THE JOURNAL OF
PHYSICAL CHEMISTRY
LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCL

Letter

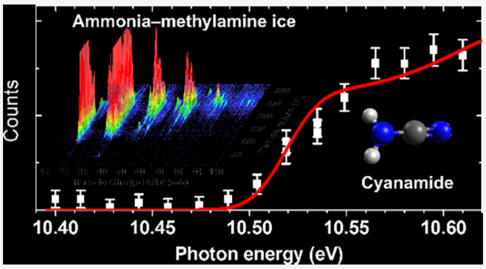
Unconventional Formation of Cyanamide, a Key Intermediate in Prebiotic Chemical Evolution, in Interstellar Ice Analogues

Jia Wang, Joshua H. Marks, André K. Eckhardt,* and Ralf I. Kaiser*

Cite This: *J. Phys. Chem. Lett.* 2026, 17, 2748–2753

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

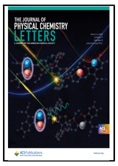


ABSTRACT: The interstellar origin and chemistry of the NCN moiety, a critical molecular backbone of nucleobases, is central to the RNA world hypothesis for the Origins of Life; however, its formation mechanisms under astrophysical conditions remain largely unexplored. Here, we report the first laboratory preparation of cyanamide (NH_2CN), a key intermediate in prebiotic chemical evolution, in low-temperature ammonia–methylamine (NH_3–CH_3NH_2) interstellar ice analogs exposed to energetic electrons, simulating secondary electrons generated by galactic cosmic rays. Utilizing tunable vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry combined with isotopic labeling, cyanamide was identified isomer-selectively in the gas phase during temperature-programmed desorption. These findings reveal nonequilibrium pathways to cyanamide in methylamine-containing interstellar ices, highlighting the pivotal role of galactic cosmic rays in forming the biorelevant NCN backbone and shedding light on the abiotic synthesis of nucleobases in astrophysical environments.

Since its very first identification toward the molecular cloud Sagittarius B2 (Sgr B2) by Turner et al. nearly half a century ago,[1] cyanamide (NH_2CN, **1**), the first interstellar molecule containing an NCN backbone, has attracted extensive interest across the prebiotic chemistry,[2] astrochemistry,[3,4] physical (organic) chemistry,[5,6] and theoretical chemistry communities.[7−11] This broad attention primarily arises from the central role of **1** in the prebiotic chemical evolution and its potential relevance to the emergence of life.[10,12−15] As one of the simplest organic molecules that features an electrophilic nitrile and a nucleophilic amino group,[9] **1** is considered as an effective prebiotic condensing agent[16] and a key building block for the synthesis of crucial biorelevant compounds such as purines and pyrimidines in interstellar ices and prebiotic chemistry (Figure 1). Upon energetic processing by galactic cosmic rays (GCRs) or ultraviolet (UV) photons, **1** can react with water (H_2O) to the biorelevant urea (NH_2CONH_2),[17,18] which has been detected toward the hot core Sgr B2(N1).[19] Dimerization of **1** yields 2-cyanoguanidine ($(NH_2)_2CNCN$),[20] a precursor to purine nucleobases such as adenine ($C_5H_5N_5$) and guanine ($C_5H_5N_5O$). Furthermore, reaction between **1** and glycolaldehyde ($HOCH_2CHO$) produces 2-aminooxazole ($C_3H_4N_2O$),[15,21] which is a pivotal prebiotic intermediate that leads to pyrimidine nucleotides such as cytidine- and uridine-2′,3′-cyclic phosphates,[22] thereby contributing to prebiotic RNA synthesis.[15,23] In prebiotic chemistry, **1** may react with cyanoacetylene (HCCCN), which has been detected toward molecular cloud Sgr B2,[24] to 4-cyanoimidazole ($C_4H_3N_3$), a key intermediate leading to purines including adenine and guanine.[25] Additionally, **1** reacts efficiently with ribose ($C_5H_{10}O_5$) to form ribosecyanamide ($C_6H_{10}O_4N_2$), which can further react with cyanoacetylene to yield pyrimidine nucleosides.[26] Consequently, elucidating the formation of **1** in the interstellar medium (ISM) is critical for constraining abiotic routes that enable the emergence and incorporation of the NCN moiety into complex organics associated with the Origins of Life. However, despite its significance, the formation routes of **1** have been inferred mainly from gas-phase chemical models[8,9] or through hypothesized grain-surface reactions,[4,10,27] whereas laboratory experiments that critically constrain its formation pathways under astrophysical conditions remain scarce.

Here, we report the very first laboratory simulation on the synthesis of cyanamide (NH_2CN, **1**) in model interstellar analog ices composed of ammonia (NH_3) and methylamine (CH_3NH_2). The low-temperature (5 K) ice mixtures were exposed to energetic electrons to simulate the secondary electrons generated by GCRs as they penetrate the interstellar ices in cold molecular clouds.[28] The applied low irradiation doses of 6.7 ± 1.0 eV per ammonia molecule and 12 ± 2 eV per methylamine molecule correspond to GCR exposures over time scales comparable to molecular cloud lifetimes of $(3.9 \pm 0.6) \times 10^7$ years.[29] Both ammonia and methylamine are

Received: January 30, 2026
Revised: February 18, 2026
Accepted: February 19, 2026
Published: February 23, 2026



ACS Publications

https://doi.org/10.1021/acs.jpclett.6c00331
J. Phys. Chem. Lett. 2026, 17, 2748–2753

