Evidence for the Formation of Pyrimidine Cations from the Sequential Reactions of Hydrogen Cyanide with the Acetylene Radical Cation

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Supporting Information

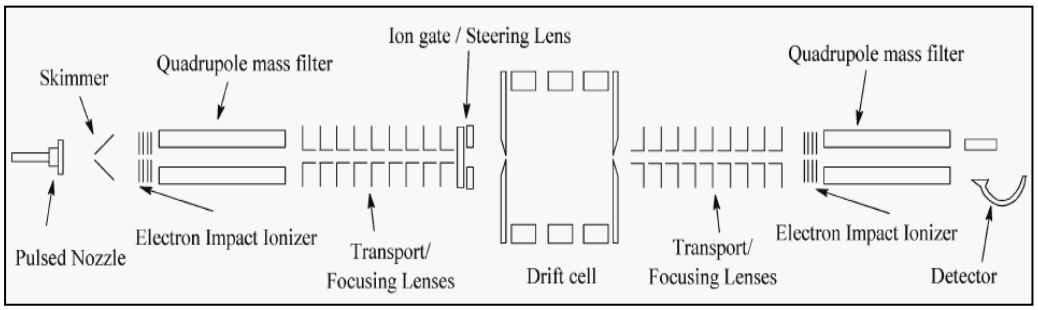

Figure S1. Schematic diagram of the mass-selected ion mobility (MSIM) system at VCU.

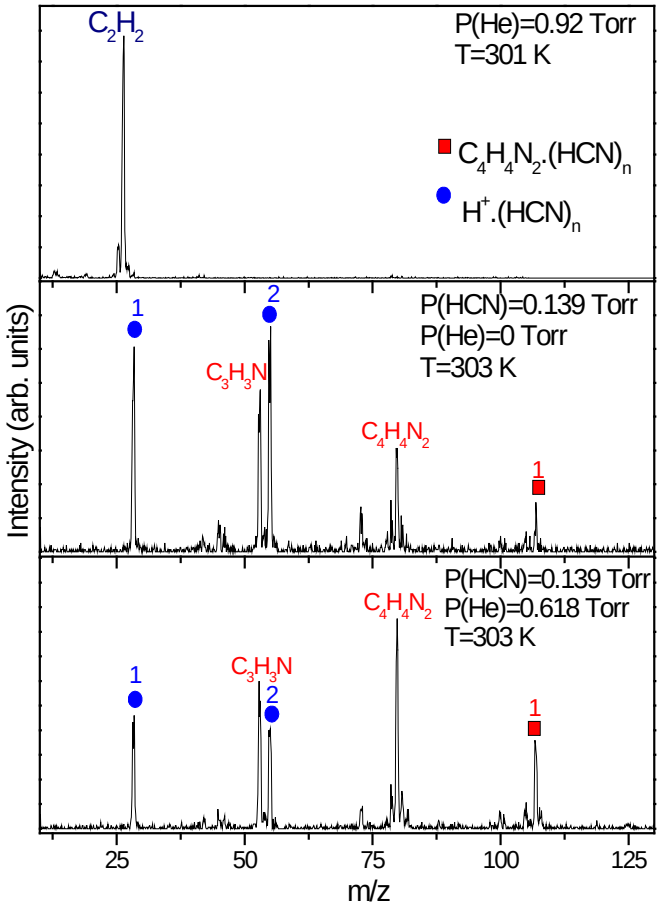

Figure S2. Mass spectra obtained upon injecting the mass-selected acetylene radical cations into the drift cell containing: (Top) 0.92 Torr He, (Middle) 0.139 Torr HCN, and (Bottom) 0.618 He and 0.139 Torr HCN. The third body collisions by He atoms enhance the addition channel leading the covalently-bonded $C_4H_4N_2$ ion and the association of HCN with the $C_4H_4N_2$ ion as shown in the bottom panel.

