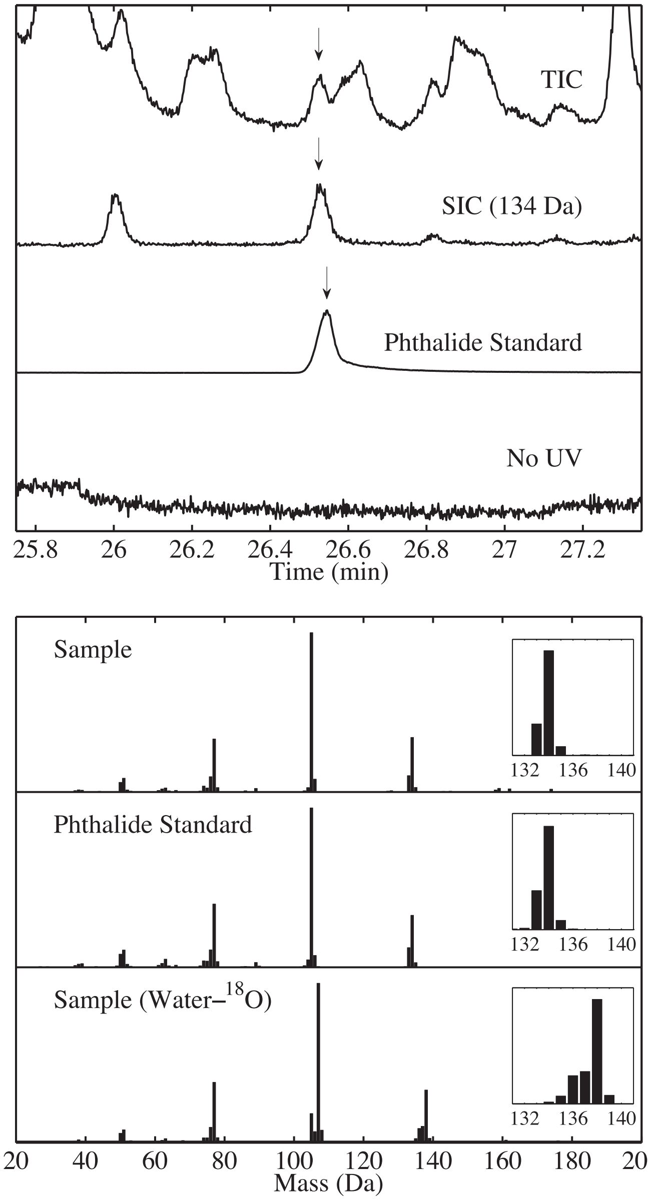


Figure 3. Top: (top)—total-ion chromatogram (TIC) of a residue produced from a UV-irradiated $H_2O:C_{10}H_8$ ice. Upper middle: mass 134 Da single-ion chromatogram (SIC) of the same residue. Lower middle: phthalide standard. Bottom: TIC of an unirradiated $H_2O:C_{10}H_8$ ice (control sample). Bottom: (top)—mass spectrum of the peak identified as phthalide in the residue produced from a UV-irradiated $H_2O:C_{10}H_8$ ice. Middle: mass spectrum of the phthalide standard. Bottom: mass spectrum of the peak identified as phthalide in the residue produced from a UV-irradiated $H_2{}^{18}O:C_{10}H_8$ ice.