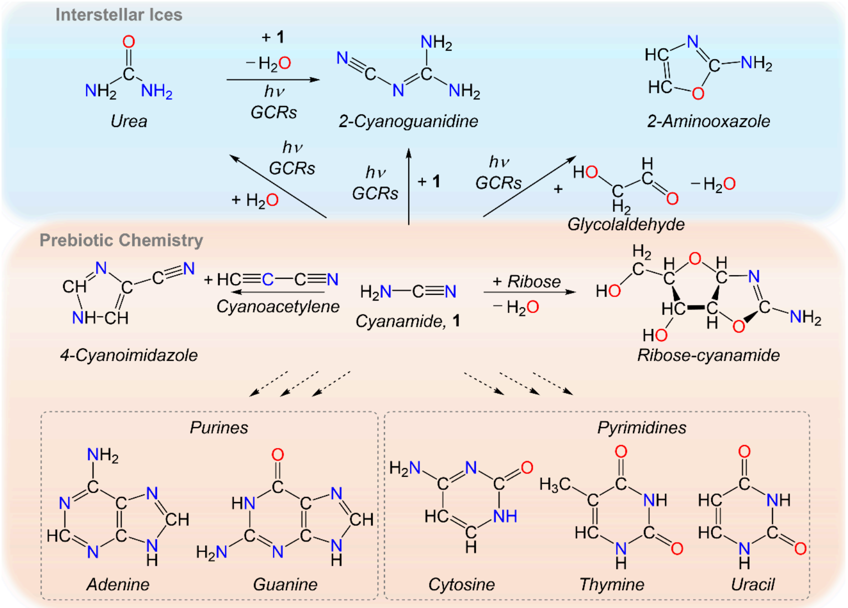


Figure 1. Cyanamide (**1**) serves as a key molecular building block in the formation of fundamental biorelevant molecules in interstellar ices and prebiotic chemistry.

ubiquitous in the ISM. Ammonia is a critical component of interstellar ices with abundances reaching up to 15% relative to water.[30] Methylamine has been detected toward high-mass star-forming regions such as NGC 6334I,[31] hot molecular cores like G10.47+0.03,[32] and molecular clouds such as Sgr B2(N) with an abundance of 3×10^{-7} relative to molecular hydrogen (H_2).[33] Laboratory experiments revealed that methylamine forms effectively in interstellar ices composed of ammonia and methane (CH_4).[34] Therefore, ammonia–methylamine ice represents a suitable model ice to probe the interstellar formation pathways of **1**. Utilizing tunable vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) combined with isotopic labeling, we identified **1** *isomer-selectively* in the gas phase during temperature-programmed desorption (TPD) of the irradiated ices. As dense molecular clouds evolve toward star formation, **1** can be released from interstellar icy nanoparticles (grains) into the gas phase. Consistently, **1** has been detected in diverse environments including molecular clouds with column densities up to 5×10^{16} cm^{-2},[35] protostars,[4] high-mass star-forming regions,[14] and extragalactic sources.[36] These findings reveal unconventional, nonequilibrium pathways to **1**—a key intermediate in prebiotic chemical evolution—in methylamine-containing interstellar ices, thereby advancing our fundamental understanding of how a biorelevant NCN backbone can form through GCR-mediated, nonequilibrium chemistry within cold molecular clouds.

Fourier-transform infrared spectra (FTIR) of ammonia–methylamine (NH_3–CH_3NH_2) and the fully deuterated labeled ices (ND_3–CD_3ND_2) were recorded before, during, and after electron irradiation at 5 K (Figures S1–S3, Tables S1–S3). The absorption features of NH_3–CH_3NH_2 ice can be attributed to the fundamental and combination vibrational modes of ammonia such as the symmetric N–H stretching (ν_1) at 3191 cm^{-1} and the degenerate N–H stretching (ν_3) at 3356 cm^{-1} and methylamine such as the symmetric stretch of the NH_2 group (ν_1) at 3284 cm^{-1} and the degenerate stretch of the CH_3 group (ν_{11}) at 2943 cm^{-1} (Figure S1). Upon electron irradiation, several new absorption bands appeared. The absorption at 3039 cm^{-1} is assigned to the C–H degenerate stretching mode (ν_3) of methane (CH_4)[37] and/or the C–H stretching (ν_2) of methanimine (CH_2NH).[38] The formation of methanimine is further supported by the absorption at 1599 cm^{-1} observed in irradiated ND_3–CD_3ND_2 ice, corresponding to the C=N stretching (ν_4) of methanimine-d_3 (Figures S2–S3).[38] Ethane (C_2H_6) was identified via its combination bands at 4132, 2740, 2653, and 2540 cm^{-1}, corresponding to $\nu_7 + \nu_{12}$, $\nu_2 + \nu_6$, $\nu_8 + \nu_{12}$, and $\nu_6 + \nu_9$ modes, respectively. In the fully deuterated ices, ethane-d_6 (C_2D_6) was detected at 1904 cm^{-1} ($\nu_3 + \nu_6$) in low-dose irradiated ND_3–CD_3ND_2 ice (Figure S2) with additional absorptions at 2973 cm^{-1} ($\nu_7 + \nu_{12}$), 2079 cm^{-1} (ν_5), 1655 cm^{-1} ($\nu_{11} + \nu_{12}$), and 1626 cm^{-1} ($\nu_6 + \nu_{12}$) emerging under high-dose irradiation (Figure S3). The absorption at 2321 cm^{-1} is attributed to the C≡N stretching vibration,[39] while bands at 2085 cm^{-1} and 2058 cm^{-1} are assigned to the C≡N stretching mode of cyanide anion (CN^{-1}).[40] In addition, the absorption feature at 1568 cm^{-1} in irradiated ND_3–CD_3ND_2 ice can be assigned to the N–C≡N stretching, which may be linked to cyanamide (**1**).[41] Because the complex organics formed in the irradiated ice mixtures exhibit strong overlapping IR functional-group absorptions, infrared spectroscopy alone does not permit isomer-specific identification of CH_2N_2 species including **1**. Consequently, a more sensitive analytical technique is required to unambiguously identify individual reaction products.[42,43]

