Supplementary material

to the paper

*Prebiotic route to thymine from formamide – a combined experimental-theoretical study*

by

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Figure S1: Separation of nucleobases thymine (T) and uracil (U) by CE. BGE: 40 mM sodium borate with 60 mM SDS (pH 9.8). Hydrodynamic injection: 50 mbar for 5 s, separation voltage: 15 kV, absorption signal at $\lambda = 260$ nm. Electropherograms of (A) pure formamide, (B) 200 μM standards T and U in formamide, (C) formamide sample with 2000 μM U before thermolysis (0 hours) and (D) after 12 hours of thermolysis.
Optimized geometries and computed electronic energies for all structures from Figure 3, main text.

structure 1 (uracil), B3LYP/6-31G* electronic energy (Hartree): -414.839207

N    -0.178893    -0.155479     0.575524
C     0.332176     0.168722     1.820444
O    -0.020908     1.157628     2.452904
N     1.277382    -0.731560     2.277197
C     1.746753    -1.887800     1.631080
O     2.598254    -2.592368     2.173427
C     1.139881    -2.124329     0.335409
C     0.211147    -1.259664    -0.137809
H     1.675714    -0.526803     3.188454
H    -0.876242     0.475903     0.198169
H     1.443917    -2.994038    -0.231708
H    -0.277300    -1.382554    -1.097632

structure 2, B3LYP/6-31G* electronic energy (Hartree): -529.367702

N    -0.006464    -0.004708     0.477130
C     0.411531     0.237260     1.773125
O     0.143162     1.264556     2.385077
N     1.162037    -0.795399     2.305224
C     1.522827    -2.001670     1.687672
O     2.214082    -2.818750     2.295460
C     1.028758    -2.155738     0.322845
C     0.288910    -1.151514    -0.212340
H     1.494205    -0.655302     3.254804
H    -0.559585     0.723768     0.041040
C     1.325657    -3.424869    -0.428352
H    -0.108895    -1.194887    -1.220793
H     1.127913    -3.271266    -1.497510
O     0.596963    -4.552997     0.071361
H     2.380249    -3.689914    -0.311817
H    -0.346890    -4.361799    -0.060114

structure 3, B3LYP/6-31G* electronic energy (Hartree): -642.709946

N     0.077549     0.085780     0.516412
C     0.366874     0.176380     1.868875
O     0.083338     1.153254     2.549524
N     1.007000    -0.944297     2.366558
C     1.373931    -2.101744     1.668216
O     1.954790    -3.018041     2.247939
C     1.015116    -2.093021     0.254127
C     0.385787    -1.009947    -0.252479
H     1.244453    -0.914485     3.353846
H    -0.386867     0.885568     0.100861
C     1.356331    -3.282555    -0.585413
H     0.096231    -0.924882    -1.295127
H     1.245276    -3.057246    -1.649524
structure 4, B3LYP/6-31G* electronic energy (Hartree): -454.131313
N   -0.216571  -0.172046  0.653766
C    0.361166   0.150685  1.837621
O    0.000837   1.073526  2.565781
N   1.421067   -0.688777  2.227237
C   1.789645   -1.895064  1.656664
O    2.593981   -2.635014  2.214759
C   1.126920   -2.192883  0.353128
C    0.431379   -1.040802  -0.331238
H    1.820674   -0.477879  3.136313
H   -0.886708   0.506643  0.312177
C    1.206162   -3.425658  -0.157184
H    1.162919   -0.464114  -0.918044
H    0.724062   -3.684049  -1.095621
H    1.763713   -4.202567  0.356478
H   -0.330475   -1.408900  -1.021468

structure 5, B3LYP/6-31G* electronic energy (Hartree): -454.514428
N     0.000569   0.051851  0.555912
C    0.424569   0.272267  1.829859
O    0.175719   1.265148  2.489932
N    1.201616   -0.779127  2.373996
C    1.573321   -1.967069  1.804541
O    2.239583   -2.826695  2.355676
C    1.069214   -2.150236  0.392122
C    0.339671   -1.081211  -0.239124
H    1.517138   -0.617652  3.328776
H   -0.533482   0.795963  0.120815
C    1.363333   -3.393982  -0.288521
H    1.032208   -0.803011  -1.076635
H   -0.527747   -1.481542  -0.794497
H    1.071090   -3.396307  -1.338387
H    0.802524   -4.179083  0.257483
H    2.415381   -3.671264  -0.134027

