Low-Temperature Formation of Pyridine and (Iso)quinoline via Neutral-Neutral Reactions

Zhenghai Yang,1 Chao He,1 Shane J. Goettl,1 Alexander M. Mebel,2\* Paulo F. G. Velloso,3 Márcio O. Alves,3 Breno R. L. Galvão,3\* Jean-Christophe Loison,4\* Kevin M. Hickson,4 Michel Dobrijevic,5 Xiaohu Li,6,7\* Ralf I. Kaiser1\*

**1** Department of Chemistry, University of Hawaii at Manoa, 2545 McCarthy Mall, Honolulu, HI 96822 (USA)

**2** Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

**3** Centro Federal de Educação Tecnológica de Minas Gerais, CEFET-MG, Av. Amazonas 5253, 30421-169 Belo Horizonte, Minas Gerais, Brazil

**4** Institut des Sciences Moléculaires, CNRS, Univ. Bordeaux, 351 Cours de la Libération, 33400 Talence, France

**5** Laboratoire d’Astrophysique de Bordeaux, Univ. Bordeaux, CNRS, B18N, Allée Geoffroy Saint-Hilaire, 33615 Pessac, France

6 Xinjiang Astronomical Observatory, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, P. R. China

7 Key Laboratory of Radio Astronomy, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, P. R. China

\* Correspondence to:

[ralfk@hawaii.edu](mailto:ralfk@hawaii.edu), [mebela@fiu.edu](mailto:mebela@fiu.edu), [brenogalvao@gmail.com](mailto:brenogalvao@gmail.com), [jean-christophe.loison@cnrs.fr](mailto:jean-christophe.loison@cnrs.fr), xiaohu.li@xao.ac.cn

The file includes:

Main text: 3838 words

Methods: 851 words

Legends: 469 words

Number of main text references: 64

Number of methods references: 8

Number of figures: 6

**Aromatic molecules represent fundamental building blocks in prebiotic chemistry and are contemplated as vital precursors to DNA and RNA nitrogen bases. However, despite the identification of some 300 molecules in extraterrestrial environments, the pathways to pyridine (C5H5N), pyridinyl (C5H4N•), and (iso)quinoline (C9H7N) – the simplest represen­tative of mono and bicyclic aromatic molecule carrying nitrogen – are elusive. Here, we afford compelling evidence on the gas-phase formation of methylene amidogen (H2CN•) and cyanomethyl (H2CCN•) radicals via molecular beam studies and electronic structure calcula­tions. The modeling of the chemistries of Taurus Molecular Cloud (TMC-1) and Titan’s atmosphere contemplates a complex chain of reactions synthesizing pyridine, pyridinyl, and (iso)quinoline from H2CN• and H2CCN• at levels of up to 75%. This study affords unique entry points to precursors of DNA and RNA nitrogen bases in hydrocarbon-rich extraterrestrial environments thus changing the way we think about the origin of prebiotic molecules in our Galaxy.**

     Since the very first discovery of biorelevant, heteroaromatic molecules such as vitamin B3 (niacin)1,2 and nucleobases (pyrimidines, purines)3 in carbonaceous chondrites including Murchison3,4, critical questions have arisen on their formation routes in extraterrestrial environments. The identification of a series of terrestri­ally rare nucleobases such as 6-diaminopurine along with the 15N/14N isotope enrichment suggests an interstellar origin4 thus providing a vital link between cold molecular clouds as their origin and their identification in our solar system. Their stem compounds - polycyclic aromatic hydrocarbons (PAHs) along with their cations and (partially) hydrogenated counterparts5-7 - have been proposed to be associated with the synthesis of these biorelevant molecules in the interstellar medium, though not having unraveled how a stable C-H moiety in PAHs can be replaced by an isoelectronic nitrogen atom (N) in NPAHs. The 6.2 μm (1613 cm-1) infrared emission band in deep space has been linked to protonated PAHs8, but has also been discussed as the result of NPAHs9 with PAHs and NPAHs accounting for up to 30 % of the cosmic carbon budget10. Whereas well-defined low-temperature (cold molecular clouds; TMC-1) and high-temperature routes (circumstellar envelopes; IRC +10216) to PAH formation have begun to emerge11, surprisingly little is known on the gas-phase synthesis of their nitrogen-substituted counterparts (NPAHs). This lack of knowledge is rather staggering considering that these aromatics carry the cyclic nitrogen-carbon skeletons of a key class of astrobiologically important molecules: nitrogen bases of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)9,12.

     Recent astrochemical models advocated that the carbon – nitrogen chemistries in molecular clouds can be linked with complex reaction networks13 of gas phase ion–molecule14 and neutral–neutral reactions15 of aromatic (AR) and reso­nant­ly stabilized free radicals (RSFR) such as phenyl (C6H5•) and propargyl (C3H3•) along with their nitrogen counterparts pyridinyl (C5H4N•) and cyanomethyl (H2CCN•)14,16-18. Further, the synthesis of pyridine (C5H5N) has been proposed to be driven by radical mediated reactions of hydrogen cyanide (HCN)19 and via de-facto methylidyne radical (CH) insertion into pyrrole (C4H5N)20. These reaction networks have been ‘borrowed’ from the planetary science community attempting to rationalize the existence of both stratospheric PAHs and NPAHs in Titan’s atmosphere determined from Cassini’s Visual and Infrared Mapping Spectrometer (VIMS) measure­ments at 3.28 µm (3,049 cm-1)21 and Composite Infrared Spectrometer (CIRS) measurements at 71.43 µm (140 cm-1)22,23, and through Cassini’s Plasma Spectrometer (CAPS)24. The latter detected positively and nega­tively charged particles with molecular weights less than 8,000 amu containing (N)PAHs along with their fundamental building blocks benzene (C6H6; m/z = 78) and pyridine (C5H5N; m/z = 79)14,24,25. Overall, to date, an understanding of the synthesis of ben­zene along with aromatics carrying up to six rings such as corannulene (C20H10)26 and helicenes (C26H16)27 is beginning to emerge11. However, the underlying elementary processes even leading to the simplest representative of mono- and bicyclic aromatic molecule carrying nitrogen, i.e. pyridine (C5H5N; **1**) and (iso)quinoline (C9H7N; **2/3**) – together with their cyanomethyl (H2CCN•; **4**) and methylene amidogen (H2CN•; **5**) precursors is still in its infancy (Figure 1). The understanding of these gas phase reactions and the formation of the first carbon – nitrogen bonds from the ‘bottom up’ is fundamental to our know­ledge of how nitrogen containing aromatics can be produced abiotically in low temperature interstellar and solar system environments from the simple closed shell nitrogen containing hydride (ammonia; NH3) and reactive carbon-based reactants in form of atomic carbon (C) and dicarbon (C2).

