Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Competition Between Stacked and Hydrogen Bonded Structures of Cytosine Aggregates

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[2] Department of Chemistry, University of La Rioja, Logroño, La Rioja, 26006, Spain.

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Figure S01. Comparison between the mass-resolved IR/UV spectrum of enol-cytosine and the simulated spectra of the tautomers of cytosine. A correction factor of 0.9483 was used to account for anharmonicity. This value was maintained for the rest of the study.

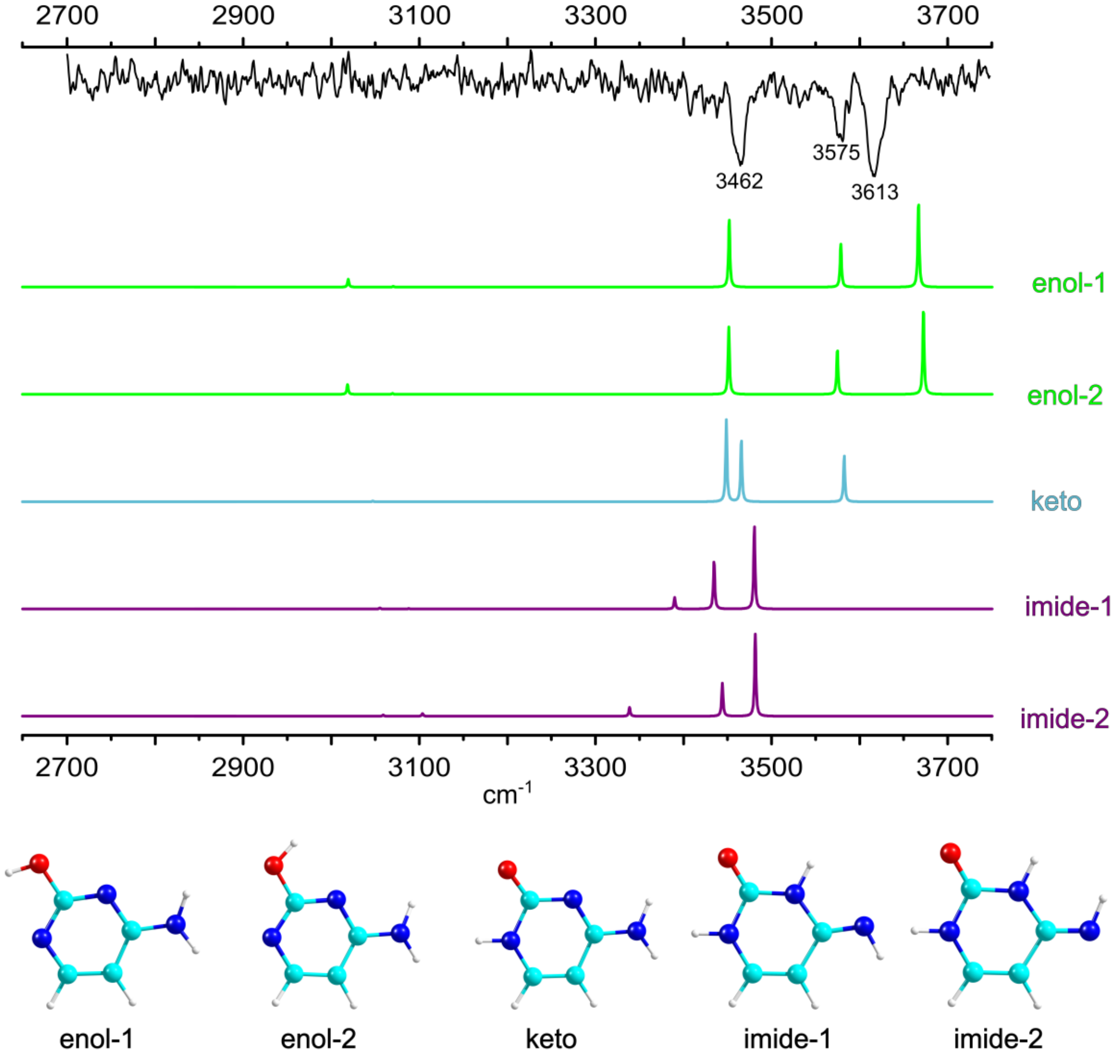


Figure S02. Comparison between the mass-resolved IR/UV spectrum of the cytosine dimer and the simulated spectra of some representative calculated structures.

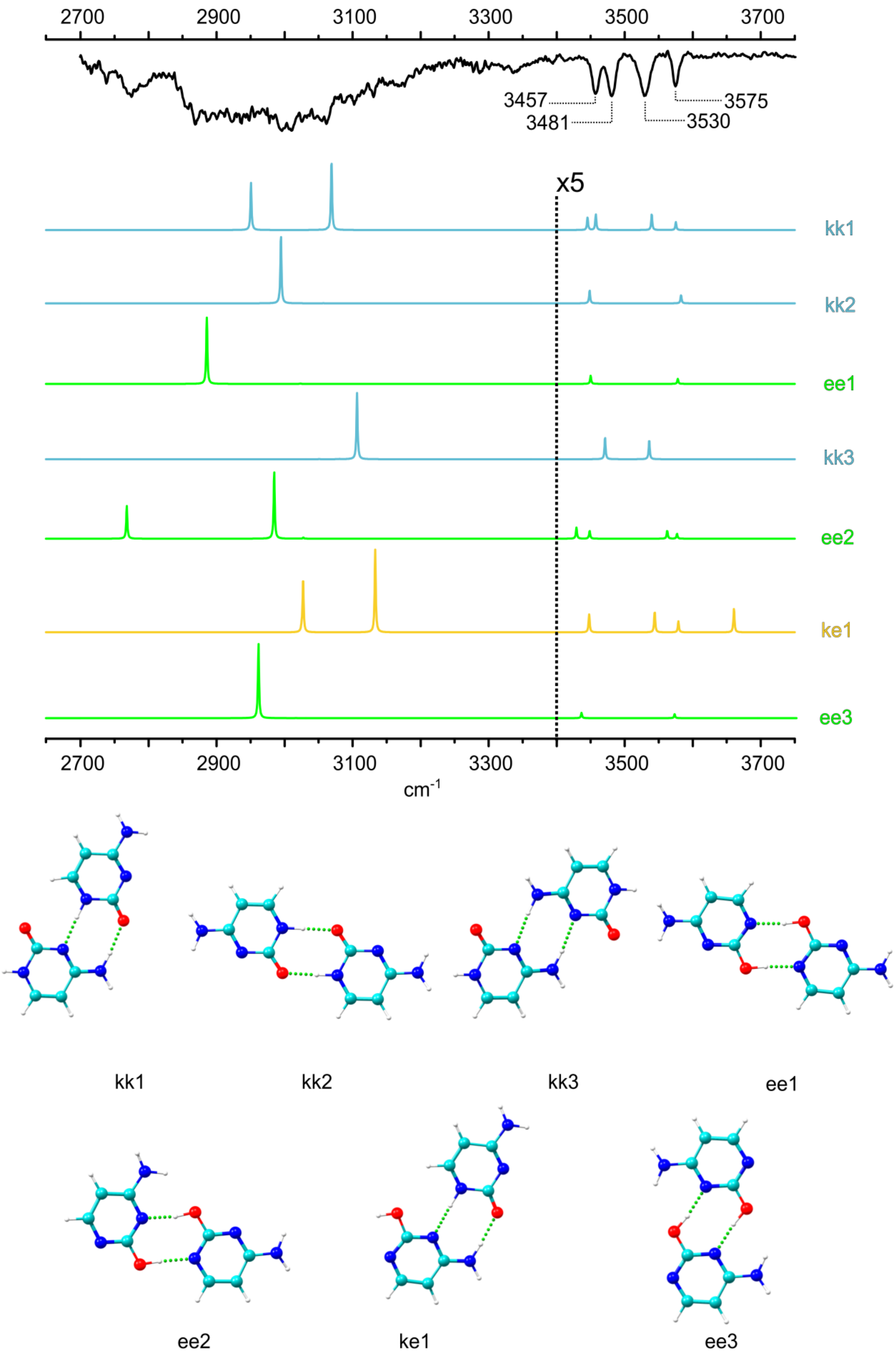
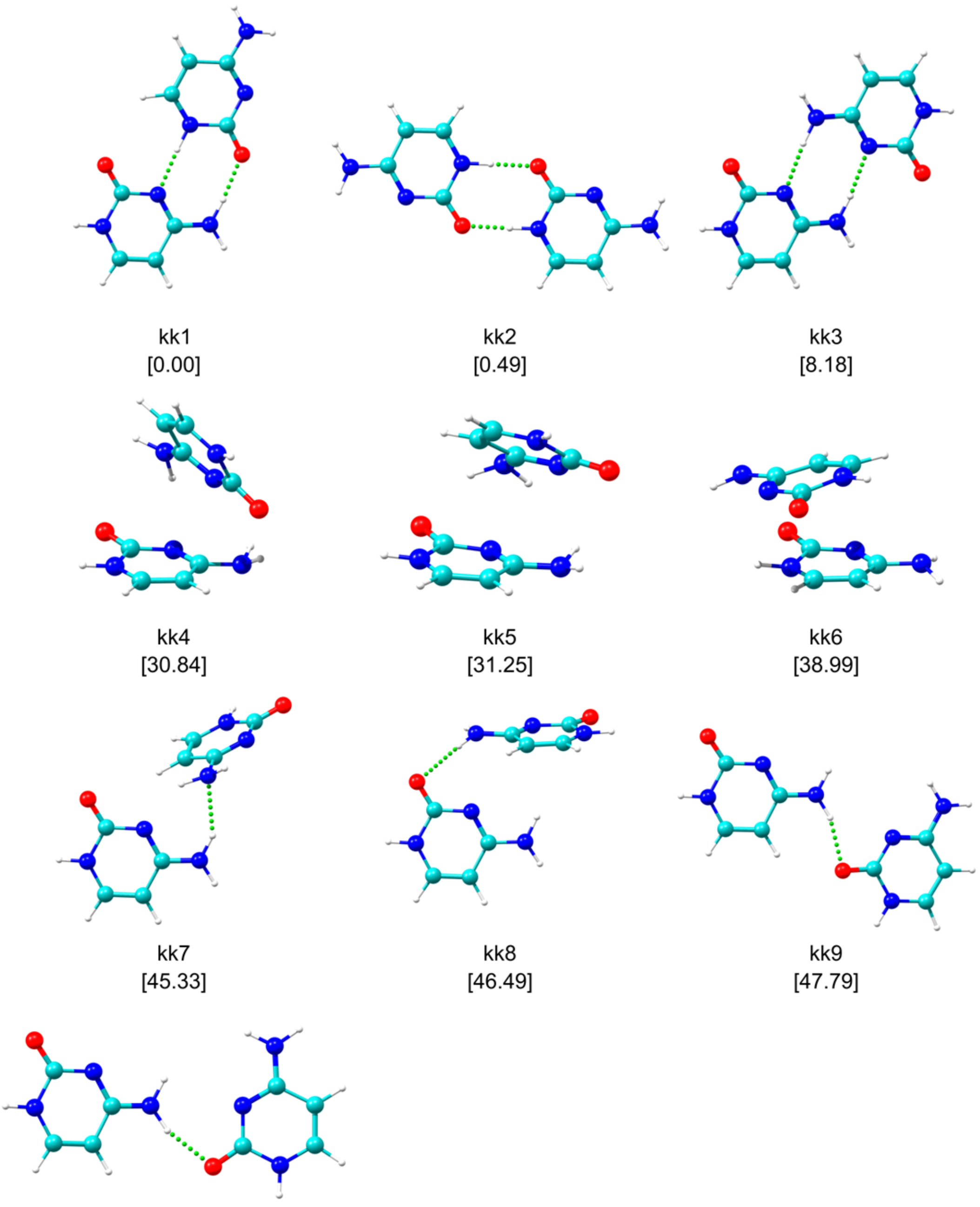


Figure S03. The 10 most stable structures of kk cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



kk1
[0.00]

kk2
[0.49]

kk3
[8.18]

kk4
[30.84]

kk5
[31.25]

kk6
[38.99]

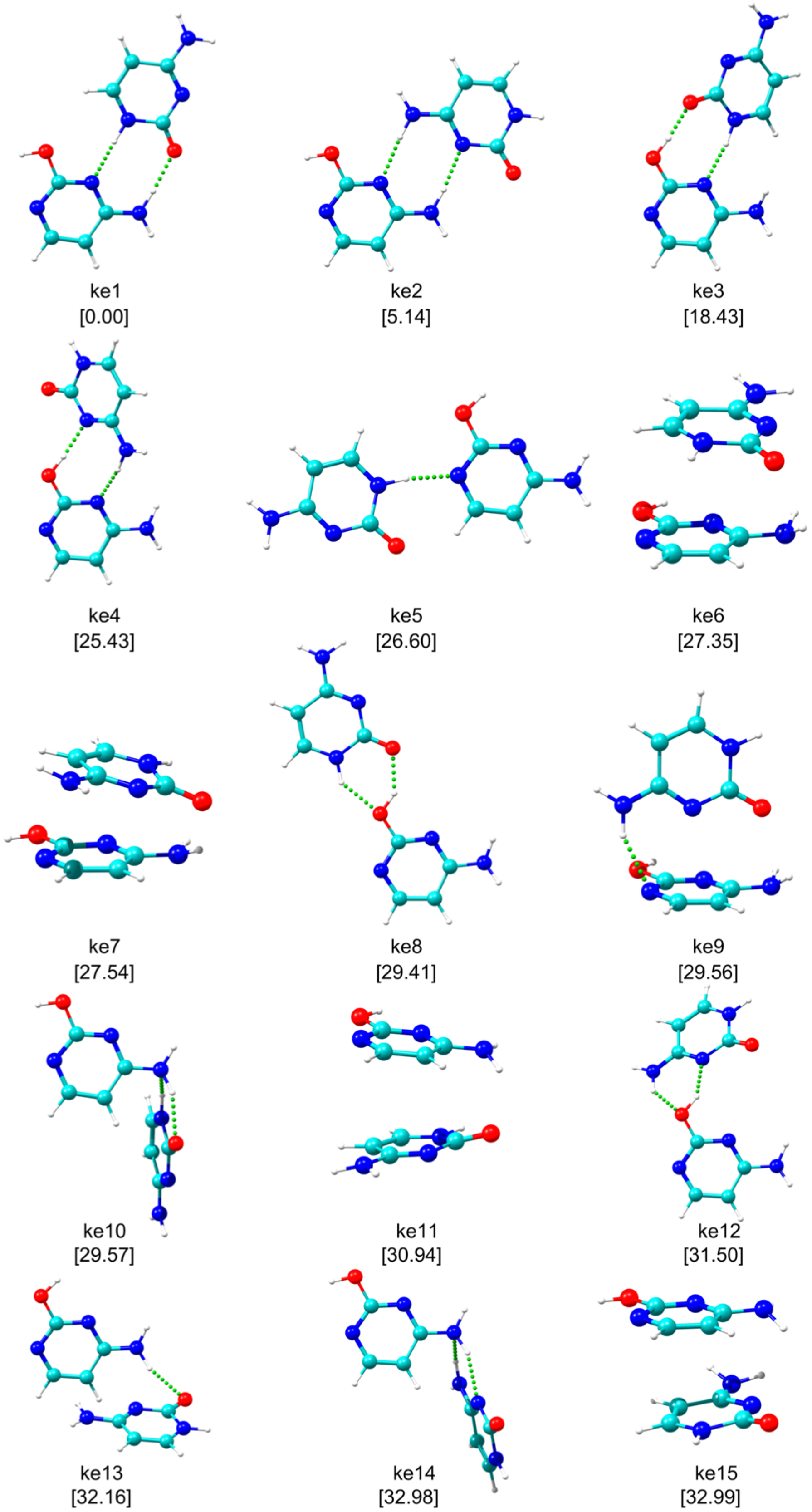
kk7
[45.33]

kk8
[46.49]

kk9
[47.79]

kk10
[48.88]

