

# Generation and UV-photolysis of *N*-methyleneformamide

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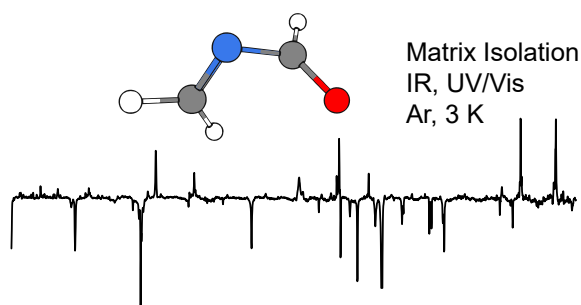
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**Keywords:** imines – matrix isolation spectroscopy – photolysis – pyrolysis – retro-aza-Diels-Alder

**Abstract.** Simple imines have been detected in space and are considered as building blocks to larger heteroaromatic, cyclic and biological relevant compounds. Herein we revisited the formation of the simplest acylimine, namely *N*-methyleneformamide, by high-vacuum flash pyrolysis (HVFP) as well as its spectroscopic characterization by cryogenic matrix isolation infrared (IR) and UV/Vis spectroscopy. *N*-methyleneformamide prefers a *gauche* over a *s-trans* conformation in contrast to parent 1,3-butadiene. In UV-photolysis experiments we identified formaldehyde:HCN and formaldimine:CO complexes as the major decomposition products. As further photolysis products we observed the HCN:CO and HNC:CO complexes. All experimental findings are supported by deuterium labeling experiments and high-level *ab initio* coupled cluster calculations. *N*-methyleneformamide should be considered as a candidate for an interstellar search. The sequence  $R_2C=N-RC=O$  also occurs in cytosine making the title compound highly relevant for prebiotic chemistry and the search for the molecular origins of life.

## TOC

### *N*-methyleneformamide



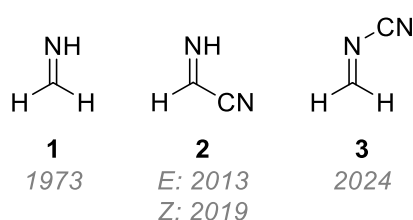
Imines are fundamental building blocks in prebiotic chemistry, e.g., in Strecker's amino acid synthesis or in the HCN dimerization and adenine forming Ferris Orgel reaction.<sup>1–3</sup> Simple imines are continuously discovered in space, including formaldimine ( $H_2C=NH$ , **1**),<sup>4</sup> cyanomethanimine ( $NCHC=NH$ , **2**)<sup>5</sup> and others (Scheme 1).<sup>6–9</sup> Only last year the high energy isomer of the HCN dimer **2**, namely *N*-cyanomethanimine ( $H_2C=NCN$ , **3**) including the prebiotically relevant NCN backbone was discovered in space.<sup>10</sup> This provides evidence that other differently substituted methanimines might also be present in space including *N*-methyleneformamide (**4**). Computational studies predict

the formation of **4** from  $\text{H}_2\text{CO}$  and  $\text{HCN}$ ,<sup>11</sup> as well as  $\text{HCNO}$  and  $\text{CH}_2$  under plausible interstellar conditions.<sup>12</sup>

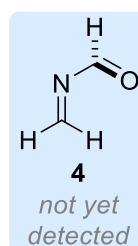
*N*-methyleneformamide is the simplest *N*-acylimine and was already part of theoretical<sup>13–19</sup> and experimental investigations.<sup>20</sup> It is noteworthy that the sequence  $\text{R}_2\text{C}=\text{N}-\text{RC}=\text{O}$  also occurs in the nucleobase cytosine, making **4** highly relevant for the field of prebiotic chemistry. *N*-methyleneformamide was previously generated from a cyclopentadiene based precursor in a retro-aza-Diels-Alder reaction at 450 °C in the gas-phase under high-vacuum and characterized using low-temperature infrared spectroscopy.<sup>20</sup> However, only the two most prominent vibrations, namely the CO and CN stretching vibration at 1735 and 1695  $\text{cm}^{-1}$ , were observed in a solid film. Even in the condensed phase and in the absence of a solvent, **4** showed propensity to polymerize at –196 °C. Due to the high reactivity, a low temperature nuclear magnetic resonance (NMR) spectrum could not be reported in contrast to other reactive *N*-acylmethanimines.<sup>20</sup> In a mass spectrometric and microwave spectroscopic study only *trans*-nitrosoethylene ( $\text{H}_2\text{CHCNO}$ ) could be identified as the elusive  $\text{C}_2\text{H}_3\text{NO}$  isomer.<sup>21</sup> To the best of our knowledge a microwave spectrum of **4** is not yet reported, despite its high dipole moment of 3.0 D (*gauche*, B3LYP/6-311+G\*\*).<sup>18</sup>

