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Authors: André Kristopher Eckhardt and Peter Richard Schreiner

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Spectroscopic Evidence for Aminomethylene ($H–\ddot{C}–NH_2$) – The Simplest Amino Carbene

André K. Eckhardt and Peter R. Schreiner*

Dedicated to Prof. A. J. Arduengo, III, on the occasion of his retirement and for his extraordinary work on amino carbenes

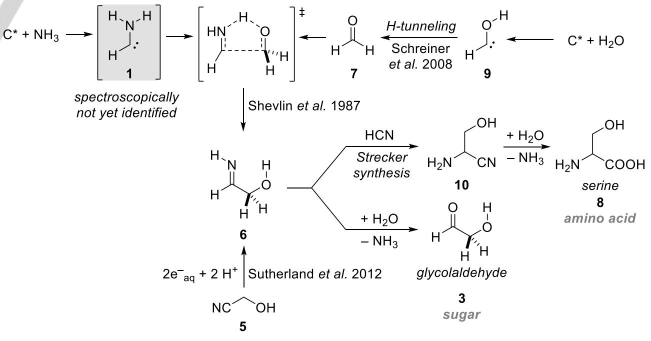
Abstract: Although N-heterocyclic carbenes have been well-studied, the simplest aminocarbene, aminomethylene $H–\ddot{C}–NH_2$, has not been spectroscopically identified yet. Here we report the gas phase preparation of aminomethylene by high-vacuum flash pyrolysis of cyclopropylamine and subsequent trapping of the pyrolysate in an inert argon matrix at 12 K. Aminomethylene was characterized by matching matrix IR and UV/Vis spectroscopic data with *ab initio* coupled cluster computations. After UV irradiation of the matrix aminomethylene rearranges to its isomer methanimine (formaldimine) $H_2C{=}NH$. Based on our experimental results and computations aminomethylene has a singlet ground state with a reaction barrier of almost 46 kcal mol^{-1} to methanimine so that H-tunneling to formaldimine is excluded.

Carbenes are neutral compounds with a divalent carbon atom whose valence shell contains only six instead of eight electrons, thereby violating the octet rule. They have turned from fleetingly existent laboratory curiosities into commonplace catalysts in organic chemistry.[1] Acyclic and N-heterocyclic carbenes (NHCs) have found multiple applications as metal ligands in, e.g., metathesis catalysis or as organocatalysts.[2] Although many NHCs have now been studied well, parent aminomethylene $H–\ddot{C}–NH_2$ (**1**, aminocarbene) has only been characterized by neutralization-reionization mass spectrometry but not yet spectroscopically.[3]

Aminomethylene has been postulated as an intermediate in the reaction of excited state atomic carbon atoms with ammonia.[4] After aqueous workup these conditions yield various amino acids including glycine, alanine, and aspartic acid. Methanimine $H_2C{=}NH$ (**2**, formaldimine), formally a tautomer of **1**, might also be an intermediate in such reactions. Despite its high reactivity several isotopologues of **2** have been spectroscopically well characterized by microwave,[5] matrix isolation and gas phase infrared[6] (IR) as well as electronic absorption spectroscopy.[7] All of its nine fundamental vibrational transitions have been observed in high-resolution gas phase experiments using laser Stark and Fourier-transform (FT) IR spectroscopy.[8] Methanimine has also been detected in interstellar media in 1973[9] and is an intermediate in Strecker amino acid synthesis.[10] Therefore, it has been suggested to be an interstellar precursor for the simplest amino acid glycine.[11]

Sutherland *et al.* showed in 2012 that the simplest sugars glycolaldehyde (**3**) and glyceraldehyde (**4**) may form through a photochemically induced disproportionation of HCN catalyzed by copper cyanide complexes;[12] subsequently, the sugars are sequestered as isocyanate adducts. A key step in this photoredox chemistry is the reduction of the cyanohydrin glycolonitrile (**5**) into glycolaldehyde imine (**6**, ethanol imine), which hydrolyzes to **3** (Scheme 1). In the reactions of excited state atomic carbon atoms with ammonia and water, or formaldehyde (**7**), Shevlin *et al.* obtained serine (**8**) in addition to glycine, alanine, and aspartic acid.[4d] They proposed that **7** forms in the first step of the reaction of excited state carbon atoms with water through intermediacy of hydroxymethylene (**9**, $H–\ddot{C}–OH$), which was spectroscopically identified only in 2008.[13] Subsequent reaction of putative **1** with **7**, should also give **6**. At high HCN concentrations **6** reacts to serine nitrile (**10**) and **8** after aqueous workup. Intermediate imine **6** unites the formation pathways of prebiotic sugars and amino acids derived from analogous building blocks under similar conditions.[12, 14]