Figure S04. The 15 most stable structures of ke cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



ke1
[0.00]

ke2
[5.14]

ke3
[18.43]

ke4
[25.43]

ke5
[26.60]

ke6
[27.35]

ke7
[27.54]

ke8
[29.41]

ke9
[29.56]

ke10
[29.57]

ke11
[30.94]

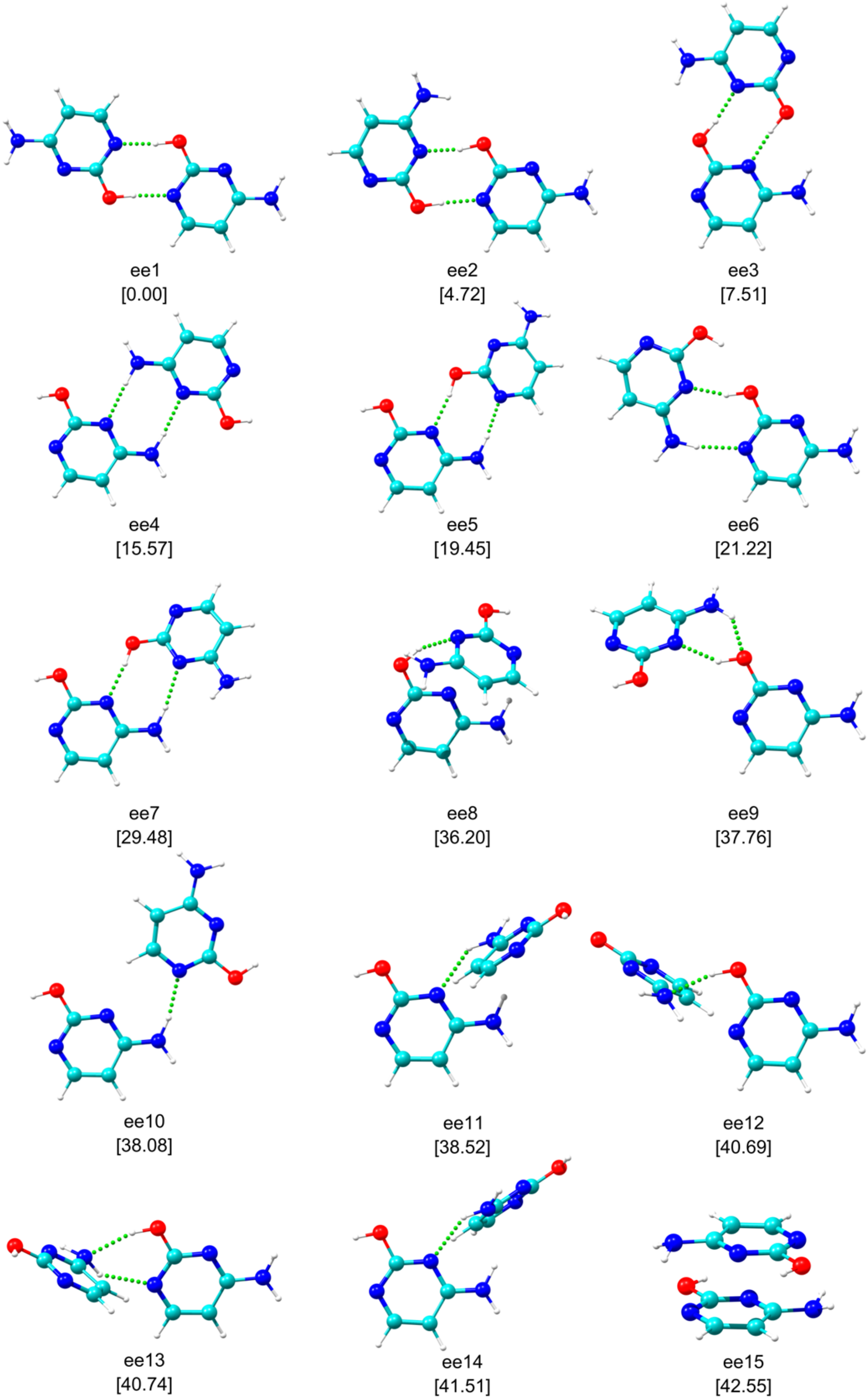
ke12
[31.50]

ke13
[32.16]

ke14
[32.98]

ke15
[32.99]

Figure S05. The 10 most stable structures of ee cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



ee1 [0.00]

ee2 [4.72]

ee3 [7.51]

ee4 [15.57]

ee5 [19.45]

ee6 [21.22]

ee7 [29.48]

ee8 [36.20]

ee9 [37.76]

ee10 [38.08]

ee11 [38.52]

ee12 [40.69]

ee13 [40.74]

ee14 [41.51]

ee15 [42.55]

Figure S06. Relative Gibbs free energy of the most stable conformations of kk cytosine dimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable.

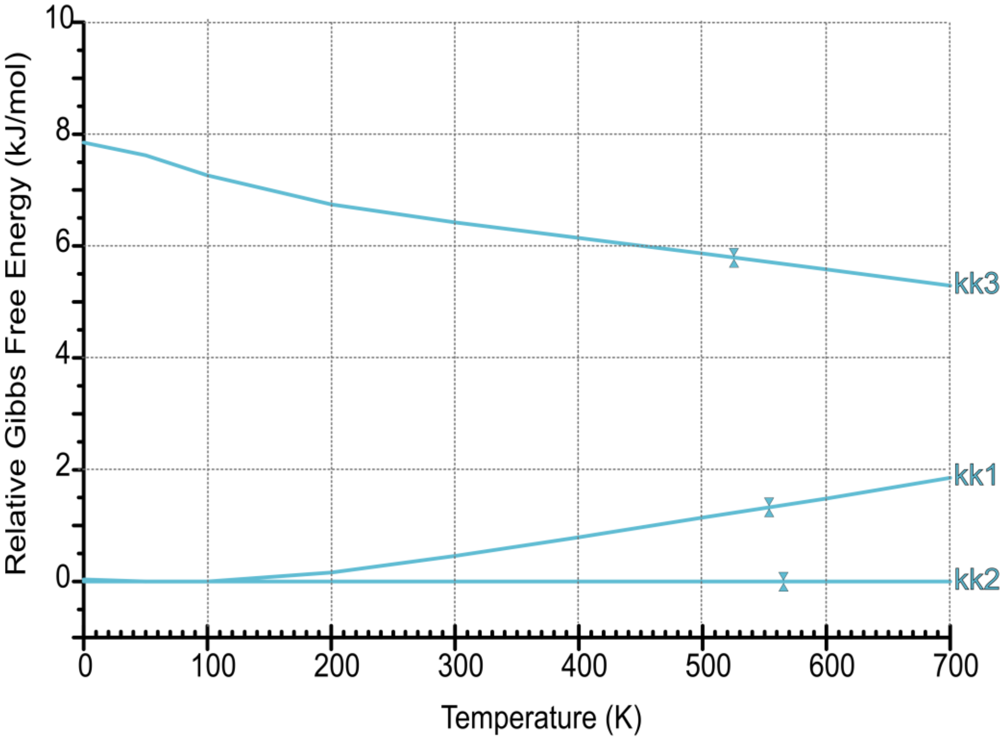


Figure S07. Relative Gibbs free energy of the most stable conformations of ke cytosine dimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable.

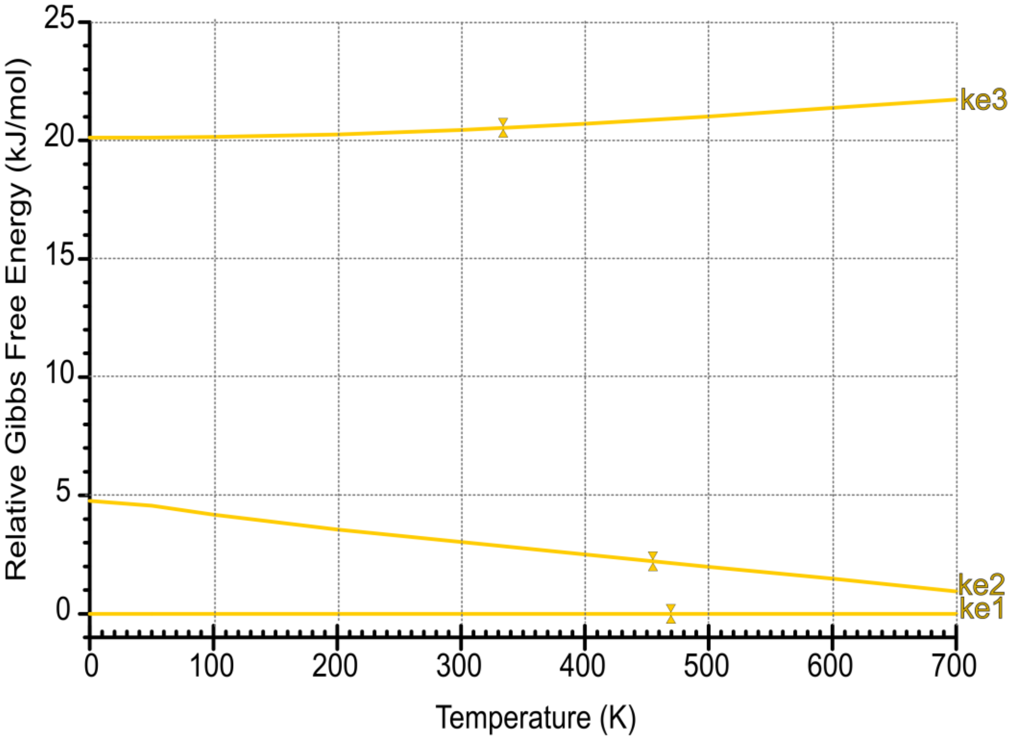


Figure S08. Relative Gibbs free energy of the most stable conformations of ee cytosine dimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable.

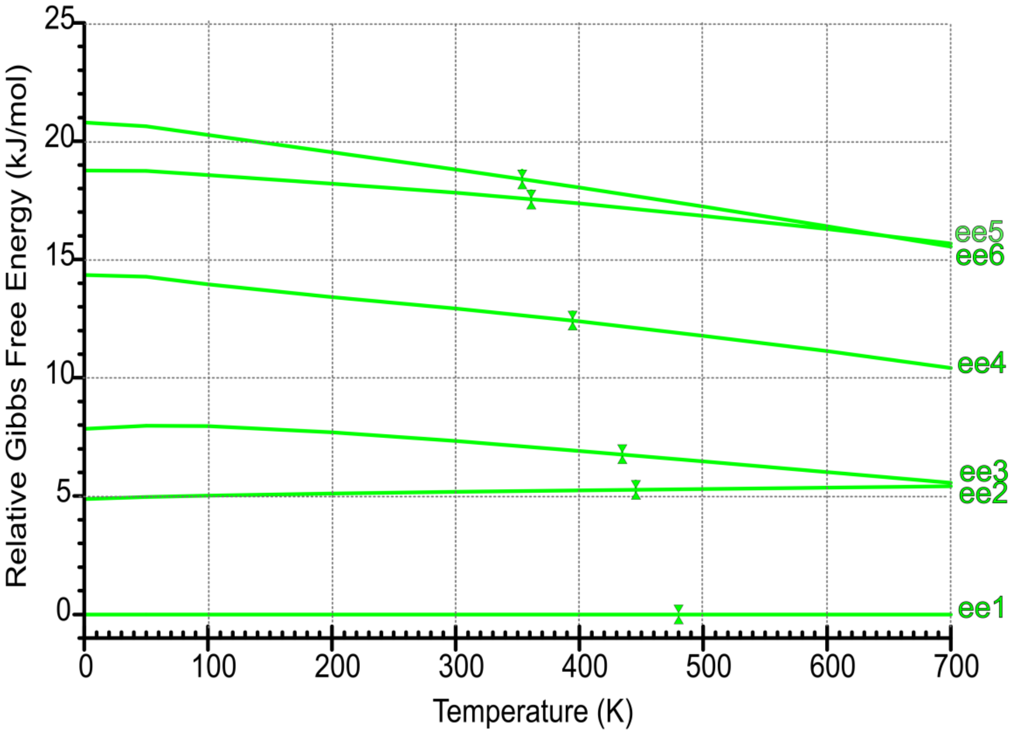


Figure S09. Relative Gibbs free energy of the most stable planar and stacked conformations of cytosine dimer.

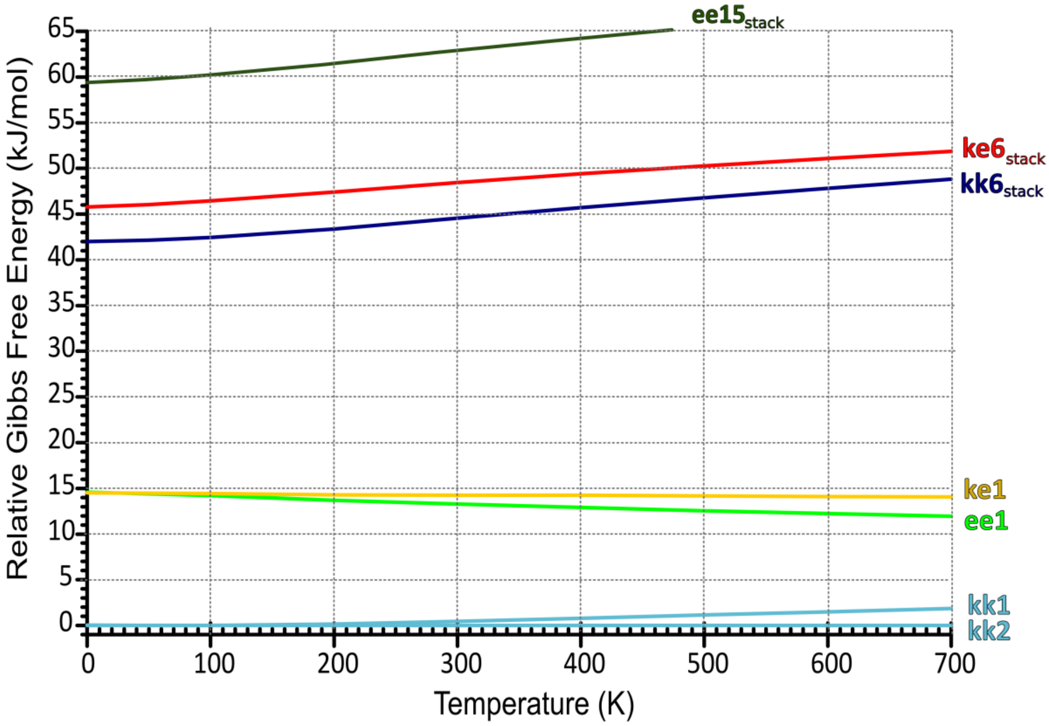


Figure S10. Comparison between the mass-resolved IR/UV spectrum of the cytosine trimer and the simulated spectra of some representative calculated cytosine trimers.