*N*-methyleneformamide is a 1,3-butadiene heteroanalog, preferring a *gauche* over a planar *s-trans* conformation according to density functional theory (DFT) calculations.<sup>18,19</sup> The presence of both, an imino and a carbonyl functional group gives **4** a rotational profile around the  $\text{C}=\text{N}-\text{C}=\text{O}$  dihedral angle, which is at odds with other (hetero)butadiene analogs.<sup>22</sup> The energetic preference for the *gauche* conformer was rationalized with electronic repulsion effects.<sup>11</sup> The repulsive interactions are greater than the conjugation effect in the two planar conformations of **4**.<sup>18,19</sup> Only recently, the non-planar *gauche* preference for parent 1,3-butadiene was demonstrated experimentally in a Fourier-transform microwave (FTMW) spectroscopy study.<sup>23</sup> The lower energy *s-trans* conformer does not possess a dipole moment and is invisible to radio astronomy. However, the cyano tagged butadiene analog, namely *s-trans-E*-1-cyano-1,3-butadiene, was observed in TMC-1 in 2023 suggesting that also more heteroatom substituted butadienes might be present in space.<sup>24</sup>

**Detected in ISM:**



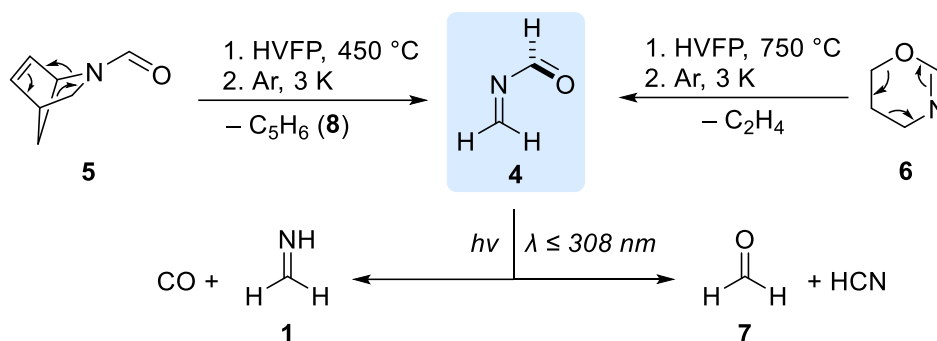
**This work:**



**Scheme 1:** Formaldimine (**1**) and the  $\text{HCN}$  dimers cyanoformaldimine (**2**) and *N*-cyanomethanimine (**3**) have been detected in the interstellar medium (ISM) while *N*-methyleneformamide (**4**) is not yet detected.

Panda et al. explored various  $\text{C}_2\text{H}_3\text{NO}$  isomers in the context of interstellar chemistry. Methylisocyanate ( $\text{H}_3\text{CNCO}$ ), glycolonitrile ( $\text{HOCH}_2\text{CN}$ ), **4** and 2-iminoacetaldehyde ( $\text{HC(O)CHNH}$ ) were identified as the lowest energy  $\text{C}_2\text{H}_3\text{NO}$  isomers.<sup>11</sup> We reported recently the spectroscopic characterization of interstellar relevant imines by UV photolysis of the corresponding azide precursors.<sup>25–27</sup> In the UV photolysis of 2-azidoacetaldehyde we identified 2-iminoacetaldehyde and two unassigned bands at 993.7 and 1469.9  $\text{cm}^{-1}$  that did not show any

photochemistry. As **4** was suggested as a viable photoproduct but IR spectroscopically only characterized by two bands, we revisited the preparation of **4** and investigated its photochemistry.