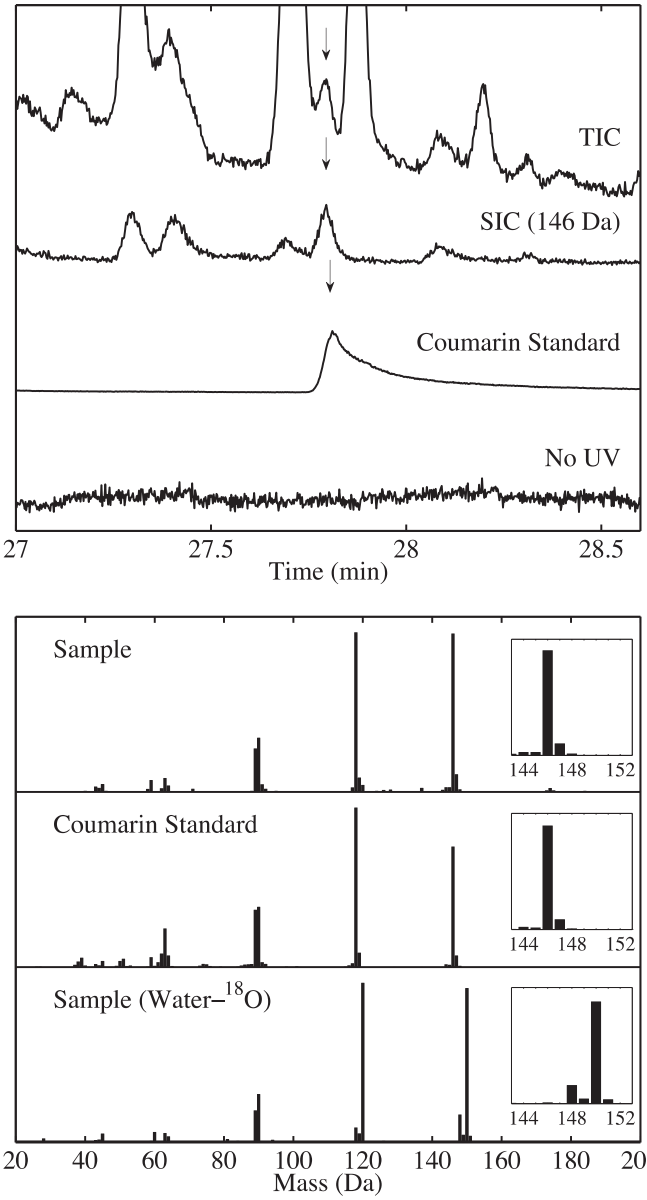


Figure 4. Top: (top)—total-ion chromatogram (TIC) of a residue produced from a UV-irradiated $H_2O:C_{10}H_8$ ice. Upper middle: mass 146 Da single-ion chromatogram (SIC) of the same residue. Lower middle: coumarin standard. Bottom: TIC of an unirradiated $H_2O:C_{10}H_8$ ice (control sample). Bottom: (top)—mass spectrum of the peak identified as coumarin in the residue produced from a UV-irradiated $H_2O:C_{10}H_8$ ice. Middle: mass spectrum of the coumarin standard. Bottom: mass spectrum of the peak identified as coumarin in the residue produced from a UV-irradiated $H_2{}^{18}O:C_{10}H_8$ ice.

which UV photons easily cleave methyl groups from methylated pyrimidine (Materese et al. 2013). (3) Ring fragmentation followed by the formation of entirely new heterocycles from the fragments.

We note that no *O*-heterocycles were detected in the $H_2O:C_6H_6$ and $H_2O:NH_3:C_6H_6$ mixtures even though they were detected in the $H_2O:C_{10}H_8$ and $H_2O:NH_3:C_{10}H_8$ mixtures. There are several possible explanations for this result: (1) A simple substitution of oxygen into the ring in place of a single carbon would yield pyran, which is not aromatic and is unstable in water or air. If this molecule were formed, it would not likely survive to be detected in the GC-MS. If a second oxygen atom were added to yield either 2- or 4-pyrone, the molecule would become much more stable, though these products have not been detected. (2) It is possible a 5-member ring variant like furan is formed in our samples, but its low boiling point and high vapor pressure make it undetectable with our GC-MS protocol.

Given the abundance of PAHs in space and the expectation that they will condense onto icy grains in cold environments (Bernstein et al. 2005), our work suggests that the production of *N*- and *O*-heterocycles in the solid phase in interstellar clouds and protostellar disks is likely. As previously stated, small *N*- and *O*-heterocycles including pyridines, pyrimidines, quinolines, isoquinolines, and benzofurans have been detected in meteorites (Komiya et al. 1993; Hayatsu 1964; Folsome et al. 1971, 1973; Hayatsu et al. 1975; van der Velden & Schwartz

