



Radical-assisted pathways for the prebiotic formation of nucleobases from plausible precursors

Sarabjeet Kaur¹, and Purshotam Sharma¹

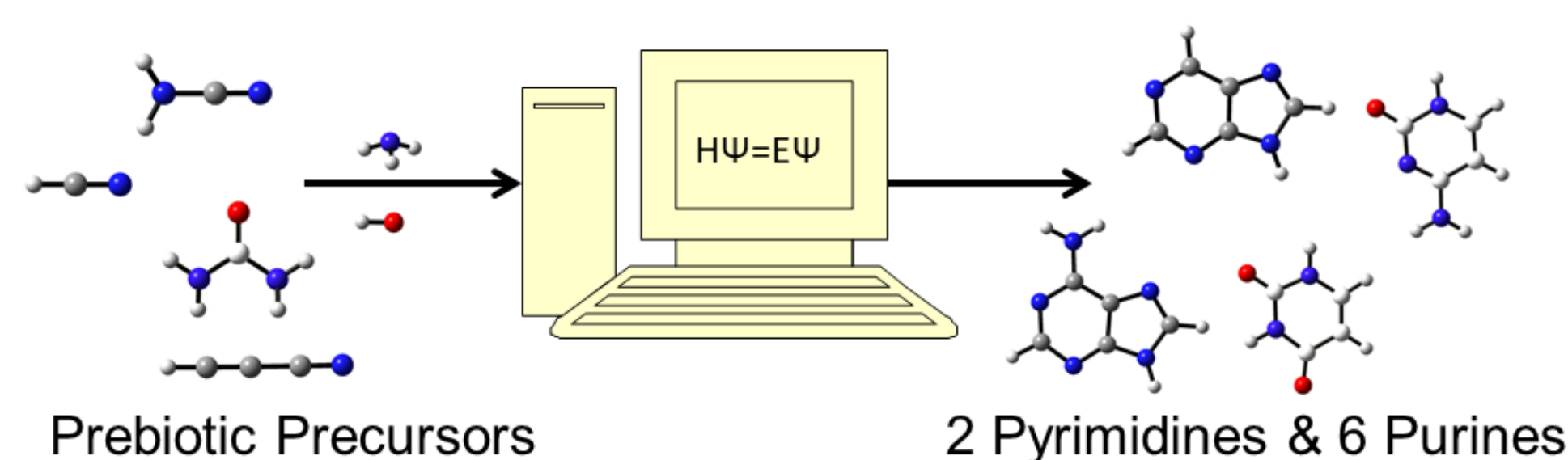
Email: sarab14jeet@gmail.com; purshotam.chem@gmail.com.

¹Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh, India.



Introduction

- Canonical nucleobases form an indispensable component of present day genetics.
- Their formation pathways on early earth have attracted attention as well as debate.
- Quantum chemical calculations can complement experimental studies on prebiotic nucleobase formation and provide some insight.
- UV radiations on primitive earth coupled with the detection of radicals in laboratory experiments suggest that nucleobase formation followed radical-based routes
- Thus, our group proposes and investigates plausible free radical pathways for nucleobase formation using quantum chemical tools.



Computational Details

- Geometry optimization and calculation of electronic energies of reactants, transition states, intermediates and products were performed in the gas (B3LYP/6–311G(d,p)) phase.
- Stationary points on the reaction surfaces as minima (reactants, intermediates and products) or saddle points (transition states) were characterized using vibrational frequency calculations.
- IRC scans confirmed the right transition state connecting reactants to products.

Formation of Purines

- Various purines can be formed through radical-assisted pathways from starting precursors *i.e.* cyanamide and cyanoacetylene via five-membered intermediate, 4-cyanoimidazole in the presence of ammonia
- Skeletal components of 4-cyanoimidazole can be solely made from initial precursors.