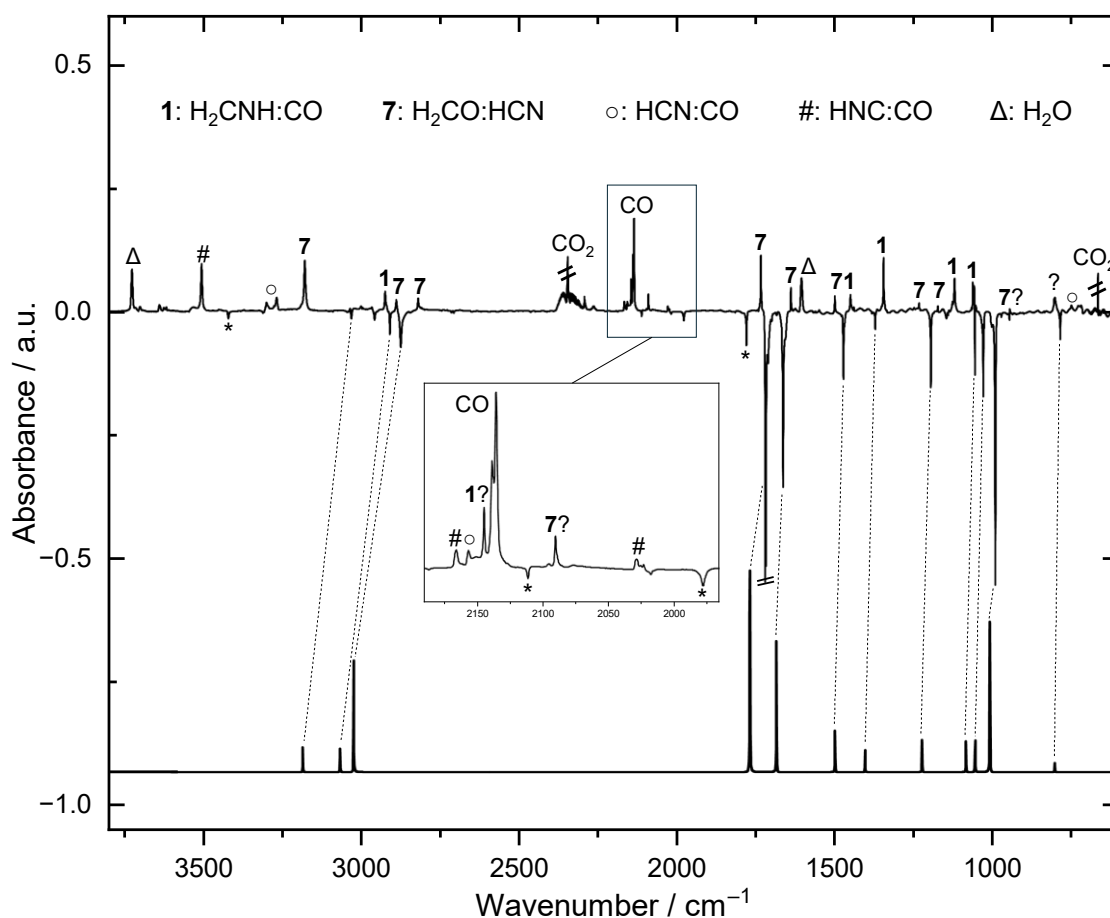


**Scheme 2:** Gas phase generation of *N*-methyleneformamide (**4**) by high-vacuum flash pyrolysis (HVFP) of *N*-formyl-2-azabicyclo[2.2.1]hept-5-ene (**5**) and 5,6-dihydro-4H-1,3-oxazine (**6**) and subsequent trapping of all pyrolysis products in solid argon at 3.4 K. UV irradiation ( $\lambda \leq 308$  nm) of the matrix leads to the decomposition of **4** into formaldimine (**1**) and CO as well as formaldehyde (**7**) and HCN.

For the generation of **4** we synthesized *N*-formyl-2-azabicyclo[2.2.1]hept-5-ene (**5**) as described by Lasne *et al.* including the 3,3-deuterium isotopically labelled compound (Scheme S1).<sup>20</sup> We performed high-vacuum flash pyrolysis (HVFP) experiments with **5** at 450 °C and directly trapped all pyrolysis products with an excess of argon on a cold matrix window at 3.4 K (Scheme 2). Besides the well-known signals of matrix isolated cyclopentadiene (**8**) in argon,<sup>28</sup> we identified another set of signals at 2956.8, 2908.0, 2873.7, 1719.4, 1664.0, 1473.1, 1372.6, 1196.1, 1057.0, 1030.5, 992.6, 786.6  $cm^{-1}$  (Table S1), which we assigned to the fundamentals of *gauche*-**4** based on our calculation of *gauche*-**4** at the CCSD(T)/cc-pVTZ level of theory (Figure S1, Table S1). There is no spectroscopic evidence for *s-trans*-**4** in our pyrolysis spectrum. Cyclopentadiene and *gauche*-**4** are the retro-aza-Diels-Alder reaction products of **5**. We irradiated the matrix with UV light ( $\lambda = 254$  nm, 40 min) and observed a 40% decomposition of *gauche*-**4** along with the reported disrotatory photoinduced intramolecular cycloaddition of **8** forming bicyclo[2.1.0]pent-2-ene (BCP) as observed by its two most intense bands at 774 and 720  $cm^{-1}$  (Figure S2).<sup>28</sup> We identified complexed formaldimine<sup>29</sup> and carbon monoxide as well as the reported HCN-formaldehyde complex<sup>30</sup> as the primary photolysis products of *gauche*-**4** (Figure S2).

