



Preparation of methanediimine ($\text{CH}_2(\text{NH}_2)_2$)—A precursor to nucleobases in the interstellar medium

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Although methanediimine ($\text{CH}_2(\text{NH}_2)_2$) has historically been the subject of theoretical scrutiny, it has never been isolated to date. Here, we report the preparation of methanediimine ($\text{CH}_2(\text{NH}_2)_2$)—the simplest diamine. Low-temperature interstellar analog ices composed of ammonia and methylamine were exposed to energetic electrons which act as proxies for secondary electrons produced in the track of galactic cosmic rays. These experimental conditions, which simulate the conditions within cold molecular clouds, result in radical formation and initiate aminomethyl ($\dot{\text{C}}\text{H}_2\text{NH}_2$) and amino (NH_2) radical chemistry. Exploiting tunable photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) to make isomer-specific assignments, methanediimine was identified in the gas phase upon sublimation, while its isomer methylhydrazine (CH_3NHNH_2) was not observed. The molecular formula was confirmed to be CH_6N_2 through the use of isotopically labeled reactants. Methanediimine is the simplest molecule to contain the NCN moiety and could be a vital intermediate in the abiotic formation of heterocyclic and aromatic systems such as nucleobases, which all contain the NCN moiety.

interstellar ice | astrochemistry | ionization potentials | radical reactions | reaction mechanism

Nitrogen represents a central element in contemporary biomolecules such as in amino sugars, amino acids, and nucleobases (1). Nitrogen is also incorporated into nearly one-third of some 300 molecules identified in the interstellar medium (ISM) and around circumstellar envelopes (2). However, most nitrogen-containing molecules in deep space carry exclusively nitrile moieties ($\text{RC}\equiv\text{N}$) which are weakly electrophilic in contrast to nucleophilic amines ($\text{RNR}'\text{R}''$), imines ($\text{R}=\text{NR}'$), and amides (RCONHR') needed for life as we know it (2–4). So far, only two closed-shell molecules have been detected astronomically which contain more than one nitrogen-carrying moiety other than nitrile: urea ($\text{CO}(\text{NH}_2)_2$) (5, 6) and carbodiimide ($\text{HN}=\text{C}=\text{NH}$) (7). An understanding of the origin and fundamental chemistry of the NCN moiety in deep space is central to the RNA world hypothesis for the origin of life (8–10) because all nucleobases found in contemporary RNA and DNA contain this very NCN moiety (Scheme 1). Here, the abiotic synthesis and gas-phase detection of methanediimine (**1**, $\text{CH}_2(\text{NH}_2)_2$) are reported as a prototype system for unraveling the origin and incorporation of the NCN moiety into complex organic molecules of potential astrobiological importance.

The bulk of prior scholarship has employed methanediimine (**1**) as a model compound to study systems containing the R–X–C–Y backbone, where X has a lone pair and Y represents any element more electronegative than carbon such as R–NHCH₂NH₂. Molecules carrying this moiety reveal a preference for the gauche configuration resulting from internal rotation along both the X–C and C–Y bonds in what is known as the generalized anomeric effect (11–19). Negative hyperconjugation, where electron density is donated from the non-bonding pair of nitrogen to the CH antibonding (σ^*) orbital, contributes to this effect and has a particularly strong influence on the conformational structure of methanediimine (**1**) (11, 13, 14, 16). Since the donation increases antibonding character, this tends to weaken the carbon–hydrogen bonds while stabilizing radicals formed by elimination of atomic hydrogen from carbon (11, 20–23). Substitution of two hydrogen atoms in methane (CH_4) with the amino group ($-\text{NH}_2$) stabilizes the diaminomethyl radical ($\dot{\text{C}}\text{H}(\text{NH}_2)_2$) by 43 kJ mol^{−1} which allows for unusual radical reactions like [1] to occur more readily (Scheme 2) (20, 23). The amines also stabilize the singlet state of diaminocarbene ($\dot{\text{C}}(\text{NH}_2)_2$) by 202 kJ mol^{−1} while increasing the energy of the triplet ($\text{C}(\text{NH}_2)_2$) by 65 kJ mol^{−1}; this results in a singlet ground state which can participate in recombination [2] or spin-allowed carbene insertion [3] (24).

Unlike methanediimine (**1**), the hydrochloride salt of methanediimine has been employed in organic preparative solution chemistry as a reactant for more than a century (25). Upon neutralization of the salt, methanediimine (**1**) is presumed to exist as a highly

Significance

Methanediimine ($\text{CH}_2(\text{NH}_2)_2$) represents a target of computational study, and while its dihydrochloride salt is used in synthetic preparations, the free diamine exists only as a transient in solution. Here, we prepare and identify methanediimine via energetic processing of low-temperature ices followed by sublimation into the gas phase. This finding shows that interstellar ices subjected to ionizing radiation, such as galactic cosmic rays and ultraviolet light, exhibit unique chemistry in which highly unstable species are produced and preserved. Both ammonia and methane are abundant in interstellar ices where radical reactions can readily produce methanediimine. Its subsequent sublimation into the gas phase in star-forming regions indicates that this species is a candidate for detection by radio telescopes.

