Guanine formation mechanism from observed interstellar chemical species

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Summary

Facts about (bio)molecules in the ISM

Methodological background

Learnings from Adenine mechanism of Synthesis

Results on the Guanine Synthesis

Conclusions

~ 150 molecules were observed in the ISM

Table 1 Interstellar molecules[a] (cumulenes and heterocumulenes are shown in bold letters)

Diatomic
AlCl, AlF, AlO, $\mathbf{CC}$, CH, CH^+, CF^+, CN, CN^-, CO, CO^+, CP, CS, CSi, FeO, HCl, HF, H_2, HN, HO, HS, KCl, LiF, MgH^+, N_2, NO, NP, NS, NSi, NaCl, NaI, O_2, OP, OS, OS^+, OSi, SH, SSi.

Triatomic
AlNC, AlOH, $\mathbf{C_3}$, $\mathbf{C_2H}$, CH_2, $\mathbf{C_2O}$, CO_2, $\mathbf{C_2P}$, $\mathbf{C_2S}$, *cyclo*-C_2Si, HCN, HCO, HCO^+, HCP, HCS, HCS^+, HDO, H_3^+, HNC, HN_2^+, HNO, H_2D^+, HD_2^+, H_2N, H_2O, H_2S, HOC^+, KCN, MgCN, MgNC, NaCN, NaOH, N_2O, OCN^-, OCS, O_3, SO_2, SiCN, SiNC.

4-atomic
CH_2O, CH_2S, C_2H_2, $\mathbf{C_2HN}$, CH_2N, $\mathbf{C_3H}$, $\mathbf{\mathit{cyclo}C_3H}$, $\mathbf{C_3N}$, $\mathbf{C_3O}$, $\mathbf{C_3S}$, $\mathbf{C_3Si}$, CH_3, $\mathbf{C_4}$, $HCNH^+$, HCNO, HNCO, HNCS, HSCN, $HOCO^+$, H_3O^+, H_2O_2, NH_3.

5-atomic
CH_4, CH_2CN, CH_2CO, CH_2NC, CH_2NH, CH_2OH^+, $\mathbf{C_3H_2}$, $\mathbf{\mathit{cyclo}C_3H_2}$, $\mathbf{HC_2CN}$, $\mathbf{HC_2NC}$, $\mathbf{C_3NH}$, HC_3N, $\mathbf{C_4H}$, $\mathbf{C_4H^-}$, $\mathbf{C_4Si}$, $\mathbf{C_5}$, HCO_2H, HCOCN, NH_2CN, SiH_4.

6-atomic
C_2H_4, CH_2CHO, CH_2CNH, *cyclo*C_3H_2O, CH_3CN, CH_3NC, CH_3OH, CH_3SH, C_3H_2N, $\mathbf{C_4H_2}$, $\mathbf{C_4HN}$, $\mathbf{C_5H}$, $\mathbf{C_5N^-}$, HC_2CNH^+, $HCONH_2$, NH_2CHO.

7-atomic
cycloC_2H_4O, CH_2CHCN, CH_2CHOH, CH_3CHO, CH_3NH_2, CH_3C_2H, $\mathbf{HC_4CN}$, $\mathbf{C_6H}$, $\mathbf{C_6H^-}$.

8-atomic
CH_2OHCHO, CH_2CHCHO, $\mathbf{CH_2CCHCN}$, CH_3CO_2H, $\mathbf{CH_3C_2CN}$, $\mathbf{C_6H_2}$, $\mathbf{C_7H}$, HCO_2CH_3, $\underline{NH_2CONH_2}$, NH_2CH_2CN.

9-atomic
CH_3CH_2CN, CH_3CH_2OH, CH_3CHCH_2, CH_3CONH_2, CH_3OCH_3, $\mathbf{CH_3C_4H}$, $\mathbf{C_7HN}$, $\mathbf{C_8H}$, $\mathbf{C_8H^-}$.

10 or more atoms
CH_3CH_2CHO, $\underline{CH_3COCH_3}$, $\mathbf{CH_3C_4CN}$, $HOCH_2CH_2OH$, $\mathbf{CH_3C_6H}$, $\mathbf{HC_8CN}$, $HCO_2C_2H_5$, nC_3H_7CN, C_6H_6, $\underline{HOCH_2COCH_2OH}$, $\mathbf{HC_{10}CN}$, $\mathbf{HC_{11}N}$, $C_{14}H_{10}$, C_{60}, C_{70}.

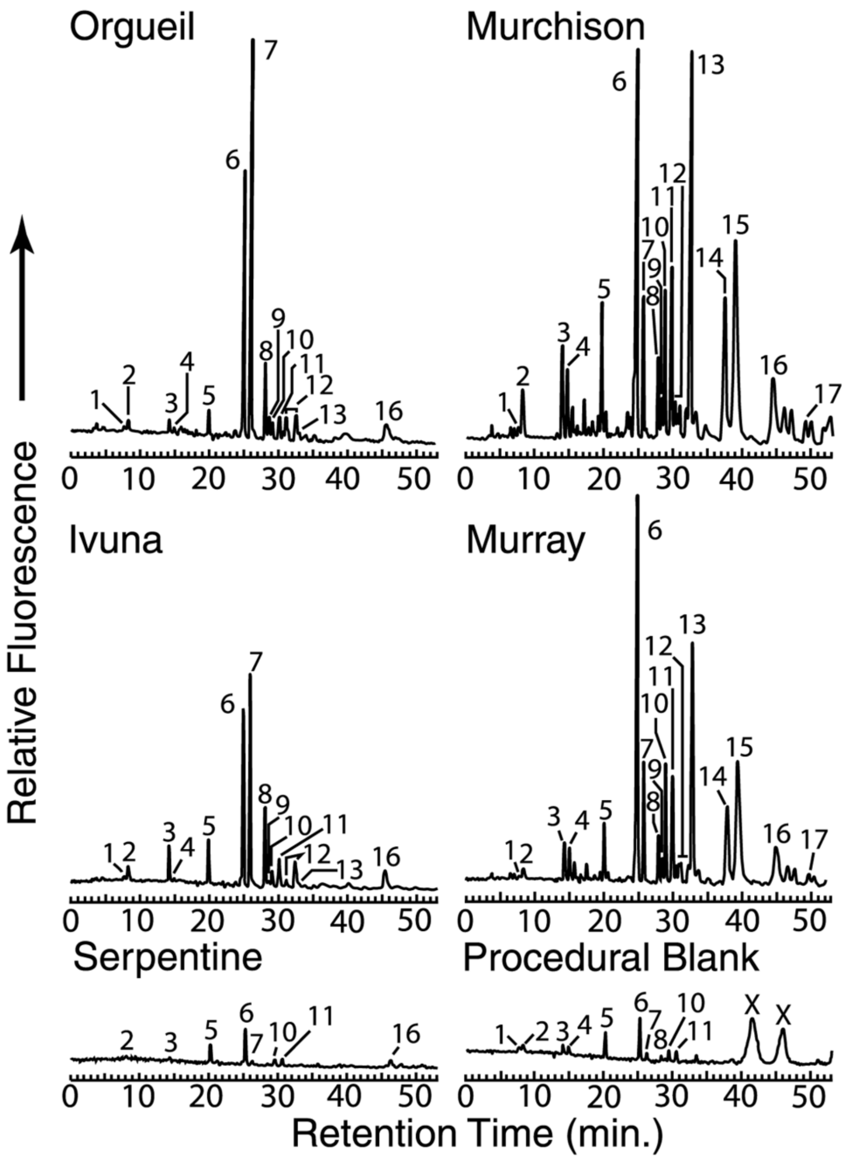
Deuterated molecules
HD, H_2D^+, HD_2^+, HDO, D_2O, DCN, DCO, DNC, N_2D^+, NH_2D, NHD_2, ND_3, HDCO, D_2CO, CH_2DC_2H, CH_3C_2D.