     Here, we report on the gas phase preparation of the methylene amidogen radical (H2CN•, X2B2) and of the resonantly stabilized cyanomethyl radical (H2CCN•, X2B1) via bimolecular reactions of atomic carbon (C, 3P) and of dicarbon (C2, X1Σg+/a3Πu) with ammonia (NH3, X1A1) exploiting crossed molecular beams experiments. Combined with electronic structure calculations and modeling of the chemistries of hydrocarbon rich environments of cold molecular clouds and atmospheres of planets and their moons exploiting the TMC-1 (10 K) and Titan (70-180 K) as benchmarks, the role of the methylene amidogen and the cyanomethyl radicals in forming pyridine (C5H5N; **1**), pyridinyl (C5H4N; **9-11**), and (iso)quinoline (C9H7N; **2/3**) are also elucidated. And a complex chain of exoergic, barrierless routes is contemplated with H2CN• and H2CCN• radicals representing fundamental molecular building blocks of pyridine and pyridinyl radicals (C5H4N•, **9-11**) synthesized through successive barrierless reactions involving propargyl (C3H3•, X2B1, **6**) and *i/n*-C4H3• (X2A', **7-8**) under low temperature conditions (Figure 1)28. Since pyridinyl radicals are isoelectronic to the phenyl radical (C6H5•), pyridinyl may play a critical role in the gas phase formation of (iso)quinoline upon reaction with vinylacetylene (C4H4) via the low-temperature hydrogen abstraction – vinyl­acetylene addition (HAVA) pathway29. These results thus offer fundamental knowledge on the previously elusive reaction routes to prototype nitrogen heteroaromatics not only in TMC-1 and atmosphereTitan, but also in low temperature, hydrocarbon and nitrogen-rich atmospheres of outer Solar System bodies such as Triton30 and Pluto31. Hence, the present work sheds light on sensible processes coupling the carbon and nitrogen chemistries eventually leading to the formation of molecular nitrogen – carbon motives of astrobiological relevance as found in, e.g., nucleobases29 in our Universe.

**Results**

**Laboratory Frame**

     Reactive scattering signal of the reaction of atomic carbon (C, 3P) with D3-ammonia (ND3, X1A1) was observed at *m/z* = 30 (D2CN+). Within our signal-to-noise, no signal was monitored at 32 (D3CN+) indicating that no D3CN adducts were formed. These data alone indicate the existence of the D loss channel (reaction (1)). Note that for technical reasons, the reaction was not conducted with ammonia (NH3, X1A1) since this would have shifted reactive scattering signal to *m/z* = 28 (H2CN+). Signal at 28 is obscured by significant background counts from carbon monoxide, which outgasses from stainless steel even under our ultra-high vacuum (UHV) conditions of 6×10-12 Torr. Therefore, angular resolved TOF spectra were recorded at 30 (D2CN+) in 5° intervals within the scattering plane, integrated, and scaled with respect to the TOF recorded at the center-of-mass (CM) angle of 35.9 ± 0.5° leading to the laboratory angular distribution (LAD). This distri­bution holds a maximum around the CM angle and is nearly forward-backward symmetric (Figure 2, a-b) implying that the carbon − D3-ammonia reaction proceeds through indirect reaction dynamics involving the formation of D3CN collision complex(es).

     Reactive scattering signal of the reaction of dicarbon (C2, X1Σg+/a3Πu) with ammonia (NH3, X1A1) was detected at *m/z* = 40 (C2NH2+) and 39 (C2NH+) (reaction (2)) with signal at 39 collected at level of 66 ± 5% compared to signal at 40. The TOF spectra at 40 and 39 are identical after scaling suggesting that signal at 39 originates from dissociative ionization of the nascent product (40 amu). Further, signal at 40 indicated the existence of a H loss and inherent formation of a molecule with the molecular formula C2NH2. Consequently, data were collected at 40 in 2.5° steps (Figure 2, c-d). The derived LAD is also nearly forward-backward symmetric revealing the existence of C2H3N intermediate(s) and indirect scattering dynamics.

1. C (12 amu) + ND3 (20 amu) → D2CN(30 amu) + D (2 amu)
2. C2 (24 amu) + NH3 (17 amu) → H2C2N(40 amu) + H (1 amu)

**Center-of-Mass Frame**

We are now elucidating the nature of the structural isomer(s) and the underlying reaction mechanism(s) by transforming the laboratory data (TOFs, LAD) into the CM reference frame32.This forward convolution approach yields the CM translational energy (*P(E*T*)*) and angular (*T(θ)*) flux distributions as detailed in Figure 3 (a-c). For C (3P) − ND3 (X1A1) system, signal at 30 could be replicated with a single D loss channel (reaction (1)). A detailed inspection of the *P(E*T*)* reveals a high-energy cutoff of 237 ± 25 kJ mol-1, which denotes the sum of the collision energy Ec (28.1 ± 0.9 kJ mol-1) plus the reaction exoergicity for molecules generated without internal excitation. Therefore, reaction (1) is suggested to be exoergic by 209 ± 26 kJ mol-1. Further, the *P(E*T*)* display a distribution maximum at 26 ± 3 kJ mol-1 suggesting a tight exit transition state upon unimolecular decomposition of the D3CN intermediate to the separated products and a significant electron density reorganization. The *T(θ)* function depicts flux across the complete angular range together with a forward-backward symmetric scattering pattern. These findings reveal indirect scattering dynamics through long-lived D3CN complex(es) holding lifetime longer than the(ir) rotational periods32.

ConsideringtheC2 (X1Σg+/a3Πu) − NH3 (X1A1) system, the laboratory data can be replicated with a single atomic hydrogen loss channel (reaction (2)) (Figure 3, d-f). The *P(E*T*)* as depicted in Figure 3d shows an *E*max of 327 ± 26 kJ mol-1; this results in an exoergicity of 310 ± 26 kJ mol-1 or 318 ± 26 kJ mol-1 considering the Ec of 17.0 ± 0.3 kJ mol-1 for dicarbon reactants in ground X1Σg+ or excited a3Πu state. It should be noted that the *P(E*T*)* peaks only slightly away from zero translational energy at 9 ± 1 kJ mol-1 indicating a loose exit transition state with only a minor rearrangement of the electron density. Finally, the *T(θ)* function exhibits a forward-backward symmetry with sideway scattering and hence a distribution maximum at 90o. These results also propose indirect scattering dynamics33.