The critical unknown structure in this reaction network is **1**, which undergoes a formal carbonyl ene reaction with **7**. We showed recently in a matrix isolation study at cryogenic temperatures that the analogous carbonyl ene reaction of **7** with methylhydroxycarbene[13b, 15] $H_3C–\ddot{C}–OH$ (**11**), the methyl derivative of **9**, are extremely facile owing to their very low reaction barriers (ca. 1 kcal mol^{-1}).[16] Isolating and characterizing **1** hence is central for supporting this mechanistic scenario. The key feature of **1** is that it acts as a nucleophilic ene-component in marked contrast to electrophilic **2**.



Scheme 1. Formation of glycolaldehyde (**3**) and serine (**8**) from similar building blocks with glycolaldehyde imine (**6**) as the key intermediate that may form by a carbonyl ene reaction of aminomethylene (**1**) and formaldehyde (**7**) or by reduction of glycolonitrile (**5**) with copper cyanide complexes as photoredox catalysts.

Carbene **1** and imine **2** are the formal hydrogenation products of HCN and HNC, respectively (Figures 3 and S17). Chiavassa *et al.* showed experimentally that the exclusive product in the hydrogenation of solid HCN with atomic hydrogen at cryogenic temperatures is methylamine (**12**); hydrogenation of **2** also gives **12**.[17] Hence, the authors concluded that **2** must be involved in the former hydrogenation process. Either the hydrogenation of **2**

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[*] M. Sc. A. K. Eckhardt, Prof. Dr. P. R. Schreiner, PhD
Institute of Organic Chemistry
Justus-Liebig University Giessen
Heinrich-Buff-Ring 17, 35392 Giessen (Germany)
E-mail: prs@uni-giessen.de

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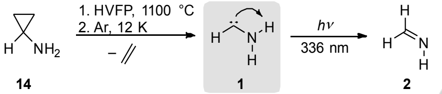
is very fast so that neither **2** nor methylnitrene (**13**, $H_3C–N$) can be trapped or **1** is the main reactive intermediate in the hydrogenation process of HCN that does not easily rearrange to **2**.[16] Surface hydrogenation reactions play an important role in the formation of molecules on interstellar ices. Methylamine, which was detected in interstellar media in 1974,[18] is suggested to be involved in the interstellar formation of glycine via a surface reaction on icy grains with CO_2 upon UV irradiation.[19]

Tsuboi *et al.* reported the pyrolysis of cyclopropylamine (**14**) at 630 °C and analyzed the pyrolysis products in a 20 cm long IR absorption cell.[20] The main products were the *E* and *Z* isomer of 1-aminopropene (**15**) but the side products allylamine (**16**), CH_4, NH_3, HCN, and ethylene (**17**) were identified in the spectra as well (Scheme S1). As the formation of **17** hints at a concerted cheletropic reaction of **14** to **17** and **1** (Scheme 2), we decided to reinvestigate the pyrolysis of **14** in combination with more sensitive matrix isolation IR spectroscopy. We confirm the formation of all pyrolysis products reported earlier. Indeed, with pyrolysis temperatures above 1000 °C we detect large amounts of **17** and **2**, identified by comparison with the reported signals,[6, 21] which deliver a strong indication of the proposed cheletropic cycloreversion. In addition, we also observed new unreported signals that we assign to **1**. Irradiation of the matrix immediately after the pyrolysis with UV light (336 or 365 nm) for a few minutes led to the disappearance of the signals of **1** while the signals of **2** increased (Figure 1).



Scheme 2. Generation of aminomethylene (**1**) by high-vacuum flash pyrolysis (HVFP) of cyclopropylamine (**14**) at 1100 °C and subsequent trapping of the pyrolysis products in solid argon at 12 K. After 5 min irradiation of the matrix with a wavelength of 336 nm the carbene rearranges to methanimine (**2**).

The strongest signals of **1** (observed in two matrix-sites) are the C–H stretching vibration at 2812.5 and 2809.1 cm^{-1} and the out-of-plane wagging vibration of the amino group at 807.3 and 806.3 cm^{-1}. Weaker signals for the asymmetric NH_2 stretching vibration with two matrix sites at 3374.0 and 3370.9 cm^{-1}, the NH_2 scissoring vibration at 1681.8 cm^{-1}, the C–N stretching vibration with three matrix-sites at 1415.1, 1412.9 and 1407.8 cm^{-1} and the H–C–N deformation vibration at 1366.7 cm^{-1} were also observed. Our signal assignments are based on an IR difference spectrum obtained from subtracting the spectrum recorded after 5 min irradiation of the matrix with a wavelength of 336 nm from the spectrum recorded before irradiation of the same matrix in combination with anharmonic AE-CCSD(T)/cc-pCVQZ coupled cluster frequency computations. The signals of disappearing **1** point downward while the increasing signal of **2** point upwards.