Molecules reported but not confirmed
HOCN, $NH_2CH_2CO_2H$, $CO(CH_2OH)_2$, $C_2H_5COCH_3$, $C_{10}H_8^+$, SiH, PH_3.

[a] This list was compiled from data listed in: http://www.astro.uni-koeln.de/cdms/molecules http://www.astrochymist.org/astrochymist_ism.html http://en.wikipedia.org/wiki/List_of_molecules_in_interstellar_space, also ref. 43.

Wand, T.; Bowie, J.H. Org. & Biomol. Chem. 10, 652(2012).

Chromatogram Samples extracted from Meteors



1 D-Aspartic Acid
2 L-Aspartic Acid
3 L-Glutamic Acid
4 D-Glutamic Acid
5 D,L-Serine
6 Glycine
7 β-Alanine
8 γ-Amino-*n*-butyric Acid (g-ABA)
9 D,L-b-Aminoisobutyric Acid (b-AIB)
10 D-Alanine
11 L-Alanine
12 D,L-β-Amino-n-butyric Acid (b-ABA)
13 α-Aminoisobutyric Acid (AIB)
14 D,L-α-Amino-n-butyric Acid (a-ABA)
15 D,L-Isovaline
16 L-Valine
17 D-Valine
X: unknown

Ehrenfreund, P. Rep. Prog. Phys., 65, 1427(2002).

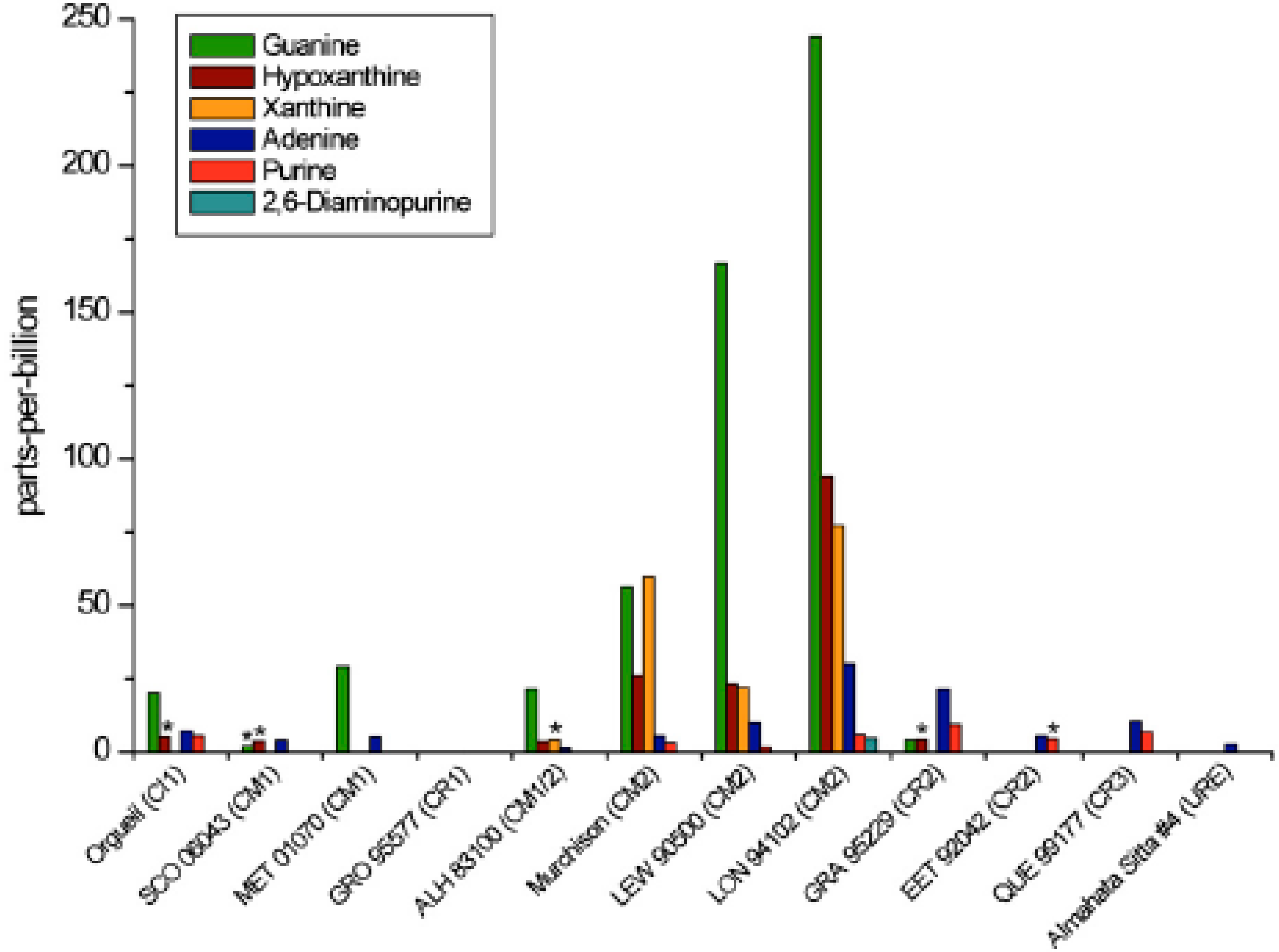


Fig. 1. Distribution of guanine, hypoxanthine, xanthine, adenine, purine, and 2,6-diaminopurine in 11 carbonaceous chondrites and one ureilite.