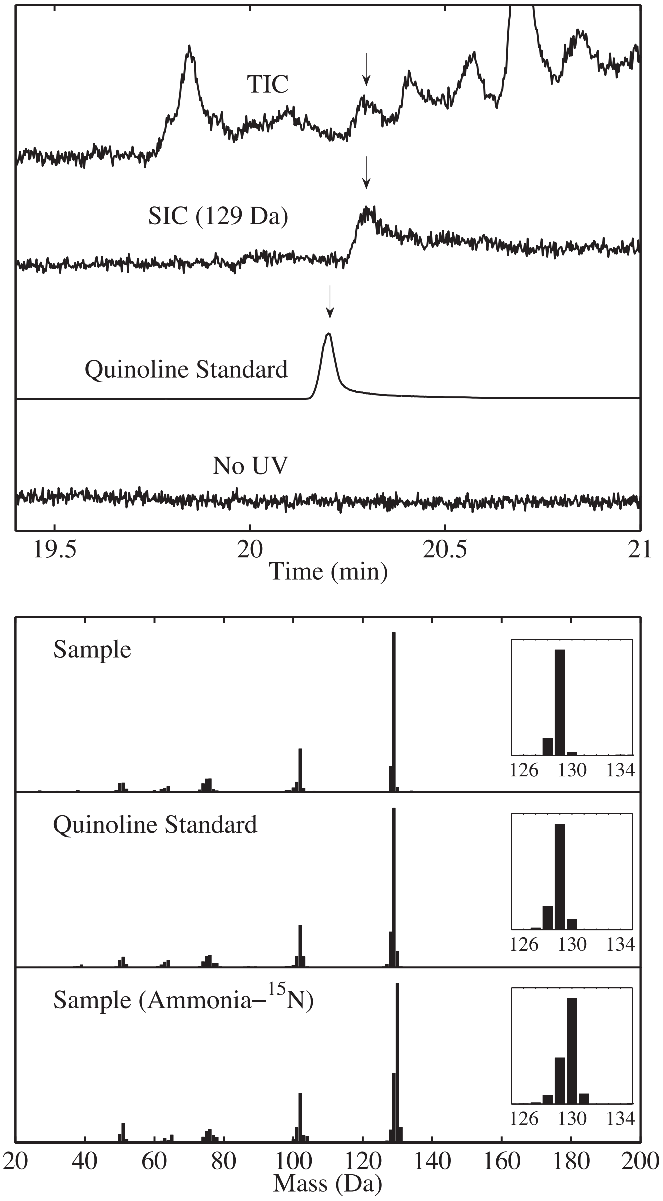


Figure 5. Top: (top)—total-ion chromatogram (TIC) of a residue produced from a UV-irradiated $H_2O:NH_3:C_{10}H_8$ ice. Upper middle: mass 129 Da single-ion chromatogram (SIC) of the same residue. Lower middle: quinoline standard. Bottom: TIC of an unirradiated $H_2O:NH_3:C_{10}H_8$ ice (control sample). Bottom: (top)—mass spectrum of the peak identified as quinoline in the residue produced from a UV-irradiated $H_2O:NH_3:C_{10}H_8$ ice. Middle: mass spectrum of the quinoline standard. Bottom: mass spectrum of the peak identified as quinoline in a residue produced from a UV-irradiated $H_2O:^{15}NH_3:C_{10}H_8$ ice.