PI-ReToF-MS data were collected at VUV photon energies of 10.70 and 10.35 eV to photoionize subliming molecules during TPD of irradiated ammonia–methylamine ices, thus enabling the gas-phase identification of **1** based on the desorption profile and adiabatic ionization energies (IEs) of CH_2N_2 isomers (Figure 2). The corresponding mass spectra are compiled in Figure S4. Since ammonia (IE = 10.02–10.06 eV)[44] and methylamine (IE = 8.77–8.97 eV)[44] can be ionized at 10.70 and 10.35 eV, their sublimation events between 73–122 K and 88–150 K, respectively, dominate the ion signals.

https://doi.org/10.1021/acs.jpclett.6c00331
J. Phys. Chem. Lett. 2026, 17, 2748–2753

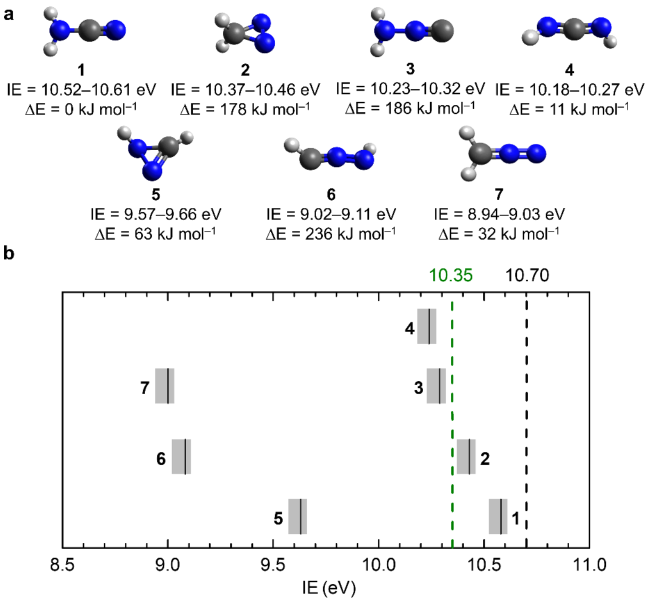


Figure 2. (a) Computed adiabatic ionization energies (IEs) and relative energies (ΔEs) of CH_2N_2 isomers **1**−**7** at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory including zero-point vibrational energy (ZPVE) corrections. (b) Compiled IEs (black solid line) and IE ranges (gray area) after error analysis. VUV photon energies of 10.70 and 10.35 eV were used to photoionize molecules subliming from irradiated ammonia−methylamine ices during TPD.

At 10.70 eV, the TPD profile of mass-to-charge ratios (m/z) of 42 from the low-dose irradiated NH_3−CH_3NH_2 ice reveals a broad sublimation event extending from 90 to 250 K with a major peak at 232 K (Figure 3a). A blank experiment conducted under identical conditions, but without irradiation, shows only a weak peak at 117 K, due to impurities co-subliming with ammonia and/or methylamine; no sublimation events above 140 K are present. Therefore, the subsequent analysis focuses on the higher-temperature region exceeding 140 K. Substituting NH_3−CH_3NH_2 ice with fully deuterated ND_3−CD_3ND_2 ice resulted in a mass shift of 2 atomic mass units (amu) from m/z = 42 to 44 (Figure 3a), demonstrating the incorporation of two hydrogen atoms and confirming that the events of m/z = 42 above 140 K are assigned to CH_2N_2 isomers. At 10.70 eV, all seven CH_2N_2 isomers—cyanamide (**1**, IE = 10.52−10.61 eV), 3*H*-diazirine (**2**, IE = 10.37−10.46 eV), isocyanamide (**3**, IE = 10.23−10.32 eV), methanediimine (**4**, IE = 10.18−10.27 eV), 1*H*-diazirine (**5**, IE = 9.57−9.66 eV), methyl-2-hydrazinyl-1-ylidene (**6**, IE = 9.02−9.11 eV), and diazomethane (**7**, IE = 8.94−9.03 eV)—can be photoionized (Figure 2, Table S4). Consequently, the TPD profile of m/z = 42 ($CH_2N_2^+$) recorded at 10.70 eV can be attributed to any of the CH_2N_2 isomers, with **1** being the thermodynamically most stable isomer in the gas phase. To facilitate the identification of **1**, higher irradiation doses were applied to enhance the formation yields, and fully deuterated ices were chosen to better separate CH_2N_2 isomers from neighboring mass channels. The TPD profile of m/z = 44 ($CD_2N_2^+$) of the high-dose irradiated ND_3−CD_3ND_2 ice at 10.70 eV exhibits a minor sublimation peak at 224 K and a dominant peak at 238 K (Figure 3b).