M. P. Callahan *et al*. PNAS, 108, 13995–13998(2011).

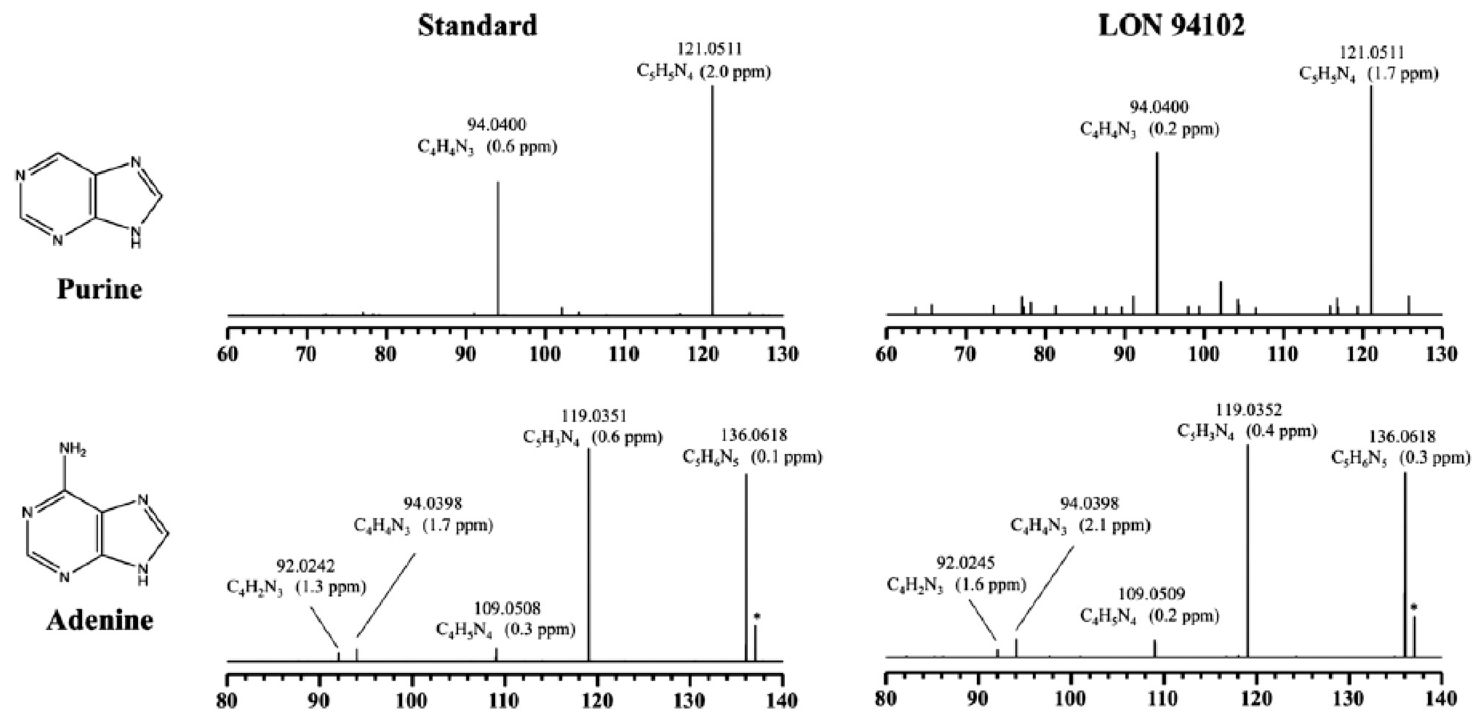


Fig. 2. Mass-selected fragmentation spectra of reference standards (left spectra) and compounds found in the meteorite LON 94102 (right spectra) measured on an LTQ Orbitrap XL hybrid mass spectrometer using an HCD (higher energy collision dissociation) setting of 90 to 100%. Purine, adenine, 2,6-diaminopurine, and 6,8-diaminopurine were identified using accurate mass measurements on the parent mass and multiple fragment masses and chromatographic retention time. Mass accuracy of less than 5 ppm allows for the unambiguous assignment of elemental formulae. The * represents inferences in the fragmentation spectra that are present in both the meteorite and reference standard spectra.

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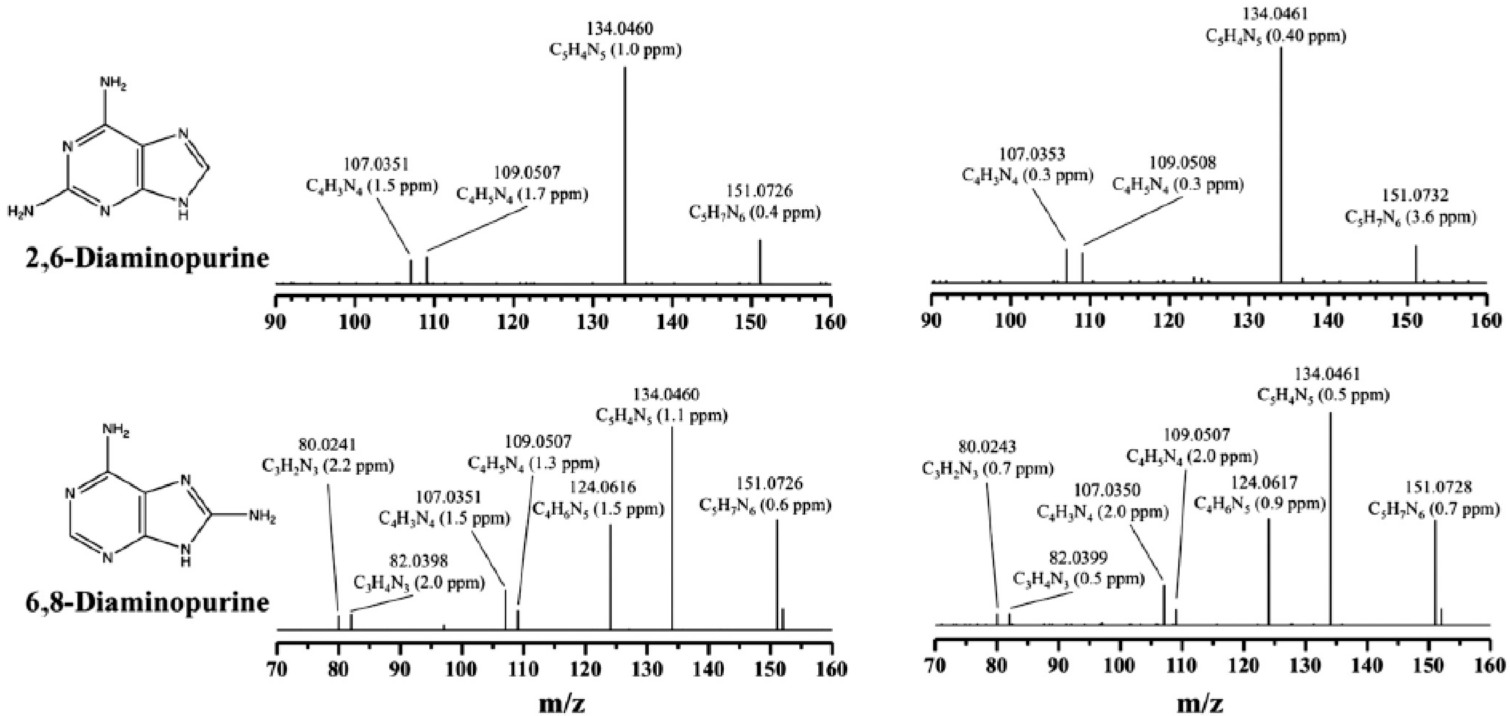