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The authors declare no competing interest.

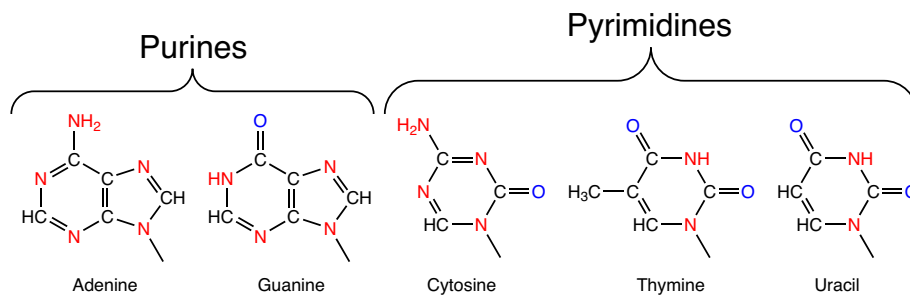
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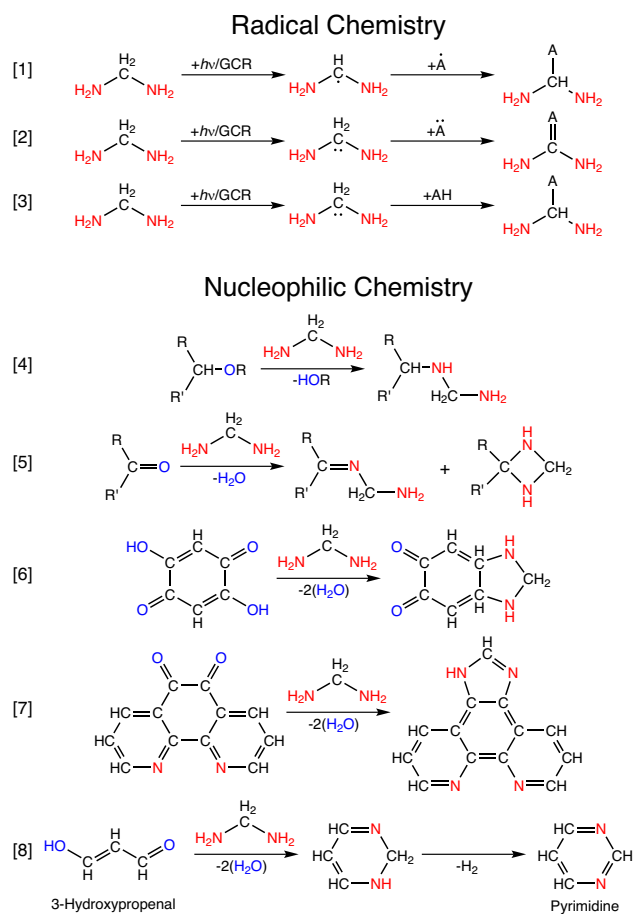


Scheme 1. Nucleotides found in RNA and DNA, all of which contain the NCN moiety exhibited by methanediamine (**1**, $\text{CH}_2(\text{NH}_2)_2$).

reactive intermediate. The nucleophilic nature of amines allows this transient to participate in substitution reactions [4]–[8] (26–29). This can take the form of substitution for an alcohol or ether in [4] (26) or substitution of an aldehyde (RCHO) or ketone (RC(O)R') via [5] by an imine (29) or a diazaspirane, respectively (30). Its bifunctional nature allows for participation in ring-closure reactions accompanied by aromatization as demonstrated in [6] (27) and [7] (28); these show that both amine and imine bonds can form resulting in nitrogen-substituted polycyclic aromatic hydrocarbons (28). The potential formation of aromatic heterocycles from methanediamine (**1**) via nucleophilic chemistry may provide a route to the abiotic formation of nucleobases in the ISM. Pyrimidine ($\alpha\text{-NCHNCHCHCH}$) forms the core structure of cytosine, thymine, and uracil (Scheme 1). Given the recent observation of 3-hydroxypropenal (OCHCHCHOH) toward the protostar IRAS 16293-2422 (28), nucleophilic substitution with

methanediamine (**1**) in reaction [8] may provide a facile route to the abiotic formation of pyrimidine via $\text{S}_{\text{N}}2$ nucleophilic substitution of amines onto aldehydes which has been demonstrated to operate in low-temperature acidic ices (31, 32).