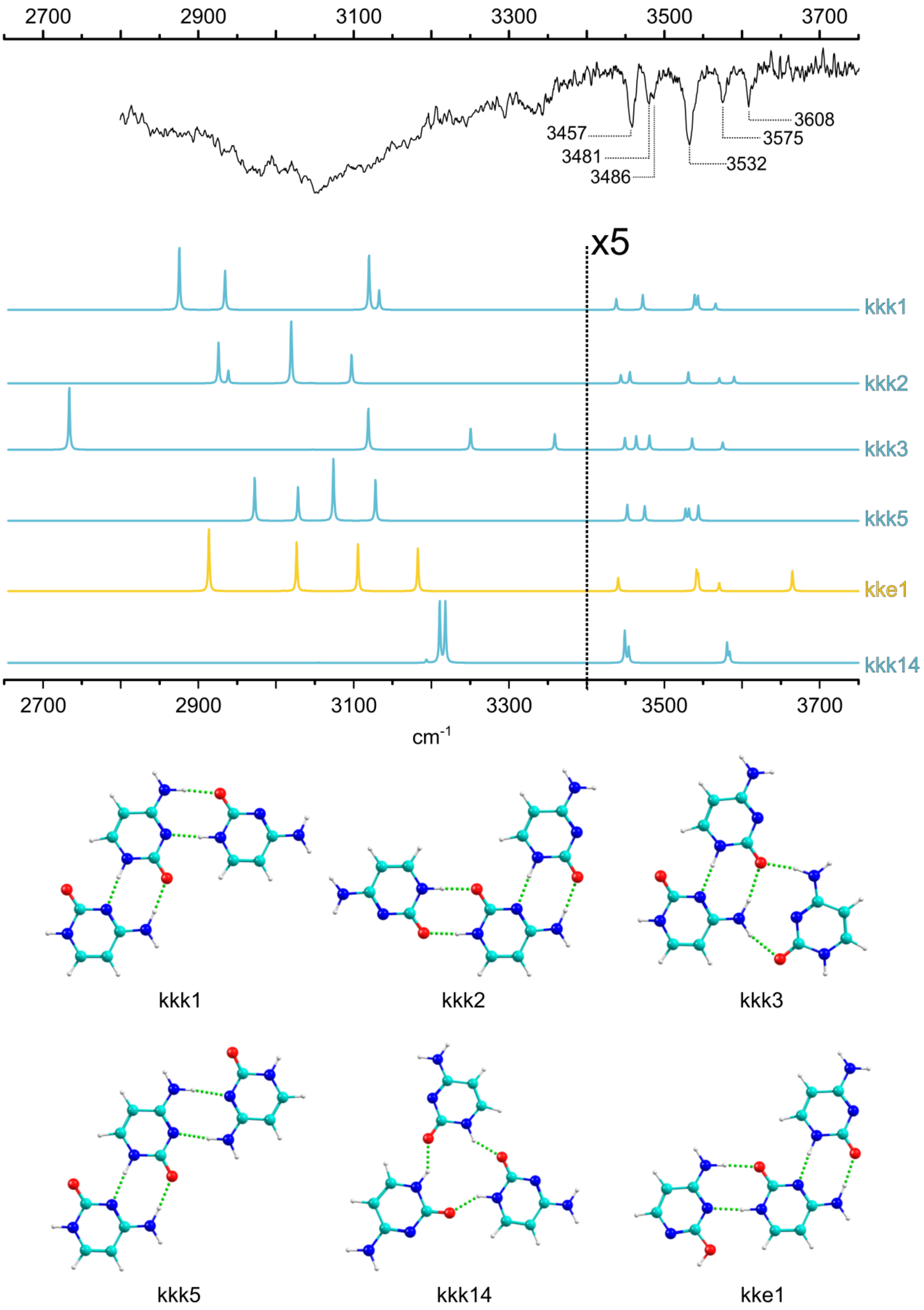
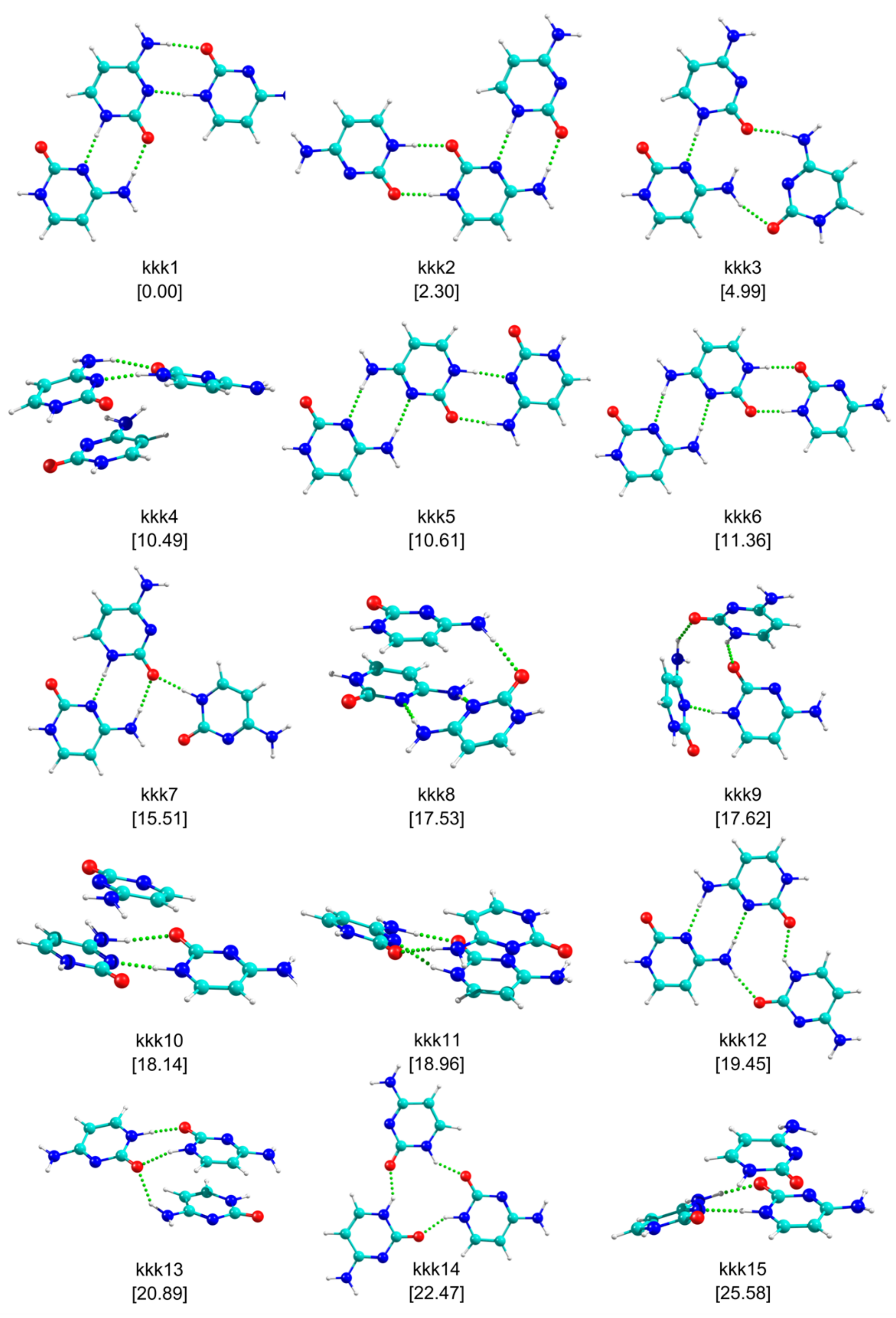


Figure S11. The 15 most stable structures of kkk cytosine trimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



kkk1
[0.00]

kkk2
[2.30]

kkk3
[4.99]

kkk4
[10.49]

kkk5
[10.61]

kkk6
[11.36]

kkk7
[15.51]

kkk8
[17.53]

kkk9
[17.62]

kkk10
[18.14]

kkk11
[18.96]

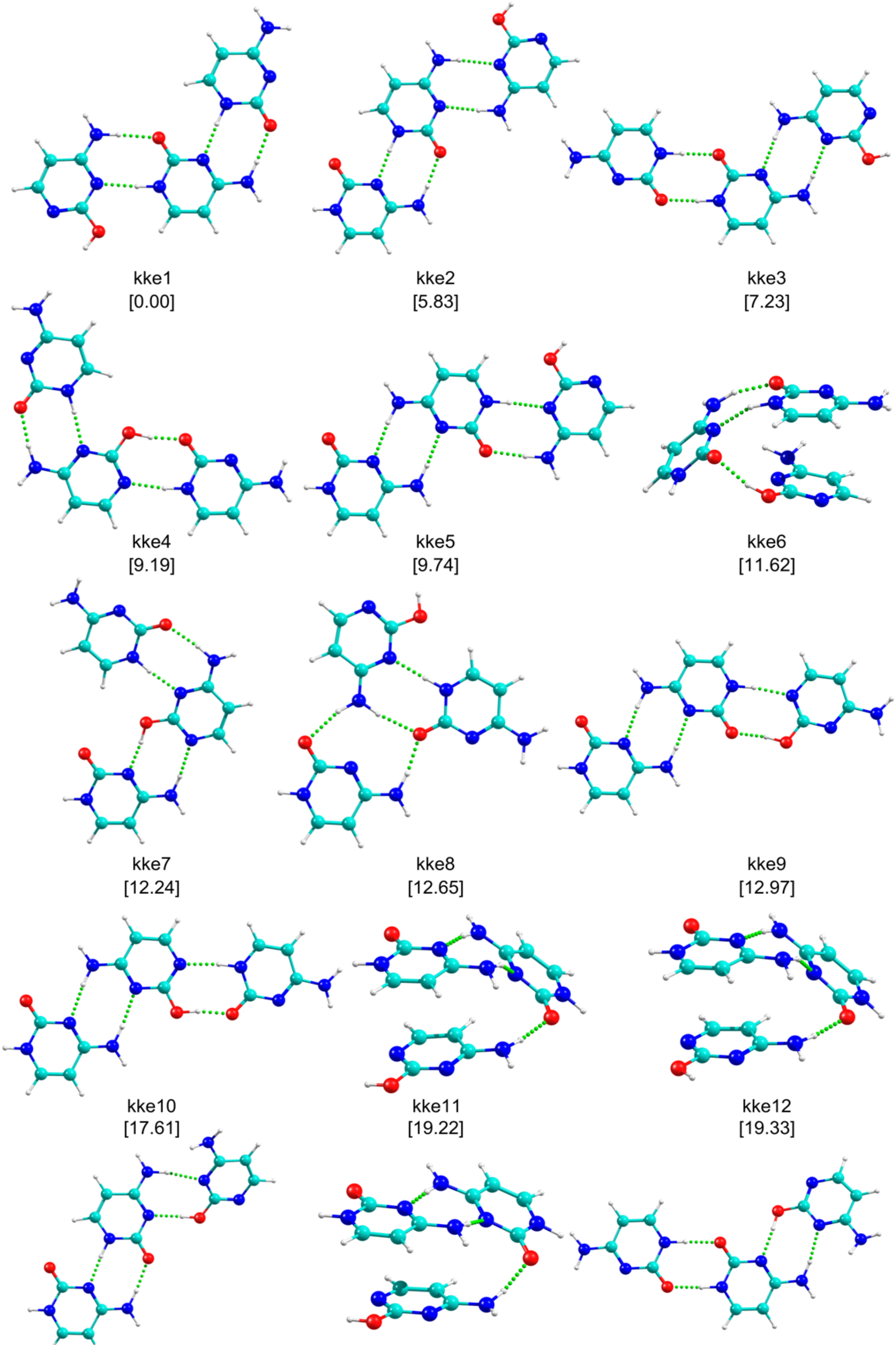
kkk12
[19.45]

kkk13
[20.89]

kkk14
[22.47]

kkk15
[25.58]

Figure S12. The 15 most stable structures of kke cytosine trimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



kke1
[0.00]

kke2
[5.83]

kke3
[7.23]

kke4
[9.19]

kke5
[9.74]

kke6
[11.62]

kke7
[12.24]

kke8
[12.65]

kke9
[12.97]

kke10
[17.61]

kke11
[19.22]

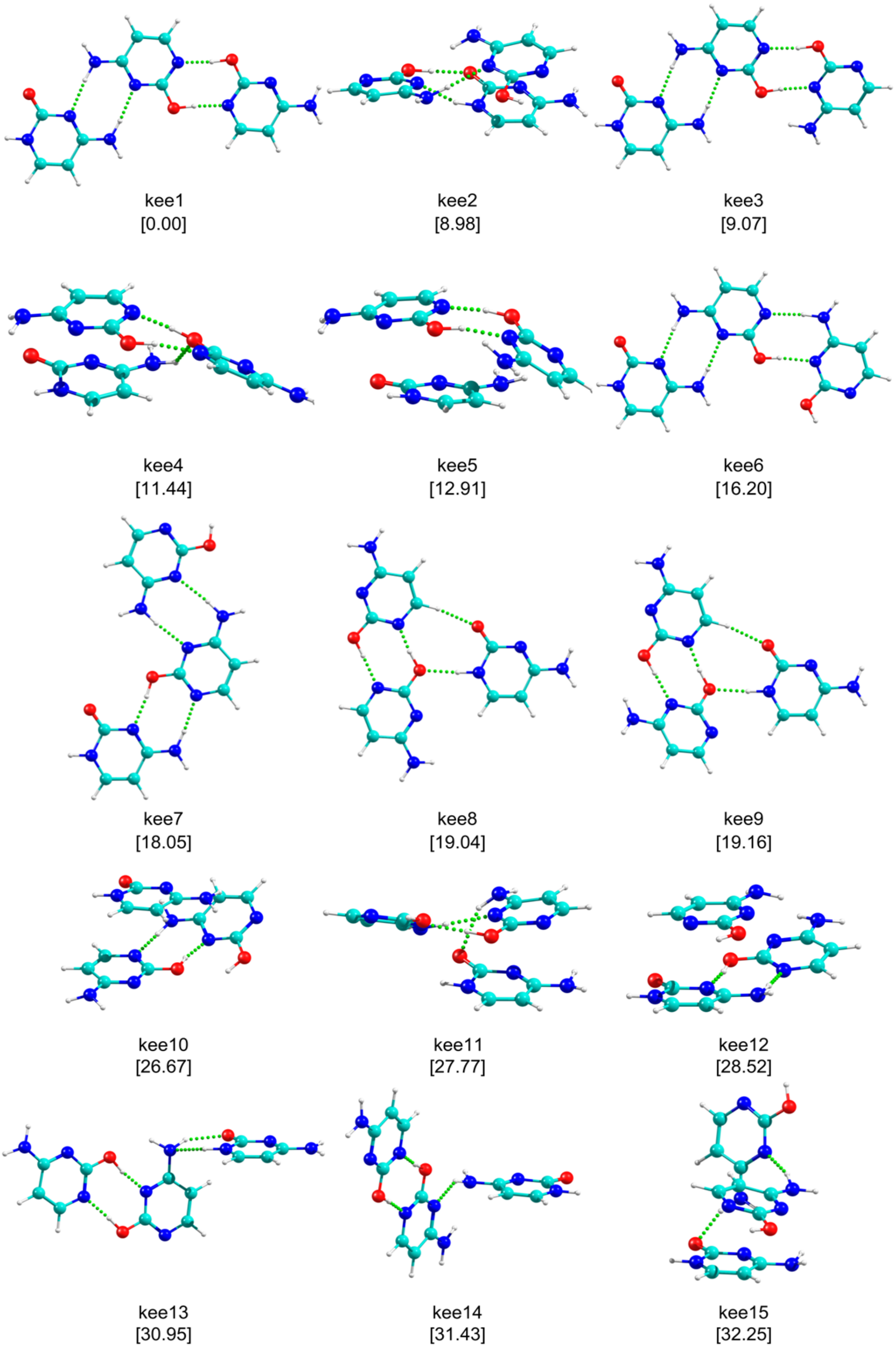
kke12
[19.33]

kke13
[20.22]

kke14
[21.63]

kke15
[22.00]

Figure S13. The 15 most stable structures of kee cytosine trimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



kee1
[0.00]

kee2
[8.98]

kee3
[9.07]

kee4
[11.44]

kee5
[12.91]

kee6
[16.20]

kee7
[18.05]

kee8
[19.04]

kee9
[19.16]

kee10
[26.67]

kee11
[27.77]

kee12
[28.52]

kee13
[30.95]

kee14
[31.43]

kee15
[32.25]

Figure S14. Relative Gibbs free energy of kkk cytosine trimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The dark blue trace corresponds to a stacking structure.