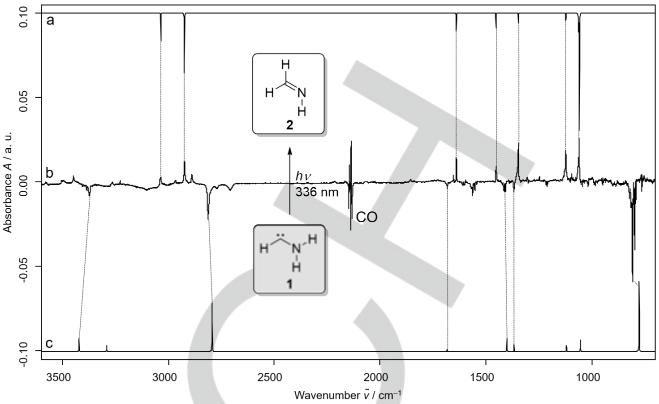


Figure 1. a) Experimentally observed vibrational frequencies of methanimine (**2**) in combination with computed AE-CCSD(T)/cc-pCVQZ harmonic intensities. b) Experimental difference spectrum between the spectrum recorded after 5 min irradiation of the matrix with a wavelength of 336 nm and the spectrum immediately recorded after 4 h pyrolysis of a gas mixture of cyclopropylamine (**14**) in argon (0.5%) at 1100 °C. c) Computed AE-CCSD(T)/cc-pCVQZ anharmonic fundamental frequencies and intensities of aminomethylene (**1**) (unscaled).

To solidify the formation of **1** we performed analogous pyrolysis experiments with **14** deuterated at the amine function (d_2-**14**). In the corresponding pyrolysis spectra we identified a mixture of amino deuterated **1** (d_2-**1**) as well as the mono amino deuterated *cis* and *trans* isotopologues after irradiation of the matrix, indicating that there is some *D*/*H* exchange of the precursor on the surface of the storage balloon or in the gas inlet capillary. The IR signal of the C–H stretching vibration of **1** remains virtually unchanged for all three isotopologues (Figure S7-S9), which can be easily identified and differentiated by the out-of-plane wagging vibration of the amino group. There is excellent agreement for the experimental and computed isotope shifts (Table S3 – S5).

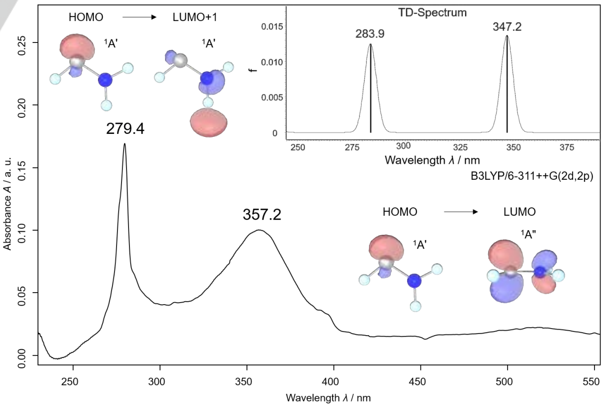


Figure 2. Experimental difference UV/Vis spectrum of aminomethylene (**1**) in argon at 12 K between the spectrum immediately recorded after 2 h pyrolysis of cyclopropylamine (**13**) at 1100 °C and the spectrum recorded after 10 min irradiation of the same matrix with a wavelength of 336 nm (see Figure S10 for raw spectra) and computed TD-Spectrum at B3LYP/6-311++G(2d,2p). The NBOs for the two electronic transitions were computed at HF/6-311++G(2d,2p) based on the AE-CCSD(T)/cc-pCVQZ optimized geometry of **1**. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital

We also support the formation of **1** with UV/Vis spectroscopy. Two transitions were experimentally observed that are assigned to a HOMO – LUMO and a HOMO – LUMO+1 transition at 357.2 and 279.4 nm, respectively. We computed the two transitions with time dependent density functional theory at B3LYP/6-311++G(2d,2p) at 347.2 nm and 283.9 nm, again in excellent agreement with experiment (Figure 2). The spectrum was obtained via subtraction of the spectrum recorded after 10 min irradiation of the matrix with a wavelength of 336 nm from the spectrum recorded before irradiation.