Here, by exploiting isomer-selective photoionization combined with reflectron time-of-flight mass spectrometry (PI-ReToF-MS), the preparation and gas-phase detection of methanediamine (**1**) is reported. Interstellar analog ices of methylamine (CH_3NH_2) and ammonia (NH_3) were exposed to proxies of galactic cosmic rays (GCRs) in the form of energetic electrons. Reactions which may form both methanediamine (**1**, $\text{CH}_2(\text{NH}_2)_2$) and methylhydrazine (**2**, CH_3NHNH_2) in this simulated interstellar environment were investigated (Fig. 1). Isotopic substitution experiments along with tunable vacuum ultraviolet light (VUV) photoionization at discrete energies reveal unambiguously the selective preparation of methanediamine (**1**) via a carbon–nitrogen bond coupling through the radical–radical reaction of aminomethyl (**A**, $\dot{\text{C}}\text{H}_2\text{NH}_2$) and amino (**C**, NH_2) radicals thus providing a facile to the previously elusive methanediamine (**1**).



Scheme 2. Representative reactions of methanediamine ($\text{CH}_2(\text{NH}_2)_2$) including radical–radical recombination [1]–[3] initiated by energetic photons ($h\nu$) or GCRs and nucleophilic substitution [4]–[8].

Results

PI-ReToF-MS data collected in these experiments are shown as a function of temperature in Fig. 2. In these experiments, single-photon ionization with VUV laser light is employed to ionize molecules as they sublime from the ice after the exposure to GCR proxies (*SI Appendix*). This is a fragmentation-free or “soft” ionization method, particularly in comparison with electron impact ionization. By using tunable VUV light, the photon energy can be selected to selectively ionize and hence to discriminate isomers with different ionization energy as molecules cannot be ionized when the photon energy is less than their adiabatic ionization energy. Furthermore, isotopic labeling was used to verify the molecular formula, and in some cases the formation mechanism, of observed molecules. By exploiting these techniques, PI-ReToF-MS experiments separate molecules by mass, sublimation temperature, and ionization energy to confidently assign the identity of reaction products in the analog ice: methanediamine (**1**).

The adiabatic ionization energy is unknown for methanediamine (**1**) and has been measured with substantial error for methylhydrazine (**2**) (33). Therefore, adiabatic ionization energies were computed for all possible conformers of both methanediamine (**1**) and methylhydrazine (**2**) with high-quality CCSD(T) complete basis set computations expected to have a maximum error of ± 0.05 eV (*SI Appendix*, Table S1) (34). Accounting for all conformers, the range of adiabatic ionization energies of methanediamine (**1**) is 8.54–8.75 eV and 7.44–7.67 eV for methylhydrazine (**2**). Photoionization with 9.20 eV photons is therefore capable of ionizing both of these molecules, while 8.00 eV photons can only ionize methylhydrazine (**2**). Collected ion counts at a