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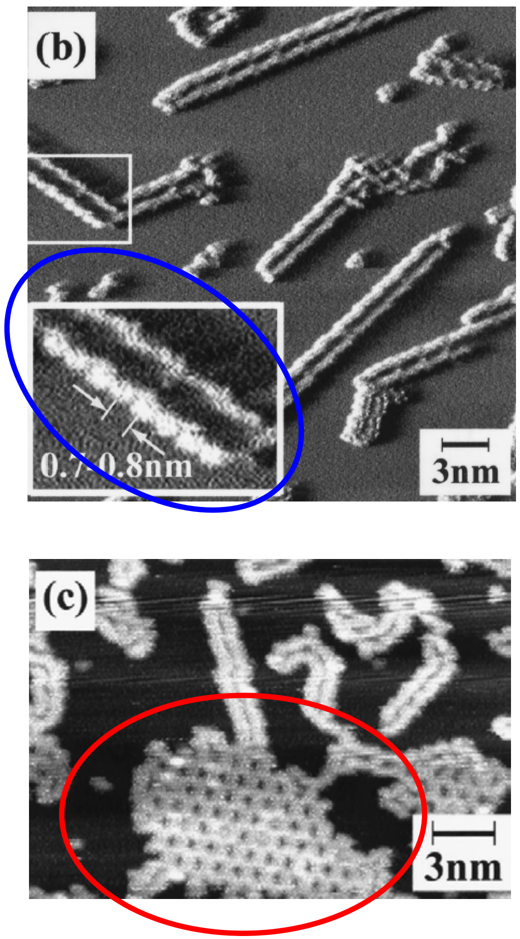
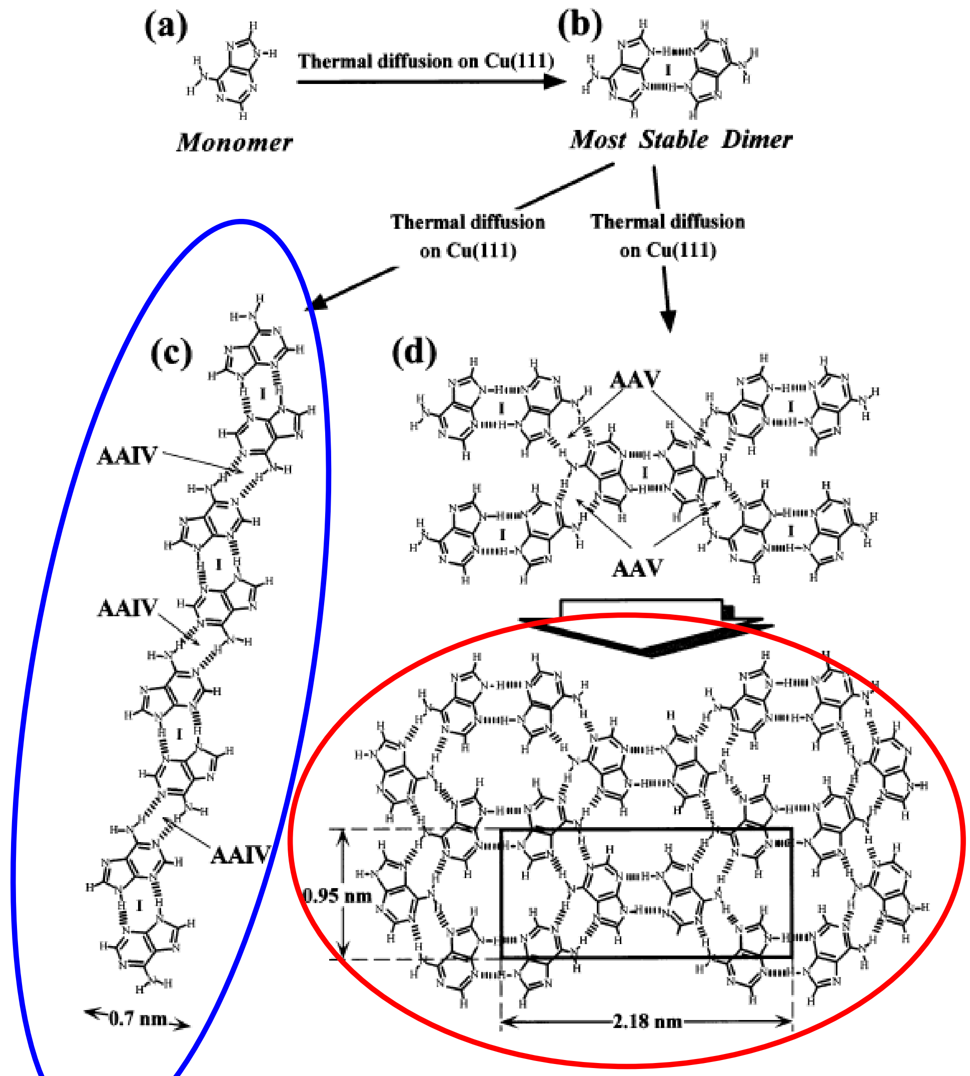
M. P. Callahan *et al*. PNAS, 108, 13995–13998(2011).

Low-dimensional of super hydrogen-bond complexes of adenine on Cu(111) surfaces



Scanning Tunneling Microscope (STM)

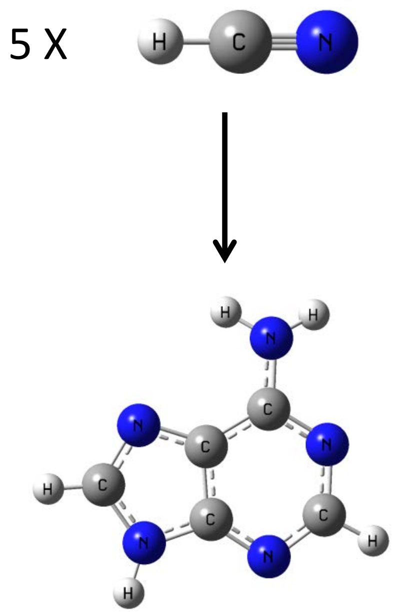


PM3 Semi-empirical Calculations

Furukawa, M.; Tanaka, H.; Kawai, T. Surface Science 445 1 (2000).

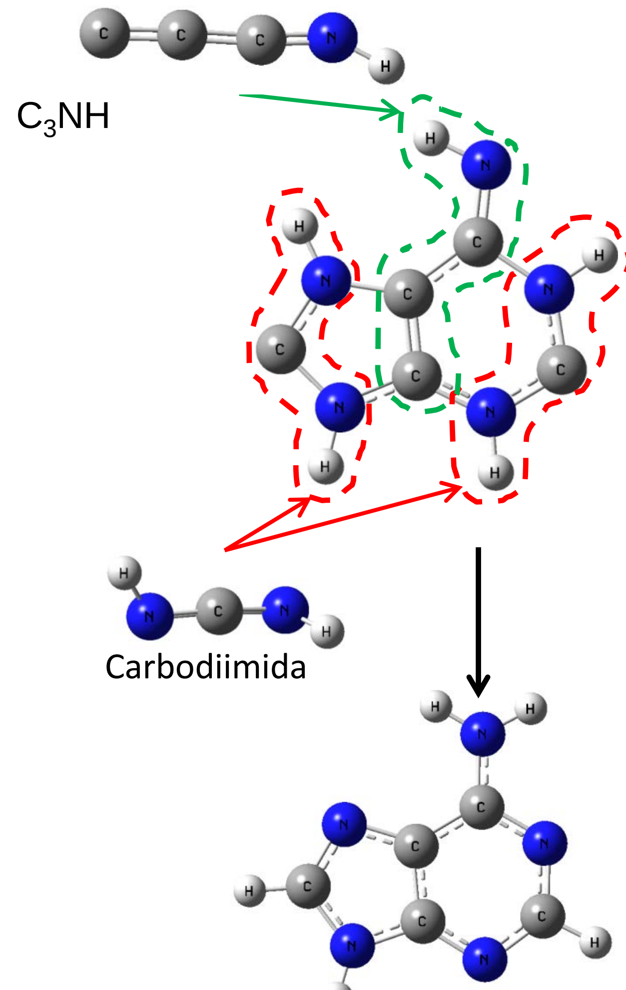
Mechanisms for the Synthesis of Adenine

D. Roy, K. Najafian, P. von R. Schleyer
***PNAS 104*, 17272 (2007).**



Adenine

J.B.P. da Silva, E. C. de Aguiar, K. M. Merz
***J. Chem. Phys. A 118*, 3637 (2014).**