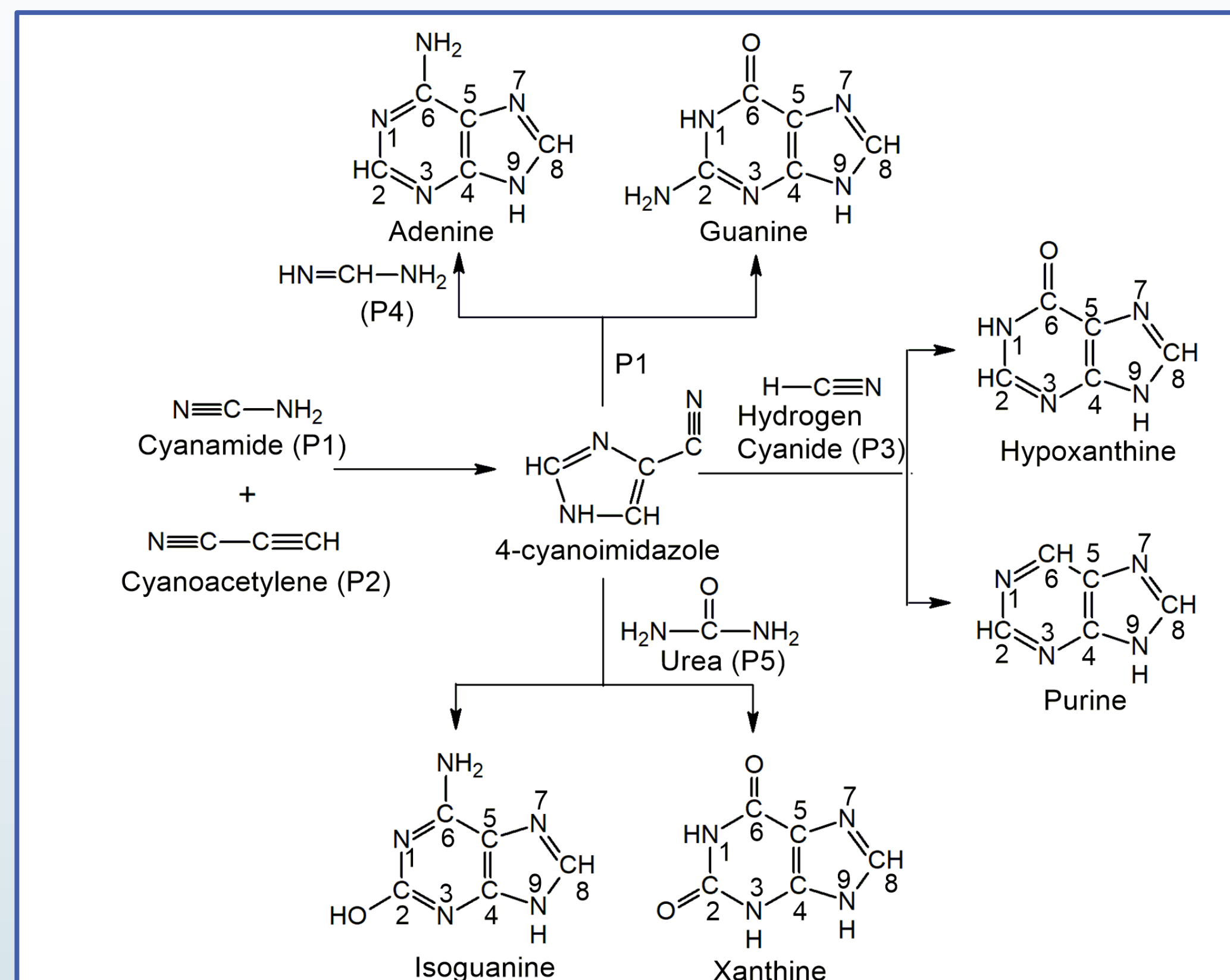


Figure 1. Formation of purines from cyanamide (P1), cyanoacetylene (P2), HCN (P3) and urea (P5).