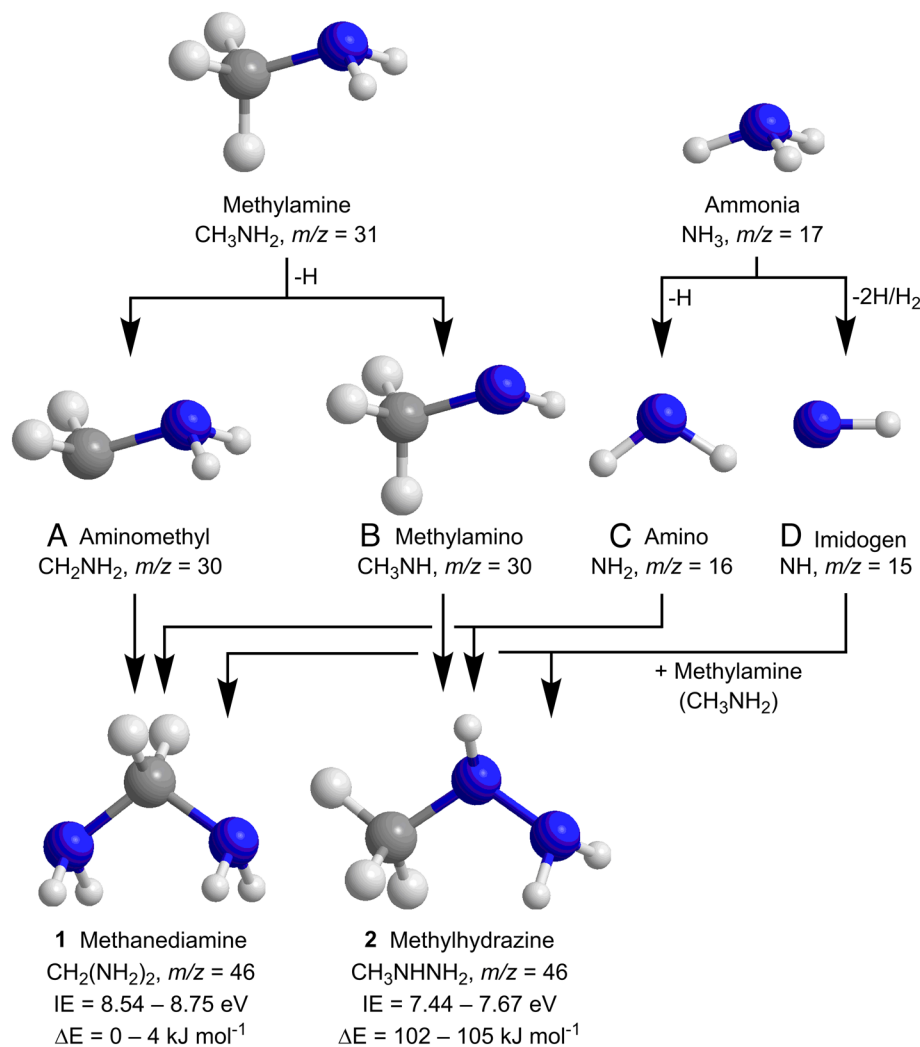


Fig. 1. Reaction scheme for radical reactions of ammonia (NH_3) and methylamine (CH_3NH_2) to form methanediaamine (**1**, $\text{CH}_2(\text{NH}_2)_2$) and methylhydrazine (**2**, CH_3NHNH_2) via radical-radical recombination or insertion of imidogen into methylamine. Computed relative (ΔE) and adiabatic ionization energies (IE) are presented as ranges that include all conformers.

mass-to-charge ratio (m/z) = 46 (CH_6N_2) are reported as a function of temperature in Fig. 3A. Photoionization at 9.20 eV produced a small peak at 120 K and a larger sublimation event at 152 K. Neither of these events is observed at 8.00 eV. This reveals that the molecule(s) responsible for these peaks must have an adiabatic ionization energy between 8.00 and 9.20 eV. Since we can eliminate the possibility of the presence of methylhydrazine (**2**), this peak must therefore be linked to methanediaamine (**1**).

To provide further evidence in the observation of this molecule, isotopic substitution experiments were carried out to ensure that the observed compound does, in fact, have the molecular formula (CH_6N_2). In detail, isotopically labeled ammonia and methylamine were used to verify the formula of the ions detected in Fig. 3A. The smaller peak at 120 K occurs at the same temperature as a major peak found at $m/z = 45$; this sublimation event is connected to dimethylamine which is present as a trace contaminant in the methylamine sample and observed here as the naturally occurring dimethylamine- ^{13}C . If it is assumed that carbon can make up to four bonds, nitrogen three, and hydrogen one, then the only possible molecular formulas for $m/z = 46$ are H_4N_3 and CH_6N_2 . When ^{15}N -ammonia–methylamine ice was examined, the peak at 152 K and $m/z = 46$ was (Fig. 3A) found to shift to $m/z = 47$ (Fig. 3B). From this isotopic shift, it is concluded that there must be at least one nitrogen present in the observed molecule which must originate in the ammonia component of the ice. Furthermore, this is in agreement with the reaction shown in Fig. 1

which demonstrates the incorporation of one nitrogen from ammonia via the amino radical (**C**, NH_2). When ammonia- d_3 -methylamine- d_5 ice was examined, the peak at 152 K was found to shift from $m/z = 46$ to 52 (Fig. 3C). This can only happen if the molecule being ionized contains six or more hydrogen atoms, which excludes the possibility that H_4N_3 is being observed and confirms that the correct molecular formula is CH_6N_2 . It was also noted that the peak of the temperature programmed desorption (TPD) profiles observed in this deuterated ice shifts from 152 K to 160 K. This is likely due to an increase of molecular weight by 6 amu resulting in an elevated sublimation temperature (35).