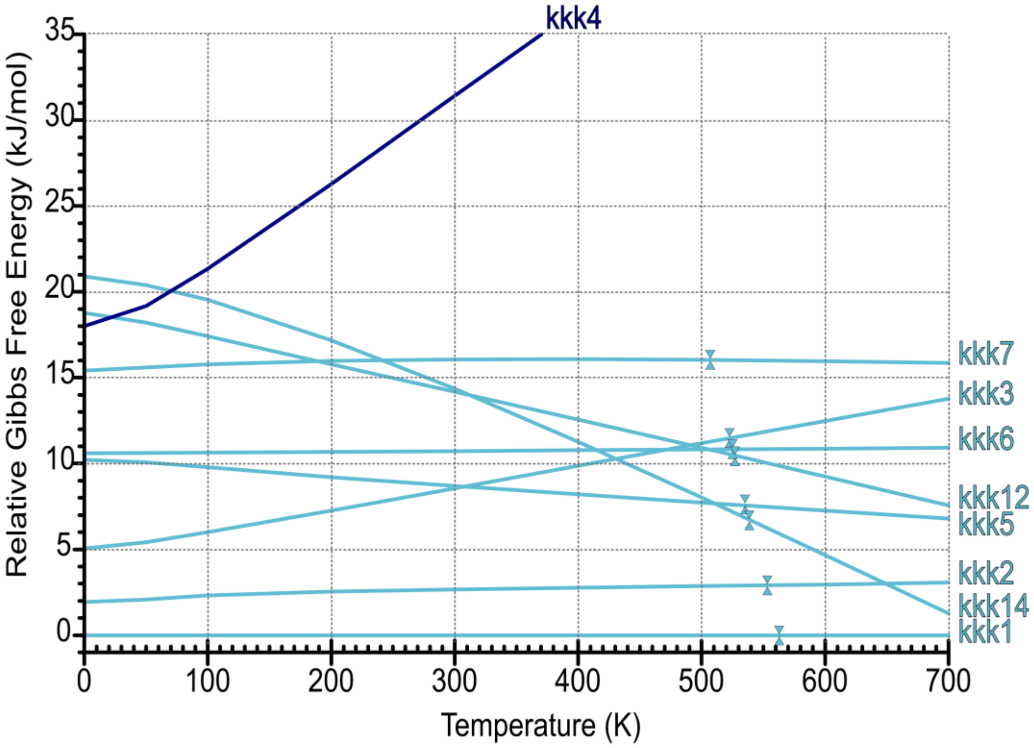


Figure S15. Relative Gibbs free energy of kke cytosine trimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The red trace corresponds to a stacking structure.

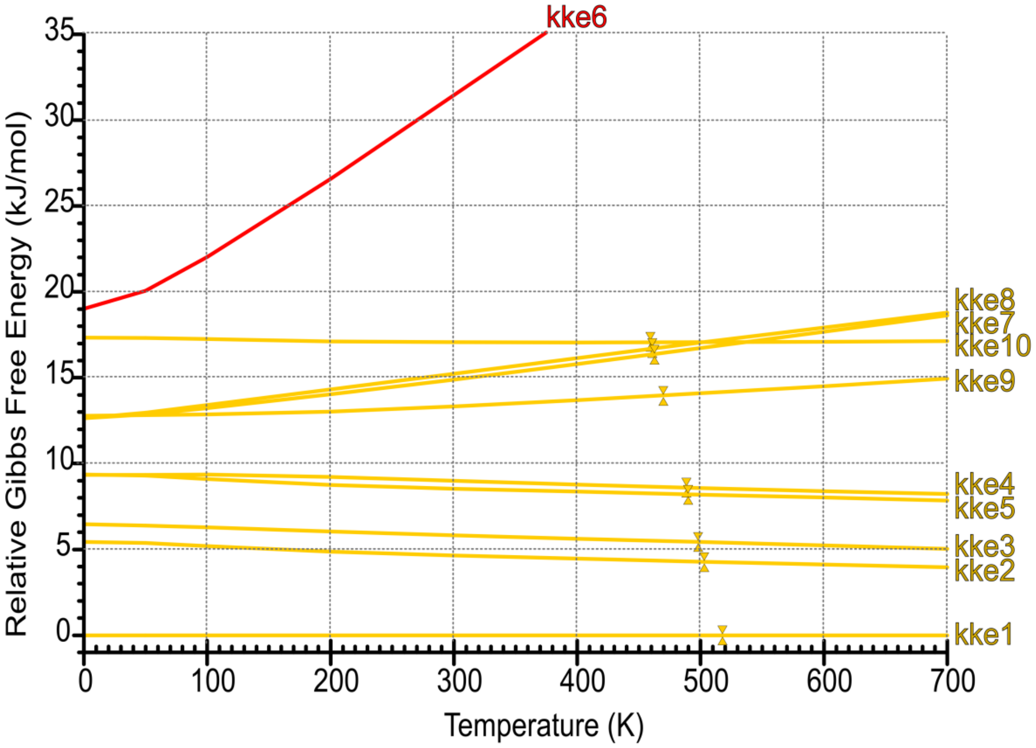


Figure S16. Relative Gibbs free energy of kee cytosine trimer. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The dark green traces correspond to stacking structures.

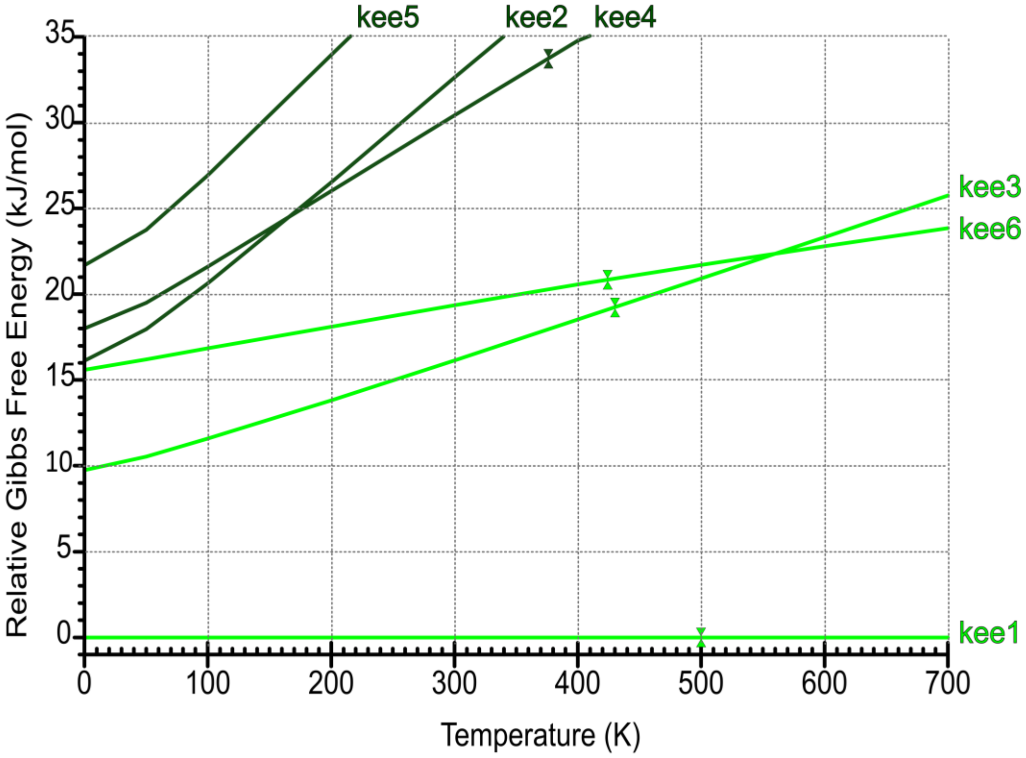


Figure S17 . Comparison between the relative Gibbs free energy of some selected calculated cytosine trimers. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable.

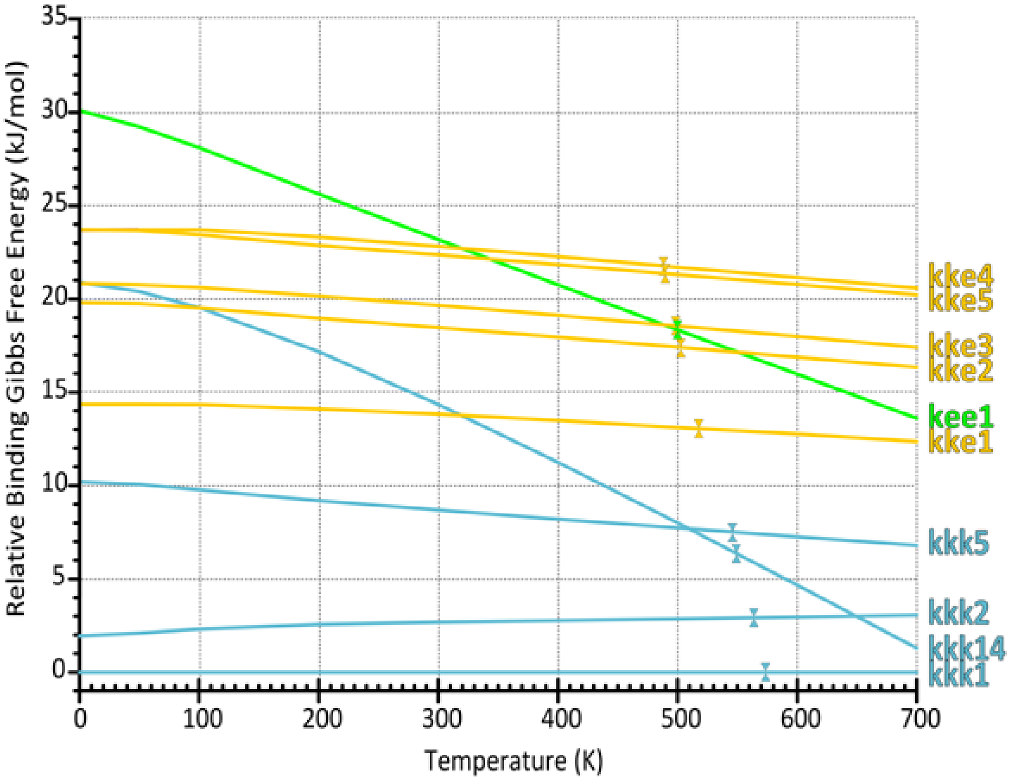


Figure S18. Comparison between the mass-resolved IR/UV spectrum of the cytosine tetramer and the simulated spectra of some selected calculated cytosine tetramers. The dark blue traces correspond to stacking structures.

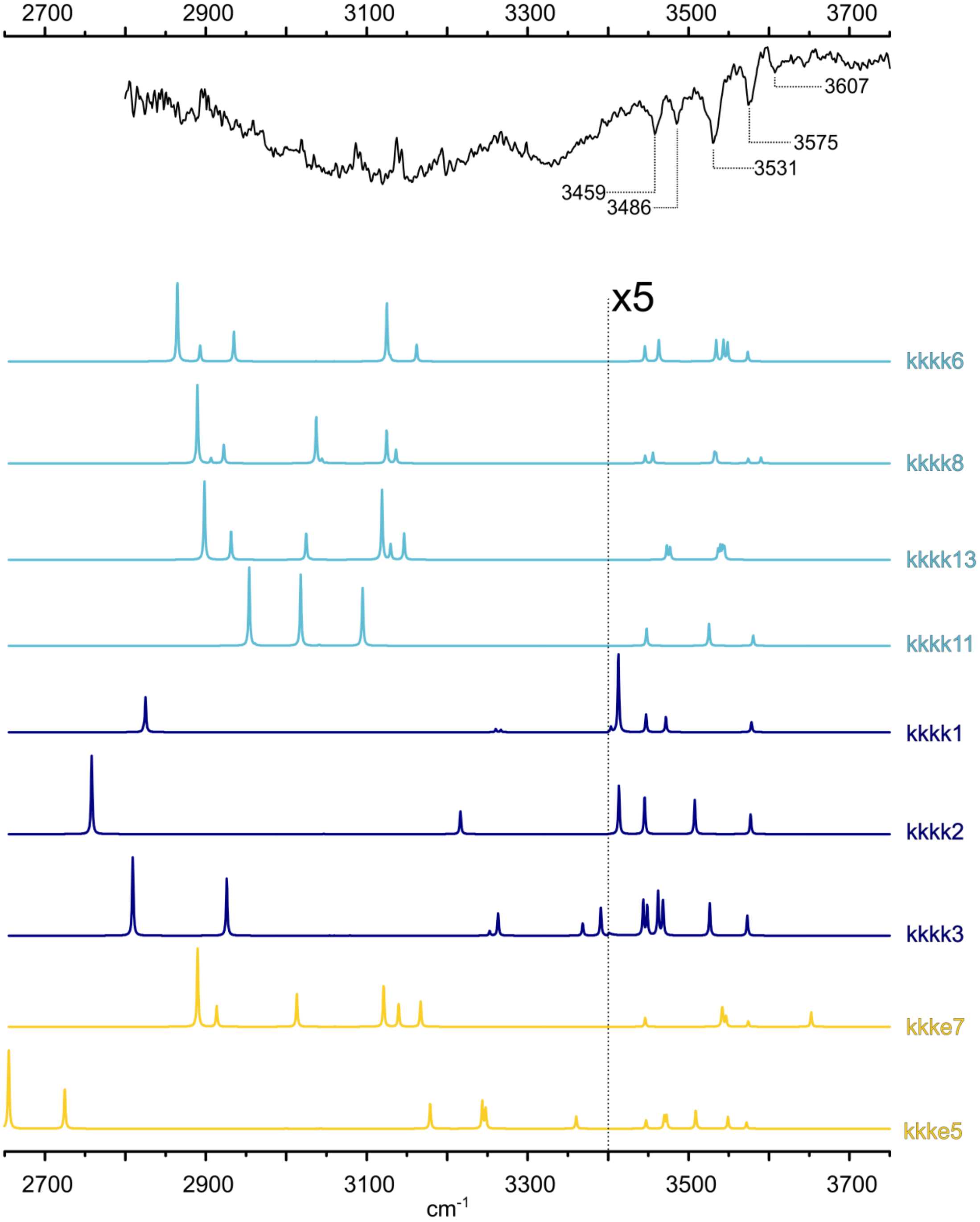
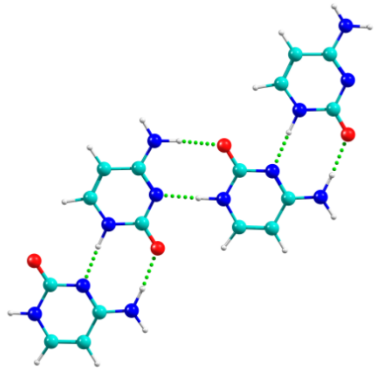
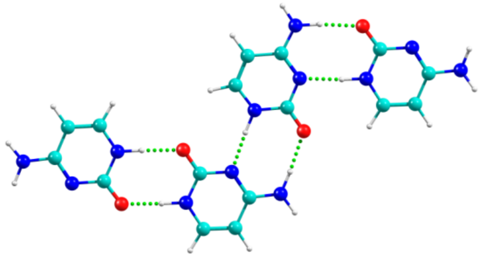


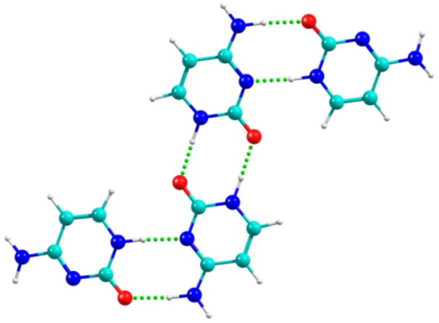
Figure S19. Structure of the cytosine tetramers calculated at the M06-2X/6-311++G(d,p) level selected for the comparison with the experimental IR spectrum.