Adenine

Mechanisms for the Synthesis of Adenine

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***PNAS 104*, 17272 (2007).**

B3LYP/6-311+G(d,p)

Rate determinant step → 71 kcal mol^{-1}

First it forms the 5-member ring, then he 6-member ring

Involves 14 steps

ΔG_R = -53.7 kcal mol^{-1}

J.B.P. da Silva, E. C. de Aguiar, K. M. Merz
***J. Chem. Phys. A 118*, 3637 (2014).**

MP2/6-311++G(d,p)

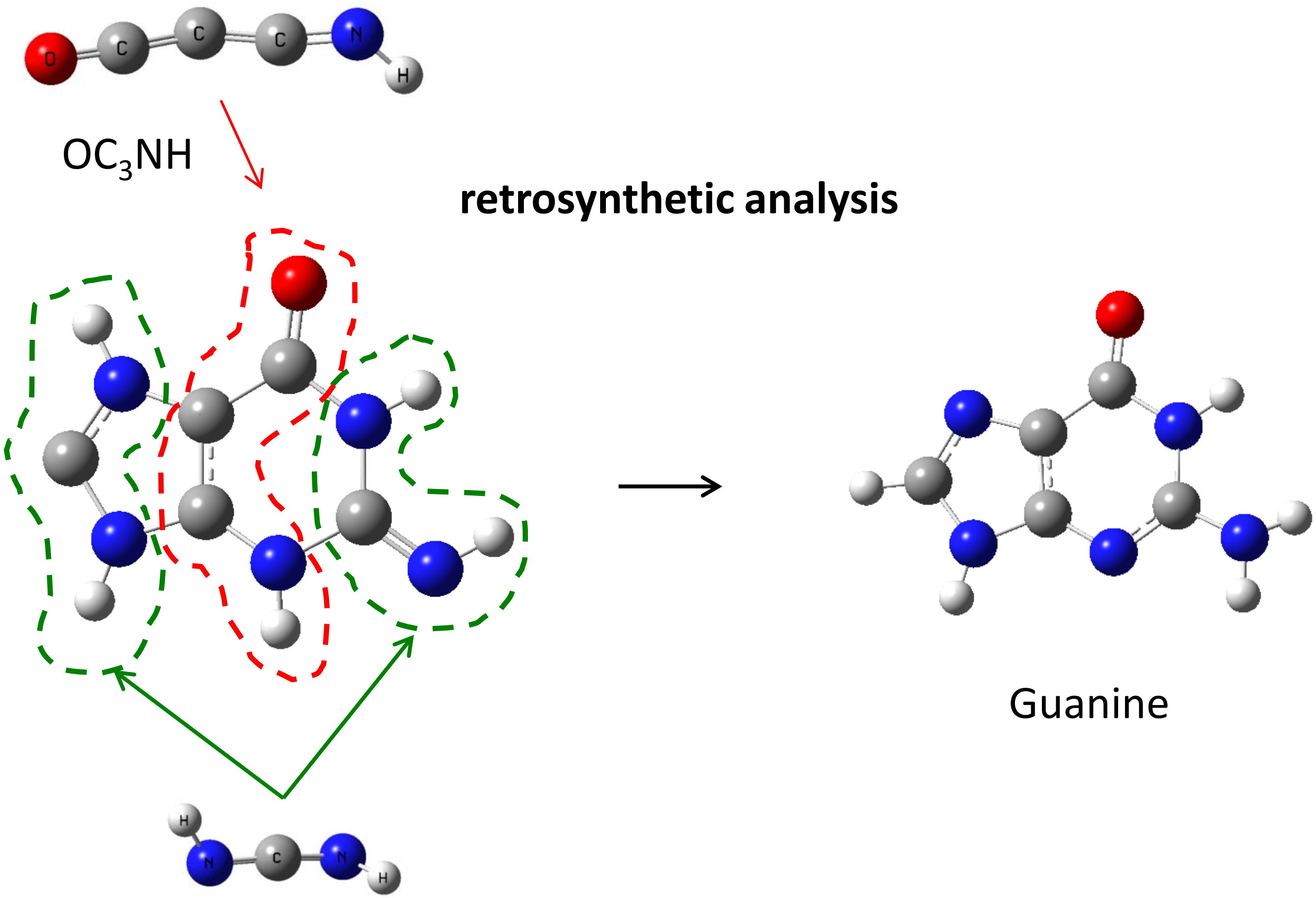
Rate determinant step → 23 kcal mol^{-1}