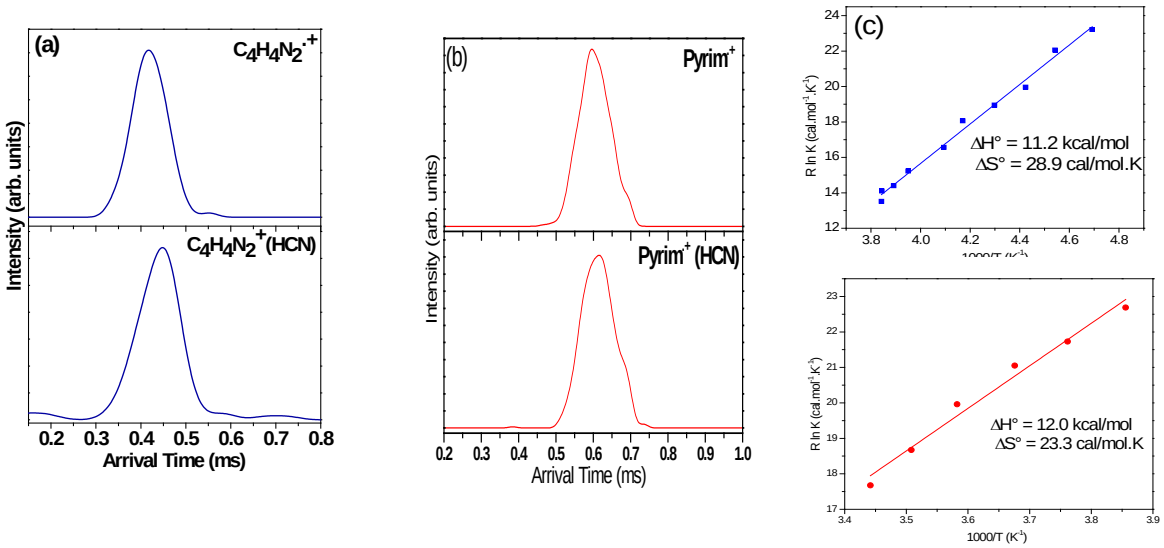

Figure S3(a). ATDs of $C_2H_2^{+\bullet}(HCN)_2$ and $C_2H_2^{+\bullet}(HCN)_3$ ions obtained at 309 K and 0.22 Torr of HCN. The applied drift field was 4.4 V/cm and the injection energy of the acetylene ion ($C_2H_2^{+\bullet}$) was 11.8 eV (Lab. frame). The nearly identical ATDs of the reactant and product ions indicate that equilibrium has been established under the experimental conditions given above.

Figure S3(b). ATDs of pyrimidine and pyrimidine$^{+\bullet}$(HCN) obtained at 298 K and 0.32 Torr of HCN. The applied drift field was 4.0 V/cm and the injection energy of the pyrimidine ion ($C_4H_4N_4^{+\bullet}$) was 12.4 eV (Lab frame). The nearly identical ATDs of the reactant and product ions indicate that equilibrium has been established under the experimental conditions given above.

Figure S3(c). van't-Hoff plot for the association reactions of the $C_4H_4N_2^{+\bullet}$and the Pyrimidine$^{+\bullet}$ ions with HCN (Reactions (1) and (2), respectively).