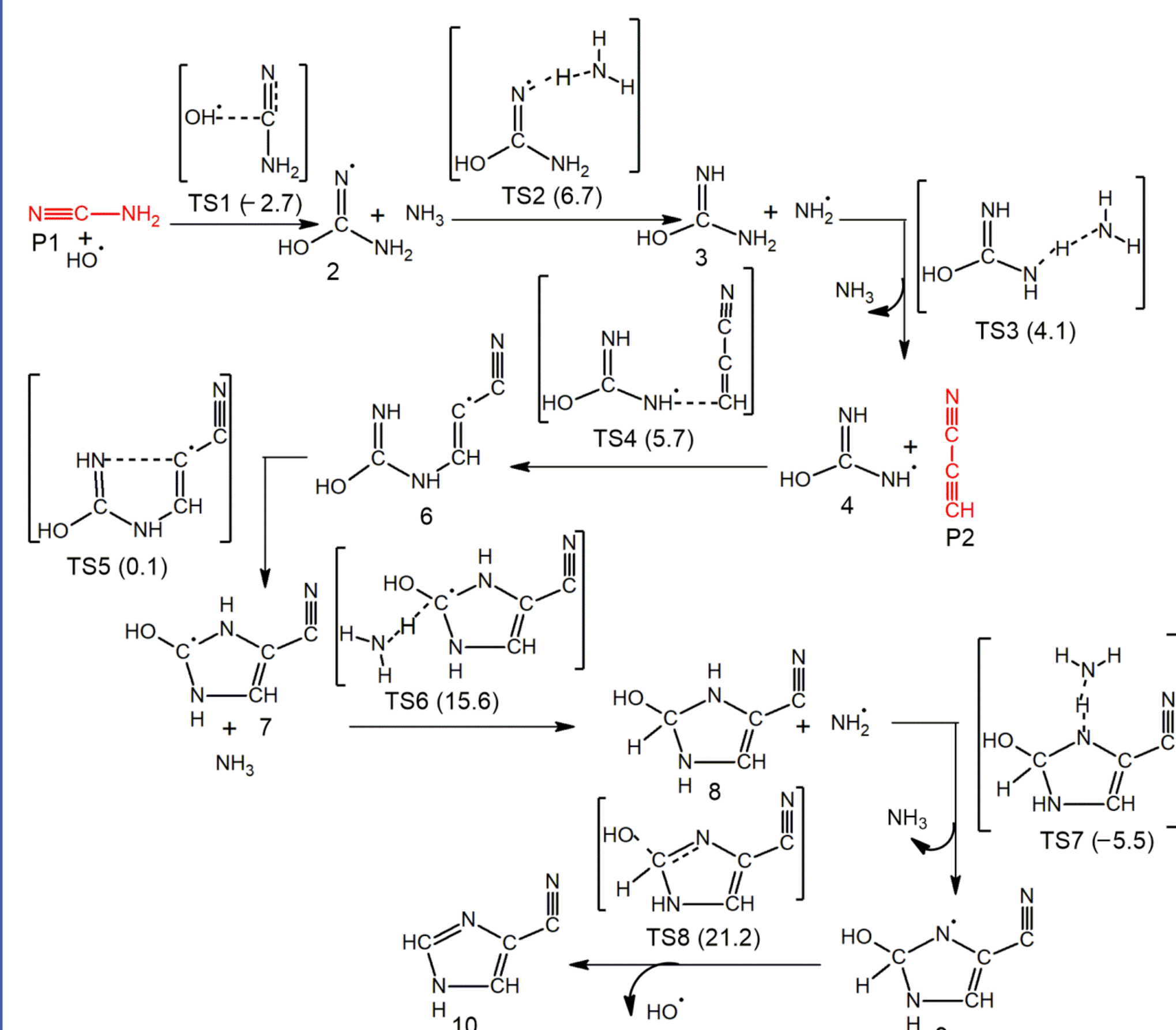


Figure 2. Formation of 4-cyanoimidazole **10** from cyanamide (P1) and cyanoacetylene (P2). Relative energies (in kcal mol⁻¹) of TSs in parenthesis.