Thereafter, the photon energy was reduced to 10.35 eV; this energy is sufficient to ionize **3**−**7** but not **1** (IE = 10.52−10.61 eV) or **2** (IE = 10.37−10.46 eV). Here, the 238 K sublimation event is eliminated (Figure 3c), indicating that this higher-temperature peak originates from **1** and/or **2**, with the

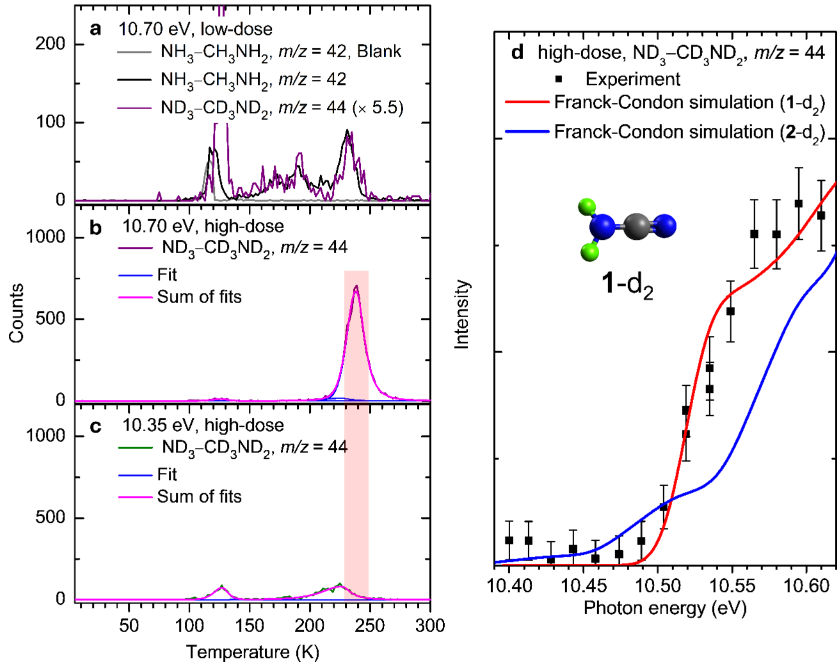


Figure 3. Ion signal recorded during TPD from ammonia−methylamine ices. TPD profiles of m/z = 42 and 44 for low-dose irradiated NH_3−CH_3NH_2 and ND_3−CD_3ND_2 ices were recorded at 10.70 (a). TPD profiles of m/z = 44 for high-dose irradiated ND_3−CD_3ND_2 ices were recorded at 10.70 (b) and 10.35 (c) eV. The red shaded region indicates the peak temperature corresponding to cyanamide. Photoionization efficiency (PIE) curve of m/z = 44 collected in the 237−255 K range during TPD after correction for temperature-dependent sublimation rate (d). Franck−Condon simulations of the PIE curves for cyanamide-d_2 (**1**-d_2) and 3*H*-diazirine-d_2 (**2**-d_2) are shown. Atoms are color-coded as deuterium (light green), carbon (gray), and nitrogen (blue).

remaining ion signals attributed to **3**−**7**. Note that the IEs of **1** and **2** are too close to be unambiguously identified using photoionization at a fixed single photon energy. To distinguish between **1** and **2**, photoionization efficiency (PIE) curves of $m/z = 44$ ($CD_2N_2^+$) were recorded during the TPD phase and corrected for the desorption profile. PIE measurements record the ion signal intensity as a function of photon energy and allow an isomer-specific identification through comparison with experimental reference PIEs or simulations.[45−47] Here, PIE curves were collected over a photon energy range of 10.40−10.61 eV in the 237−255 K range (Figure 3d). The measured PIE curve agrees well with the Franck−Condon simulations of cyanamide-d_2 (**1**-d_2), thus confirming its formation. The ionization onset was determined to be 10.50 ± 0.01 eV, which is close to the computed IE of **1**, providing further evidence for its assignment. The detected ion signals of cyanamide-d_2 in the high-dose irradiated ND_3−CD_3ND_2 ice recorded at 10.70 eV were 6700 ± 700 counts. Further analysis by fitting the experimental data with combined Franck−Condon simulated PIE curves of **1**-d_2 and **2**-d_2 shows that up to 7% of the total ion signal can be attributed to **2**-d_2 (Figure S5), indicating its tentative formation.

Having provided compelling evidence for the formation of cyanamide (**1**) in ammonia−methylamine ices exposed to GCR proxies in the form of energetic electrons, we now turn to its possible formation pathways. It is worth noting that 5 keV electrons were employed to simulate the energy deposition processes induced by GCRs in ices, as their linear energy transfer is similar to that of 10−20 MeV GCR protons interacting with interstellar ices.[28,48] First, electron irradiation of methylamine-containing ices produces methanimine (CH_2NH),[49] which was identified also in the present work via the C−H stretching of methanimine (CH_2NH, ν_2)[38] at 3039 cm^{-1} and the C═N stretching of methanimine-d_3 (CD_2ND, ν_4)[38] at 1599 cm^{-1} (Supporting Information, Figures S1−S3). Upon interaction with GCRs, unimolecular decomposition of ammonia (reaction 1) and methanimine (reaction 2) yield the amino (NH_2)[46,47,50] and iminomethyl (CHNH) radical, respectively; these processes are endoergic by 444 and 395 kJ mol^{-1}.[51] Within the ice matrix, amino and the iminomethyl radicals that adopt a favorable geometry can recombine barrierlessly at 5 K to form formamidine (NH_2CHNH) via reaction 3; this reaction is exoergic by 402 kJ mol^{-1}.[51,52] Alternatively, electron-irradiated ammonia−methylamine ices produce methanediamine ($NH_2CH_2NH_2$),[50] which can subsequently form formamidine via unimolecular decomposition (reaction 4), an endoergic process requiring 479 mol^{-1}.[51,52]