**Electronic Structure Calculations and Reaction Mechanisms**

*First*, our computations on the triplet CND3 potential energy surface (PES) reveal four reaction intermediates (**i1-i4**), four product channels (**p1-p4**), and ten transition states. These high-level calculations predict relative energies of the transition states, local minima, and products within 8 kJ mol-1.34,35 Four deuterium atom (D) loss pathways lead to D2-methylene amidogen (**p1**, D2CN•, C2ν, X2B2), trans-D2-iminomethyl (**p2**, DCND, Cs, X2A'), cis-D2-imino­methyl (**p3**, DCND, Cs, X2A'), and D2-aminomethylidyne (**p4**, D2NC, C2ν, X2B2). The relative energies of these isomers are within 3 kJ mol-1 compared to two previous studies36,37. A comparison of the theoretically predicted reaction energies (Figure 4) with our experimentally derived exoergicity of 209 ± 26 kJ mol-1 reveals that at least the thermodynamically most stable product **p1** is formed. Contributions from high energy isomers **p2**-**p4** might be masked in the low-energy section of the *P(E*T*)* and cannot be eliminated. The reaction is predicted to be initiated via a barrierless addition of the carbon atom to the non-bonding electron pair at the nitrogen atom of ammonialeading to **i1** (CND3, D3-ammoniamethylidyne) bound by 103 kJ mol-1. This collision complex may eliminate a deuterium atom forming **p4** by passing a transition state located only 2 kJ mol-1 below the separated reactants, or isomerizes to **i2** (DCND2, D3-aminomethylidene) via deuterium migration from nitrogen to carbon. The transition state resides 11 kJ mol-1 below the separated reactants and hence is preferred compared to the unimolecular decomposition of **i1** to **p4** plus D. **i2** can fragment via D loss to **p2** or **p3** through tight transition states; **p4** may be formedbarrierlessly, too. Alternatively, **i2** may isomerize to **i3** (D2CND, D3-methanimine) via a deuterium shift. This intermediate can undergo three distinct decomposition pathways through deuterium loss leading to **p3, p2,** and/or the thermodynamically most stable isomer **p1** involving tight exit transition states (**i3**→**p3** 20 kJ mol-1; **i3**→**p2** 22 kJ mol-1; **i3**→**p1** 29 kJ mol-1; the numbers indicate barrier with respect to the products). Finally, **i3** may undergo a deuterium shift to **i4** (D3CN, D3-methylnitrene), the global minimum of the D3CN PES, followed by unimolecualr decomposition to **p1**.

    Statistical Rice–Ramsperger–Kassel–Marcus (RRKM) calculations were also conducted to predict the branching ratios of **p1**-**p4** theoretically34. Within the limit of a complete energy randomization, **p1**, **p2**, **p3**, and **p4** contribute 7 %, 33 %, 29 %, and 31%, respectively, at the experimental collision energy of 28.1 kJmol-1. At the low temperature conditions of TMC-1 and Titan, fractions of 8 %, 41 %, 33 %, and 18 % are predicted. Under the atmospheric conditions of Titan, one peculiarity exists. Rapid suprathermal hydrogen-atom assisted isomeri­zation pro­ces­ses can efficiently convert the high-energy isomers **p3** and **p4** to **p1**38,39. These processes are very efficient due to absence of a barrier of **p4 + H → i2** and a small barrier of only 20 kJmol-1 for **p3 + H → i3**. As depicted in Extended Data Fig. 1, the elevated rate constants of **p3** + H of a few 10-10 cm3s-1 can be reached with suprathermal hydrogen atoms possessing high kinetic energies (Supplementary Note 1).

*Second*, for the C2-NH3 system, the primary reactant beam contains dicarbon in its electronic ground state (X1Σg+), but also in its first electronically excited state (a3Πu). The calculations reveal that C2 (a3Πu) does not form any bound intermediates upon collision with ammonia, but rather reacts in a direct fashion via hydrogen abstraction forming the ethynyl radical (C2H•, X2Σ+) plus the amino radical (NH2•, X2B1) in an exoergic reaction (-36 kJmol-1) through a barrier of 22 kJmol-1. However, on the singlet surface, dicarbon adds barrierlessly to the non-bonding electron pair of the nitrogen atom of ammonia to **i1'** (CCNH3, ammoniaethynyl). Among the product isomers, **p1'** (H2CCN•; cyanomethyl;*C*2*ν*; 2B1) represents the thermo­dyna­mically most stable isomer followed by **p2'** (H2CNC; isocyanomethyl; *C*2*ν*; 2B1) and **p3'** (HCCNH; imidogenacetylene; *C*s; 2A''). The calculated relative energies of the C2H2N isomers agree well with previous calculations40. A comparison of these energies with the experimentally extracted exoergicity of 310 ± 26 kJ mol-1 proposed that at least **p1'** is formed under single collision conditions. Contributions from high energy isomers **p2'**-**p5'** might be hidden in the low-energy section of the *P(E*T*)* and cannot be eliminated. **i1'** can isomerize to an exotic cyclic intermediate **i2'** (HC(NH2)C) via ring closure along with a hydrogen shift from the nitrogen to the carbon or to **i4'** (HCCNH2, aminoacetylene) through hydrogen migration. Our calculations also identify a loose H loss channel to **p7'** (CCNH2; aminoethynyl; *C*2*ν*; 2B1) from **i1'**. Extensive hydrogen migration and ring opening pathway access intermediates **i3'** to **i9'**. The experimentally detected product **p1'** can eventually be accessed via H loss from **i6'** (H2CCNH, aminovinyl) and/or **i7' (**CH3CN,acetonitrile) through loose transition states. Overall, the experimentally predicted loose exit transition state agrees well with the computational predictions of two open channels to **p1'** (H2CCN•; cyanomethyl) via simple bond rupture processes on the singlet surface (Extended Data Fig. 2).

**From the Laboratory to Titan’s Atmosphere**

*First*, in Titan’s atmosphere, the carbonaceous reactants (atomic carbon, dicarbon) originate from photolysis of methane (CH4) and acetylene (C2H2), respectively14,41. Carbon can also be generated from dissociative electron – ion (CH2+, CH3+) recombination in atmospheric layers above 1,200 km18. Ammonia abundances have been inferred indirectly via the Cassini’s Ion and Neutral Mass Spectrometer (INMS) detection of the ammonium cation (NH4+) predicting high mole fraction of ammonia of (3-4)×10-5 at around 1000 km42 (Supplementary Note 2). *Second*, the chemical reactions relevant to Titan’s atmospheric chemistry must be exoergic, proceed without an entrance barrier, and involve transition states with lower energy than the separated reactants. All these benchmarks are fulfilled in the formation of holding rate constants of, e.g., a few 10-10 cm3 s-1 for the carbon – ammonia system at 50 K43. *Third*, the aforementioned radicals are isoelectronic with the vinyl (C2H3•, X2A') and propargyl (C3H3•, X2B1) radical. . The molecular mass growth processes in Titan’s atmosphere involving the H2CN• and the H2CCN• radicals are in strong analogy to the C2H3•-C4H3•16,44 and C3H3•-C3H3•45 systems which access the phenyl radical (C6H5•) under single collision conditions and benzene along with its isomers through collision with a third body. This conclusion is verified through electronic structure calculation for the H2CN•-C4H3•, H2CN•-C4H3•, and H2CCN•-C3H3• systems synthesizing three distinct pyridinyl radicals and pyridine under low-temperature conditions (Extended Data Fig. 3-4, Supplementary Note 3). In the presence of a dense atmosphere such as of Titan, pyridine can be stabilized by a third body with the bath molecule such as molecular nitrogen. Once stabilized, pyridine can be photolyzed to pyridinyl radicals (o, m, p; C5H4N•) (Figure 1) followed by barrierless reactions with vinylacetylene (C4H4) to (iso)quinoline (C9H7N)29. *Finally*, previous photochemical models suggest that H2CN• is produced via the reaction of atomic nitrogen with the methyl radical (CH3)46,47. However, thereactions of atomic carbon and dicarbon with ammonia are not included due to the foregoing lack of reliable data of the C/NH3 and C2/NH3 systems, whereas extensive computational and experimental data exist for the N/CH3 system37,48,49. Here, our results indicate the potential significant role of C/NH3 in the prebiotic chemistry of Titan.