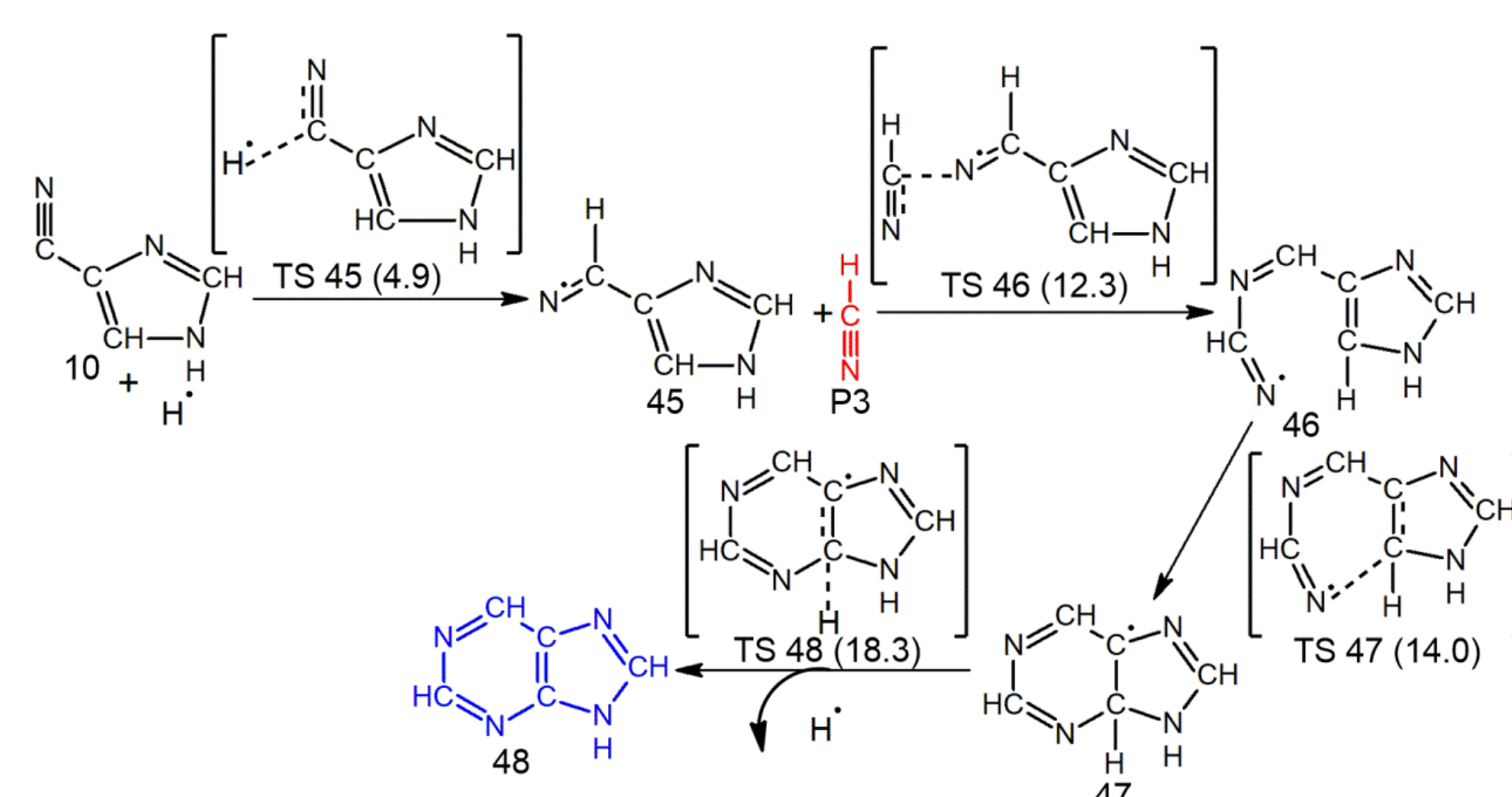


Figure 3. Formation of Purine **48** from 4-cyanoimidazole **10**. Relative energies (in kcal mol⁻¹) of TSs in parenthesis.

Formation of Pyrimidines

- Starting precursors- cyanoacetaldehyde and urea.
- Cyanoacetaldehyde acts as a source of –NH₂ group of cytosine and of the –C=O group of uracil and the NH–CO–NH skeleton of urea converts into N–C–N segment of the pyrimidine ring.

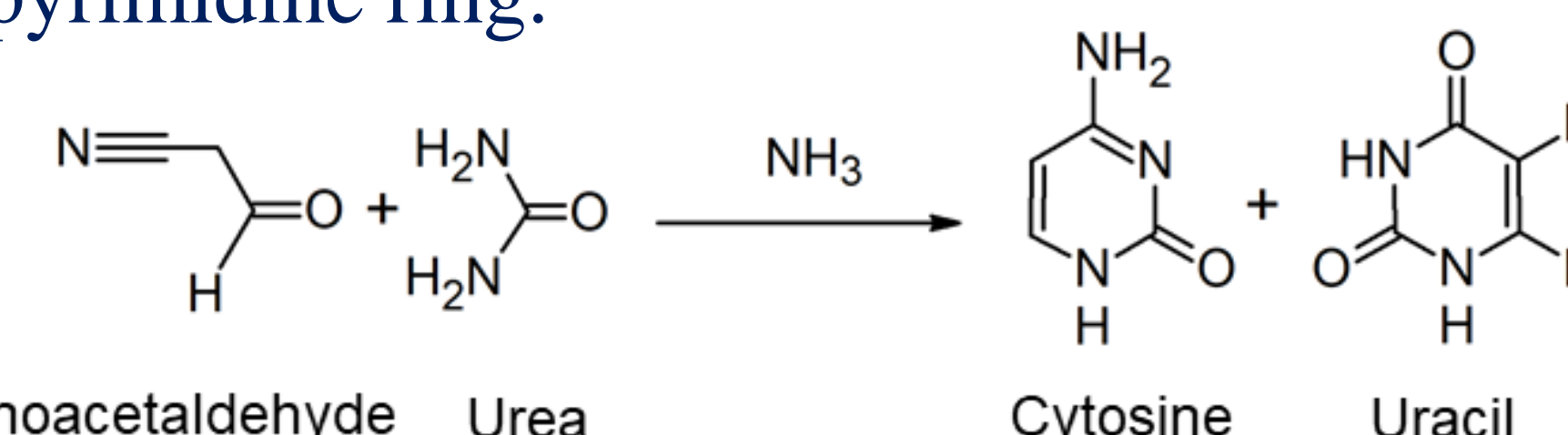


Figure 4. Formation of cytosine and uracil from cyanoacetaldehyde and urea.