First it forms the 6-member ring, then he 5-member ring

Involves 6 steps

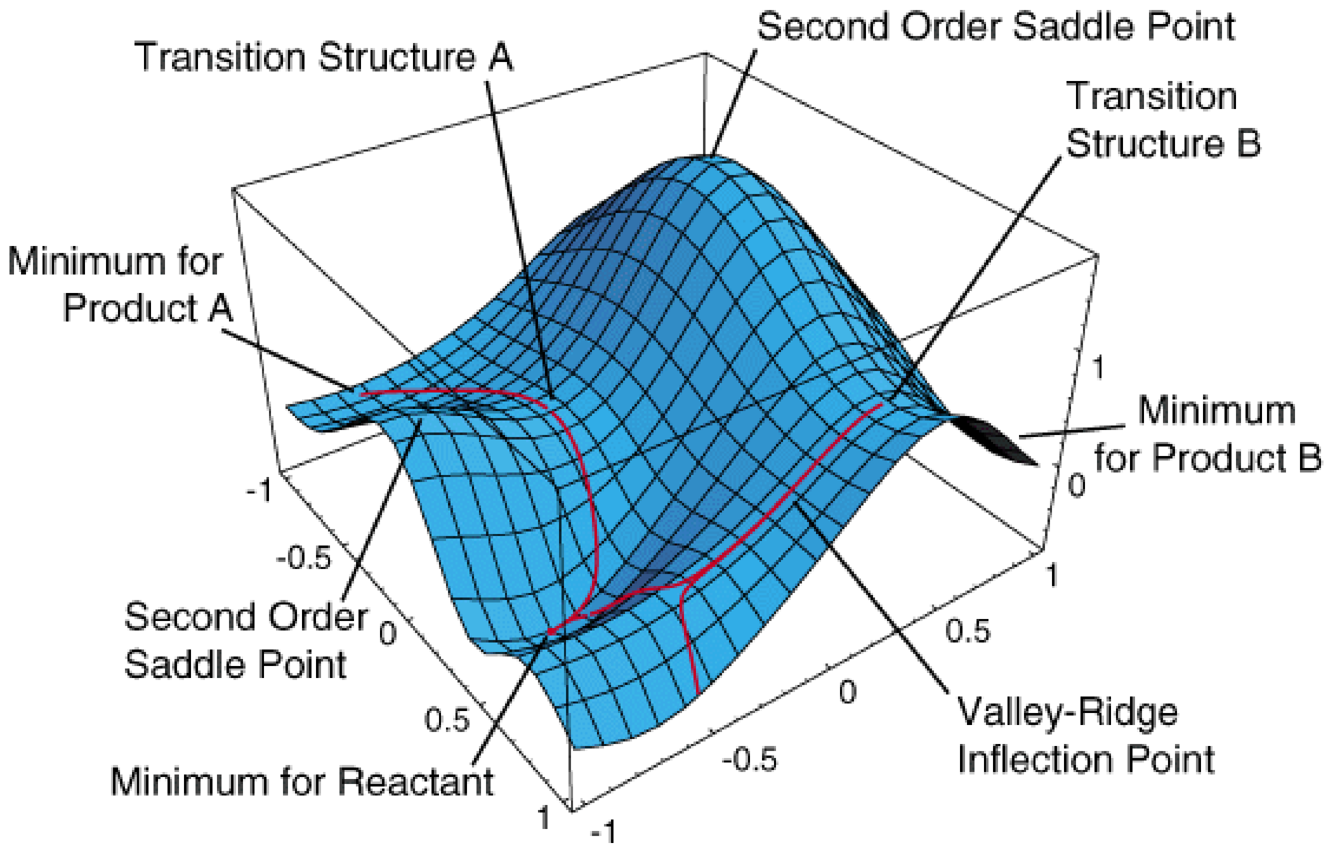
ΔG_R = -142.2 kcal mol^{-1}

Mechanism for the Synthesis of Guanine

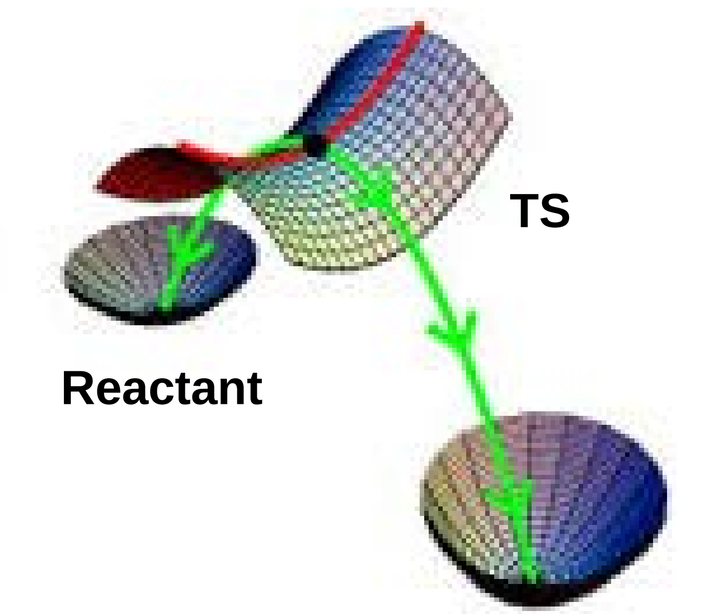


Carbodiimida

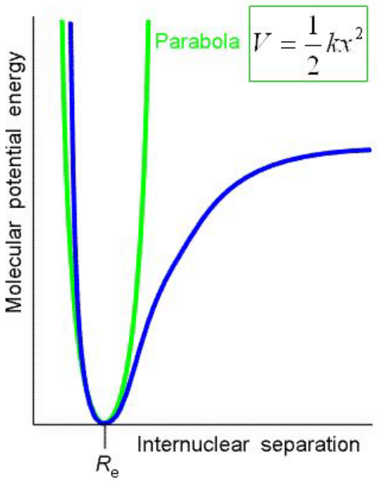
Potencial Energy Surface (PES)



Potencial Energy Surface (PES)



Harmonic approximation



$$f(x) = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

$$k = \left(\frac{\partial^2 V}{\partial x^2}\right)_0$$

For real reactants and products k > 0 → f(x) is a real number

For saddle point k <0 → f(x) is a imaginary number

Methodological background

Target: Solve the time independent Schrödinger equation

$$H\Psi = E\Psi$$

$$H = \sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right) + \sum_{A=1}^{N}\left(-\frac{\hbar^2}{2M_A}\nabla_A^2\right) + \sum_{i=1}^{n}\sum_{A=1}^{N}\left(-\frac{Ze^2}{r_{iA}}\right) + \sum_{i=1}^{n}\sum_{j>1}^{n}\frac{e^2}{r_{ij}} + \sum_{A=1}^{N}\sum_{B>A}^{N}\frac{Z_A Z_B e^2}{R_{AB}}$$

$K_{electrons}$ K_{nuclei} $V_{el.-nucl.}$ $V_{el.-el..}$ $V_{nucl.-nucl.}$

Ψ – wave funtion; E – total energy of the system

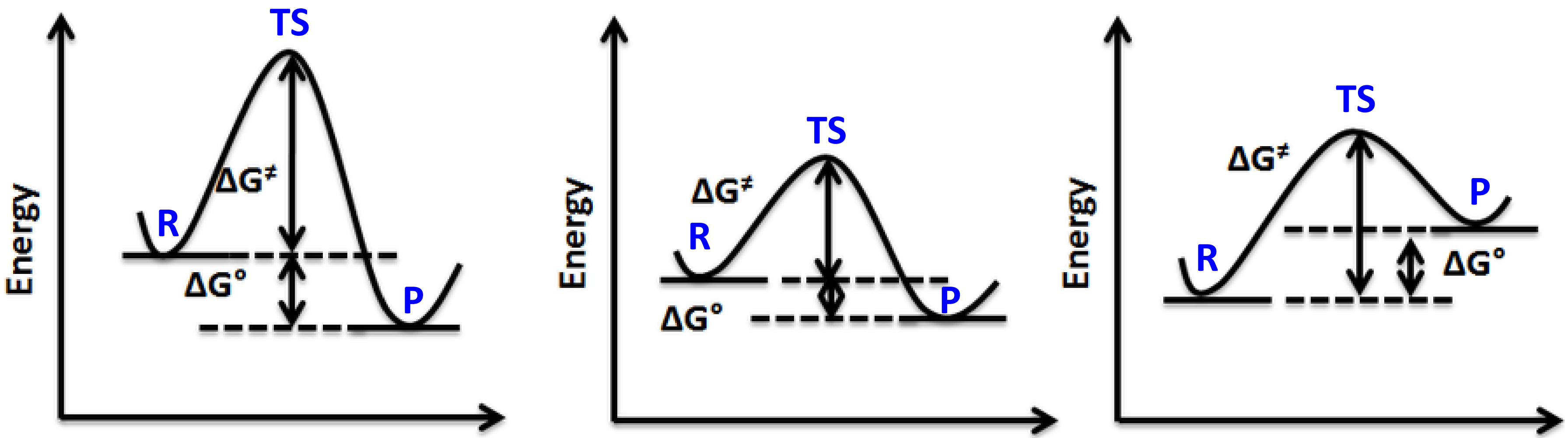
H = E + KT G = H - TS

Computation

G09, MP2/6-311++G(d,p), gas phase, default internal criteria of convergence,

energy in kcal mol^{-1}. **T = 10 K** **P = 1 bar**

Methodological background

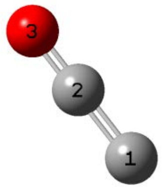


Large ΔG≠ , ΔG° < 0
Slow and favorable

Small ΔG≠ , ΔG° < 0
Fast and favorable

Small ΔG≠ , ΔG° > 0
Fast and unfavorable

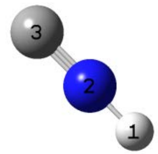
MP2/6-311++G(2d,2p)