$$NH_3 \rightarrow NH_2 + H, \quad \Delta H_r^\circ\ (0\ K) = +444\ kJ\ mol^{-1} \tag{1}$$

$$CH_2NH \rightarrow CHNH + H, \quad \Delta H_r^\circ\ (0\ K) = +395\ kJ\ mol^{-1} \tag{2}$$

$$NH_2 + CHNH \rightarrow NH_2CHNH, \quad \Delta H_r^\circ\ (0\ K) = -402\ kJ\ mol^{-1} \tag{3}$$

$$NH_2CH_2NH_2 \rightarrow NH_2CHNH + 2H, \quad \Delta H_r^\circ\ (0\ K) = +479\ kJ\ mol^{-1} \tag{4}$$

Second, the decomposition of formamidine produces the methyl, aminoimino (NH_2CNH) radical through reaction 5 or the amidogen, aminomethylene (NH_2CHN) radical via reaction 6, processes that are endoergic by 359 and 336 kJ mol^{-1}, respectively.[51−53] Once formed, these radicals become trapped in the ice matrix at 5 K due to limited molecular mobility,[54] serving as precursors to yield **1** through N−H (reaction 7) or C−H (reaction 8) bond dissociation, which are endoergic by 152 and 176 kJ mol^{-1}, respectively.[51,53] These energies can be provided by GCR-induced secondary electrons, highlighting the pivotal role of nonequilibrium chemistry in the synthesis of **1** in interstellar ices. We note that the ammonia−methylamine ice serves as a suitable model system to study low-temperature reaction pathways leading to cyanamide rather than to reproduce the exact relative abundances of these species in interstellar ices. Given that water, carbon monoxide (CO), and carbon dioxide (CO_2) are major components of interstellar ices, future experiments can investigate the formation of cyanamide in more complex ice mixtures containing these compounds. In irradiated ammonia−methylamine−water ices, hydroxyl (OH) radical formed from water may react with amino and iminomethyl radicals to yield hydroxylamine (NH_2OH)[55] and methanimidic acid (HOCHNH), respectively, thereby competing with the formation pathways leading to formamidine, the precursor to cyanamide.

$$NH_2CHNH \rightarrow NH_2CNH + H, \quad \Delta H_r^\circ\ (0\ K) = +359\ kJ\ mol^{-1} \tag{5}$$

$$NH_2CHNH \rightarrow NH_2CHN + H, \quad \Delta H_r^\circ\ (0\ K) = +336\ kJ\ mol^{-1} \tag{6}$$

$$NH_2CNH \rightarrow NH_2CN\ (\mathbf{1}) + H, \quad \Delta H_r^\circ\ (0\ K) = +152\ kJ\ mol^{-1} \tag{7}$$

$$NH_2CHN \rightarrow NH_2CN\ (\mathbf{1}) + H, \quad \Delta H_r^\circ\ (0\ K) = +176\ kJ\ mol^{-1} \tag{8}$$

In conclusion, we present the very first laboratory preparation of cyanamide (NH_2CN, **1**)—a key intermediate in prebiotic chemical evolution—in ammonia−methylamine interstellar ice analogs. Electron irradiation of low-temperature (5 K) ices, mimicking secondary electrons generated by GCRs, induces nonequilibrium chemistry that enables the synthesis of **1** from two ubiquitous interstellar nitrogen-containing species. Utilizing tunable PI-ReToF-MS combined with isotopic labeling, we identified **1** *isomer-selectively* in the gas phase during TPD. These findings reveal unconventional, nonequilibrium pathways to **1** in methylamine-containing interstellar ices, highlighting the pivotal role of GCR-driven chemistry in forming the biorelevant NCN backbone central to the RNA-world hypothesis.[50,56] Once formed in interstellar ices, **1** can serve as a key precursor to biorelevant compounds including urea, 2-cyanoguanidine, and 2-aminooxazole (Figure 1), all of which could be incorporated into planetesimals and comets and eventually delivered to early Earth, as evidenced by the detection of **1** in comet C/1995 O1 (Hale-Bopp).[57] Such exogenous delivery provides plausible prebiotic routes for the abiotic formation of purines and pyrimidines, potentially contributing to the emergence of nucleotides on early Earth.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.6c00331.

> Experimental and computational sections, PI-ReToF-MS data, FTIR spectra of ammonia–methylamine ices and their assessments, PIE curve and fittings, error analysis of IEs and relative energies, experimental conditions, VUV generation parameters and Cartesian coordinates, vibrational frequencies, and infrared intensities of calculated structures (PDF)

AUTHOR INFORMATION

Corresponding Authors

André K. Eckhardt – *Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Bochum 44801, Germany;* orcid.org/0000-0003-1029-9272;
Email: Andre.Eckhardt@ruhr-uni-bochum.de

Ralf I. Kaiser – *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States;* orcid.org/0000-0002-7233-7206;
Email: ralfk@hawaii.edu

Authors

Jia Wang – *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

Joshua H. Marks – *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States;* orcid.org/0000-0003-0492-2494

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpclett.6c00331

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

R.I.K. acknowledges support from the U.S. National Science Foundation (NSF), Division of Astronomical Sciences, under grant AST-2403867 for the experiments. A.K.E. thanks the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for support of the calculations under Germany's Excellence Strategy - EXC 2033 - 390677874 – RESOLV.