Discussion

Since the ionization energy and the molecular formula match only those of methanediaamine (**1**), this constitutes the conclusive observation of this molecule. No signal is observed at $m/z = 46$ with a photon energy of 8.00 eV. Therefore, if methylhydrazine (**2**, IE = 7.44–7.67 eV) is produced, it is not present in detectable quantities. If the reaction proceeds by radical–radical recombination, this would suggest a lack of formation of the methylamino radical (**B**, CH_3NH). Prior experiments, in which pure methylamine ice was irradiated under similar conditions as the present experiment, did not observe reaction products from recombination of the methylamino radical, i.e., 1,2-dimethylhydrazine ($\text{CH}_3\text{NHNHCH}_3$) or *N*-methylmethanediaamine ($\text{CH}_3\text{NHCH}_2\text{NH}_2$) (36). The only

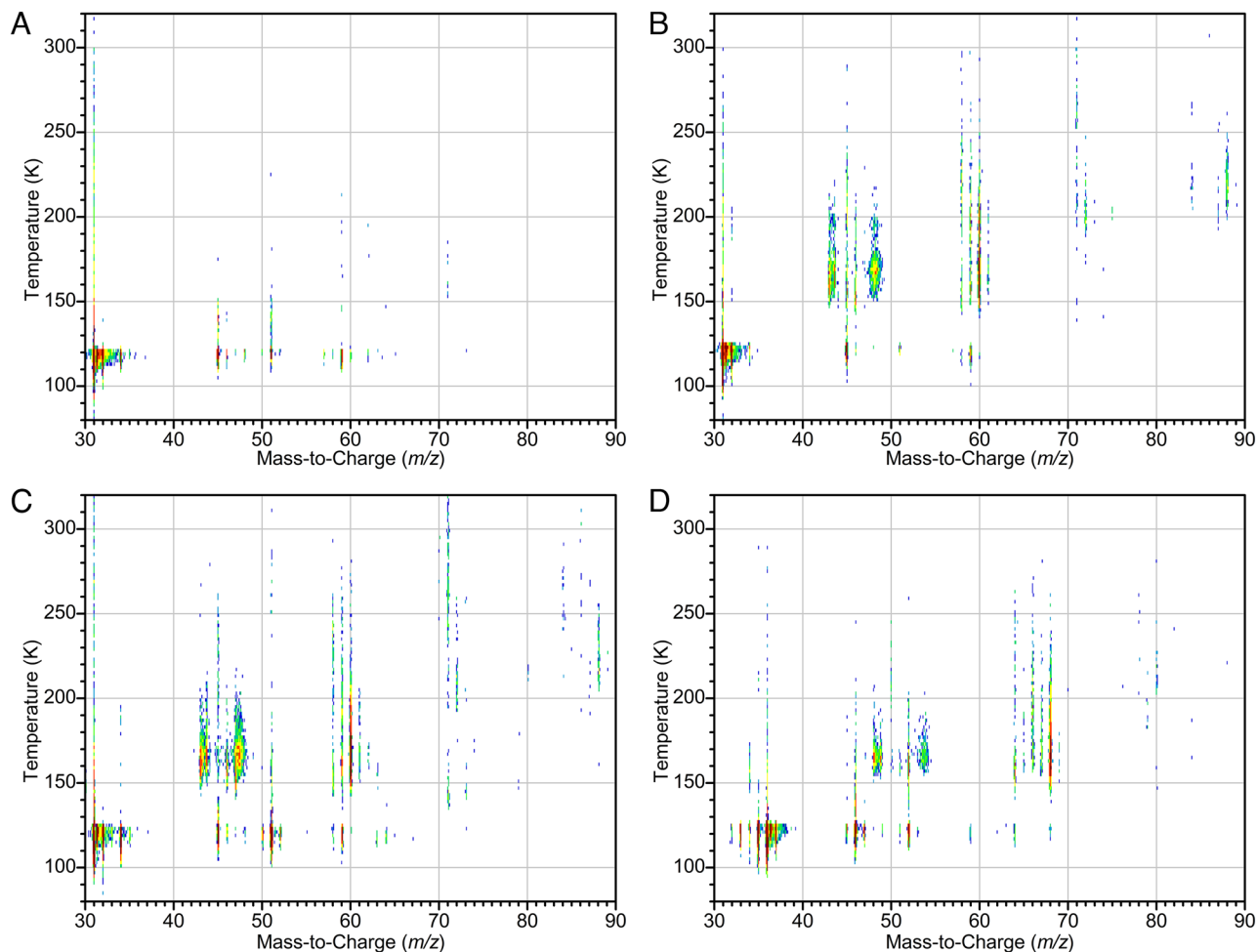
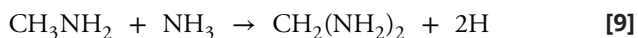


Fig. 2. Photoionization reflectron time-of-flight (PI-ReToF) mass spectra measured during TPD plotted as a function of temperature. Experiments were conducted with (A) ammonia–methylamine ice without irradiation, and with irradiation of 0.21 ± 0.02 eV molecule⁻¹ for ammonia and 0.38 ± 0.04 eV molecule⁻¹ for methylamine in (B) ammonia–methylamine ices, (C) ¹⁵N-ammonia–methylamine ice, and (D) ammonia-d₃-methylamine-d₅ ice.

reaction product identified was ethylenediamine (NH₂CH₂CH₂NH₂), which originates from radical–radical recombination of aminomethyl radicals (**B**, $\dot{\text{C}}\text{H}_2\text{NH}_2$) (36). Since solely reaction products from aminomethyl (**B**) have been observed in pure methylamine and mixed ammonia–methylamine ices, the reaction mechanism responsible likely proceeds by radical–radical recombination (Fig. 1).