1

G = -150.885159
μ = 1.29 D
ν_1 = 318.06 cm^{-1}

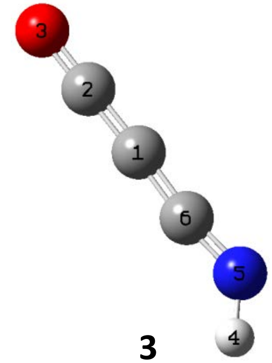
\+



2

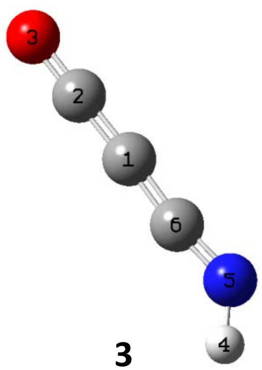
G = -93.179530
μ = 3.28 D
ν_1 = 440.23 cm^{-1}

-123.78 →



3

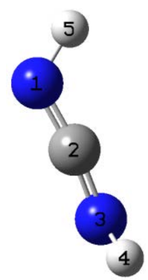
G = -244.261938
μ = 2.83 D
ν_1 = 32.72 cm^{-1}



3

G = -244.261938
μ = 2.83 D
ν_1 = 32.72 cm^{-1}

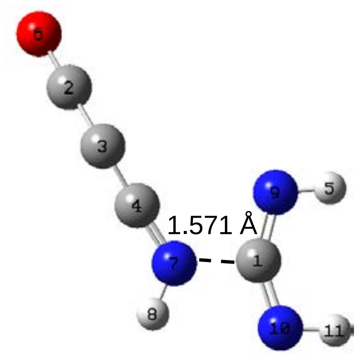
\+



4

G = -148.425378
μ = 2.03 D
ν_1 = 535.15 cm^{-1}

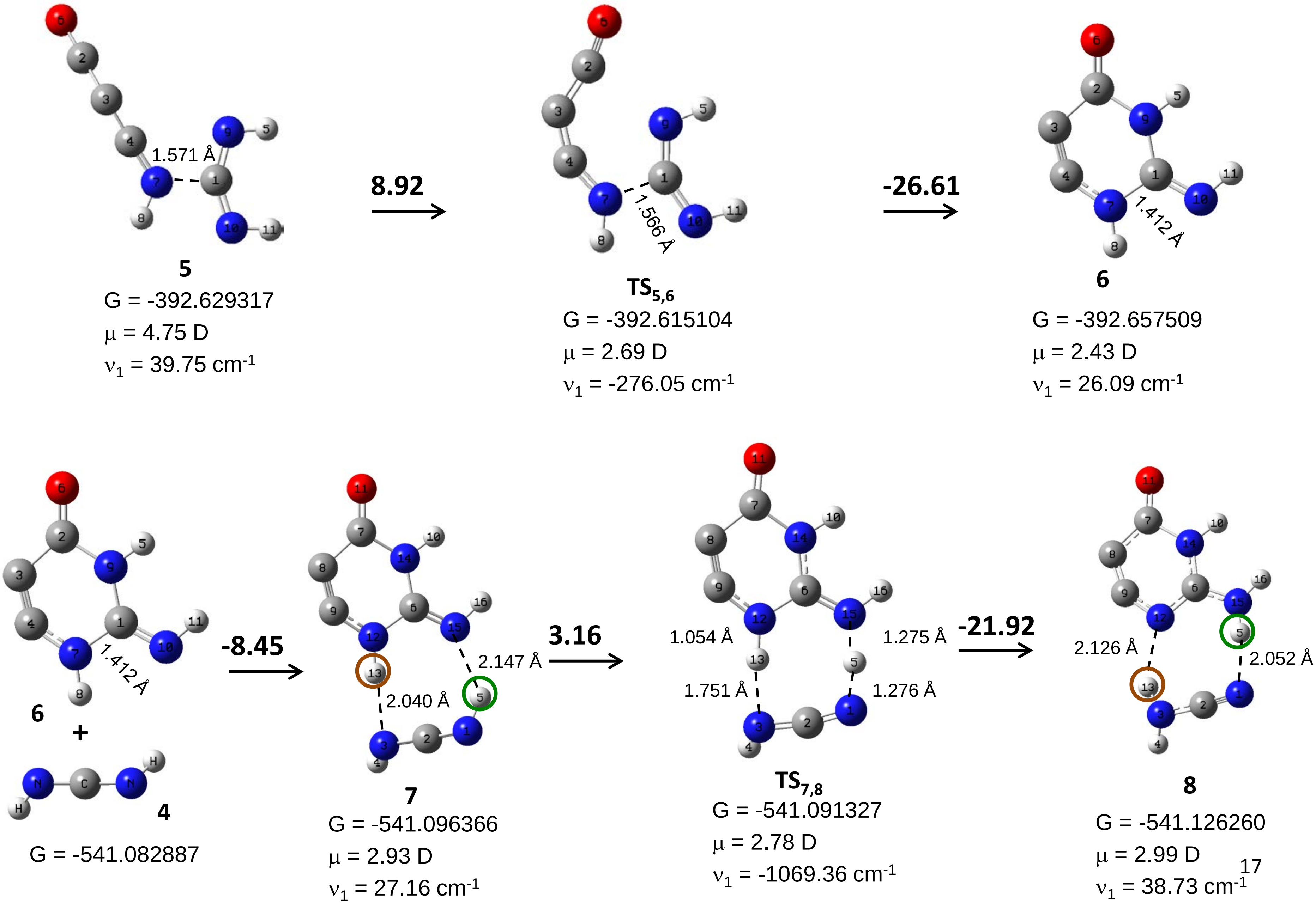
36.39 →



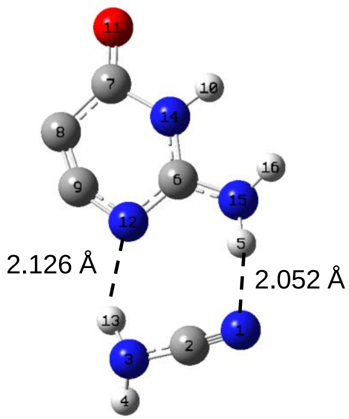
5

G = -392.629317
μ = 4.75 D
ν_1 = 39.75 cm^{-1}

MP2/6-311++G(2d,2p)



MP2/6-311++G(2d,2p)