The aforementioned findings are implemented into a one-dimensional photochemical atmos­pheric model of Titan to evaluate the eventual formation of pyridine (C5H5N) and (iso)quinoline (C9H7N) (Supplementary Note 2). This model incorporates an unbiassed chemistry of neutrals and cations along with the coupling between them from the lower atmos­phere to the ionosphere50,51. The chemical scheme operated in the present model has been enhanced with the new reactions studied included51-53. To evaluate the uncertainties of the nominal model profiles, a Monte Carlo simulation was performed according to the method described in Benne et al.52 (Figure 5). These photochemical models yield exciting results. First, these studies reveal that two C5H5N isomers, pyridine (C5H5N) and ethylcyanoacetylene (C2H5CCCN), display significant mole fractions of 1.4 × 10-7 and 2.3 × 10-7 in the ionosphere of Titan, respectively. The maximum mole fraction for (iso)quinoline is predicted to be 1.7 × 10-11 around 1,100 km, which should be obser­vable spectroscopically. These models also predict that the mole fraction of (1.5 ± 0.3) × 10-9 at m/z = 80 (C5H5NH+) derived from the Cassini INMS data18,54 agrees well with the sum of mole fractions of C5H5NH+ and C2H5C3NH+ of the atmospheric models ranging between 2.5 × 10-9 to 5.4 × 10-10. Although the atmospheric models provide compelling constrains on the abundances of pyridine and (iso)quinoline, we have to concede that the uncertain abundances of ammonia in Titan’s atmosphere, which may vary over at least two orders of magnitude, make it difficult to quantify the contributions of distinct pathways to the H2CN• radical. With a low predicted ammonia mole fraction of a few 10-7, the carbon-ammonia reaction hardly competes with the nitrogen-methyl system providing small fractions of up to one percent at most. However, considering the bimolecular nature of the carbon-ammonia system, an increase of the fractional abundance of ammonia will lead to an enhancement of H2CN• radicals. Only future direct spectroscopic measurements of ammonia can resolve this issue. In fact, based on the nominal model results, it can be determined that at least 10% of H2CN• radicals are produced by the carbon -ammonia reaction under conditions of high ammonia mole fraction derived from the INMS data 42. There­fore, fundamental bimo­lecular reactions including atomic carbon and dicarbon with ammonia may initiate a chain of barrierless reactions ultimately to pyridine and (iso)qui­noline. These processes are not limited to Titan, but represent versatile pathways eventually leading to NPAHs in atmospheres of planets and their moons in the outer Solar systems such as on Triton30 and Pluto31 with organic haze layers recently detected by the *New Horizons* mission55. Only recently, NPAH product quinolizinium+ (C9H8N+) was formed via reaction of the pyridine cation with acetylene in low-temperature pathways, highlighting the role of ion-molecule reactions in the NPAH formation in Titan’s atmosphere56. The combined ion-molecule and neutral-neutral reaction network may finally reproduce the astronomical detected abundances of PAHs which are drastically underestimated in the current modeling57. Thus our understanding of fundamental low-temperature molecular mass growth processes to nitrogen substituted aromatics and their radicals is deepened.

**From the Laboratory to Cold Molecular Clouds: TMC-1**

     . To explore the chemistry leading eventually to nitrogen heteroaromatics, we untangled the role of the cyanomethyl (H2CCN•) and methylene amidogen (H2CN•) radicals in the formation of pyridine (C5H5N), pyridinyl (C5H4N•), (iso)quinoline (C9H7N) using the *UMIST* Database (RATE2012)58 operated with the single-point time-dependent astrochemical models27 (Supplementary Information text). The predictive capabilities of the model are verified by comparing the relevant species observed with modeled fractional abundances.

     These models revealed fascinating findings (Figure 6). First, the remarkable performance of the astrochemical model for TMC-1 can be benchmarked for the methylene amidogen radical (H2CN•)59, the cyanomethyl radical (H2CCN•)60, vinyl cyanide (C2H3CN)61, and methyl cyanide (CH3CN)62 with astronomically observed fractional abundances of (1.1 ± 0.9) × 10-10, (3.5 ± 1.5) × 10-9, (7.0 ± 1.0) × 10-10, and (6.0 ± 3.0) × 10-10 relative to molecular hydrogen. Predicted peak abundances of H2CN• and of H2CCN• of (3.3 ± 0.3) × 10-10 at 1.3 × 105 years and (6.0 ± 0.4) × 10-9 at 2.0 × 105 years replicate the astronomical observations nicely. Here, the carbon – ammonia system can account for 30 % to 75 % of the observed methylene amidogen radicals; generally spoken, as the initial abundances of nitrogen increase or carbon decreases, the fraction of methylene amidogen rises. Even for standard abundances of carbon versus nitrogen in TMC-1 without grain ejection, the reaction of dicarbon with ammonia contributes up to 75 % to the peak abundance of the cyanomethyl radical (H2CCN•) (Supplementary Note 4). Second, a complex chain of reactions initiated by barrierless reactions of the cyanomethyl (H2CCN•) and methylene amidogen (H2CN•) radicals drive molecular mass growth processes to pyridine (C5H5N), pyridinyl (C5H4N•), and (iso)quinoline (C9H7N) with predicted peak fractional abundances of (6.0 ± 0.3) × 10-9 (6.3 × 105 years), (1.2 ± 0.1) × 10-10 (3.2 × 105 years), and (6.0 ± 0.4) × 10-12 (6.3 × 105 years), respectively. The H2CN•/C4H3• and H2CCN• /C3H3• reactions produce 46 % and 54 % of the predicted abundances of pyridinyl (C5H4N•), respectively. These results suggest that at least pyridine (C5H5N) and pyridinyl (C5H4N•) might be detectable by radio telescopes such as the Green Bank Observatory and Yebes Radio Telescope in TMC-1.