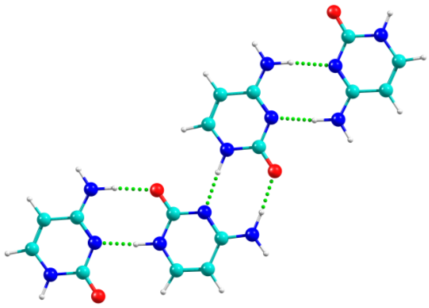
kkkk6



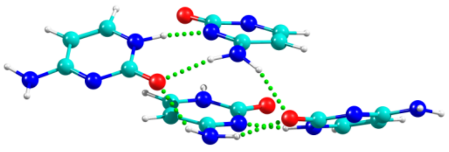
kkkk8



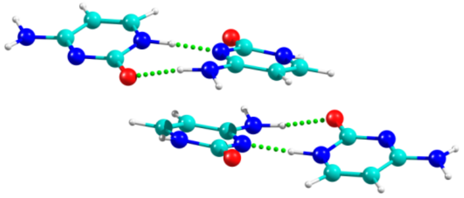
kkkk11



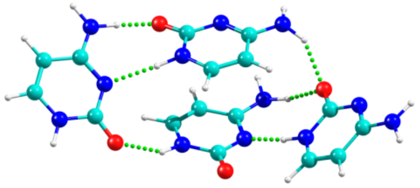
kkkk13



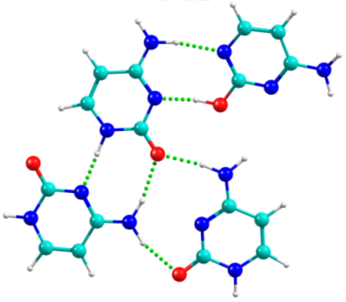
kkkk1



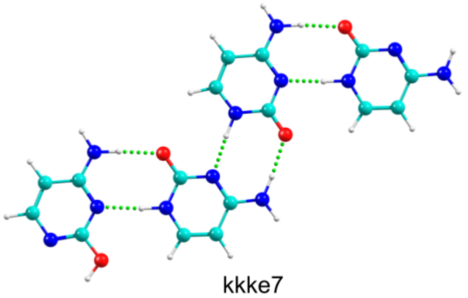
kkkk2



kkkk3

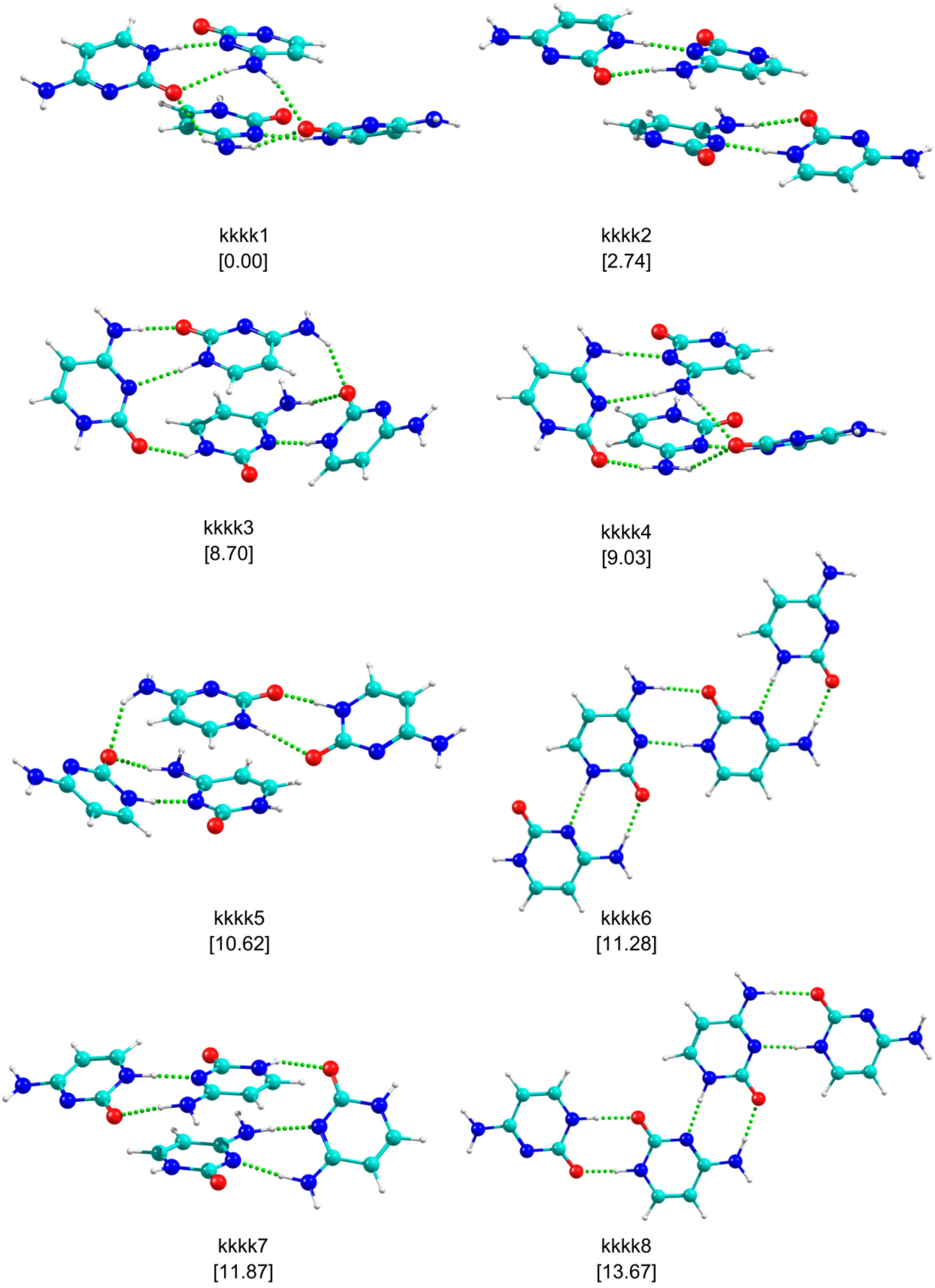


kkke5



kkke7

Figure S20. The 15 most stable structures of kkkk cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



kkkk1
[0.00]

kkkk2
[2.74]

kkkk3
[8.70]

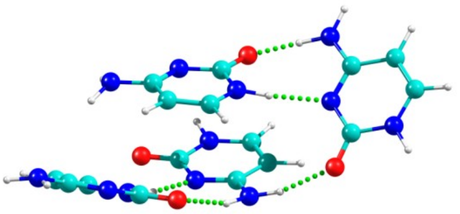
kkkk4
[9.03]

kkkk5
[10.62]

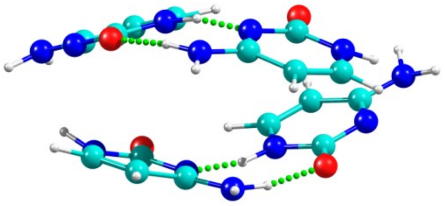
kkkk6
[11.28]

kkkk7
[11.87]

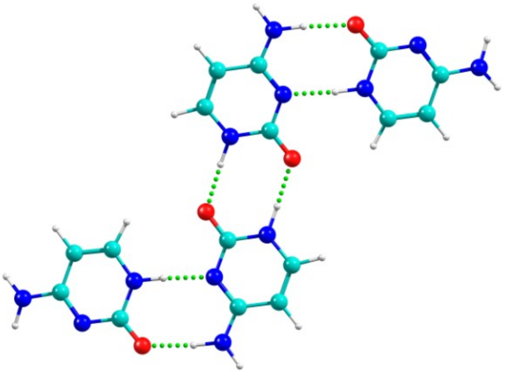
kkkk8
[13.67]



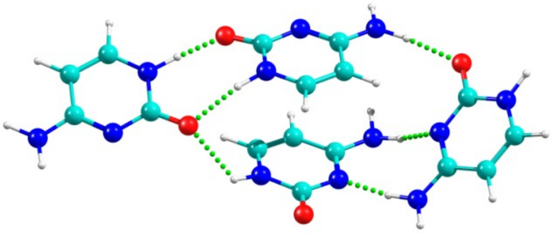
kkkk9
[14.31]



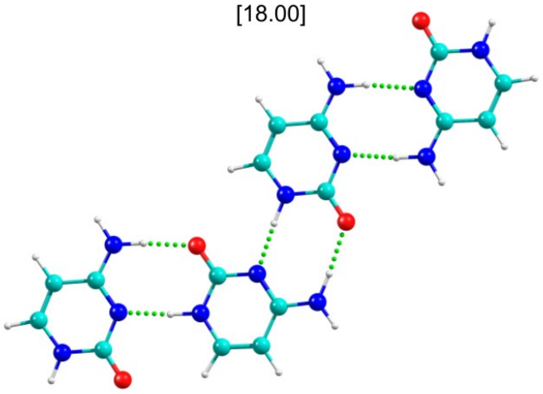
kkkk10
[14.67]



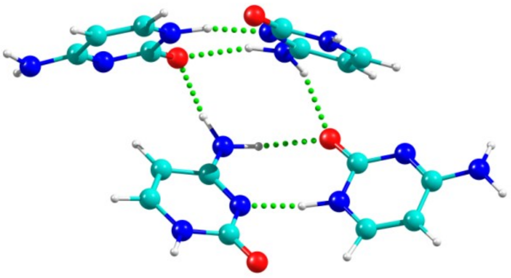
kkkk11
[18.00]



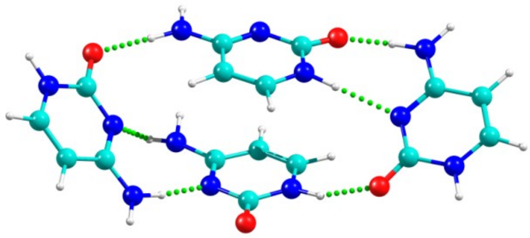
kkkk12
[19.63]



kkkk13
[19.85]

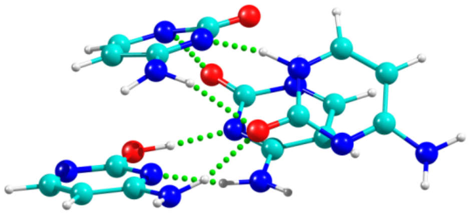


kkkk14
[20.64]



kkkk15
[21.21]

Figure S21. The 15 most stable structures of kkke cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



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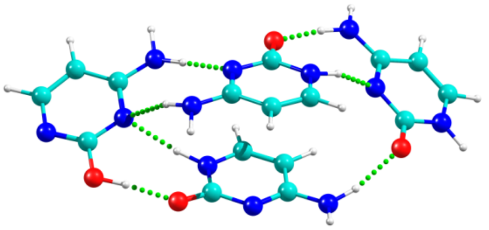
[0.00]



kkke2
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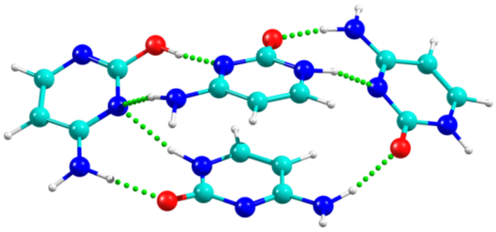
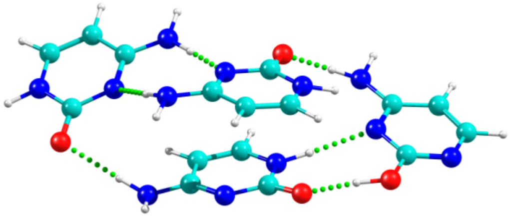


kkke3
[4.19]



kkke4
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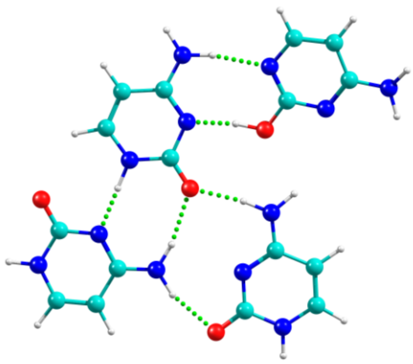
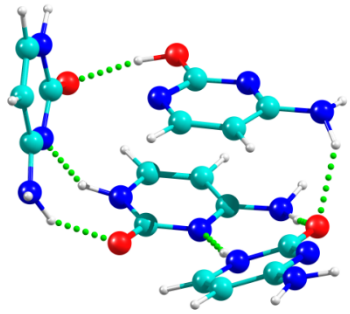
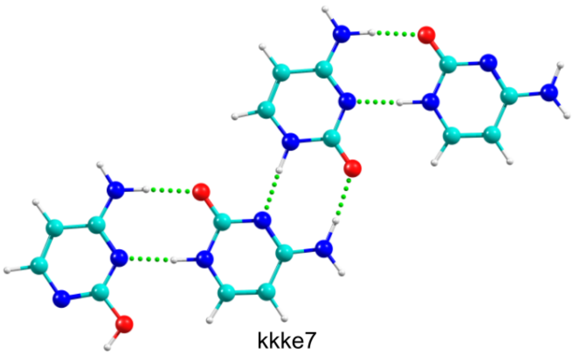


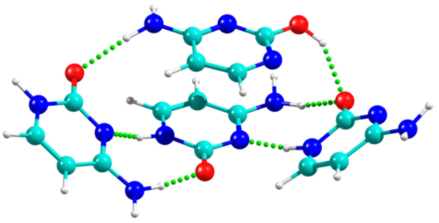
kkke5
[7.88]



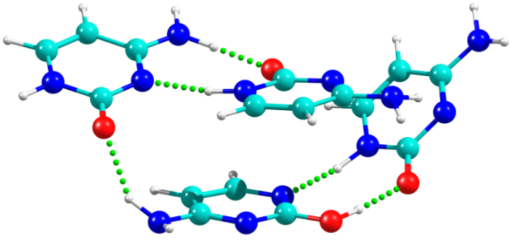
kkke6
[8.47]



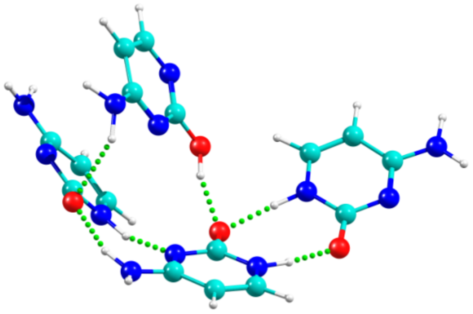
kkke7
[10.73]



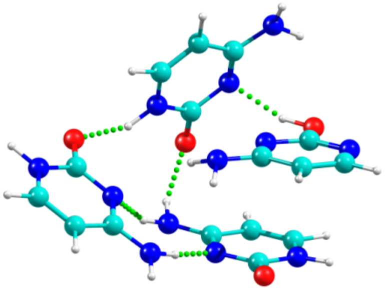
kkke8
[11.39]



kkke9
[13.21]



kkke10
[14.72]



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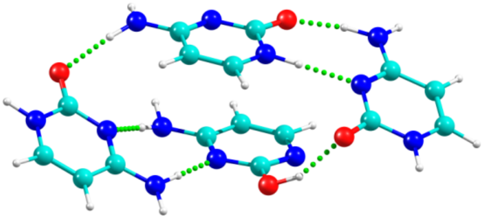
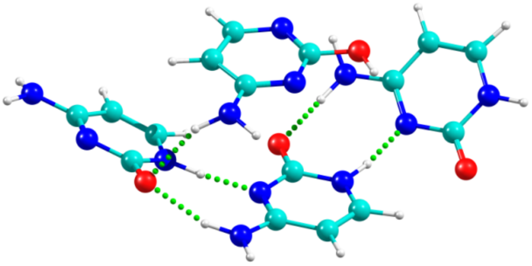
[14.88]



kkke12
[15.25]