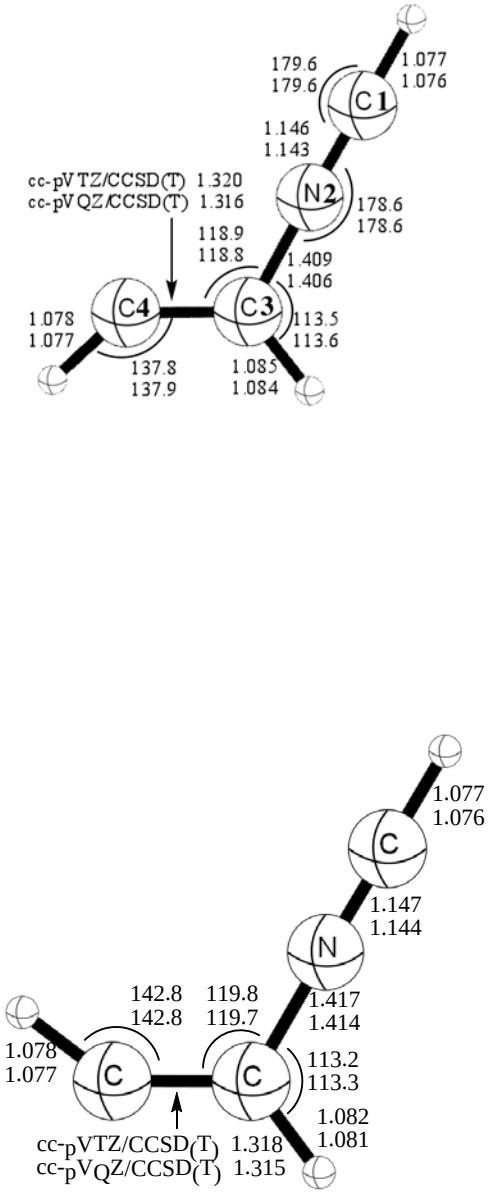

Figure S4. Structures of the *cis*- and *trans*-isomers of the $HCCHNCH^{+\cdot}$ ion obtained from Refernce 26 (Bera, P. P.; Lee, T. J.; Schaefer, H. F. Are isomers of the vinyl cyanide ion missing links for interstellar pyrimidine formation? *J. Chem. Phys*. **2009**, 131, 074303).