**Conclusion**

To conclude, our studies provided persuasive evidence on the formation of the methylene amidogen radical (H2CN•, X2B2) and of the resonantly stabilized cyanomethyl radical (H2CCN•, X2B1) via bimolecular reactions of atomic carbon (C; 3P) and of dicarbon (C2; X1Σg+/a3Πu) with ammonia (NH3; X1A1) in low temperature extraterrestrial environments. Combined with modeling, these findings reveal further that both the methylene amidogen and the cyanomethyl radicals can initiate a complex chain of reactions leading to pyridine (**1**), pyridinyl radicals (**9-11**), and eventually to (iso)quinoline (**2/3**) as the simplest prototype NPAHs and potential feedstock for more complex nitrogen-based aromatics in deep space. Whereas the elementary reactions of carbon and dicarbon with ammonia can account for up to 75 % of the methylene amidogen and of the cyanomethyl radical in TMC-1, their contributions in Titan’s atmosphere are less constrained; this is predominantly based on the uncertain abundances of atmospheric ammonia diverging by at least two orders of magnitude. This can only be solved through future in situ observations by, e.g., the prospective *Dragon Fly* mission. However, pyridine (**1**) and (iso)quinoline (**2/3**) – the most primitive nitrogen aromatics – have been detected in the Murchison (CM2) carbonaceous chondrite with abundances of up to 0.5 µg g-1 (ppm)63,64 thus providing a critical link between the low temperature chemistry in cold molecular clouds and their delivery to our solar system in form of meteorites. Overall, the present study provides a template for a systematic investigation of elementary reactions so that a comprehensive picture of the low temperature chemistry leading to biorelevant molecules in extraterrestrial environments emerges.

**Methods**

**Crossed Molecular Beams**

**C-ND3 system**

The bimolecular reaction of ground-state atomic carbon (C; 3P) with D3-ammonia (ND3; X1A1) was explored under single collision conditions employing a crossed molecular beams machine (Supplementary Fig. 1)32. A supersonic beam of atomic carbon was produced by ablating a rotating graphite rod at 266 nm (Nd:YAG, 10-12 mJ pulse-1, 30 Hz). The ablated carbon species were seeded in helium gas (99.9999%, 4 atm, 60 Hz). The primary carbon beam was velocity-selected by a chopper wheel (120 Hz) after passed through a skimmer revealing a well-defined *v*p (peak velocity) of 2512 ± 49 m s-1 and S (speed ratio) of 2.9 ± 0.3 (Supplementary Table 1). Carbon atoms in the primary beam are only in the ground state (3P) under these conditions. Operation conditions were optimized that dicarbon in the primary beam was reduced to levels of less than 5%, which does not interfere with the scattering signal. The secondary beam of D3-ammonia (ND3; Sigma-Aldrich; 99% D) was released with a backing pressure of 550 Torr and 60 Hz, characterized by a *v*p of 1091 ± 25 m s-1 and S of 10.1 ± 1.3. Finally, the carbon beam crossed the ND3 beam perpendicularly in the interaction region resulting in a collision energy (EC) of 28.1 ± 0.9 kJ mol-1 and a CM angle (ΘCM) of 35.9 ± 0.5°.

**C2-NH3 system**

A pulsed supersonic dicarbon beam [C2 (X1Σg+/a3Πu)] was produced exploiting the same ablation source described above. Briefly, the graphite rod was ablated by focusing the 266 nm laser output at 30 Hz and energy of 8-10 mJ pulse-1. The ablated species were seeded in Neon (Ne, 4 atm, 99.9999%). Operation conditions and delay times were optimized to maximize dicarbon concentrations in the primary beam. Laser-induced fluorescence (LIF) of dicarbon revealed both singlet ground state (X1Σg+) and the lowest lying triplet state (a3Πu) along with the ro-vibrational distribution. The rotational temperature (Trot) for the vibrational levels of ν = 0, 1 of the a3Πu state were measured to be 240 ± 30 and 190 ± 30 K with fractions of 0.67 ± 0.05 and 0.33 ± 0.05, respectively, via the Swan band transition (d3Πg-a3Πu). The singlet state was detected via the Mulliken excitation (D1Σu+-X1Σg+) and the bimodal rotational distributions of both ν = 0, 1 were revealed at fractions of 0.83 ± 0.10 and 0.17 ± 0.04, respectively. Rotational temperature of the first and second vibrational levels was derived to be 200 K with population fraction of 0.44 ± 0.05 and 0.06 ± 0.02 together with 1000 K with fraction of 0.39 ± 0.05 and 0.11 ± 0.02, respectively65. The secondary ammonia (NH3, Matheson, 99.99%) beam was released with 550 Torr backing pressure. The peak velocities, speed ratios of the primary and secondary beam along with the derived collision energy and CM angles of the C2-NH3 system are tabulated in Supplementary Table 1.

    For both reactions, the products were detected by a rotatable detection system at ultrahigh-vacuum conditions (6×10-12 Torr). In detail, the neutral species were ionized with an electron impact ionizer (80 eV; 2 mA) before they are mass-selected by a quadrupole mass spectrometer (QMS) in the time-of-flight (TOF) mode (Supplementary Fig. 2). The ions at a selected *m/z* will eventually lead to the signal detected and filtered by a photomultiplier tube (PMT; model 8850; -1.35 kV) and a discriminator (1.6 mV). Finally, a multichannel scaler is used to collect the TOF spectra at different angles. These laboratory data are converted into the CM frame with a forward-convolution method yielding the CM translational energy (*P(E*T*)*) and angular (*T(θ)*) flux distributions, with which the information of the reaction dynamics can be extracted32. The reactive differential cross section, *I(u, θ) ~* *P(u) × T(θ)*,whichreports the product intensity (*I*) as a function of the center-of-mass angle *θ* and the velocity *u*, represents an overall image of the reaction and contains all the information of the scattering process32.

