Observation of spontaneous N-bearing PAH formation using an ion trap: A new formation pathway in the interstellar medium

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Synopsis We present an ion-neutral kinetic study of the reaction between pyrimidine cations and acetylene utilizing a 22-pole RF ion trap apparatus. This approach enables the investigation of sequential ion-molecule reactions under conditions that closely mimic those found in space, thereby providing critical experimental constraints for astrochemical models.

Nitrogen-bearing polycyclic aromatic hydrocarbons (N-PAHs) are key precursors to complex organic molecules in both the interstellar medium and the nitrogen-rich planetary atmospheres. Despite the recent detections of nitrogen-functionalized astromolecules, their formation pathways remain an open question. The discrepancies between their predicted and observed abundances point to unknown mechanisms such as ion-molecule reactions that govern their evolution in the astrophysical environments. Employing an ion trap technique (schematic of the experimental setup shown in Fig. 1 [1, 2]) in conjunction with electronic structure calculations, we unravel multiple barrier-less reactions between gas-phase pyrimidine cations ($C_4H_4N_2^+$) and acetylene (C_2H_2). The second-order rate coefficient for the first acetylene addition was determined to be $(1.3 \pm 0.3) \times 10^{-10}$ cm^3 s^{-1}. Subsequent addition of a second acetylene molecule proceeds with a rate coefficient of $(2.2 \pm 0.9) \times 10^{-12}$ cm^3 s^{-1}, yielding a hitherto unreported endocyclic N-PAH cation ($C_8H_7N_2^+$), through an exothermic reaction pathway with $\Delta H = -2.73$ eV. The calculated infrared absorption spectrum of this final product, particularly the C=C stretching band, appeared at 6.16 μm, which is in close agreement with the 6.2 μm emission band observed in the interstellar infrared emission spectrum. This support the inclusion of N-PAHs in the astrochemical models aimed at explaining the origin of the 6.2 μm interstellar emission feature [3]. The present measurements on reactions involving a double-nitrogen substituted aromatic heterocycle have implications to the astrochemistry of both the Titan's atmosphere and the interstellar medium.

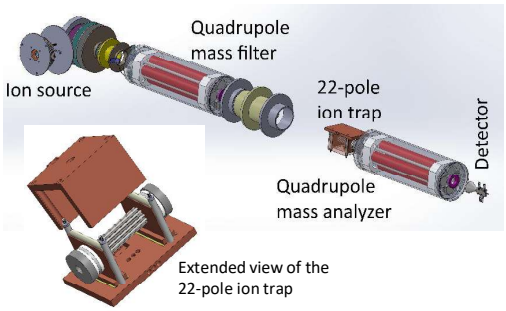


Figure 1. Schematic drawing of the modified 22-pole radio frequency ion trap setup. The ions are produced between the first two plates of the ion guide by electron impact ionization and repelled towards the QMS-1. Mass-selected ions are injected into the 22-pole trap. The trap is equipped with neutral and pulsed buffer gas input ports. A neutral density measurement gauge (Pfeiffer CMR 375) is also connected to the trap volume. After a specified trapping time, the ions are mass-analyzed by QMS-2 and counted in the CEM detector.

References

[1] Siddhartha S P *et al.* 2026 *ApJ* **1008** 212
[2] Nihar R B *et al.* 2024 *RSI* **95** 013201
[3] Sloan G C *et al.* 2003 *ApJS* **147** 379

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