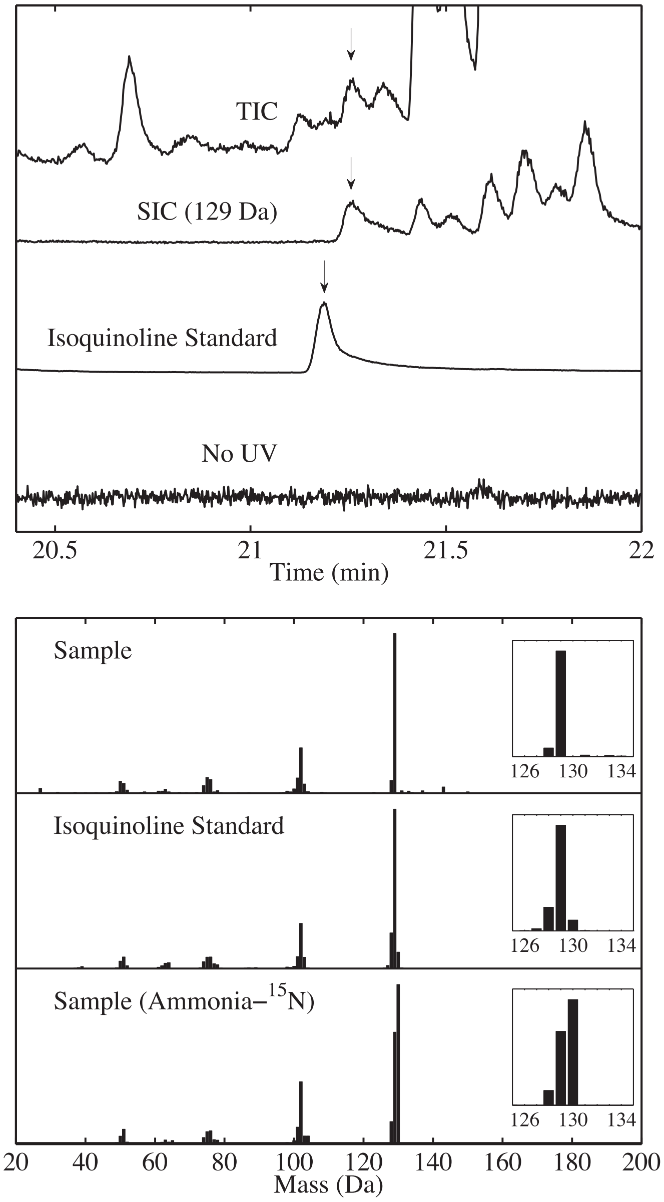


Figure 6. Top: (top)—total-ion chromatogram (TIC) of a residue produced from a UV-irradiated $H_2O:NH_3:C_{10}H_8$ ice. Upper middle: mass 129 Da single-ion chromatogram (SIC) of the same residue. Lower middle: isoquinoline standard. Bottom: TIC of an unirradiated $H_2O:NH_3:C_{10}H_8$ ice (control sample). Bottom: (top)—mass spectrum of the peak identified as isoquinoline in a residue produced from a UV-irradiated $H_2O:NH_3:C_{10}H_8$ ice. Middle: mass spectrum of the isoquinoline standard. Bottom: mass spectrum of the peak identified as isoquinoline in a residue produced from a UV-irradiated $H_2O:^{15}NH_3:C_{10}H_8$ ice.

1977; Stoks & Schwartz 1979, 1981, 1982; Callahan et al. 2011). The method for the production of *N*- and *O*-heterocycles described in the present work could explain their production in presolar/protosolar ices, followed by their incorporation into asteroidal or cometary parent bodies, independent of the presence of gas-phase *N*-heterocycles in interstellar/circumstellar environments. Therefore, such molecules are expected to be present in forming planetary systems and could be an important source of abiotically produced nucleobases.

Pyrimidine and purine are both simple *N*-heterocycles that are important for biology, since the five nucleobases found in terrestrial RNA and DNA are based on these molecules. Uracil, cytosine, and thymine are derivatives of pyrimidine functionalized by OH, NH_2, and CH_3 groups, while adenine and guanine are derivatives of purine functionalized by OH and NH_2 groups. Previous UV irradiation experiments of pyrimidine in H_2O, NH_3, CH_3OH, and CH_4 ices have demonstrated the formation of uracil, cytosine, and thymine (Nuevo et al. 2009, 2012, 2014; Materese et al. 2013). For these experiments to be relevant to astrophysical environments, the presence of pyrimidine in these starting ices was assumed. Although the presence of pyrimidine has not been confirmed in our ices, it is reasonable to assume that the process described in this work could produce pyrimidine through successive nitrogen insertions into the benzene ring. Future work should focus on the formation of heterocycles involving the insertion of multiple heteroatoms and on the formation of any nucleobases.