**Electronic Structure Calculations**

The electronic structure calculations reported in this work for the carbon and dicarbon reactions with ammonia (Figure 3, Extended Data Fig. 2, Supplementary Data 1) were performed with the MOLPRO66 software. The geometry optimizations and harmonic frequencies calculations employed the coupled-cluster singles and doubles plus perturbative triples – CCSD(T) – method67. For such optimizations and frequencies, the augmented correlation consistent family basis set aug-cc-pV*X*Z68 was employed, with a quadruple-zeta (*X=Q*) basis being used for the CNH3 system, and a triple-zeta (*X=T*) for CCNH3. For both systems, a final single point energy calculation was performed at the optimized geometries with the explicitly correlated CCSD(T)-F12 method35 with the quadruple-zeta basis set cc-pVQZ-F1269. Using the conventional notation, the reported energies for the carbon-ammonia system are therefore CCSD(T)-F12/cc-pVQZ-F12//CCSD(T)/aug-cc-pVQZ+ZPE(CCSD(T)/aug-cc-pVQZ) and for dicarbon-ammonia CCSD(T)-F12/cc-pVQZ-F12//CCSD(T)/aug-cc-pVTZ+ZPE(CCSD(T)/aug-cc-pVTZ). For the larger C5H5N system where the potential energy surface is accessed by the C3H3 + H2CCN, C4H3 + H2CN, and C4H3 + cis-HCNH reactions (Extended Data Figs. 3-4), geometry optimizations and harmonic frequencies calculations used the density functional (DFT) B3LYP method70,71 with the cc-pVTZ basis and single-point energies refined at the CCSD(T)-F12/cc-pVTZ-F12 level. Thus, the reported energies for C5H5N species are obtained at CCSD(T)-F12/cc-pVTZ-F12//B3LYP/cc-pVTZ+ZPE(B3LYP/cc-pVTZ) employing the Gaussian 1672 and MOLPRO66 software packages.

**Data availability**

All data generated in this study are available in the main text and the supplementary materials.

**Acknowledgements**

This work was supported by the U.S. Department of Energy, Basic Energy Sciences, by Grants No. DE-FG02-03ER15411 to the University of Hawaii at Manoa. The support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Grant 311508/2021-9 and 405524/2021-8, is also acknowledged. We would like to acknowledge fruitful discussions on the fractional abundances of ammonia with Drs. Conor A. Nixon (NASA Goddard) and Karen Willacy (JPL).

**Author Contributions**

R.I.K. designed the experiments; Z.Y., C.H., and S.J.G. preformed the experiments; A.M.M., P.F.G.V., M.O.A., and B.R.L.G. conducted the electronic structure calculations; J.-C.L, K.M.H., and M.D. conducted the atmospheric modeling of Titan; X.L. performed the astrochemical modeling of TMC-1; Z.Y. and R.I.K. analyzed data and wrote the manuscript. All authors discussed the data.

**Competing interests**

The authors declare no competing interests.

Figure Legends

**Figure 1**. **Pathways to pyridine and (iso)quinoline.** A chain of reactions initiated through the formation of methylene amidogen (H2CN• **5**) and cyanomethyl (H2CCN• **4**) lead to the simplest representative of mono and bicyclic aromatic molecules carrying nitrogen. The reactions of atomic carbon and dicarbon with ammonia to H2CN• and H2CCN• are investigated via crossed molecular beam machine; our calculations predict the formation of pyridine (**1**) and pyridinyl radicals (**9**-**11**) through the reactions of H2CN• with i/n-C4H3 and of H2CCN•with propargyl (C3H3). The reactions of pyridinyl radicals (**9**-**11**) with vinylacetylene (C4H4) forming (iso)quinoline are depicted in Ref. 29.

**Figure 2**. **Laboratory data of the C-ND3 and C2-NH3 reactions**. Laboratory angular distributions (a, c), and time-of-flights (b, d) for the C-ND3 (a, b) and C2-NH3 (c, d) reactions. The solid circles with their error bars in (a) and (c) represent the normalized experimental distribution with ±1σ uncertainty (s.d. of the integrals of the TOF spectra for the respective angle); the open circles indicate the experimental data. To obtain reasonable signal-to-noise ratios, for C-ND3 and C2-NH3 systems, at each angle, 3 × 106 (30 hours) and 2 × 106 (20 hours) TOF spectra had to be averaged, respectively. The red lines represent the best fits obtained. Atoms are color coded as follows: carbon, gray; nitrogen, blue; deuterium, light blue; and hydrogen, white.

**Figure 3**. **CM functions of the C-ND3 and C2-NH3 reactions**. CM translational energy distributions (*P(E*T*)*; a, d), angular flux distributions (*T(θ)*; b, e), and the corresponding flux contour map (c, f) for the C-ND3 (a, b, c) and C2-NH3 (d, e, f) reactions. The red lines represent the best-fit; shaded areas depictthe error limits of the best fits. The flux contour map represents the flux intensity as a function of product velocity (*u*) and CM scattering angle (*θ*). The color bar indicates the flux gradient from high (H) to low (L) intensity.

**Figure 4**. **Potential energy surfaces of the reactions of C-ND3.** Energies provided in black are relative energies for the deuterated reactants, whereas the energies in red refer to the hydrogenated reactants.

**Figure 5**. **Results of the astrochemical model for Titan’s atmosphere.** Mole fraction profiles for six species obtained from a one-dimensional photochemical model of Titan’s atmosphere. The solid black lines represent the nominal model results, with 280 runs of the Monte Carlo analysis displayed as cyan lines. Please confer to the text for details on the error analysis and the assignment of the species.

**Figure 6**. **Results of the astrochemical model for TMC-1.** The fractional abundance of the gas-phase methylene amidogen (H2CN, red), cyanomethyl (H2CCN, blue), methyl cyanide (CH3CN, purple), vinyl cyanide (C2H3CN, olive), pyridinyl (C5H4N, navy), pyridine (C5H5N, orange), and (iso)quinoline (C9H7N, pink) are plotted as a function of time. Astronomically observed fractional abundances of the four species are visualized with the colored horizontal bars.

**References**

1 Pizzarello, S., Huang, Y. & Fuller, M. The carbon isotopic distribution of Murchison amino acids. *Geochim. Cosmochim. Acta* **68**, 4963-4969 (2004).

2 Smith, K. E., Callahan, M. P., Gerakines, P. A., Dworkin, J. P. & House, C. H. Investigation of pyridine carboxylic acids in CM2 carbonaceous chondrites: potential precursor molecules for ancient coenzymes. *Geochim. Cosmochim. Acta* **136**, 1-12 (2014).

3 Martins, Z. *et al.* Extraterrestrial nucleobases in the Murchison meteorite. *Earth Planet. Sci. Lett.* **270**, 130-136 (2008).

4 Burton, A. S., Stern, J. C., Elsila, J. E., Glavin, D. P. & Dworkin, J. P. Understanding prebiotic chemistry through the analysis of extraterrestrial amino acids and nucleobases in meteorites. *Chem. Soc. Rev.* **41**, 5459-5472 (2012).

5 Andrews, H., Candian, A. & Tielens, A. G. G. M. Hydrogenation and dehydrogenation of interstellar PAHs: Spectral characteristics and H2 formation. *Astron. Astrophys.* **595**, A23 (2016).

6 Tsuge, M., Bahou, M., Wu, Y.-J., Allamandola, L. & Lee, Y.-P. The infrared spectrum of protonated ovalene in solid para-hydrogen and its possible contribution to interstellar unidentified infrared emission. *Astrophys. J.* **825**, 96 (2016).

7 Tielens, A. G. G. M. Interstellar polycyclic aromatic hydrocarbon molecules. *Annu. Rev. Astron. Astrophys.* **46**, 289-337 (2008).