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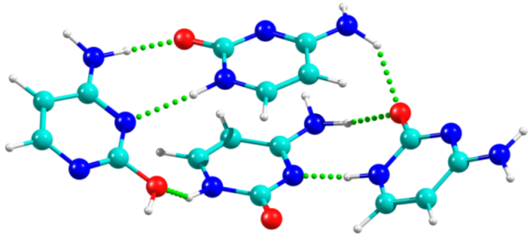

kkke14
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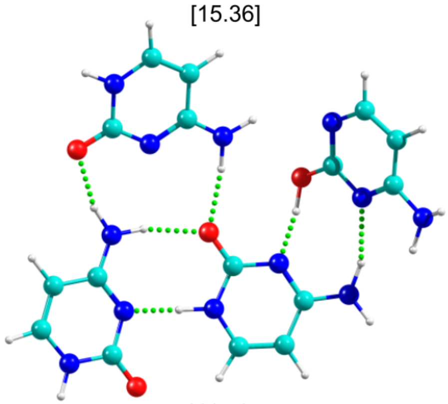
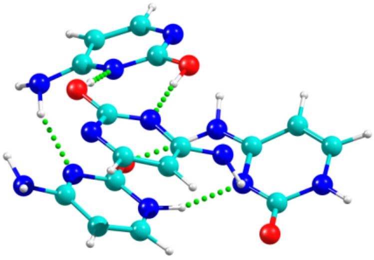
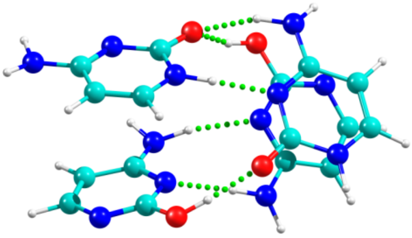


kkke15
[16.27]

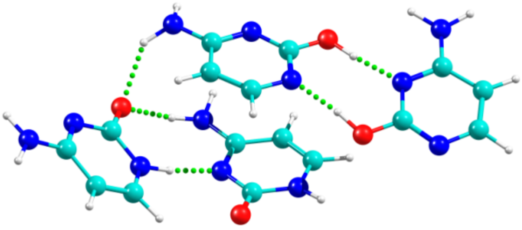
Figure S22. The 15 most stable structures of kkee cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



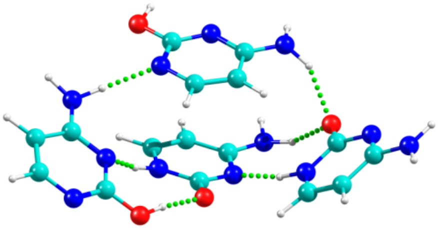
kkee1
[0.00]



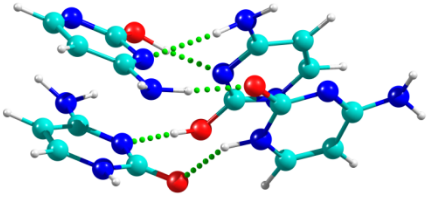
kkee2
[4.06]



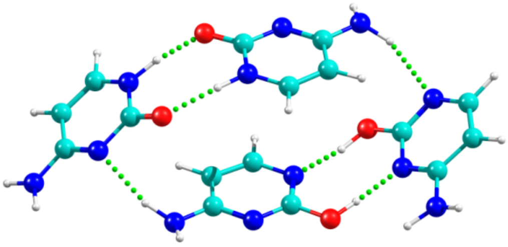
kkee3
[5.74]



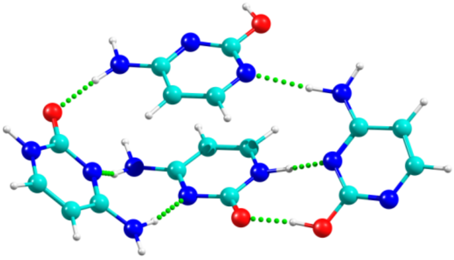
kkee4
[9.27]



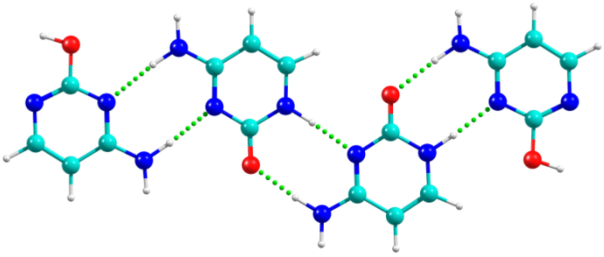
kkee5
[11.94]



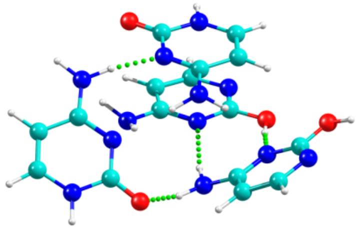
kkee6
[13.64]



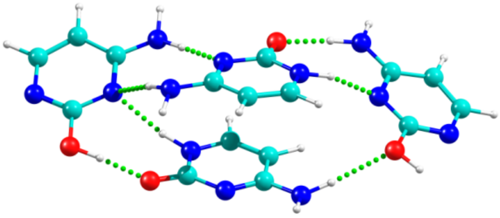
kkee7
[13.93]



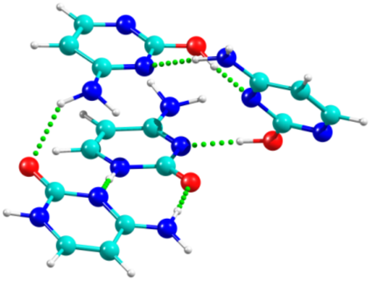
kkee8
[13.95]



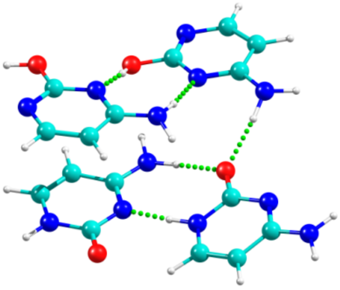
kkee9
[14.62]



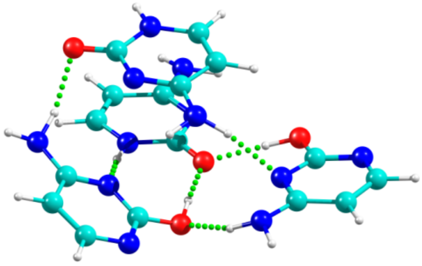
kkee10
[15.64]



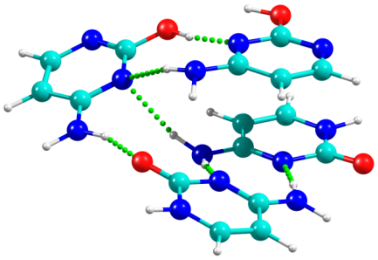
kkee11
[15.66]



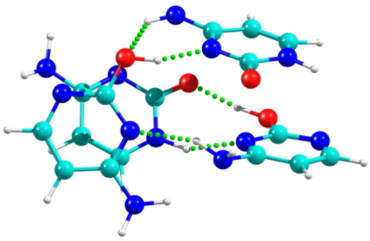
kkee12
[16.18]



kkee13
[17.32]

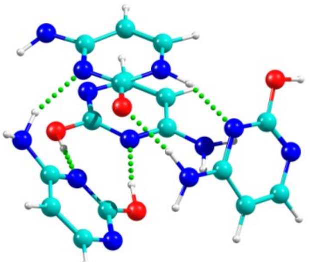


kkee14
[17.83]

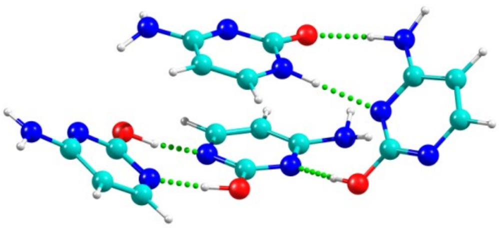


kkee15
[18.11]

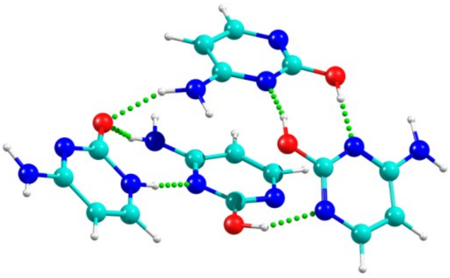
Figure S23. The 15 most stable structures of keee cytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



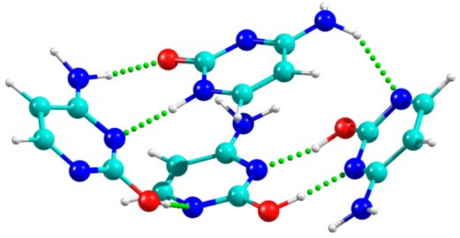
keee1
[0.00]



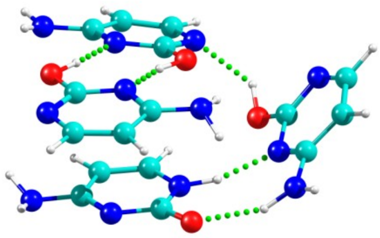
keee2
[3.46]



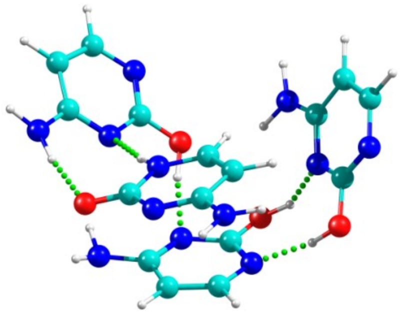
keee3
[7.44]



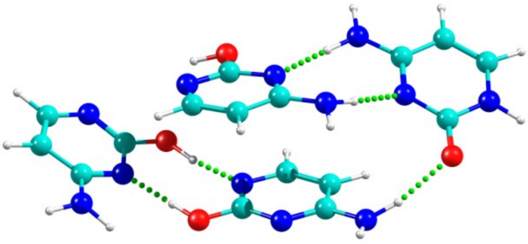
keee4
[7.56]



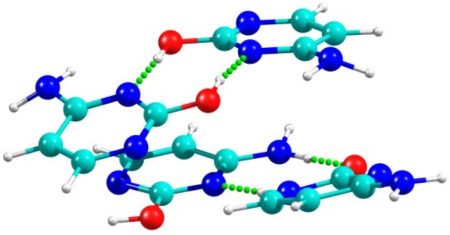
keee5
[8.65]



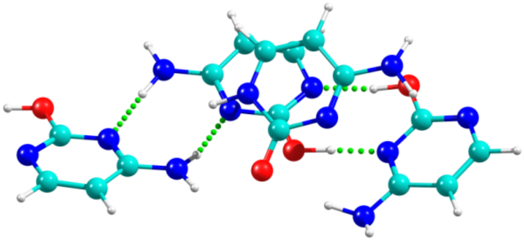
keee6
[9.14]



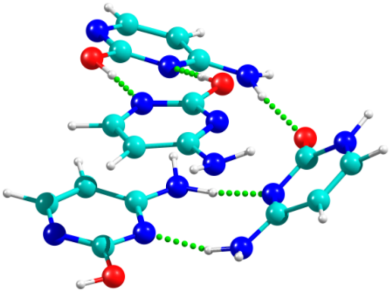
keee7
[10.33]



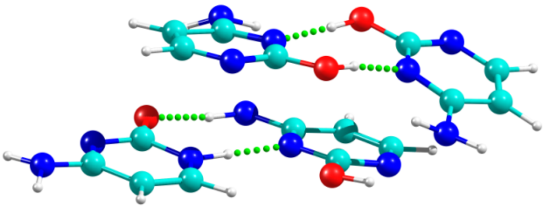
keee8
[11.32]



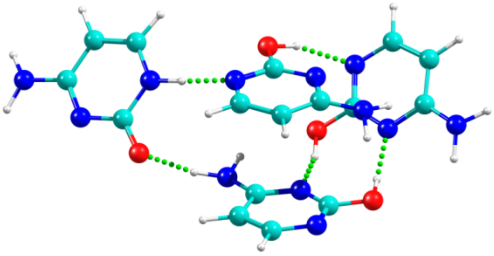
keee9
[11.69]



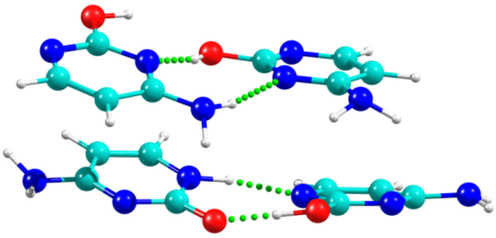
keee10
[12.43]



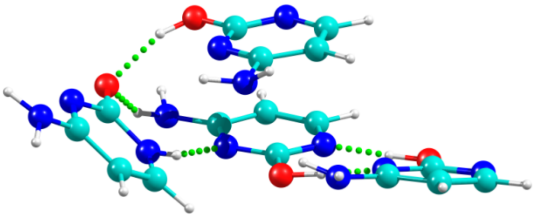
keee11
[13.49]



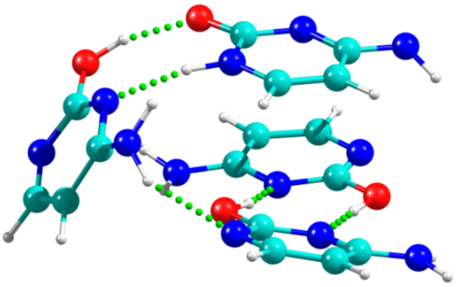
keee12
[15.59]



keee13
[19.75]



keee14
[19.81]



keee15
[21.24]

Figure S24. Relative Gibbs free energy of the computed kkkk cytosine tetramers. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The dark blue traces correspond to stacking structures.

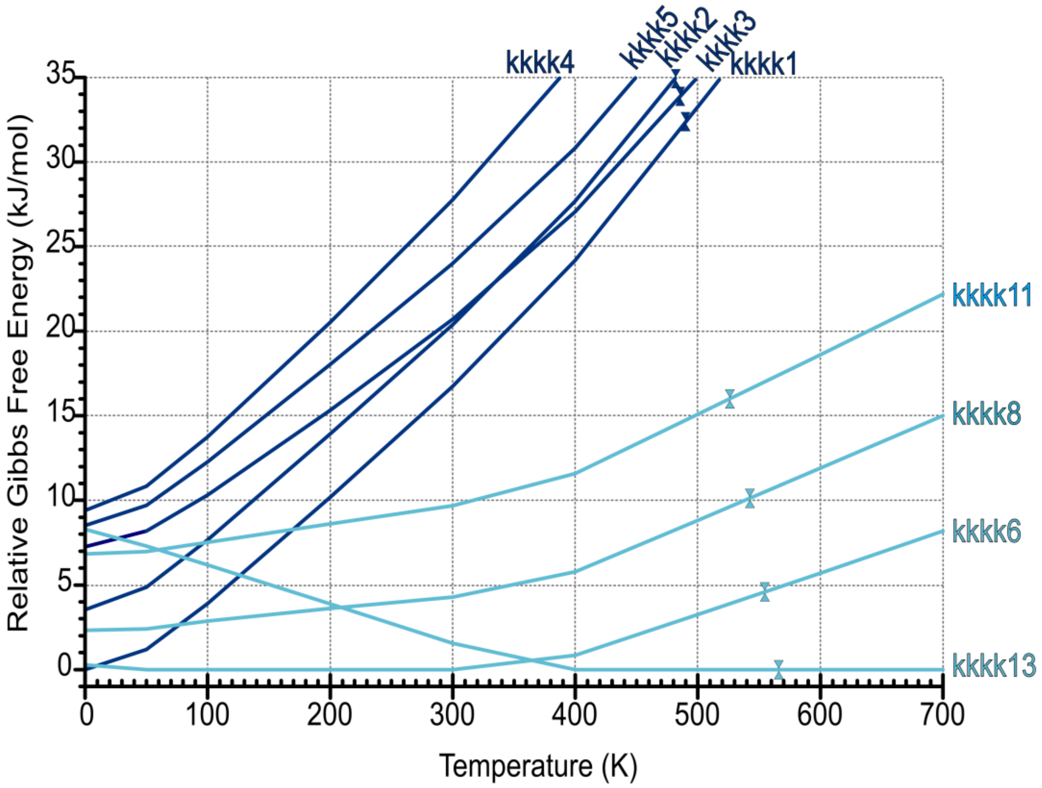


Figure S25 . Relative Gibbs free energy of the computed kkke cytosine tetramers. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The red traces correspond to stacking structures.