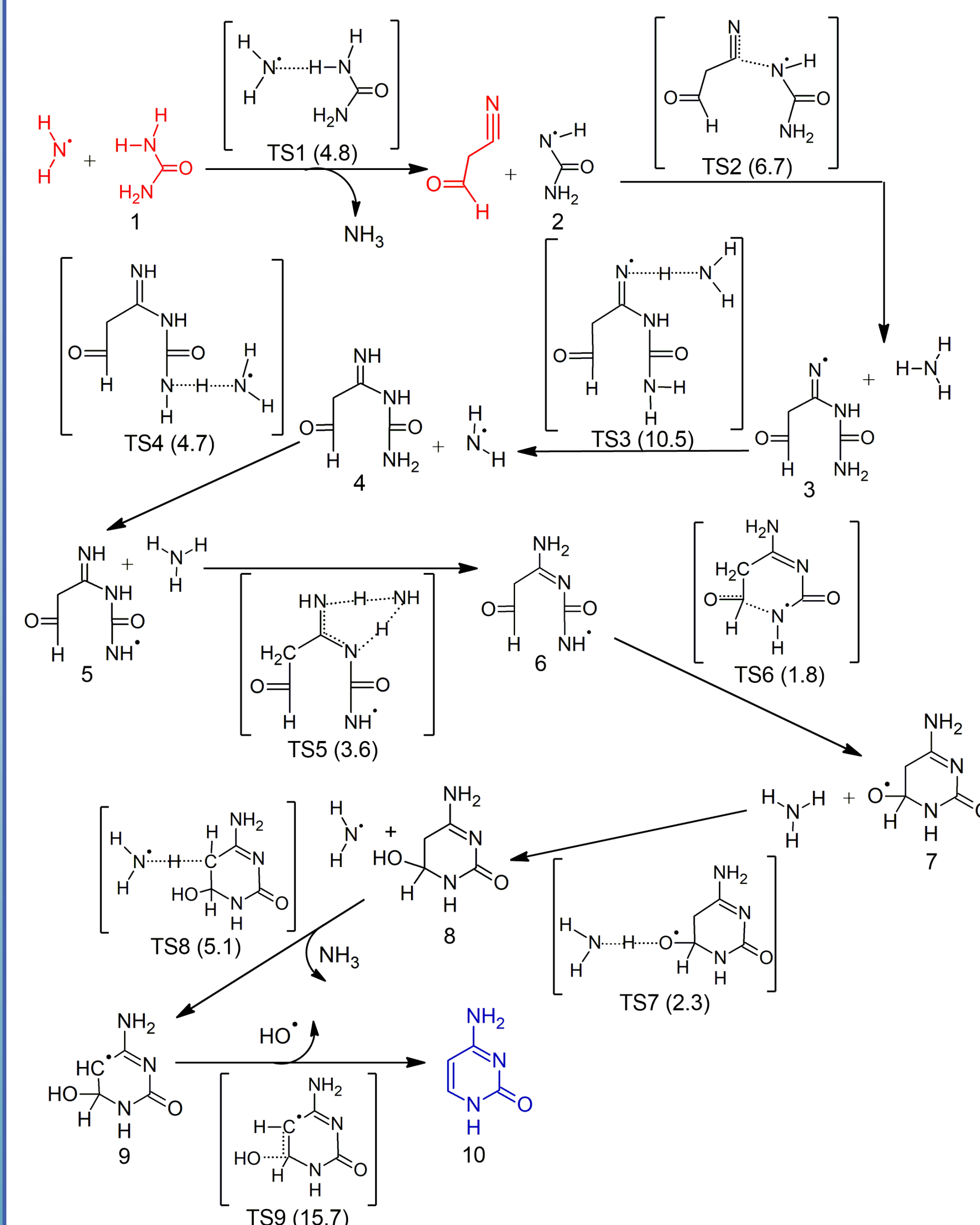


Figure 5. Formation of cytosine **10** from cyanoacetaldehyde and urea. Relative energies (in kcal mol⁻¹) of TSs in parenthesis.

Note: In figures 1–4, reactants are in red and product in blue colour.

Acknowledgements

PS thanks the DST and UGC, New Delhi for financial support through the DST INSPIRE and the UGC FRP programs, respectively. SK thanks the DST for financial support through WOS-A.