As we observed critical overlaps in the IR spectrum of *gauche*-**4** with **8** and its photochemistry, we investigated another precursor for the generation of *gauche*-**4**. In the [4+2] retro-aza-Diels-Alder reaction of **5**, cyclopentadiene takes the role of the diene and **4** of the dienophile. We synthesized 5,6-dihydro-4H-1,3-oxazine (**6**) as an alternative precursor (Scheme S2). In the corresponding [4+2] retro-aza-Diels-Alder reaction ethylene and **4** should be the reaction products as dieneophile and diene, respectively. The oxazine heterocycle is highly sensitive and polymerizes as a neat liquid even at  $-26$  °C in the dark within three days. We conducted HVFP experiments with **6** in the 450-750 °C temperature range (Scheme 2). The compound is more stable than **5** and starts decomposing at around 650 °C. At 750 °C we identified the same set of signals for *gauche*-**4** as described in the pyrolysis of **5** as the major pyrolysis product along with the characteristic sets of signals for ethylene,<sup>31</sup> HCN, formaldehyde, formaldimine, CO and not decomposed starting material (Figure S3). In contrast to **8**, ethylene and the other pyrolysis side products do not show

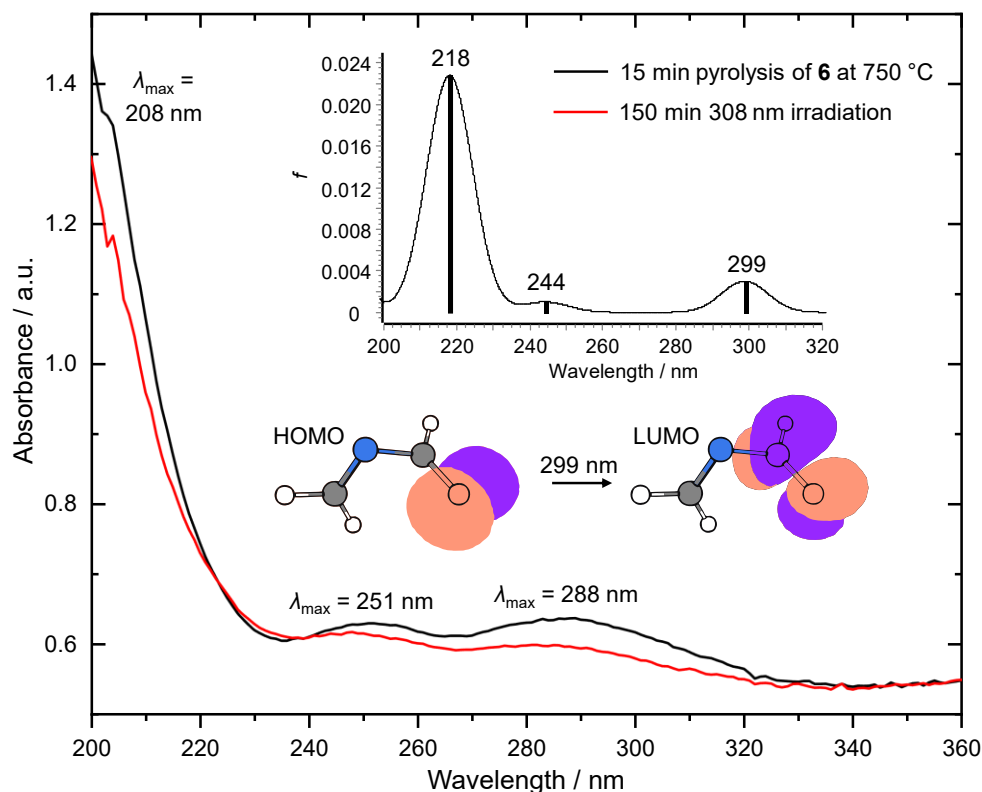
any photochemistry after UV irradiation ( $\lambda > 254$  nm), and we observed a difference spectrum after photolysis of *gauche*-4 only (Figure 1). The tiny signals in Figure 1, which are pointing downwards and are marked with an asterisk (\*) at 3419.0, 2111.6, and 1978.3  $\text{cm}^{-1}$  are assigned to the corresponding overtone signals of the fundamentals of *gauche*-4 at 1719.4, 1057.0, and 992.6  $\text{cm}^{-1}$ . The characteristic signal in the carbonyl region at 1779.2  $\text{cm}^{-1}$  is a combinational band of the fundamentals at 992.6 and 786.6  $\text{cm}^{-1}$ . After prolonged photolysis we also identified the HCN:CO and HNC:CO complexes as further photolysis products.<sup>32</sup> We assume that IR inactive dihydrogen forms together with these complexes.