REFERENCES

(1) Turner, B. E.; Liszt, H. S.; Kaifu, N.; Kisliakov, A. G. Microwave detection of interstellar cyanamide. *Astrophys. J.* **1975**, *201*, L149–L152.

(2) Das, T.; Ghule, S.; Vanka, K. Insights into the origin of life: Did it begin from HCN and H_2O? *ACS Cent. Sci.* **2019**, *5*, 1532–1540.

(3) Duvernay, F.; Chiavassa, T.; Borget, F.; Aycard, J.-P. Carbodiimide production from cyanamide by uv irradiation and thermal reaction on amorphous water ice. *J. Phys. Chem. A* **2005**, *109*, 603–608.

(4) Coutens, A.; Willis, E. R.; Garrod, R. T.; Müller, H. S. P.; Bourke, T. L.; Calcutt, H.; Drozdovskaya, M. N.; Jørgensen, J. K.; Ligterink, N. F. W.; Persson, M. V.; et al. First detection of cyanamide (NH_2CN) towards solar-type protostars. *Astron. Astrophys.* **2018**, *612*, A107.

(5) Duvernay, F.; Chiavassa, T.; Borget, F.; Aycard, J.-P. Experimental study of water-ice catalyzed thermal isomerization of cyanamide into carbodiimide: Implication for prebiotic chemistry. *J. Am. Chem. Soc.* **2004**, *126*, 7772–7773.

(6) Tanzer, K.; Pelc, A.; Huber, S. E.; Czupyt, Z.; Denifl, S. Low energy electron attachment to cyanamide (NH_2CN). *J. Chem. Phys.* **2015**, *142*, 034301.

(7) Puzzarini, C.; Gambi, A. A theoretical study on CH_2N_2 isomers: structure and energetics. *Theor. Chem. Acc.* **2012**, *131*, 1135.

(8) Sleiman, C.; El Dib, G.; Rosi, M.; Skouteris, D.; Balucani, N.; Canosa, A. Low temperature kinetics and theoretical studies of the reaction CN + CH_3NH_2: a potential source of cyanamide and methyl cyanamide in the interstellar medium. *Phys. Chem. Chem. Phys.* **2018**, *20*, 5478–5489.

(9) Ramal-Olmedo, J. C.; Menor-Salván, C. A.; Miyoshi, A.; Fortenberry, R. C. Gas-phase molecular formation mechanisms of cyanamide (NH_2CN) and its tautomer carbodiimide (HNCNH) under Sgr B2(N) astrophysical conditions. *Astron. Astrophys.* **2023**, *672*, A49.

(10) Zhang, X.; Quan, D.; Li, R.; Esimbek, J.; Chen, L.-F.; Zhao, G.; Zhou, Y. Chemical models of adenine precursors cyanamide and carbodiimide in the interstellar medium. *Mon. Not. R. Astron. Soc.* **2023**, *521*, 1578–1589.

(11) Chataigner, I.; Pauzat, F.; Tasseau, O.; Ellinger, Y.; Guillemin, J.-C. Thermodynamical stability of [CNN and NCN] sequences as indication of most abundant structures in the ISM. *Astron. Astrophys.* **2024**, *689*, A118.

(12) Steinman, G.; Lemmon, R. M.; Calvin, M. Cyanamide: A possible key compound in chemical evolution. *Proc. Natl. Acad. Sci. U.S.A.* **1964**, *52*, 27–30.

(13) Parker, E. T.; Zhou, M.; Burton, A. S.; Glavin, D. P.; Dworkin, J. P.; Krishnamurthy, R.; Fernández, F. M.; Bada, J. L. A plausible simultaneous synthesis of amino acids and simple peptides on the primordial earth. *Angew. Chem., Int. Ed.* **2014**, *53*, 8132–8136.

(14) Ligterink, N. F. W.; El-Abd, S. J.; Brogan, C. L.; Hunter, T. R.; Remijan, A. J.; Garrod, R. T.; McGuire, B. M. The family of amide molecules toward NGC 6334I. *Astrophys. J.* **2020**, *901*, 37.

(15) Yi, R.; Tran, Q. P.; Ali, S.; Yoda, I.; Adam, Z. R.; Cleaves, H. J.; Fahrenbach, A. C. A continuous reaction network that produces RNA precursors. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 13267–13274.

(16) Lohrmann, R.; Orgel, L. E. Prebiotic synthesis: Phosphorylation in aqueous solution. *Science* **1968**, *161*, 64–66.

(17) Kilpatrick, M. L. A mechanism for the hydrolysis of cyanamide in acid solution. *J. Am. Chem. Soc.* **1947**, *69*, 40–46.

(18) Powner, M. W.; Gerland, B.; Sutherland, J. D. Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* **2009**, *459*, 239–242.

(19) Belloche, A.; Garrod, R. T.; Müller, H. S. P.; Menten, K. M.; Medvedev, I.; Thomas, J.; Kisiel, Z. Re-exploring molecular complexity with ALMA (ReMoCA): Interstellar detection of urea. *Astron. Astrophys.* **2019**, *628*, A10.

(20) Schimpl, A.; Lemmon, R. M.; Calvin, M. Cyanamide formation under primitive earth conditions. *Science* **1965**, *147*, 149–150.