To determine the energetics for **1** and the barrier for the photo-chemical rearrangement to **2** we computed the corresponding potential energy surface at AE-CCSD(T)/cc-pCVQZ including zero-point vibrational energies (ZPVE) (Figure 2). Aminomethylene is a planar C_s symmetric molecule that has a closed-shell singlet ^{1}A' electronic ground state. The lowest triplet state is much higher in energy (T_0 = 33.7 kcal mol^{-1}). The C–N bond length of **1** of 1.31 Å is much shorter than a typical C–N bond (e.g., 1.47 Å in **12**[22]) due to π-type stabilization of the electron-deficient carbene center through the adjacent nitrogen *p* lone pair (Figure S13). The bond is also shorter than the C–N bond in the first "bottleable" NHC *N*,*N*'-diadamantylimidazol-2-ylidene (**18**) (1.37 Å).[1b] This is also represented in the experimentally observed C–N stretching vibration of **1** that is blue shifted in comparison to the single bond in **11**[23] (1415 vs. 1052 cm^{-1}) but red shifted in comparison to the double bond in **2**[6, 8, 21] (1415 vs. 1640 cm^{-1}). A Wiberg bond index of approx. 1.5 is computed for the CN bond in **1**, indicating zwitterionic character. A natural resonance theory (NRT) analysis favors the zwitterionic resonance contributor (see SI for details).

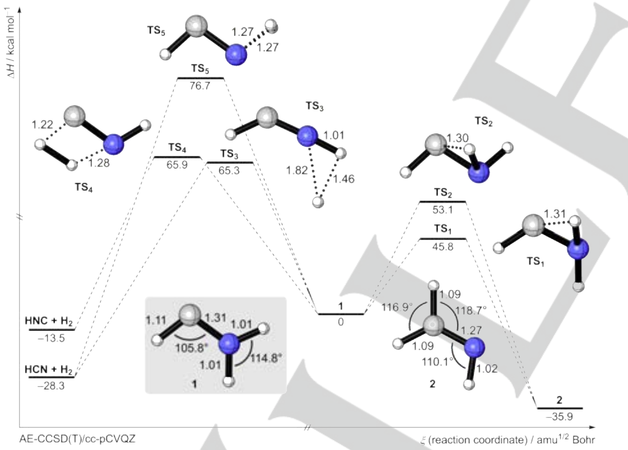
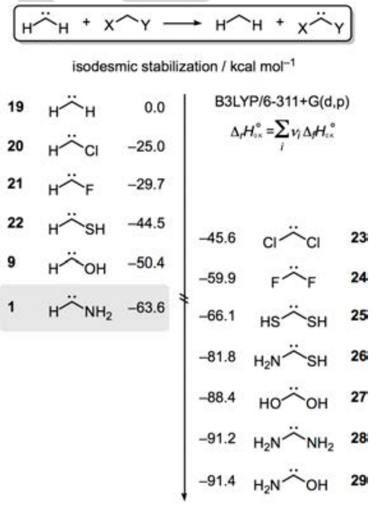


Figure 2. Potential energy surface around aminomethylene (**1**) (color code: carbon: grey, nitrogen: blue, hydrogen: white) at AE-CCSD(T)/cc-pCVQZ + ZPVE. For an extended version of the PES see Figure S16.

As there are two distinct amino hydrogen atoms, there are also two transition states **TS$_1$** and **TS$_2$** connecting **1** with **2** that differ by 7.3 kcal mol^{-1} in energy. The barrier for lower-lying **TS$_1$** is 45.8 in the forward and 81.7 kcal mol^{-1} in the reverse direction. In comparison to the hydroxycarbenes, which can be isolated in cryogenic inert gas matrices after pyrolysis of the corresponding α-ketocarboxylic acids and then rearrange through a quantum mechanical hydrogen tunneling (QMT) process to the corresponding aldehydes, the reaction barrier for the [1,2]H-shift is approximately 15 kcal mol^{-1} higher and the barrier width approximately 25% larger.[13] Therefore, QMT was experimentally not observed: After five days in the dark the matrix spectrum remained unchanged. The experimental results are supported by a semiclassical one dimensional Wentzel-Kramers-Brillouin (WKB) tunneling analysis [24] that predicts a tunneling half-life of several billion years (see SI for details). Transition states **TS$_3$** and **TS$_4$** for the dissociation of **1** into HCN and H$_2$, and HNC and H$_2$, respectively, are almost equal in energy (approx. 66 kcal mol^{-1}). A second transition state **TS$_5$** (C_s) for the dissociation of **1** into HCN and H$_2$ is 10 kcal mol^{-1} higher in energy (76.7 kcal mol^{-1}).