8 Knorke, H., Langer, J., Oomens, J. & Dopfer, O. Infrared spectra of isolated protonated polycyclic aromatic hydrocarbon molecules. *Astrophys. J.* **706**, L66 (2009).

9 Hudgins, D. M., Bauschlicher Jr, C. W. & Allamandola, L. J. Variations in the peak position of the 6.2 μm interstellar emission feature: a tracer of N in the interstellar polycyclic aromatic hydrocarbon population. *Astrophys. J.* **632**, 316 (2005).

10 Herbst, E. & Van Dishoeck, E. F. Complex organic interstellar molecules. *Annu. Rev. Astron. Astrophys.* **47**, 427-480 (2009).

11 Kaiser, R. I. & Hansen, N. An Aromatic Universe–A Physical Chemistry Perspective. *J. Phys. Chem. A* **125**, 3826-3840 (2021).

12 Peeters, Z., Botta, O., Charnley, S. B., Ruiterkamp, R. & Ehrenfreund, P. The astrobiology of nucleobases. *Astrophys. J.* **593**, L129 (2003).

13 Hörst, S. M. Titan's atmosphere and climate. *J. Geophys. Res.* **122**, 432-482 (2017).

14 Vuitton, V., Yelle, R. V., Klippenstein, S. J., Hörst, S. M. & Lavvas, P. Simulating the density of organic species in the atmosphere of Titan with a coupled ion-neutral photochemical model. *Icarus* **324**, 120-197 (2019).

15 Loison, J. C. *et al.* The neutral photochemistry of nitriles, amines and imines in the atmosphere of Titan. *Icarus* **247**, 218-247 (2015).

16 Kislov, V. V., Nguyen, T. L., Mebel, A. M., Lin, S. H. & Smith, S. C. Photodissociation of benzene under collision-free conditions: An ab initio/Rice–Ramsperger–Kassel–Marcus study. *J. Chem. Phys.* **120**, 7008-7017 (2004).

17 Lin, M.-F. *et al.* Photodissociation dynamics of pyridine. *J. Chem. Phys.* **123**, 054309 (2005).

18 Vuitton, V., Yelle, R. V. & McEwan, M. J. Ion chemistry and N-containing molecules in Titan's upper atmosphere. *Icarus* **191**, 722-742 (2007).

19 Ricca, A., Bauschlicher Jr, C. W. & Bakes, E. A computational study of the mechanisms for the incorporation of a nitrogen atom into polycyclic aromatic hydrocarbons in the Titan haze. *Icarus* **154**, 516-521 (2001).

20 Soorkia, S. *et al.* Direct detection of pyridine formation by the reaction of CH (CD) with pyrrole: a ring expansion reaction. *Phys. Chem. Chem. Phys.* **12**, 8750-8758 (2010).

21 López-Puertas, M. *et al.* Large abundances of polycyclic aromatic hydrocarbons in Titan's upper atmosphere. *Astrophys. J.* **770**, 132 (2013).

22 Anderson, C. M. & Samuelson, R. E. Titan’s aerosol and stratospheric ice opacities between 18 and 500 μm: Vertical and spectral characteristics from Cassini CIRS. *Icarus* **212**, 762-778 (2011).

23 Sebree, J. A., Trainer, M. G., Loeffler, M. J. & Anderson, C. M. Titan aerosol analog absorption features produced from aromatics in the far infrared. *Icarus* **236**, 146-152 (2014).

24 Ali, A., Sittler Jr, E. C., Chornay, D., Rowe, B. R. & Puzzarini, C. Organic chemistry in Titan׳ s upper atmosphere and its astrobiological consequences: I. Views towards Cassini Plasma Spectrometer (CAPS) and Ion Neutral Mass Spectrometer (INMS) experiments in space. *Planet. Space Sci.* **109**, 46-63 (2015).

25 Mathé, C., Gautier, T., Trainer, M. G. & Carrasco, N. Detection opportunity for aromatic signature in Titan’s aerosols in the 4.1–5.3 μm range. *Astrophys. J. Lett.* **861**, L25 (2018).

26 Zhao, L. *et al.* Gas-phase synthesis of corannulene–a molecular building block of fullerenes. *Phys. Chem. Chem. Phys.* **23**, 5740-5749 (2021).

27 Kaiser, R. I. *et al.* Gas-phase synthesis of racemic helicenes and their potential role in the enantiomeric enrichment of sugars and amino acids in meteorites. *Phys. Chem. Chem. Phys.* **24**, 25077-25087 (2022).

28 Parker, D. S. N. & Kaiser, R. I. On the formation of nitrogen-substituted polycyclic aromatic hydrocarbons (NPAHs) in circumstellar and interstellar environments. *Chem. Soc. Rev.* **46**, 452-463 (2017).

29 Zhao, L. *et al.* A molecular beam and computational study on the barrierless gas phase formation of (iso)quinoline in low temperature extraterrestrial environments. *Phys. Chem. Chem. Phys.* **23**, 18495-18505 (2021).

30 Broadfoot, A. L. *et al.* Ultraviolet spectrometer observations of Neptune and Triton. *Science* **246**, 1459-1466 (1989).

31 Moores, J. E., Smith, C. L., Toigo, A. D. & Guzewich, S. D. Penitentes as the origin of the bladed terrain of Tartarus Dorsa on Pluto. *Nature* **541**, 188-190 (2017).

32 Yang, Z. *et al.* Gas-Phase Formation of 1, 3, 5, 7-cyclooctatetraene (C8H8) through ring expansion via the aromatic 1, 3, 5-cyclooctatrien-7-yl radical (C8H9•) transient. *J. Am. Chem. Soc.* **144**, 22470-22478 (2022).

33 Yang, Z. *et al.* Gas-phase formation of the resonantly stabilized 1-indenyl (C9H7•) radical in the interstellar medium. *Sci. Adv.* **9**, eadi5060 (2023).

34 Zhang, J. & Valeev, E. F. Prediction of Reaction Barriers and Thermochemical Properties with Explicitly Correlated Coupled-Cluster Methods: A Basis Set Assessment. *J. Chem. Theory Comput.* **8**, 3175-3186 (2012).

35 Adler, T. B., Knizia, G. & Werner, H.-J. A simple and efficient CCSD(T)-F12 approximation. *J. Chem. Phys.* **127**, 221106 (2007).

36 Bourgalais, J. *et al.* The C(3P) + NH3 reaction in interstellar chemistry. I. Investigation of the product formation channels. *Astrophys. J.* **812**, 106 (2015).

37 Chiba, S., Honda, T., Kondo, M. & Takayanagi, T. Direct dynamics study of the N(4S)+ CH3(2A2″) reaction. *Comput. Theor. Chem.* **1061**, 46-51 (2015).