(21) Fahrenbach, A. C.; Giurgiu, C.; Tam, C. P.; Li, L.; Hongo, Y.; Aono, M.; Szostak, J. W. Common and potentially prebiotic origin for precursors of nucleotide synthesis and activation. *J. Am. Chem. Soc.* **2017**, *139*, 8780–8783.

(22) Stairs, S.; Nikmal, A.; Bučar, D.-K.; Zheng, S.-L.; Szostak, J. W.; Powner, M. W. Divergent prebiotic synthesis of pyrimidine and 8-oxo-purine ribonucleotides. *Nat. Commun.* **2017**, *8*, 15270.

(23) Jiménez-Serra, I.; Martín-Pintado, J.; Rivilla, V. M.; Rodríguez-Almeida, L.; Alonso Alonso, E. R.; Zeng, S.; Cocinero, E. J.; Martín, S.; Requena-Torres, M.; Martín-Domenech, R.; et al. Toward the RNA-world in the interstellar medium—Detection of urea and search of 2-amino-oxazole and simple sugars. *Astrobiology* **2020**, *20*, 1048–1066.

(24) Turner, B. E. Detection of interstellar cyanoacetylene. *Astrophys. J.* **1971**, *163*, L35.

(25) Kaur, S.; Ohri, A.; Sharma, P. Could purines be formed from cyanamide and cyanoacetylene in a prebiotic earth environment? *ACS Omega* **2019**, *4*, 12771−12781.

(26) Ingar, A.-A.; Luke, R. W. A.; Hayter, B. R.; Sutherland, J. D. Synthesis of cytidine ribonucleotides by stepwise assembly of the heterocycle on a sugar phosphate. *ChemBioChem.* **2003**, *4*, 504−507.

(27) Manna, A.; Pal, S. Detection and chemical modeling of complex prebiotic molecule cyanamide in the hot molecular core G31.41 + 0.31. *ACS Earth Space Chem.* **2024**, *8*, 665−674.

(28) Kaiser, R.; Roessler, K. Theoretical and laboratory studies on the interaction of cosmic-ray particles with interstellar ices. I. Synthesis of polycyclic aromatic hydrocarbons by a cosmic-ray-induced multicenter mechanism. *Astrophys. J.* **1997**, *475*, 144.

(29) Yeghikyan, A. G. Irradiation of dust in molecular clouds. II. Doses produced by cosmic rays. *Astrophysics* **2011**, *54*, 87−99.

(30) Gibb, E. L.; Whittet, D. C. B.; Boogert, A. C. A.; Tielens, A. G. G. M. Interstellar ice: The infrared space observatory legacy. *Astrophys. J., Suppl. Ser.* **2004**, *151*, 35−73.

(31) Bøgelund, E. G.; McGuire, B. A.; Hogerheijde, M. R.; van Dishoeck, E. F.; Ligterink, N. F. W. Methylamine and other simple N-bearing species in the hot cores NGC 6334I MM1−3. *Astron. Astrophys.* **2019**, *624*, A82.

(32) Ohishi, M.; Suzuki, T.; Hirota, T.; Saito, M.; Kaifu, N. Detection of a new methylamine (CH_3NH_2) source: Candidate for future glycine surveys. *Publ. Astron. Soc. Jpn.* **2019**, *71*, 86.

(33) Nummelin, A.; Bergman, P.; Hjalmarson, Å.; Friberg, P.; Irvine, W. M.; Millar, T. J.; Ohishi, M.; Saito, S. A three-position spectral line survey of Sagittarius B2 between 218 and 263 GHz. II. Data analysis. *Astrophys. J., Suppl. Ser.* **2000**, *128*, 213.

(34) Förstel, M.; Bergantini, A.; Maksyutenko, P.; Góbi, S.; Kaiser, R. I. Formation of methylamine and ethylamine in extraterrestrial ices and their role as fundamental building blocks of proteinogenic α-amino acids. *Astrophys. J.* **2017**, *845*, 83.

(35) Belloche, A.; Müller, H. S. P.; Menten, K. M.; Schilke, P.; Comito, C. Complex organic molecules in the interstellar medium: IRAM 30 m line survey of Sagittarius B2(N) and (M). *Astron. Astrophys.* **2013**, *559*, A47.

(36) Aladro, R.; Martín, S.; Martín-Pintado, J.; Mauersberger, R.; Henkel, C.; Ocaña Flaquer, B.; Amo-Baladrón, M. A. A $\lambda = 1.3$ mm and 2 mm molecular line survey towards M 82. *Astron. Astrophys.* **2011**, *535*, A84.

(37) Maity, S.; Kaiser, R. I.; Jones, B. M. Formation of ketene (H_2CCO) in interstellar analogous methane (CH_4)-carbon monoxide (CO) ices: A combined FTIR and reflectron time-of-flight mass spectroscopic study. *Astrophys. J.* **2014**, *789*, 36.

(38) Jacox, M. E.; Milligan, D. E. The infrared spectrum of methylenimine. *J. Mol. Spectrosc.* **1975**, *56*, 333−356.

(39) Socrates, G. *Infrared and raman characteristic group frequencies: Tables and charts*; John Wiley & Sons, Ltd., 2004.

(40) Gerakines, P. A.; Moore, M. H.; Hudson, R. L. Ultraviolet photolysis and proton irradiation of astrophysical ice analogs containing hydrogen cyanide. *Icarus* **2004**, *170*, 202−213.