Scheme 3. Stabilization enthalpies of various heterocarbenes.

The stability of **1** and other substituted heterocarbenes was estimated by an isodesmic equation (Scheme 3). Nitrogen is by far the best π-donor,[25] making **1** the most stable mono heteroatom-substituted carbene. It is even more stabilized than the doubly heteroatom substituted dichloro (**23**) and difluorocarbene (**24**), as well as various other heterocarbenes (Schemes 3 and S2). The most stabilized doubly heteroatom substituted carbene is aminohydroxycarbene[13b] (**29**) almost equal in energy with diaminocarbene (**28**) and 3 kcal mol^{-1} more stabilized than dihydroxycarbene[13b, 26] (**27**). Hence, the second nitrogen atom stabilizes the carbene center less than the first one.

We present the first spectroscopic characterization of the simplest amino carbene aminomethylene by matrix isolation IR and UV/Vis spectroscopy. Based on our experimental results and AE-CCSD(T)/cc-pCVQZ computations aminomethylene is a C_s symmetric singlet ground state carbene. In contrast to the familiar hydroxycarbene H-tunneling aminomethylene does not undergo a [1,2]H-shift reaction to methanimine; this isomerization can be induced photochemically by irradiating the carbene with UV light. These findings let us suggest to consider aminomethylene as a viable interstellar molecule that may be an intermediate in prebiotic sugar and amino acid synthesis (Scheme 1).

Experimental Section

Matrix isolation studies. We used an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF_2 windows for UV/Vis measurements. The matrix temperature was controlled by a Scientific Instruments 9600-1 Si-diode temperature controller. For irradiations a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used (band width ca. 10 nm). IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500 – 400 cm^{-1}, resolution 0.7 cm^{-1}), while UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer. For the combination of HVFP with matrix isolation we employed a homebuilt, water-cooled oven directly connected to the vacuum shroud of the cryostat. The pyrolysis zone consisted of an empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a thermocoax wire. The temperature was controlled by a Ni/CrNi thermocouple. At a distance of approximately 50 mm, all pyrolysis products were condensed on the surface of the matrix window at 12 K. In a typical pyrolysis experiment a gaseous mixture of cyclopropylamine with argon (0.5%) was passed through the hot pyrolysis tube (1000–1100 °C). The gas flow was regulated by a Pfeiffer EVN 116 gas dosing valve with separate shut-off. For all experiments we used Ar of 99.999% purity.

Cyclopropylamine (98%, received from Sigma Aldrich) was further purified through distillation and degassed by repeated freeze-pump-thaw cycles. Amino-deuterated cyclopropylamine was obtained by three cycles of dissolving 0.5 mL cyclopropylamine in 2 mL sodium deuteroxide solution (40 wt. % in D_2O, 99.5 atom % D, received from Sigma Aldrich) and removing the solvent in vacuo.

Computations. All coupled cluster computations used with the CFOUR program.[27] All electron coupled cluster level of theory[28] including single, double, and perturbatively included triple excitations [AE-CCSD(T)] utilizing the Dunning correlation consistent split valence basis set cc-pCVQZ[29] was used for geometry optimizations and frequency computations. All B3LYP[30] computations employed the Gaussian09[31] program.

Acknowledgments

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Keywords: amino acids • matrix isolation • origin of life • prebiotic chemistry • sugars

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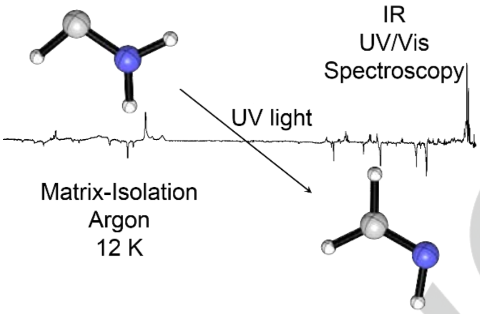
Entry for the Table of Contents

COMMUNICATION

The simplest aminocarbene, aminomethylene H–C̈–NH$_2$, has been spectroscopically characterized in solid Ar at 12 K by matrix isolation IR and UV/Vis spectroscopy. Aminomethylene rearranges by irradiation with UV light to methanimine, formaldimine H$_2$C=NH but does not undergo tunneling isomerization.



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