**Figure 1:** Top: Experimental IR difference spectrum between the matrix IR spectrum at 3.4 K recorded after 84 min pyrolysis of **6** at 750 °C and irradiation of the matrix with UV light ( $\lambda = 308$ -254 nm) for 270 min. Bottom: Calculated harmonic IR spectrum of *gauche*-4 at the CCSD(T)/cc-pVTZ level of theory. After UV irradiation *gauche*-4 decomposes into formalimine:CO (**1**) and HCN:formaldehyde (**7**) complexes, which presumably further decompose into dihydrogen (IR inactive) and HCN:CO (○) and HNC:CO (#) complexes.

To provide further spectroscopic evidence for the generation of *gauche*-4, we synthesized 3,3-deuterium labelled *N*-formyl-2-azabicyclo[2.2.1]hept-5-ene (**5-d<sub>2</sub>**). The compound can easily be prepared by reducing Vince lactam<sup>33</sup> (2-azabicyclo[2.2.1]hept-5-en-3-one, **9**) with lithium aluminum deuteride (LiAlD<sub>4</sub>) and subsequent formylation (Scheme S1).<sup>20</sup> We carried out the pyrolysis experiments with the deuterium labeled compound in a similar fashion and assigned a

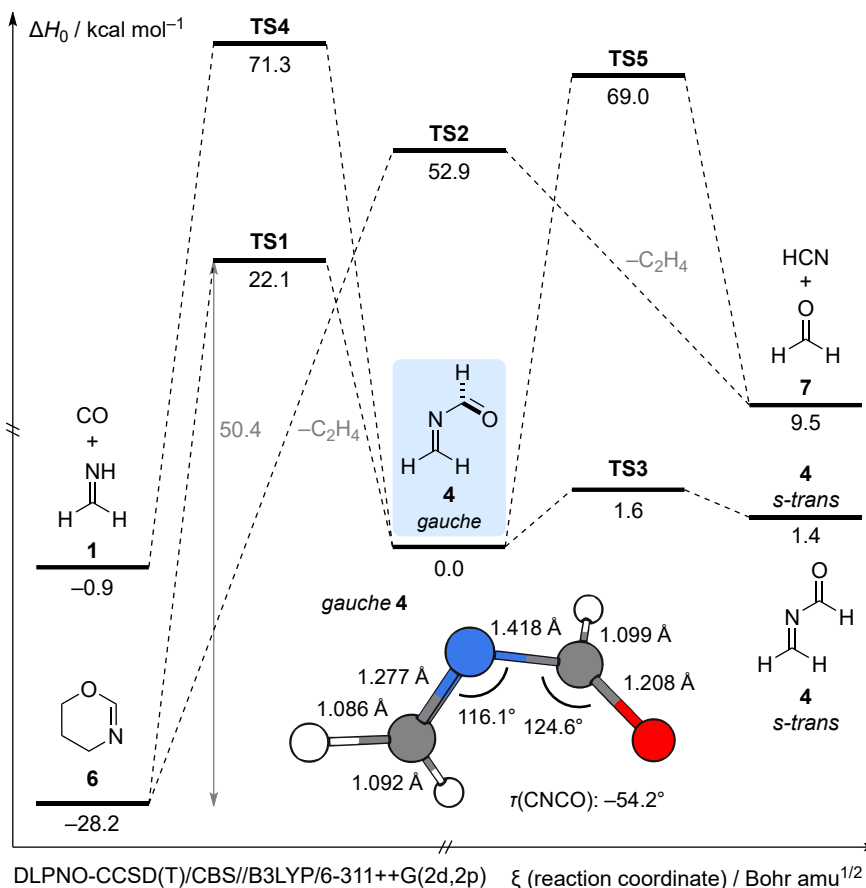
new set of signals at 2281.0, 2159.8, 1711.9, 1623.3, 1121.4, 1039.1, 979.3, 926.6, 847.6, 707.8  $\text{cm}^{-1}$  to deuterium labeled *gauche*-4- $d_2$  ( $\text{D}_2\text{CNHCO}$ ) based on our CCSD(T)/cc-pVTZ frequency calculations (Table S2, Figure S4). Irradiation of the matrix with 254 nm results in disappearance of the described signals and the formation of complexed formalimine- $d_2^{29}$  ( $\text{D}_2\text{CNH}$ ) and CO as well as a DCN:formaldehyde- $d_1$  complex (Figure S5).