The process to form methanediamine (**1**) via radical–radical reaction [9] is endoergic by 488 ± 3 kJ mol⁻¹; this energy can be imparted by the impinging electrons. The distance between the ice surface and the ionization region of 2.0 ± 0.5 mm along with the range of sublimation temperatures implies that methanediamine (**1**) has to “live” at least an average of 7.6 ± 1.9 μs. However, lifetimes of the ions must be at least 26.88 ± 0.07 μs to be detected. Note that the “thermal” decomposition of methanediamine (**1**) to methanimine (H₂CNH) plus ammonia (NH₃) [10] is calculated to be endoergic by 46 ± 3 kJ mol⁻¹, also supporting its gas-phase stability.



Previous experimental investigations in ices have shown that isolectronic molecules methanediol (37) (CH₂(OH)₂) and aminomethanol (38) (NH₂CH₂OH) form in irradiated ices and survive into the gas phase and upon photoionization. The

minimum energy conformers (Scheme 3) (37, 38) of these molecules demonstrate significant variation in bond angles. Methanediamine (**1**) exhibits an NCN angle of 119.0°, while the NCO angle in aminomethanol is the smallest at 110.6°. Both of which are larger than the ideal 109.5° tetrahedral angle for the central carbon atom. Such behavior indicates that electrostatic repulsion from the non-bonding electron pairs along with steric repulsion is present in all three molecules but is more significant for the NH₂ than for the OH moiety. While the CH, NH, and OH bond lengths vary little between these molecules, in aminomethanol the C–N single bond is 3 pm shorter, but the C–O bond is 3 pm longer compared to methanediamine (**1**) and methanediol. These variations in bond lengths are likely the result of enhanced transfer of electron density from –NH₂ to –OH in aminomethanol upon increasing electronegativity from nitrogen to oxygen. The calculations employed here improve on prior efforts (11, 13, 14) to study methanediamine (**1**) computationally. While the gauche configuration was previously expected to be more stable, higher-level ab initio calculations employed herein indicate the trans configuration across both C–N bonds to be most stable. The discrepancy in relative energies between calculations reported here and prior studies demonstrate the need for the testing and further development of computational methods. The existence of the previously “hypothetical” molecules in Scheme 3 reveals an opportunity for future experimental measurements and detection utilizing the PI-ReToF-MS approach which would aid

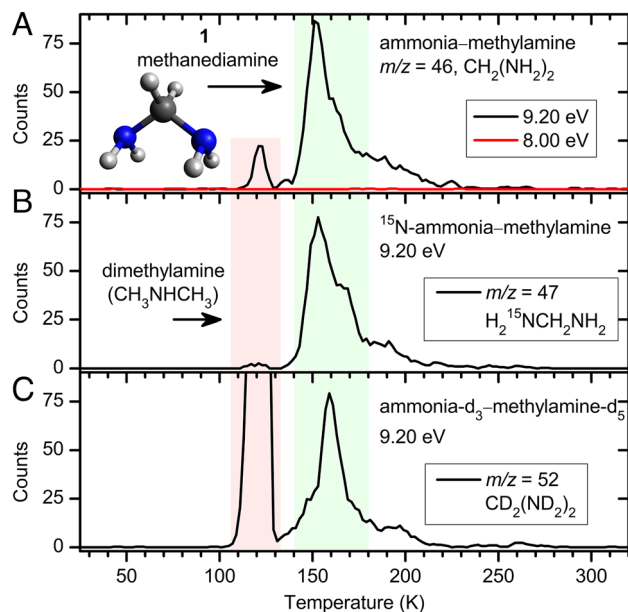


Fig. 3. TPD profiles measured during photoionization reflectron time-of-flight (PI-ReToF) mass spectra measurement of ammonia-methylamine ices. Ices formed with natural isotopic abundance (A) were examined with photon energy of 9.20 and 8.00 eV and at 9.20 eV with isotopic labeled ices (B) ^{15}N -ammonia-methylamine, and (C) ammonia- d_3 -methylamine- d_5 .

in benchmarking the accuracy of quantum chemical calculations and contribute to the development of more accurate and predictive quantum chemical methods.