(41) Davies, M.; Jones, W. J. The infra-red spectrum and structure of cyanamide and dimethylcyanamide. *Trans. Faraday Soc.* **1958**, *54*, 1454−1463.

(42) Turner, A. M.; Kaiser, R. I. Exploiting photoionization reflectron time-of-flight mass spectrometry to explore molecular mass growth processes to complex organic molecules in interstellar and solar system ice analogs. *Acc. Chem. Res.* **2020**, *53*, 2791−2805.

(43) Wang, J.; Marks, J. H.; Turner, A. M.; Nikolayev, A. A.; Azyazov, V.; Mebel, A. M.; Kaiser, R. I. Mechanistical study on the formation of hydroxyacetone (CH_3COCH_2OH), methyl acetate (CH_3COOCH_3), and 3-hydroxypropanal ($HCOCH_2CH_2OH$) along with their enol tautomers (prop-1-ene-1,2-diol ($CH_3C(OH)CHOH$), prop-2-ene-1,2-diol ($CH_2C(OH)CH_2OH$), 1-methoxyethen-1-ol ($CH_3OC(OH)CH_2$) and prop-1-ene-1,3-diol ($HOCH_2CHCHOH$)) in interstellar ice analogs. *Phys. Chem. Chem. Phys.* **2023**, *25*, 936−953.

(44) Linstrom, P. J.; Mallard, W. G. NIST standard reference database number 69. In *NIST Chemistry WebBook*; 2013.

(45) Zhu, C.; Wang, H.; Medvedkov, I.; Marks, J.; Xu, M.; Yang, J.; Yang, T.; Pan, Y.; Kaiser, R. I. Exploitation of synchrotron radiation photoionization mass spectrometry in the analysis of complex organics in interstellar model ices. *J. Phys. Chem. Lett.* **2022**, *13*, 6875−6882.

(46) Marks, J. H.; Wang, J.; Kleimeier, N. F.; Turner, A. M.; Eckhardt, A. K.; Kaiser, R. I. Prebiotic synthesis and isomerization in interstellar analog ice: Glycinal, acetamide, and their enol tautomers. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202218645.

(47) Wang, J.; Nikolayev, A. A.; Marks, J. H.; Turner, A. M.; Chandra, S.; Kleimeier, N. F.; Young, L. A.; Mebel, A. M.; Kaiser, R. I. Interstellar formation of nitrogen heteroaromatics [indole, C_8H_7N; pyrrole, C_4H_5N; aniline, $C_6H_5NH_2$]: Key precursors to amino acids and nucleobases. *J. Am. Chem. Soc.* **2024**, *146*, 28437−28447.

(48) Ferrari, B. C.; Slavicinska, K.; Bennett, C. J. Role of suprathermal chemistry on the evolution of carbon oxides and organics within interstellar and cometary ices. *Acc. Chem. Res.* **2021**, *54*, 1067−1079.

(49) Zhu, C.; Frigge, R.; Turner, A. M.; Abplanalp, M. J.; Sun, B.-J.; Chen, Y.-L.; Chang, A. H.; Kaiser, R. I. A vacuum ultraviolet photoionization study on the formation of methanimine (CH_2NH) and ethylenediamine ($NH_2CH_2CH_2NH_2$) in low temperature interstellar model ices exposed to ionizing radiation. *Phys. Chem. Chem. Phys.* **2019**, *21*, 1952−1962.

(50) Marks, J. H.; Wang, J.; Fortenberry, R. C.; Kaiser, R. I. Preparation of methanediamine ($CH_2(NH_2)_2$—A precursor to nucleobases in the interstellar medium. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119*, No. e2217329119.

(51) Ruscic, B.; Bross, H. *Active Thermochemical Tables (ATcT)*; values based on ver. 1.220 of the Thermochemical Network (accessed 9 January, 2026); https://atct.anl.gov/Thermochemical%20Data/version%201.220/index.php.

(52) Seasholtz, M. B.; Thompson, T. B.; Rondan, N. G. Energetics of imino compounds calculated at the G2 level of theory for deriving benson's group contributions. *J. Phys. Chem.* **1995**, *99*, 17838−17843.

(53) Meads, R. F.; Maclagan, R. G. A. R.; Phillips, L. F. Kinetics, energetics, and dynamics of the reactions of cyanogen with ammonia and ammonia-d_3. *J. Phys. Chem.* **1993**, *97*, 3257−3265.

(54) Wang, J.; Zhang, C.; Marks, J. H.; Evseev, M. M.; Kuznetsov, O. V.; Antonov, I. O.; Kaiser, R. I. Interstellar formation of lactaldehyde, a key intermediate in the methylglyoxal pathway. *Nat. Commun.* **2024**, *15*, 10189.

(55) Zheng, W.; Kaiser, R. I. Formation of hydroxylamine (NH_2OH) in electron-irradiated ammonia-water ices. *J. Phys. Chem. A* **2010**, *114*, 5251−5255.

(56) Orgel, L. E. Prebiotic chemistry and the origin of the RNA world. *Crit. Rev. Biochem. Mol. Biol.* **2004**, *39*, 99−123.

(57) Crovisier, J.; Bockelée-Morvan, D.; Colom, P.; Biver, N.; Despois, D.; Lis, D. C.; Team for target-of-opportunity radio observations of comet. The composition of ices in comet C/1995 O1 (Hale-Bopp) from radio spectroscopy. *Astron. Astrophys.* **2004**, *418*, 1141−1157.