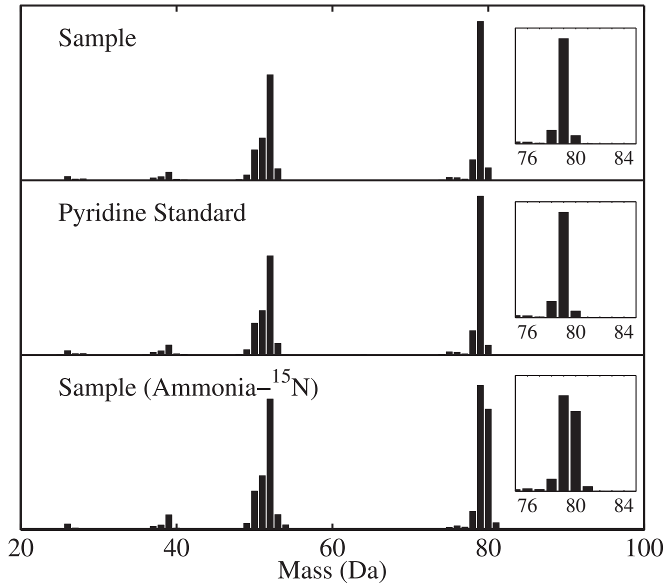


Figure 7. Top: mass spectrum of the peak identified as pyridine in the residue produced from a UV-irradiated H_2O:NH_3:C_5H_5N ice. Middle: mass spectrum of a pyridine standard. Bottom: mass spectrum of the peak identified as pyridine in a residue produced from a UV-irradiated H_2O:$^{15}NH_3$:C_5H_5N ice.

5. CONCLUSION

This study demonstrates that *N*- and *O*-heterocycles can form from the UV irradiation of benzene and naphthalene in simple H_2O and H_2O:NH_3 ices at low temperature. It shows a new way to produce these types of molecules, and has important implications for astrochemistry, astrophysics, and astrobiology. Unfortunately, these experiments do not allow us to probe the reaction mechanism(s) responsible for the production of these heterocycles. Theoretical calculations might provide significant insight into this issue.

This work also suggests that it is far easier to exchange a nitrogen atom from within the skeleton of an *N*-heterocycle with a nitrogen atom from the surrounding ice than it is to exchange a carbon atom from an aromatic ring with a nitrogen atom in the ice. This is consistent with the fact that small *N*-heterocycles tend to be less stable with respect to UV irradiation than their homocyclic counterparts. These results are of astrochemical interest because they demonstrate a means for the in situ production and sequestration of small heterocycles in icy grains without requiring that they be formed in or condense from the gas phase, in which they would be more easily photodestroyed. By extension, these results also suggest a possible explanation for the non-observation of heterocycles in the gas phase of astrophysical environments and for the presence of some of them in meteorites. Finally, these results are important from an astrobiological point of view, because of the essential role played by *N*-heterocycles including nucleobases in biological and, presumably, prebiotic systems. Indeed, such compounds may have been delivered to the primitive Earth via meteorites and played an important role in the origin of life.

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APPENDIX

OTHER COMPOUNDS TENTATIVELY IDENTIFIED IN THE REFRACTORY RESIDUES

This Appendix contains a list of other compounds that have been tentatively identified in the refractory residues discussed in this manuscript.