Conclusion

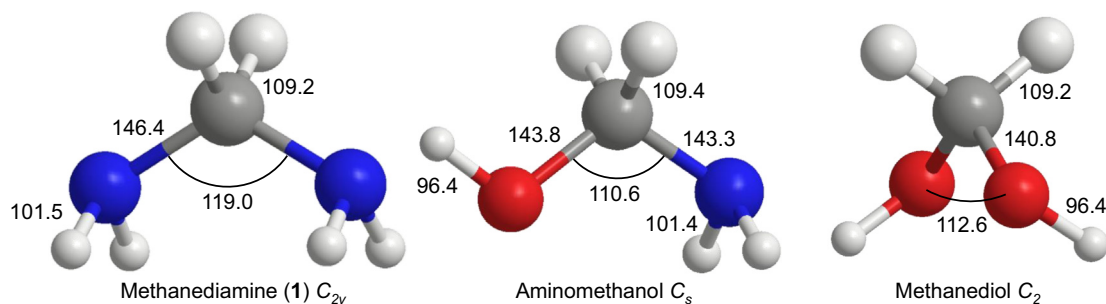
These experiments revealed that methanediimine (**1**) can be produced in interstellar ices and is able to sublime intact not only in the laboratory but also in star-forming regions such as Sagittarius B2 (Sgr B2) where its signal may be explored by radio telescopes. Rotational spectroscopy of methanediimine (**1**) in the millimeter and sub-millimeter wave regions would be necessary for the identification of this previously elusive molecule in deep space and should be pursued, and dipole moments are reported in *SI Appendix, Table S1* to aid in this search. Of the necessary reactants, ammonia is abundant in interstellar ices at fractions of regularly above 15% relative to water as determined in, e.g., the c2d Spitzer survey (39). Methylamine has been detected in the gas phase toward the Sgr B2(N) molecular cloud on the order of 10^{-7} relative to molecular hydrogen (40, 41). While much less abundant than ammonia, methylamine has been shown to form in ices from ammonia and methane (42), and methane is nearly as prevalent as ammonia in interstellar ices being found with abundances of

up to 13% observed toward EC 92 (43). Therefore, the synthesis and sublimation of methanediimine (**1**) reported here along with the prior detection in interstellar space of its precursors indicate that its preparation in interstellar ices is plausible with ring-closure reactions (Scheme 2) suggesting that methanediimine (**1**) can play a vital role in the abiotic formation of heterocycles and nucleobases in particular.

Methods and Materials

Experimental. All experiments were carried out at the W. M. Keck Research Laboratory in Astrochemistry (44–46). The apparatus consists of a hydrocarbon-free stainless steel ultra-high vacuum chamber with pressures maintained at a few 10^{-11} Torr (47). A closed cycle helium refrigerator (Sumitomo Heavy Industries, RDK-415E) is used to maintain a polished silver wafer (12.6×15.1 mm) at 5.0 ± 0.2 K. Ices were prepared by passing ammonia (ammonia, Matheson, 99.99%; ^{15}N -ammonia, Sigma-Aldrich, 98% ^{15}N ; ammonia- d_3 , Sigma-Aldrich, 99% D) at a partial pressure of 1×10^{-8} Torr and methylamine (methylamine, 99.5% Matheson TriGas; methylamine- d_5 , Cambridge Isotope Laboratories, 98% D) at a partial pressure of 1.5×10^{-8} through separate 10 mm diameter glass capillary arrays. Prior to deposition of deuterated gases, all tubing was filled with deuterated water vapor (D_2O) which was also flowed through the capillary arrays to prevent isotope exchange from reducing % D purity. The ice thickness was determined to be 720 ± 30 nm by monitoring the ice deposition with a helium–neon laser (CVI Melles-Griot, 25-LHP-230, 632.8 nm) at a 4° angle of incidence and measuring variations in reflected power due to thin film interference by the ice (48). Ice index of refraction was approximated to be 1.35, by the average of the indexes of refraction of the two components, 1.33 for ammonia and 1.38 for methylamine in amorphous ices at 18 K (49). Fourier transform infrared (FTIR) spectra (Thermo Electron, Nicolet 6700) were measured in the range 6000 to 500 cm^{-1} after ice deposition at 5.0 ± 0.2 K and used to calculate the relative abundance of the two components (*SI Appendix, Figs. S1–S3* and *Table S2*). Relative concentrations of ammonia and methylamine in ices (*SI Appendix, Table S3*) were determined using integrated infrared absorptions of ν_2 of ammonia (1070 cm^{-1} , $2.1 \times 10^{-17} \text{ cm molecule}^{-1}$) and ν_6 (1420 cm^{-1} , $1.8 \times 10^{-19} \text{ cm molecule}^{-1}$), combined ν_5 and ν_{12} (1433 to 1520 cm^{-1} , $1.73 \times 10^{-18} \text{ cm molecule}^{-1}$), and the CH stretching region with ν_3 , ν_2 , and ν_{11} (2727 to 3015 cm^{-1} , $2.3 \times 10^{-17} \text{ cm molecule}^{-1}$) for methylamine (49, 50).