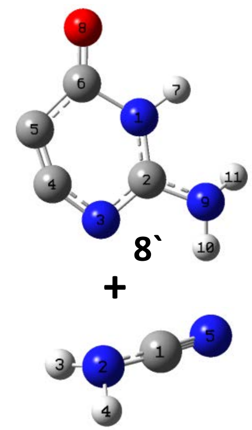
8

G = -541.126260

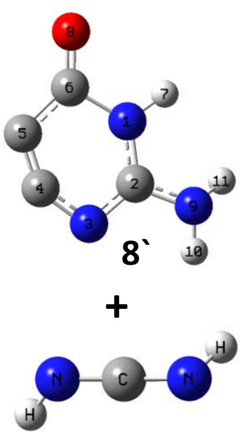
μ = 2.99 D

ν_1 = 38.73 cm^{-1}

10.78 →

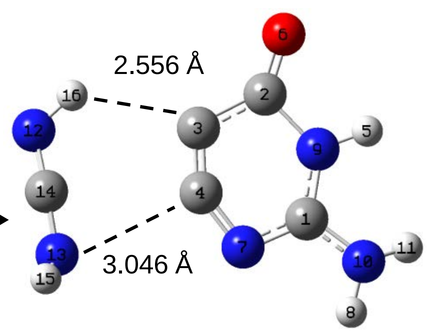


G = -541.109074



G = -541.102331

-3.77 →



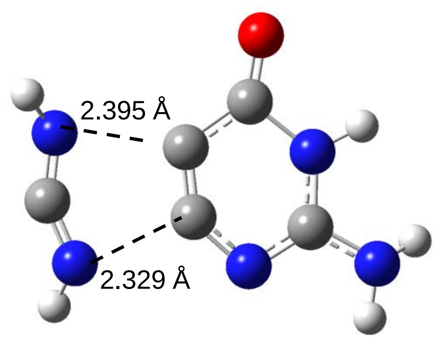
9

G = -541.108340

μ = 6.39 D

ν_1 = 16.96 cm^{-1}

6.80 →



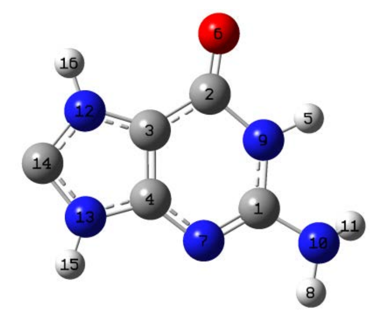
$TS_{9,10}$

G = -541.102291

μ = 3.14 D

ν_1 = -182.06 cm^{-1}

-77.42 →



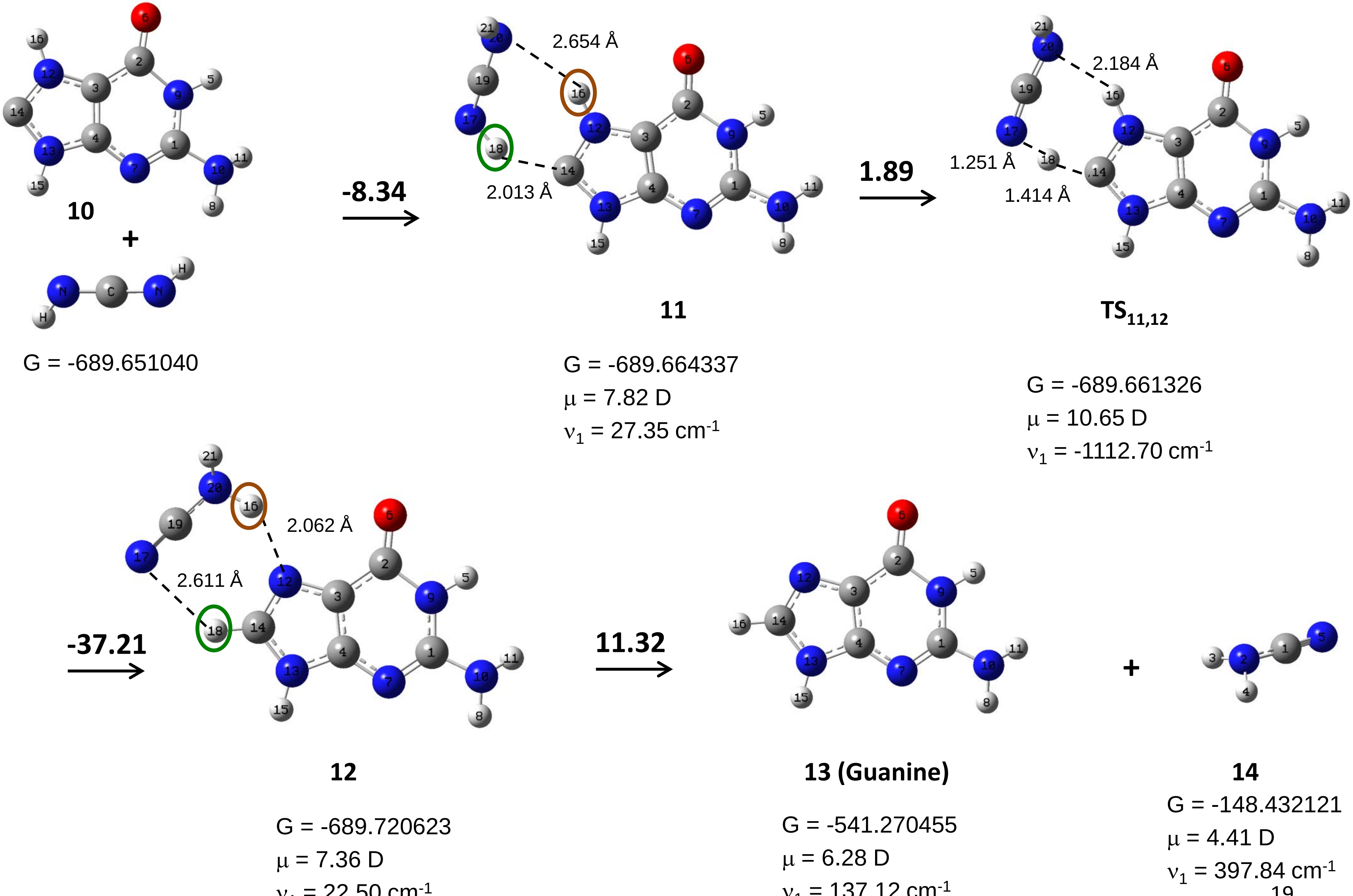
10

G = -541.225662

μ = 5.55 D

ν_1 = 143.27 cm^{-1}

MP2/6-311++G(2d,2p)



MP2/6-311++G(2d,2p)

$$CCO\ (g) + HCN\ (g) + 4\ HNCNH\ (g) \rightarrow C_5N_5H_5O\ (g) + 2\ H_2NCN\ (g)$$

(Guanine)

$\Delta_R G^\circ(guanine)$ = -228.2 kcal mol^{-1}

$\Delta_R G^\circ(adenine)$ = -142.2 kcal mol^{-1}

$$H_2NCN\ (g) \rightarrow HNCNH\ (g)$$

$\Delta_R G^\circ(HNCNH)$ = 4.8 kcal mol^{-1}

$E_a(HNCNH)$ = 78.7 kcal mol^{-1}

Conclusion

1 – A new mechanism for the formation of guanine in gas phase was proposed considering the species observed in the ISM: CCO, HCN and HNCNH.

2 – The new mechanism has **6 steps** and involves only bimolecular reactions.

3 – HNCNH plays a key rule for H-bond assisted proton transfer process.

4 – We propose first the formation of the 6-membered heterocyclic ring and then the formation of the 5-membered ring.

5 – The rate determinant step involves a energy barrier *c.a.* 36 kcal mol^{-1}.

6 – This new mechanism is very exergonic, ΔG_R = -228.24 kcal mol^{-1} .

7 – Formation of guanine may be more spontaneous than adenine at the ISM .

Acknowledgments

VIRTUS IMPAVIDA

dQF
Departamento
de Química Fundamental

GQ
TC
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CENAPADUFC

da Silva
Fundation