Table A1

List of Other Compounds Tentativly Identified in the Refractory Residues

Species	Formula	R_t (GC-MS) (minutes)	Parent Peak (Da)	Isotopically Labeled Parent (Da)	Ice Mixture
Methylpyridine (unknown isomer)	C_6H_7N	8.4	93	94	2
Methylpyridine (unknown isomer)	C_6H_7N	10.2	93	94	2
Phenol	C_6H_6O	12.3	94	96	1, 2
Benzenamine	C_6H_7N	13.5	93	94	2
Indene	C_9H_8	13.9	116	–	3, 4
(1*Z*)-*N*-Hydroxy-2-cyclohexen-1-imine	C_6H_9NO	14.1	111	112	2
4-Cyclohexene-1,2-diol	$C_6H_{10}O_2$	15.4	(114)	(118)	1
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	16.0	132	–	4
Dihydronaphthalene (unknown isomer)	$C_{10}H_{10}$	16.5	130	–	3, 4
Dihydronaphthalene (unknown isomer)	$C_{10}H_{10}$	16.8	130	–	3, 4
4-Cyclohexene-1,3-diol	$C_6H_{10}O_2$	17.4/17.6	(114)	(118)	1, 2
Naphthalene	$C_{10}H_8$	18.0	128	–	3
Benzenediol unknown isomer	$C_6H_6O_2$	18.3	110	114	1
Benzenediamine (unknown isomer)	$C_6H_8N_2$	19.7	108	110	2
Naphthol (unknown isomer)	$C_{10}H_8O$	19.8	144	–	4
Benzenediol unknown isomer	$C_6H_6O_2$	20.6	110	114	1
1,2,3,4-Tetrahydro-1-naphthalenamine	$C_{10}H_{13}N$	21.3	147	148	4
Biphenyl	$C_{12}H_{10}$	21.7	154	–	1
1,2,3,4-Tetrahydro-1-naphthalenol	$C_{10}H_{12}O$	21.8	148	150	3
1,2,3,4-Tetrahydro-2-naphthalenol	$C_{10}H_{12}O$	22.6	148	150	3, 4
5,6,7,8-tetrahydronaphthol (unknown isomer)	$C_{10}H_{12}O$	23.6	148	150	3
5,8-Dihydronaphthol	$C_{10}H_{10}O$	23.7	146	148	3

Table A1
(Continued)

Species	Formula	R_t (GC-MS) (minutes)	Parent Peak (Da)	Isotopically Labeled Parent (Da)	Ice Mixture
3,4-Dihydro-2(1*H*)-naphthalenone	$C_{10}H_{10}O$	24.1	146	148	3
3,4-Dihydro-1(2*H*)-naphthalenone	$C_{10}H_{10}O$	24.4	146	148	3, 4
2-Phenylphenol	$C_{12}H_{10}O$	24.5	170	172	1, 2
5,6,7,8-Tetrahydro-1-naphthylamine	$C_{10}H_{13}N$	24.6	147	148	4
1-Naphthalenol/2-Naphthalenol	$C_{10}H_8O$	25.2	144	146	3, 4
1-Naphthalenol/2-Naphthalenol	$C_{10}H_8O$	25.6	144	146	3, 4
1,4-Naphthoquinone	$C_{10}H_6O_2$	25.8	158	162	3
1,3-Isobenzofurandione	$C_8H_4O_3$	26.3	148	154	3
Azobenzene (unknown isomer)	$C_{12}H_{10}N_2$	26.6	182	184	2
Napthylamine (unknown isomer)	$C_{10}H_9N$	26.8	143	144	4
Napthylamine (unknown isomer)	$C_{10}H_9N$	27.3	143	144	4
5-Hydroxy-1,4-naphthoquinone	$C_{10}H_6O_3$	27.3	174	180	3
3-Phenylcyclohexanone	$C_{12}H_{14}O$	28.3	174	176	1
3-Biphenylol/4-Biphenylol	$C_{12}H_{10}O$	28.4	170	172	1, 2
3-Biphenylol/4-Biphenylol	$C_{12}H_{10}O$	28.6	170	172	1
Dihydronaphthoquinone	$C_{10}H_8O_2$	27.9	160	164	3, 4
Dihydroxynaphthalene (unknow isomer)	$C_{10}H_8O_2$	29.4	160	164	3
Biphenylamine (unknown isomer)	$C_{12}H_{11}N$	30.1	169	170	2
1,6-Diphenyl-1,3,5-hexatriene (unknown isomer)	$C_{18}H_{16}$	31.4	232	–	1
1,6-Diphenyl-1,3,5-hexatriene (unknown isomer)	$C_{18}H_{16}$	31.5	232	–	1
Naphthalenediamine (unknown isomer)	$C_{10}H_{10}N_2$	31.7	158	160	4
Naphthalenediamine (unknown isomer)	$C_{10}H_{10}N_2$	33.2	158	160	4

Notes. Parentheses indicate that the parent mass is not observed. Symbol "–" indicates that there is no isotopically labeled variant that could be produced, i.e., the molecule contains no O or N.

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