structure 6 (TS), B3LYP/6-31G* electronic energy (Hartree): -454.513642
N   -0.100235   0.000058  0.581205
C    0.380262   0.259244  1.841891
O    0.100723   1.246762  2.492791
N    1.236302   -0.739559  2.343962
C    1.629909   -1.917146  1.756862
O    2.362158   -2.736597  2.280259
C     1.027779    -2.158710     0.389581  
C     0.286622    -1.099155    -0.194516  
H     1.602280    -0.556136     3.276348  
H    -0.669938     0.721028     0.151345  
C     1.301442    -3.426031    -0.288443  
H     1.334193    -0.914124    -0.706308  
H    -0.364947    -1.319248    -1.042794  
H     0.979788    -4.180919     0.259874  
H     2.349194    -3.719709    -0.173433

structure 7, B3LYP/6-31G* electronic energy (Hartree): -454.566478

N    -0.222422    -0.131067     0.577656  
C     0.227297     0.089585     1.939494  
O    -0.311502     0.930026     2.613161  
N     1.259086    -0.723594     2.317954  
C     1.902039    -1.701385     1.554897  
O     2.798642    -2.365636     2.026519  
C     1.413398    -1.870803     0.122570  
C     0.289532    -0.987170    -0.242480  
H     1.591367    -0.597411     3.272617  
H    -0.998980     0.469103     0.288743  
C     1.080315    -3.352679    -0.205270  
H     2.244240    -1.572444    -0.539369  
H    -0.143799    -1.039903    -1.238825  
H     0.831087    -3.450355    -1.264513  
H     0.241025    -3.702444     0.400827  
H     1.963383    -3.954874     0.013940

structure 8 (thymine), B3LYP/6-31G* electronic energy (Hartree): -454.158855

N    -0.119468    -0.111207     0.570646  
C     0.446285     0.233606     1.780445  
O     0.188852     1.275167     2.376225  
N     1.334356    -0.715670     2.253876  
C     1.693075    -1.928895     1.651320  
O     2.505625    -2.673022     2.203436  
C     1.039425    -2.199665     0.375552  
C     0.166487    -1.277563    -0.100262  
H     1.775733    -0.503473     3.143432  
H    -0.778690     0.550411     0.177928  
C     1.365537    -3.479070    -0.341007  
H     2.436466    -3.541059    -0.568944  
H     0.807877    -3.552651    -1.278840  
H     1.119828    -4.350726     0.277483  
H    -0.360438    -1.402873    -1.039763

formaldehyde, B3LYP/6-31G* electronic energy (Hartree): -114.506883

C    -0.795053    -4.583845    -1.319591
formic acid, B3LYP/6-31G* electronic energy (Hartree): -189.766497
H  0.819434  -5.606883  -1.066310  
O  0.322520  -4.924999  -0.568063  
C  -0.765703  -4.592124  -1.272899  
O  -1.075872  -5.061045  -2.346376  
H  -1.340179  -3.827509  -0.733563

water, B3LYP/6-31G* electronic energy (Hartree): -76.420739
O  0.000000   0.000000  -0.018996  
H  -0.535846   0.535846  -0.625502  
H   0.535846  -0.535846  -0.625502

carbon dioxide, B3LYP/6-31G* electronic energy (Hartree): -188.584272
C   0.177800  -0.120305  -0.079257  
O   0.378076   0.314578   0.987080  
O  -0.022476  -0.555187  -1.145591

formamide, B3LYP/6-31G* electronic energy (Hartree): -169.904509
N   0.105906  -4.435505  -0.369358  
C  -0.806776  -4.368756  -1.356825  
H  -1.122593  -3.332181  -1.569587  
O  -1.258714  -5.333915  -1.972785  
H   0.478971  -5.330612  -0.076129  
H   0.435057  -3.600472   0.096024

protonated formamide, B3LYP/6-31G* electronic energy (Hartree): -170.324450
N   0.350935  -4.429801  -0.545384  
C  -0.865565  -4.355145  -1.435784  
H  -1.016764  -3.343702  -1.829565  
O  -1.520585  -5.327195  -1.629261  
H   0.475197  -5.384964  -0.186649  
H   0.263218  -3.784459   0.254223  
H   1.201933  -4.155704  -1.059390

H3O+, B3LYP/6-31G* electronic energy (Hartree): -76.834834
O  -0.159933  -0.085066  -0.087310  
H  -0.465208   0.710549  -0.585344  
H   0.706749  -0.365260  -0.467558  
H  -0.011757   0.179187   0.851921