**Figure 2:** Experimental matrix isolation UV/Vis spectrum at 3.4 K after 15 min pyrolysis of **6** (black curve) at 750 °C and after 150 min UV irradiation ( $\lambda = 308$  nm) (red curve). Inset top: Calculated TD-DFT spectrum of **4** at the TD-B3LYP/6-311++G(2d,2p) level of theory. Inset bottom: Frontier natural bond orbitals of **4** (contour value: 0.0432) calculated at the HF/STO-3G level of theory based on the optimized CCSD(T)/cc-pVTZ geometry. HOMO = Highest Occupied Molecular Orbitals; LUMO = Lowest Unoccupied Molecular Orbital. Color code: carbon: grey; hydrogen: white; nitrogen: blue; oxygen: red (covered by orbitals).

We also repeated the pyrolysis experiments with **6** and conducted UV/Vis spectroscopy experiments with the trapped pyrolysis products. As the UV/Vis absorptions of **8** show critical overlaps in the UV region with the calculated transitions of *gauche*-4, precursor **6** is more suitable for UV/Vis experiments than **5**. The major pyrolysis side product, ethylene, shows absorption below 200 nm,<sup>34</sup> as well as the other minor by-products formaldehyde,<sup>35</sup> HCN,<sup>36</sup> and CO.<sup>37</sup> Only methylene imine has a transition at around 250 nm,<sup>38</sup> however in the pyrolysis IR spectrum it is observed only in traces (Figure S3). Precursor **6** has a calculated weak transition at  $\lambda = 218$  nm (oscillator strength  $f = 0.006$ ) at the TD-B3LYP/6-311++G(2d,2p) level of theory that is in a very good agreement with our experimental UV/Vis spectrum in argon ( $\lambda_{\text{max}} = 211$  nm, Figure S11). For *gauche*-4 we calculated transitions at the same level of theory at  $\lambda = 299$  nm ( $f = 0.003$ ),  $\lambda = 244$  nm ( $f = 0.001$ ), and  $\lambda = 218$  nm ( $f = 0.023$ ) (Table S3). After 15 min pyrolysis of **6**, we recorded the black spectrum depicted in Figure 2 with three absorption maxima at  $\lambda_{\text{max}} = 288$  nm,  $\lambda_{\text{max}} = 251$  nm,

and  $\lambda_{\text{max}} = 203$  nm. The two experimental absorptions at  $\lambda_{\text{max}} = 288$  and  $\lambda_{\text{max}} = 251$  nm are in good agreement with the calculated transition while the absorption maximum at  $\lambda_{\text{max}} = 203$  nm overlaps with the absorption of undecomposed precursor **6** (Figure S11). After irradiation of the matrix with  $\lambda = 308$  nm for 150 min all bands decreased while no new signals appeared (*vide supra*) as depicted in the red curve in Figure 2.



**Figure 3:** Most essential part of the potential energy surface (PES) around *N*-methyleneformamide (**4**) at the DLPNO-CCSD(T)/CBS//B3LYP/6-311++G(2d,2p) level of theory including zero-point vibrational energy (ZPVE) corrections. The depicted geometry of *gauche*-**4** is optimized at the CCSD(T)/cc-pVTZ level of theory. Color code: carbon: grey; hydrogen: white; nitrogen: blue; oxygen: red.

We calculated the most essential part of the potential energy surface (PES) around **4** at the DLPNO-CCSD(T)/CBS//B3LYP/6-311++G(2d,2p) level of theory including zero-point vibrational energy (ZPVE) corrections (Figure 3). The barrier for the decomposition of **6** in the retro-aza-Diels-Alder reaction is 50.4 kcal mol<sup>-1</sup> (TS1) and is associated with the formation of **4** and ethylene. We located another transition state TS2 that is much higher in energy (81.1 kcal mol<sup>-1</sup>) and connects precursor **6** directly to **7**, CO and ethylene. The imaginary frequency of TS2 resembles a ring breathing vibration in **6**. For **5** the barrier for the retro-aza-Diels-Alder reaction is 43.3 kcal mol<sup>-1</sup> (TS6, Figure S31). This is in good agreement with our experimental results, as **5** already decomposed at much lower temperature (*vide supra*). There are two conformers for **4**, namely *gauche* and *s-trans*. The planar *s-trans* conformer is 1.4 kcal mol<sup>-1</sup> higher in energy, while the planar *s-cis* conformation represents a transition state (1.6 kcal mol<sup>-1</sup>), which connects two *gauche* minima of **4** in a double valley (*c.f.* Figure S32 for a relaxed scan of the electronic energy of the  $\tau(\text{CNCO})$  dihedral angle).