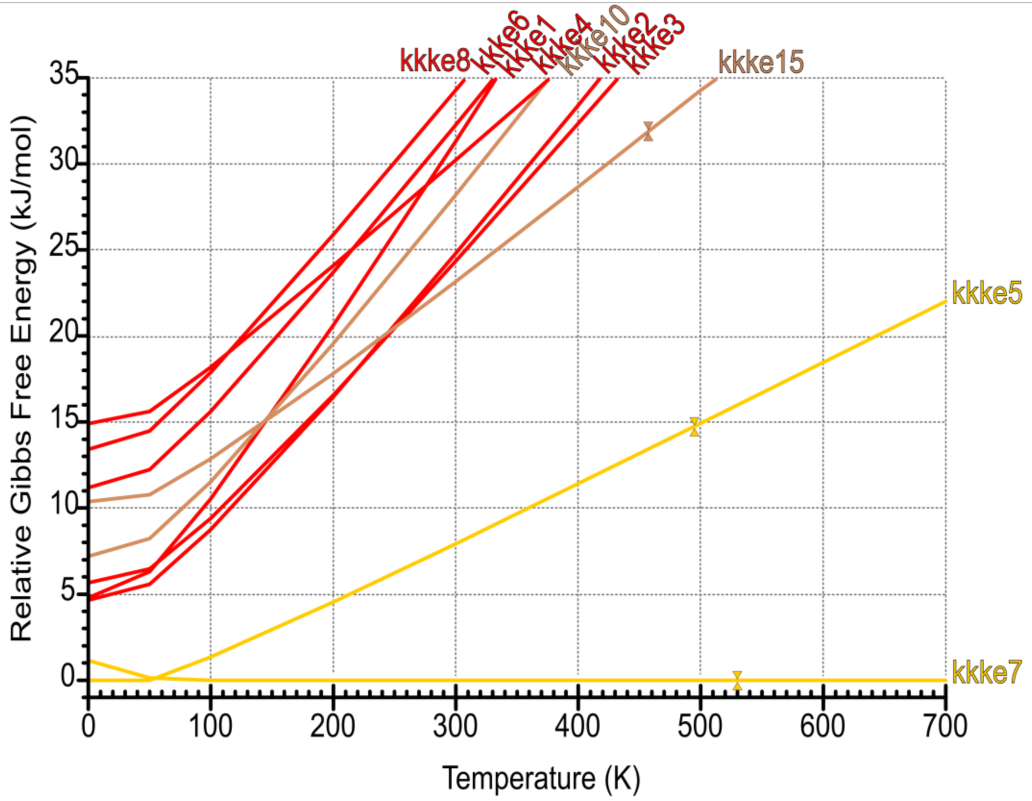


Figure S26. Relative Gibbs free energy of the computed kkee cytosine tetramers. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. The dark green traces correspond to stacking structures.

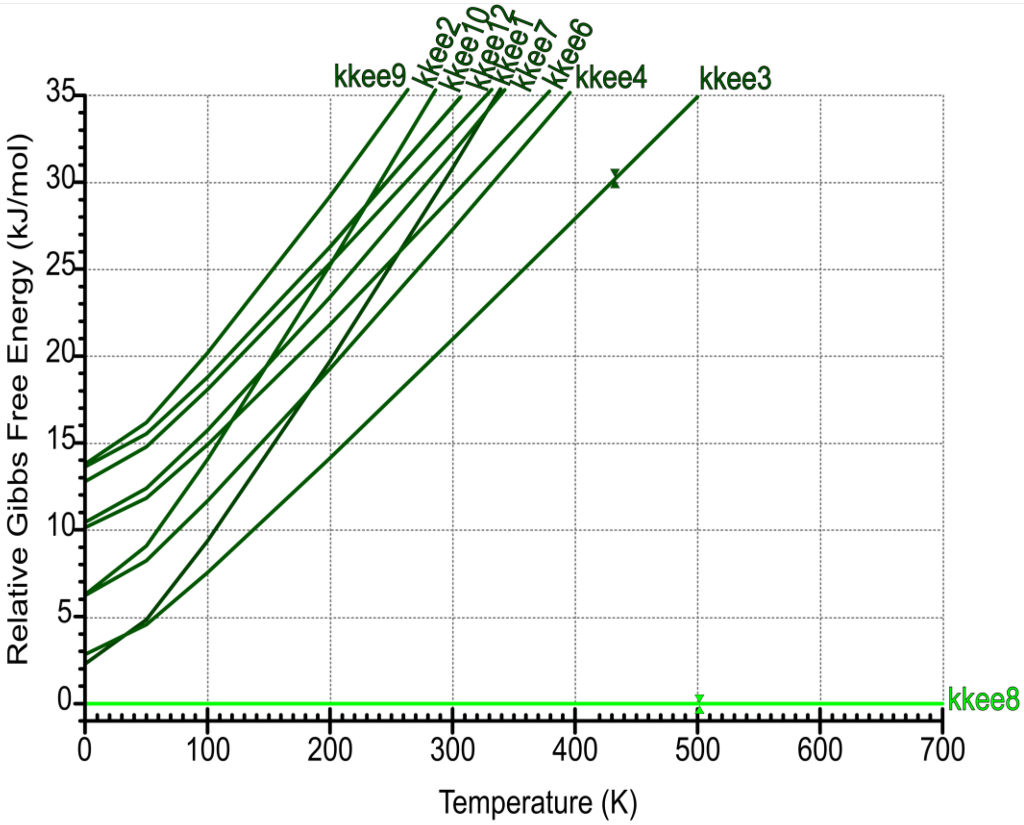
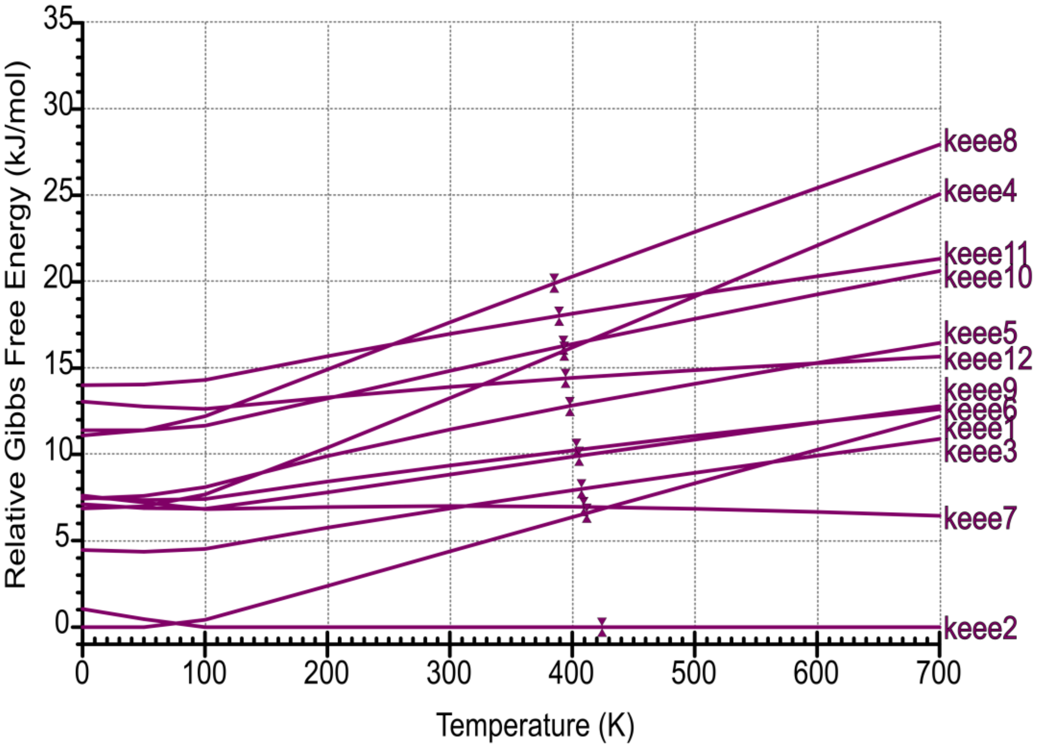
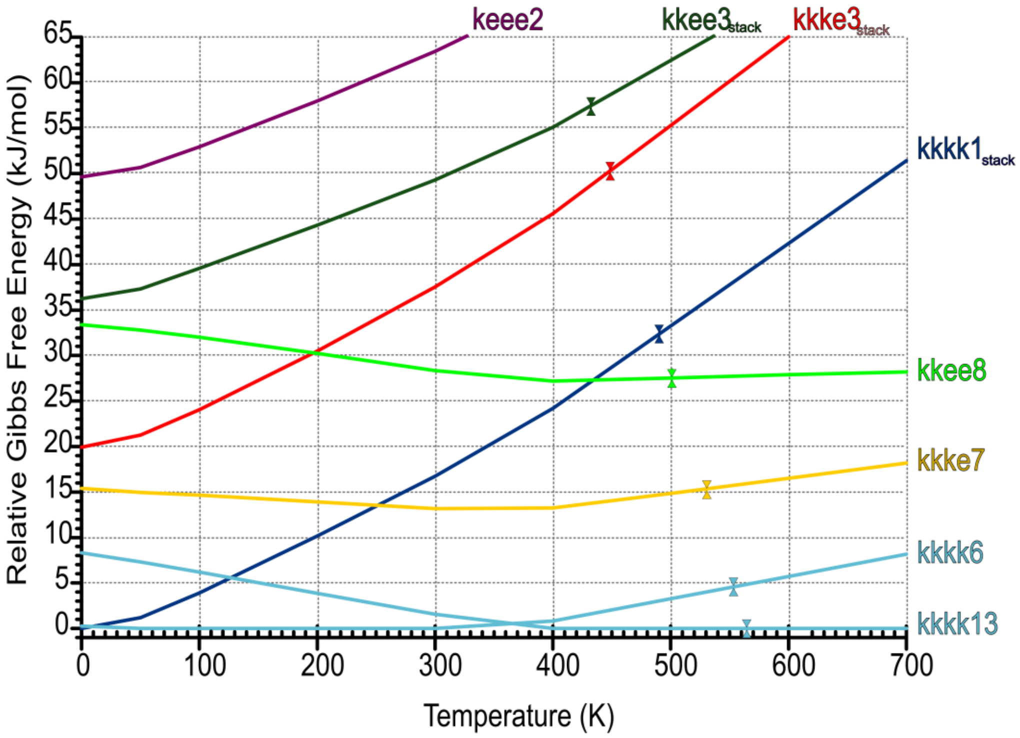


Figure S27. Relative Gibbs free energy of the computed keee cytosine tetramers. The triangles indicate the temperature at which ΔG = 0 and therefore, above such temperature the cluster is no longer stable. All the computed structures are non-planar.



FigureS28 . Comparison between the Gibbs relative free energy of the most stable planar and stacked conformers of each possible combination of tautomers of cytosine tetramer. Clearly, planar structures are favoured by entropy.



FigureS29 . Comparison between the Gibbs relative free energy of some selected calculated structures of cytosine tetramer.

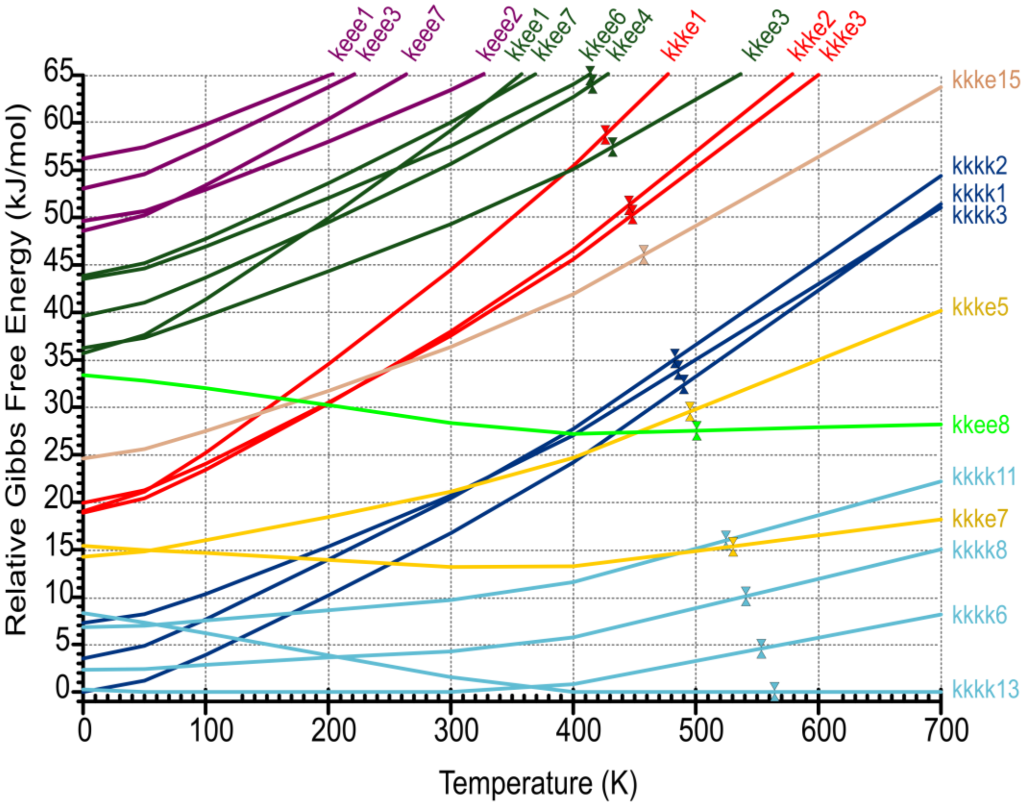
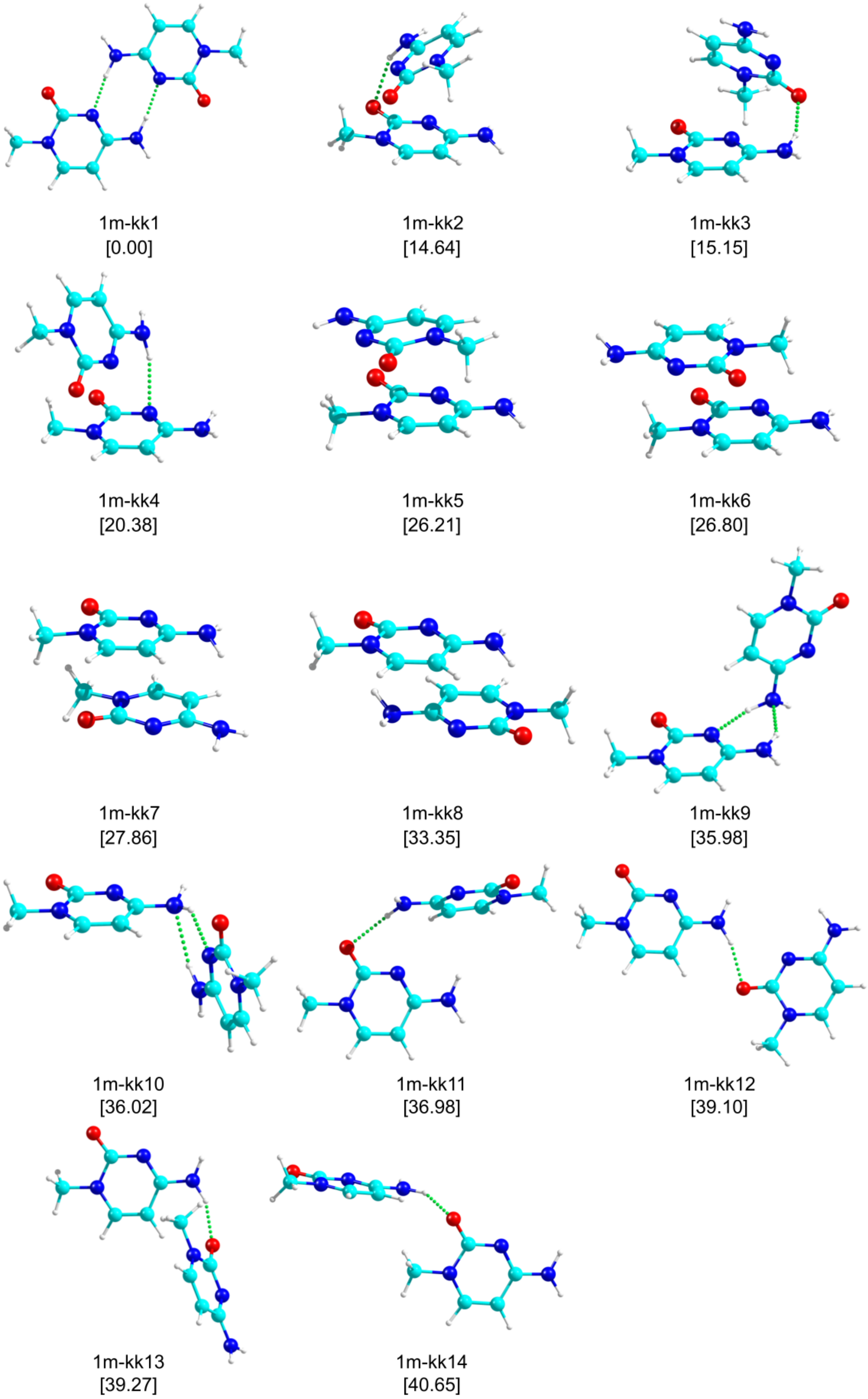


Figure S30. The 14 most stable structures of kk 1-methylcytosine dimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



1m-kk1
[0.00]

1m-kk2
[14.64]

1m-kk3
[15.15]

1m-kk4
[20.38]

1m-kk5
[26.21]

1m-kk6
[26.80]

1m-kk7
[27.86]

1m-kk8
[33.35]

1m-kk9
[35.98]

1m-kk10
[36.02]

1m-kk11
[36.98]

1m-kk12
[39.10]

1m-kk13
[39.27]

1m-kk14
[40.65]

Figure S31. Relative Gibbs free energy of the computed kk 1-methylcytosine dimers. The dark blue traces correspond to stacking structures.