After deposition, ices were irradiated with 5 keV electrons (SPECS, EQ PU-22) with electron currents and times as listed in *SI Appendix, Table S3* over an area 160 mm^2 at a 70° angle of incidence for an effective dose of $0.20 \pm 0.02 \text{ eV molecule}^{-1}$ for



Scheme 3. CCSD(T)/aug-cc-pVTZ optimized structures of methanediimine (**1**, $\text{CH}_2(\text{NH}_2)_2$), methanolamine ($\text{H}_2\text{NCH}_2\text{OH}$), and methanediol ($\text{CH}_2(\text{OH})_2$) with bond lengths (pm) and selected angles (degrees).

ammonia and 0.37 ± 0.04 eV molecule⁻¹ for methylamine in ices without isotopic labeling. A penetration depth of 348 ± 10 nm was determined for ices without isotopic labeling with the aid of Monte Carlo simulations conducted with CASINO 2.42 (51) using parameters detailed in *SI Appendix, Table S4*. For the purposes of the simulation, the average density of the ice components, 0.680 g cm⁻³ at 18 K for ammonia and 0.732 g cm⁻³ for methylamine at 18 K, was used as an approximation for the unknown density of the mixed ices (49). Variations in density due to isotopic labeling were taken into account. The average penetration depth (288 to 358 nm, *SI Appendix, Table S4*) is significantly less than the ice thickness (730 ± 30 nm) by design to prevent energetic electron initiated interactions between the ice and the silver substrate. Energetic doses reported in *SI Appendix, Table S3* represent the calculated total absorbed dose averaged over all molecules between the ice surface and the average penetration depth. FTIR spectra were measured before, during, and after irradiation to verify changes in the spectrum due to reactions and to determine new functional groups and smaller species produced.

Photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) utilized in this research has been discussed in detail previously (44). Ices were heated to 320 K with TPD at a rate of 1 K min⁻¹. During TPD, pulsed 30 Hz coherent VUV light was passed 2 mm above the surface of the ice to photoionize subliming molecules. VUV light was produced via several resonant four-wave mixing ($\omega_{\text{VUV}} = 2\omega_1 \pm \omega_2$) schemes detailed in *SI Appendix, Table S5*. After generation of the selected ω_1 and ω_2 , the lasers were made collinear and focused (Thorlabs, LA5479, $f = 300$ mm) into a jet of rare gas in the VUV generation vacuum chamber. Coherent VUV light exiting this chamber was separated from ω_1 and ω_2 by passing the collinear beams through an off-axis lithium fluoride (LiF) biconvex lens (Korth Kristalle, $R_1 = R_2 = 131.22$ mm) which collimates the light, imparts an angular separation between the three wavelengths, and directs the VUV light through an aperture to the ionization region. VUV intensity is measured by a Faraday cup on the opposite side of the ionization region, and ion counts were corrected for variations in VUV power based on the average power recorded during each mass spectrum accumulation. Ions formed are mass-analyzed in a reflectron time-of-flight mass spectrometer (ReToF-MS; Jordan TOF Products) and detected with a microchannel plate (MCP) detector (Jordan TOF

Products). MCP signal was amplified (Ortec, 9305) before discrimination and amplification to 4 V (Advanced Research Instruments Corp., F100-TD) and recorded by a multichannel scaler (FAST ComTec, MCS6A) interfaced to a personal computer. Ion arrival times were recorded to 3.2 ns accuracy, mass spectra were repeated at a rate of 30 Hz, and new mass spectra were accumulated every 2 minutes during TPD until the temperature of the sample reached 320 K.

Computational. The optimized geometries and harmonic zero-point vibrational energies (ZPVEs) are determined with coupled cluster theory at the singles, doubles, and perturbative triples level [CCSD(T)] (52) along with the aug-cc-pVTZ basis set (53). The CCSD(T)/aug-cc-pVQZ single point energies at these same geometries are then extrapolated to the complete basis set limit via a two-point formula (54). The closed-shell neutral molecules employ restricted Hartree–Fock reference wavefunctions, while the open-shell doublet radical cations employ restricted open-shell Hartree–Fock references. The relative energies are computed as adiabatic differences between the energies plus corresponding ZPVEs of the optimized neutrals and the C_{2v} CH₂(NH₂)₂ energy + ZPVE. The adiabatic ionization potentials are computed as the adiabatic energy + ZPVE differences between the neutrals and corresponding cations. All computations utilize the MOLPRO 2019.2 quantum chemistry program (55–57).

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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