The dihedral angle  $\tau(\text{CNCO})$  in *gauche* **4** is  $(-)\text{54.2}^\circ$  calculated at the CCSD(T)/cc-pVTZ level of theory (Figure 3). The *gauche* and *s-trans* conformers of **4** are connected via **TS4** and a small 1.6 kcal mol<sup>-1</sup> barrier. The small barrier and the high energy nature of *s-trans* **4** (1.4 kcal mol<sup>-1</sup>) are a reasonable explanation why we only observed the *gauche* conformer in our low temperature matrix isolation experiments. We located two high energy transition states **TS4** (71.3 kcal mol<sup>-1</sup>) and **TS5** (69.0 kcal mol<sup>-1</sup>) that are associated with the dissociation of **4** into **1** and CO as well as **7** and HCN. All dissociation products were identified in our pyrolysis spectrum.

In summary, we report the full matrix isolation IR and UV/Vis spectroscopic characterization of *gauche* *N*-methyleneformamide and its photochemical UV light induced fragmentation into formaldehyde:HCN and formaldimine:CO complexes. As further decomposition products we observed the HCN:CO and HNC:CO complexes. In contrast to parent 1,3-butadiene *N*-methyleneformamide prefers a *gauche* over a *s-trans* conformation. *N*-methyleneformamide is a promising candidate for interstellar detection. To facilitate an interstellar search, the molecule should be characterized by rotational spectroscopy to provide the necessary laboratory rotational transitions. If this compound is formed in laboratory astrochemistry experiments or is directly observed in space, it would suggest a possible connection between simple acylimines and larger biologically relevant molecules, such as cytosine as a nucleobase in which the sequence  $\text{R}_2\text{C}=\text{N}-\text{RC}=\text{O}$  appears. This discovery could potentially increase the complexity of prebiotic molecules of interest to astrobiology and the search for the molecular origins of life.

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## Supporting Information

The Supporting Information file to this article includes:

- Selected IR and UV/Vis spectra, IR and UV/Vis spectroscopic data, synthetic procedures, NMR spectra, Coordinates and energies of calculated structures

## References

- 1 A. Strecker, *Justus Liebigs Ann. Chem.*, 1850, **75**, 27–45.
- 2 A. Strecker, *Justus Liebigs Ann. Chem.*, 1854, **91**, 349–351.
- 3 J. P. Ferris and L. E. Orgel, *J. Am. Chem. Soc.*, 1966, **88**, 3829–3831.
- 4 P. D. Godfrey, R. D. Brown, B. J. Robinson and M. W. Sinclair, *Astrophys. Lett.*, 1973, **13**, 119.
- 5 D. P. Zaleski, N. A. Seifert, A. L. Steber, M. T. Muckle, R. A. Loomis, J. F. Corby, O. Martinez, K. N. Crabtree, P. R. Jewell, J. M. Hollis, F. J. Lovas, D. Vasquez, J. Nyiramahirwe, N. Sciortino, K. Johnson, M. C. McCarthy, A. J. Remijan and B. H. Pate, *Astrophys. J. Lett.*, 2013, **765**, L10.