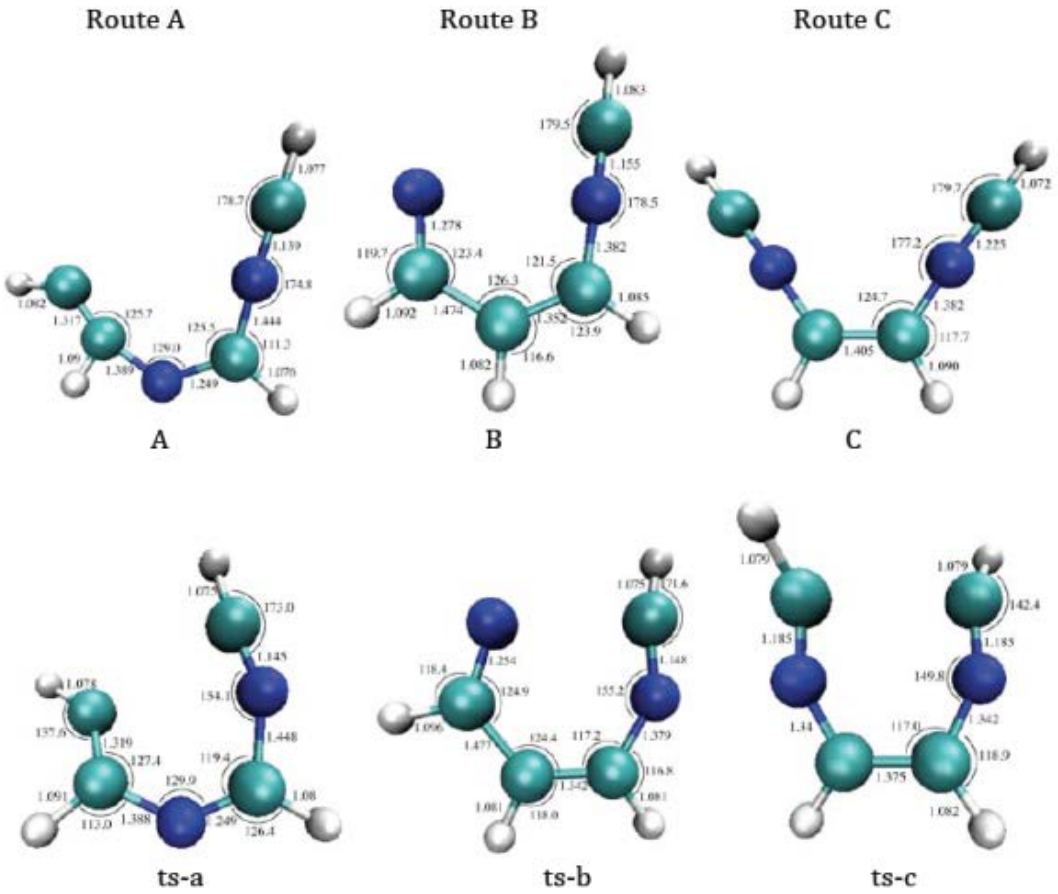

Figure S5. Intermediates A, B and C and the transition state ts-a, ts-b and ts-c leading to the pyrimidine and pyrazine ion isomers computed using B3LYP/cc-pVTZ level of theory. Bond lengths are in Å, and angles are in degrees.

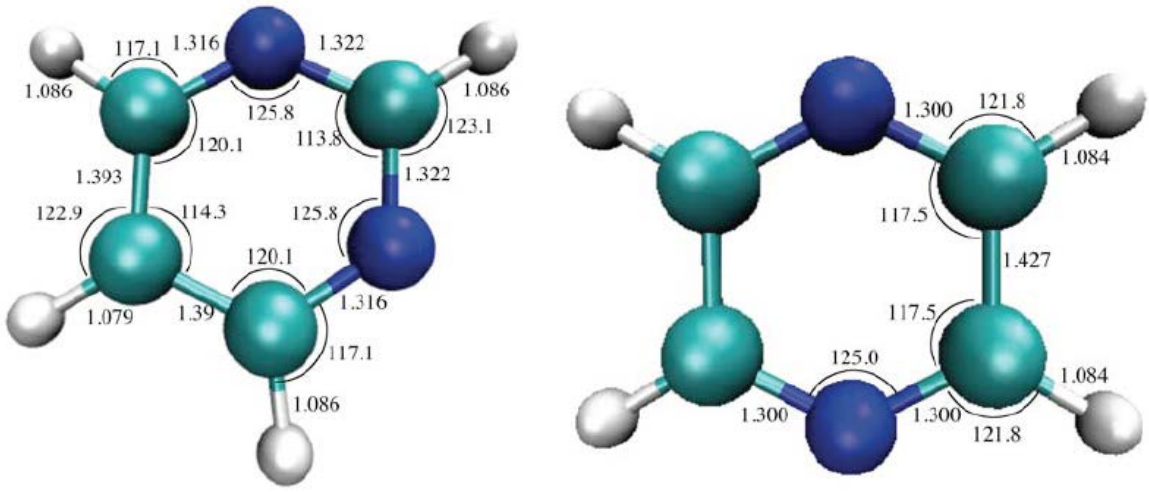

Figure S6. Structures of the Pyrimidine$^+$ and Pyrazine$^+$ ions computed using B3LYP/cc-pVTZ level of theory. Bond lengths are in Å, and angles are in degrees.

Table S1. Energies of intermediates, transition states and products (pyrimidine$^+$ and its isomer – pyrazine$^+$) using B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ.

	B3LYP/cc-pVTZ		CCSD(T)/cc-pVTZ	
	Absolute (Hartree)	Relative (Kcal/mol)	Absolute (Hartree)	Relative (Kcal/mol)
Pyrimidine	-264.081385	0	-263.521417	0
Pyrazine	-264.075586	3.63	-263.513822	4.77
Intermediate A	-263.962402	74.66	-263.407217	71.66
Intermediate B	-264.013324	42.71	-263.459385	38.93
Intermediate C	-264.018184	39.65	-263.447372	46.46
ts-a (int A:pyr)	-263.960322	75.96	-263.405253	72.80
ts-b (int B:pyr)	-264.010620	44.41	-263.457263	40.26
ts-c (int C:pyra)	-263.998718	51.87	-263.435382	53.99

- pyr = Pyrimidine and pyra = Pyrazine
- All energies are relative to pyrimidine, which is arbitrarily taken to be zero