38 Mebel, A. M., Georgievskii, Y., Jasper, A. W. & Klippenstein, S. J. Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene. *Faraday Discuss.* **195**, 637-670 (2016).

39 Jasper, A. W. & Hansen, N. Hydrogen-assisted isomerizations of fulvene to benzene and of larger cyclic aromatic hydrocarbons. *Proc. Combust. Inst.* **34**, 279-287 (2013).

40 Lau, K.-C., Li, W.-K., Ng, C. Y. & Chiu, S.-W. A Gaussian-2 study of isomeric C2H2N and C2H2N+. *J. Phys. Chem. A* **103**, 3330-3335 (1999).

41 Willacy, K., Allen, M. & Yung, Y. A new astrobiological model of the atmosphere of Titan. *Astrophys. J.* **829**, 79 (2016).

42 Cui, J. *et al.* Analysis of Titan's neutral upper atmosphere from Cassini Ion Neutral Mass Spectrometer measurements. *Icarus* **200**, 581-615 (2009).

43 Hickson, K. M. *et al.* The C(3P) + NH3 reaction in interstellar chemistry. II. Low temperature rate constants and modeling of NH, NH2, and NH3 abundances in dense interstellar clouds. *Astrophys. J.* **812**, 107 (2015).

44 Pope, C. J. & Miller, J. A. Exploring old and new benzene formation pathways in low-pressure premixed flames of aliphatic fuels. *Proc. Combust. Inst.* **28**, 1519-1527 (2000).

45 Zhao, L. *et al.* Gas-phase synthesis of benzene via the propargyl radical self-reaction. *Sci. Adv.* **7**, eabf0360 (2021).

46 Pearce, B. K. D., Ayers, P. W. & Pudritz, R. E. A consistent reduced network for HCN chemistry in early earth and Titan atmospheres: Quantum calculations of reaction rate coefficients. *J. Phys. Chem. A* **123**, 1861-1873 (2019).

47 Pearce, B. K. D., He, C. & Hörst, S. M. An experimental and theoretical investigation of HCN production in the Hadean Earth atmosphere. *ACS Earth Space Chem.* **6**, 2385-2399 (2022).

48 Marston, G., Nesbitt, F. L., Nava, D. F., Payne, W. A. & Stief, L. J. Temperature dependence of the reaction of nitrogen atoms with methyl radicals. *J. Phys. Chem.* **93**, 5769-5774 (1989).

49 Marston, G., Nesbitt, F. L. & Stief, L. J. Branching ratios in the N + CH3 reaction: formation of the methylene amidogen (H2CN) radical. *J. Chem. Phys.* **91**, 3483-3491 (1989).

50 Dobrijevic, M., Loison, J. C., Hickson, K. M. & Gronoff, G. 1D-coupled photochemical model of neutrals, cations and anions in the atmosphere of Titan. *Icarus* **268**, 313-339 (2016).

51 Loison, J. C., Dobrijevic, M. & Hickson, K. M. The photochemical production of aromatics in the atmosphere of Titan. *Icarus* **329**, 55-71 (2019).

52 Benne, B., Dobrijevic, M., Cavalié, T., Loison, J.-C. & Hickson, K. M. A photochemical model of Triton's atmosphere with an uncertainty propagation study. *Astron. Astrophys.* **667**, A169 (2022).

53 Vanuzzo, G. *et al.* Reaction N(2D) + CH2CCH2 (allene): An experimental and theoretical investigation and implications for the photochemical models of Titan. *ACS Earth Space Chem.* **6**, 2305-2321 (2022).

54 Teolis, B. D. *et al.* A revised sensitivity model for Cassini INMS: Results at Titan. *Space Sci. Rev.* **190**, 47-84 (2015).

55 Gladstone, G. R. & Young, L. A. New Horizons observations of the atmosphere of Pluto. *Annu. Rev. Earth Planet. Sci.* **47**, 119-140 (2019).

56 Rap, D. B., Schrauwen, J. G., Marimuthu, A. N., Redlich, B. & Brünken, S. Low-temperature nitrogen-bearing polycyclic aromatic hydrocarbon formation routes validated by infrared spectroscopy. *Nat. Astron.* **6**, 1059-1067 (2022).

57 McGuire, B. A. *et al.* Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering. *Science* **371**, 1265-1269 (2021).

58 McElroy, D. *et al.* The UMIST database for astrochemistry 2012. *Astron. Astrophys.* **550**, A36 (2013).

59 Ohishi, M., McGonagle, D., Irvine, W. M., Yamamoto, S. & Saito, S. Detection of a new interstellar molecule, H2CN. *Astrophys. J.* **427**, L51-L54 (1994).

60 Thaddeus, P., Vrtilek, J. M. & Gottlieb, C. A. Laboratory and astronomical identification of cyclopropenylidene, C3H2. *Astrophys. J.* **299**, L63-L66 (1985).

61 Cernicharo, J. *et al.* Discovery of CH2CHCCH and detection of HCCN, HC4N, CH3CH2CN, and, tentatively, CH3CH2CCH in TMC-1. *Astron. Astrophys.* **647**, L2 (2021).

62 Tennis, J. D. *et al.* Detection and modelling of CH3NC in TMC-1. *Mon. Not. R. Astron. Soc.* **525**, 2154-2171 (2023).

63 Stoks, P. G. & Schwartz, A. W. Basic nitrogen-heterocyclic compounds in the Murchison meteorite. *Geochim. Cosmochim. Acta* **46**, 309-315 (1982).

64 Sephton, M. A. Organic compounds in carbonaceous meteorites. *Nat. Prod. Rep.* **19**, 292-311 (2002).

65 Dangi, B. B., Maity, S., Kaiser, R. I. & Mebel, A. M. A combined crossed beam and ab initio investigation of the gas phase reaction of dicarbon molecules (C2; X1Σg+/a3Πu) with propene (C3H6; X1A′): identification of the resonantly stabilized free radicals 1-and 3-vinylpropargyl. *J. Phys. Chem. A* **117**, 11783-11793 (2013).

66 Werner, H. *et al.* MOLPRO, version 2015.1, a package of ab initio programs. *University of Cardiff Chemistry Consultants (UC3): Cardiff, Wales, UK* (2015).

67 Knowles, P. J., Hampel, C. & Werner, H. J. Coupled cluster theory for high spin, open shell reference wave functions. *J. Chem. Phys.* **99**, 5219-5227 (1993).

68 Dunning Jr, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **90**, 1007-1023 (1989).

69 Peterson, K. A., Adler, T. B. & Werner, H.-J. Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B–Ne, and Al–Ar. *J. Chem. Phys.* **128**, 084102 (2008).

70 Becke, A. D. Density-functional thermochemistry. III. the role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993).

71 Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785 (1988).

72 Frisch, M. J. *et al.* Gaussian 16, revision C.1. (2019).