- 6 R. A. Loomis, D. P. Zaleski, A. L. Steber, J. L. Neill, M. T. Muckle, B. J. Harris, J. M. Hollis, P. R. Jewell, V. Lattanzi, F. J. Lovas, O. M. Jr, M. C. McCarthy, A. J. Remijan and B. H. Pate, *Astrophys. J.*, 2013, **765**, L9.
- 7 P. D. Gensheimer, *Astrophys. Space Sci.*, 1997, **251**, 199–202.
- 8 F. J. Lovas, J. M. Hollis, A. J. Remijan and P. R. Jewell, *Astrophys. J.*, 2006, **645**, L137.
- 9 L. Bizzocchi, D. Prudeniano, V. M. Rivilla, A. Pietropolli-Charmet, B. M. Giuliano, P. Caselli, J. Martín-Pintado, I. Jiménez-Serra, S. Martín, M. A. Requena-Torres, F. Rico-Villas, S. Zeng and J.-C. Guillemin, *Astron. Astrophys.*, 2020, **640**, A98.
- 10 D. S. Andrés, V. M. Rivilla, L. Colzi, I. Jiménez-Serra, J. Martín-Pintado, A. Megías, Á. López-Gallifa, A. Martínez-Henares, S. Massalkhi, S. Zeng, M. Sanz-Novato, B. Tercero, P. de Vicente, S. Martín, M. A. Requena-Torres, G. Molpeceres and J. G. de la Concepción, *Astrophys. J.*, 2024, **967**, 39.
- 11 S. Panda, A. Chiranjibi, D. Awasthi, S. Ghosal and A. Anoop, *ACS Earth Space Chem.*, 2023, **7**, 1739–1752.
- 12 H. Ji, A. Rágyanszki and R. A. Fournier, *ChemRxiv*, 2023, preprint, DOI: 10.26434/chemrxiv-2023-kpm5r.
- 13 K. B. Wiberg, P. R. Rablen and J. H. Baraban, *J. Org. Chem.*, 2018, **83**, 8473–8482.
- 14 R. Allmann, R. Kupfer, M. Nagel and E.-U. Würthwein, *Chem. Ber.*, 1984, **117**, 1597–1605.
- 15 V. A. Petukhov, N. E. Agafonov and I. A. Abronin, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1984, **33**, 414–417.
- 16 W. Förner, J. Ladik, P. Otto and J. Čížek, *Chem. Phys.*, 1985, **97**, 251–262.
- 17 M. A. McAllister and T. T. Tidwell, *J. Chem. Soc. Perkin Trans. 2*, 1994, 2239.
- 18 H. M. Badawi, *J. Mol. Struct. THEOCHEM*, 2002, **617**, 9–15.
- 19 D. Yu. Afanas'yev and A. V. Prosyanyk, *J. Mol. Struct. THEOCHEM*, 2005, **730**, 45–49.
- 20 M. C. Lasne, J. L. Ripoll and A. Thuillier, *J. Chem. Res. Synop.*, 1982, **8**, 214–215.
- 21 T. Sakaizumi, M. Nishikawa, A. Usami, H. Satoh and O. Ohashi, *J. Anal. Appl. Pyrolysis*, 1995, **34**, 219–227.
- 22 K. B. Wiberg, P. R. Rablen and M. Marquez, *J. Am. Chem. Soc.*, 1992, **114**, 8654–8668.
- 23 J. H. Baraban, M.-A. Martin-Drumel, P. B. Changala, S. Eibenberger, M. Nava, D. Patterson, J. F. Stanton, G. B. Ellison and M. C. McCarthy, *Angew. Chem. Int. Ed.*, 2018, **57**, 1821–1825.
- 24 I. R. Cooke, C. Xue, P. B. Changala, H. T. Shay, A. N. Byrne, Q. Y. Tang, Z. T. P. Fried, K. L. Kelvin Lee, R. A. Loomis, T. Lamberts, A. Remijan, A. M. Burkhardt, E. Herbst, M. C. McCarthy and B. A. McGuire, *Astrophys. J.*, 2023, **948**, 133.
- 25 A. K. Eckhardt, *Chem. Commun.*, 2022, **58**, 8484–8487.
- 26 V. Paczelt, R. C. Wende, P. R. Schreiner and A. K. Eckhardt, *Angew. Chem. Int. Ed.*, 2023, **62**, e202218548.
- 27 V. D. Drabkin, V. Paczelt and A. K. Eckhardt, *Chem. Commun.*, 2023, **59**, 12715–12718.
- 28 J. Miyazaki and Y. Yamada, *J. Mol. Struct.*, 2004, **692**, 145–153.
- 29 M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, 1975, **56**, 333–356.
- 30 S. B. H. Bach and B. S. Ault, *J. Phys. Chem.*, 1984, **88**, 3600–3604.
- 31 E. Rytter and D. M. Gruen, *Spectrochim. Acta Part Mol. Spectrosc.*, 1979, **35**, 199–207.
- 32 S. V. Kameneva, D. A. Tyurin and V. I. Feldman, *Phys. Chem. Chem. Phys.*, 2017, **19**, 24348–24356.
- 33 R. Singh and R. Vince, *Chem. Rev.*, 2012, **112**, 4642–4686.
- 34 J. R. Platt, H. B. Kleven and W. C. Price, *J. Chem. Phys.*, 1949, **17**, 466–469.
- 35 D. C. Moule and A. D. Walsh, *Chem. Rev.*, 1975, **75**, 67–84.
- 36 G. Herzberg and K. K. Innes, *Can. J. Phys.*, 1957, **35**, 842–879.
- 37 H. Lefebvre-Brion, C. Moser and R. K. Nesbet, *J. Chem. Phys.*, 1961, **35**, 1702–1707.
- 38 A. Teslja, B. Nizamov and P. J. Dagdigian, *J. Phys. Chem. A*, 2004, **108**, 4433–4439.