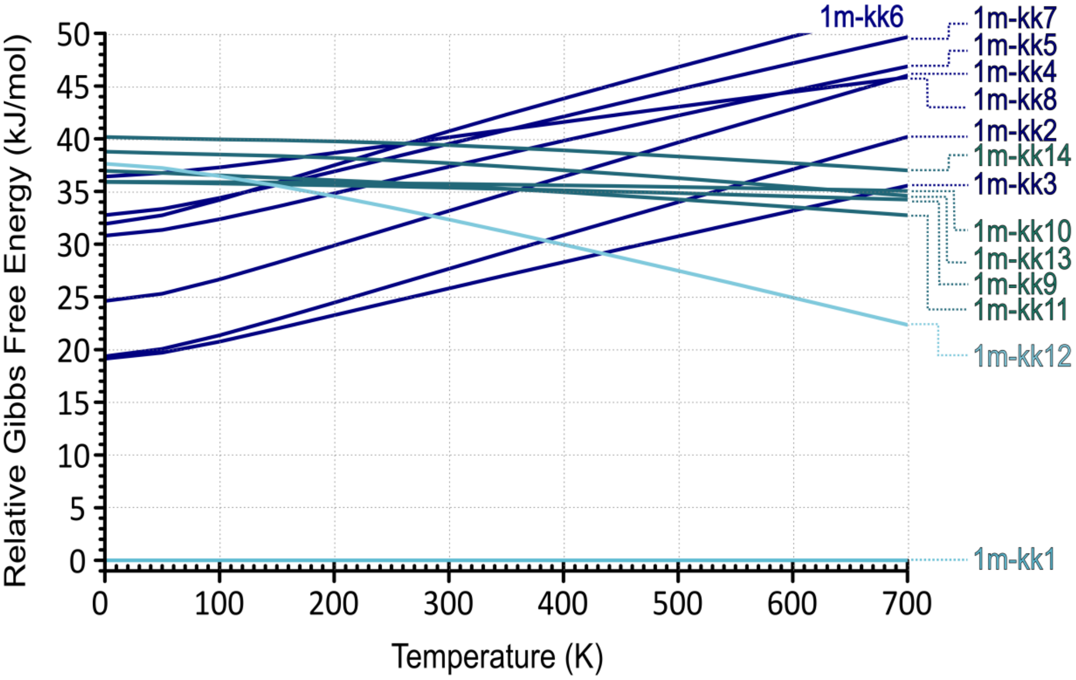
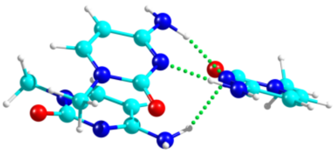
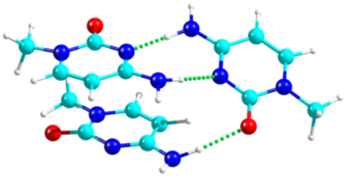


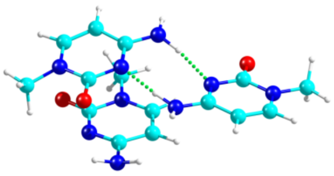
Figure S32. The 15 most stable structures of kkk 1-methylcytosine trimer, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



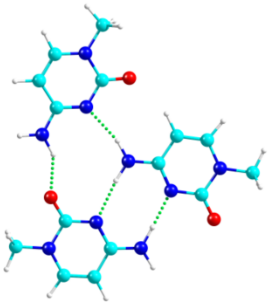
1m-kkk1
[0.00]



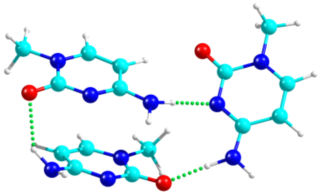
1m-kkk2
[0.22]



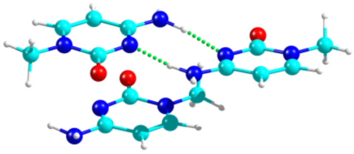
1m-kkk3
[4.70]



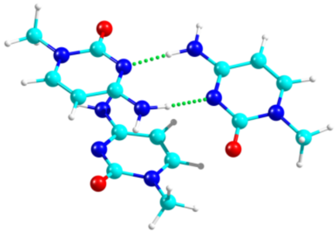
1m-kkk4
[6.21]



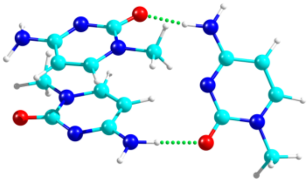
1m-kkk5
[10.30]



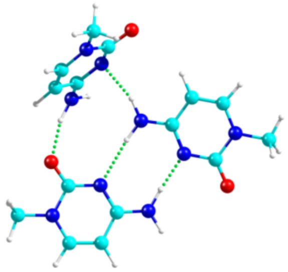
1m-kkk6
[11.42]



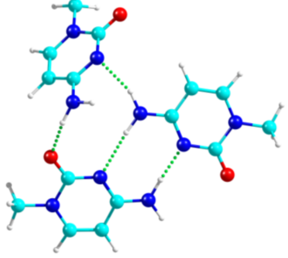
1m-kkk7
[13.40]



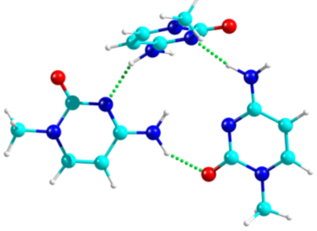
1m-kkk8
[16.24]



1m-kkk9
[16.87]



1m-kkk10
[17.95]



1m-kkk11
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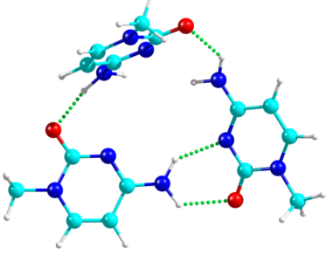
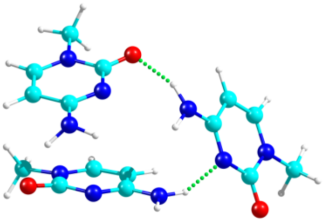
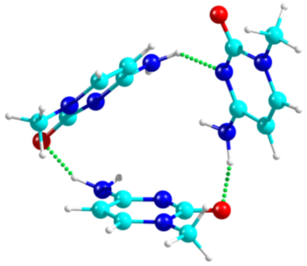


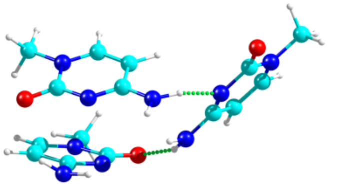
1m-kkk12
[19.26]



1m-kkk13
[21.30]



1m-kkk14
[21.68]



1m-kkk15
[22.51]

Figure S33. Relative Gibbs free energy of the computed kkk 1-methylcytosine trimers. The dark blue traces correspond to stacking structures.

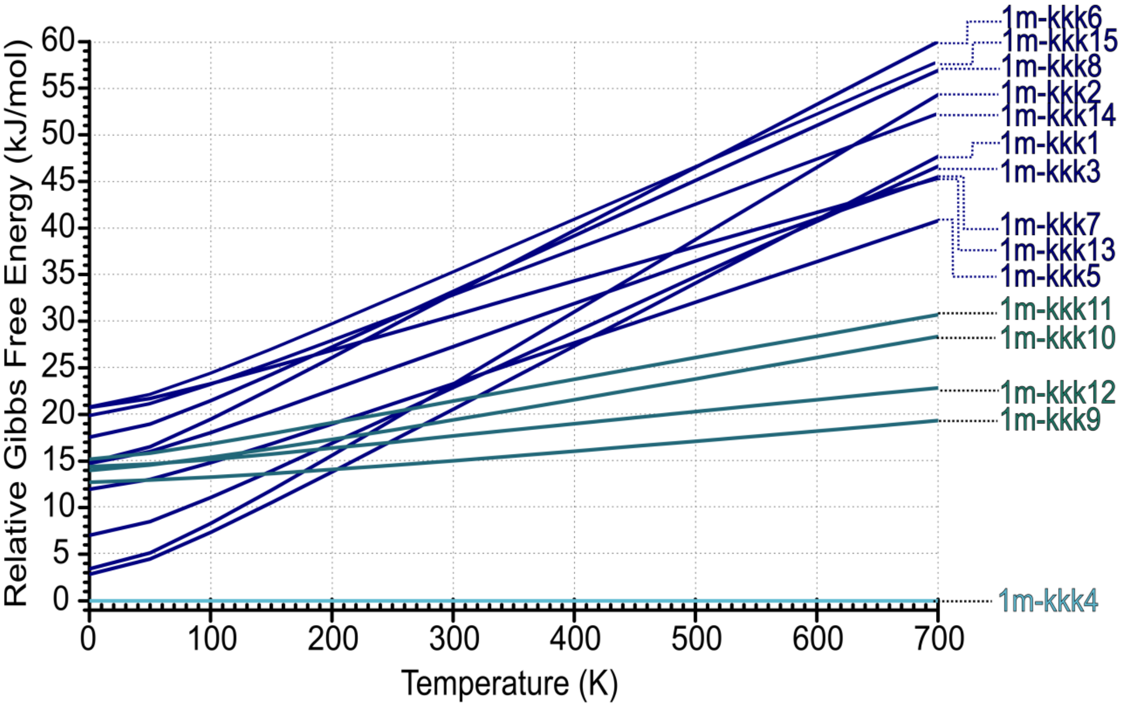
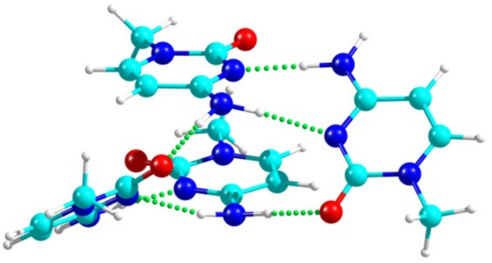
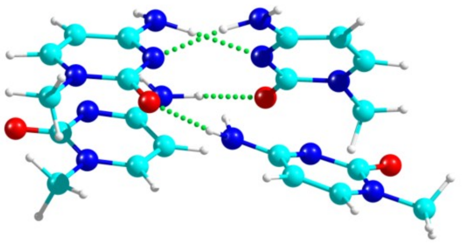


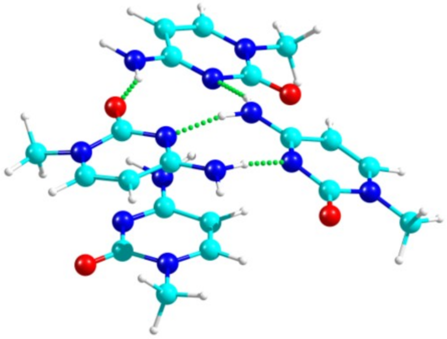
Figure S34. The 15 most stable structures of kkkk 1-methylcytosine tetramer and the first planar structure, calculated at M06-2X/6-311++G(d,p) level, together with their relative stability (ΔH, in kJ mol^{-1}) in brackets. ZPE correction was applied to the energy values.



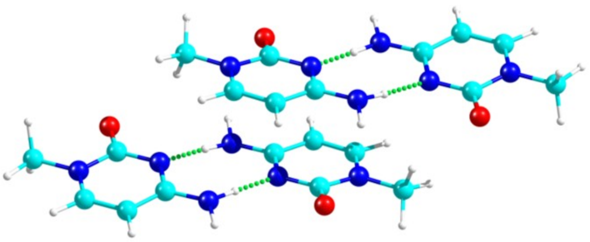
1m-kkkk1
[0.00]



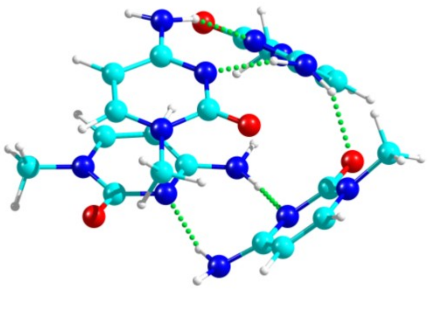
1m-kkkk2
[7.84]



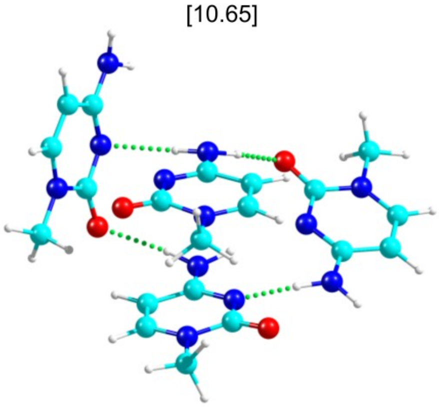
1m-kkkk3
[9.12]



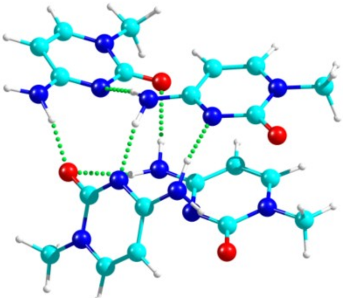
1m-kkkk4
[10.65]



1m-kkkk5
[11.42]



1m-kkkk6
[13.56]



1m-kkkk7
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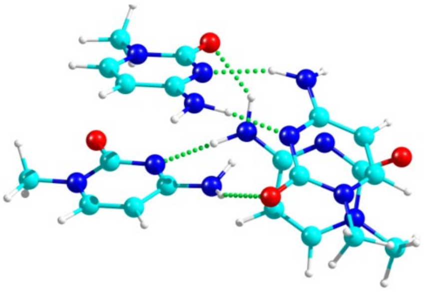
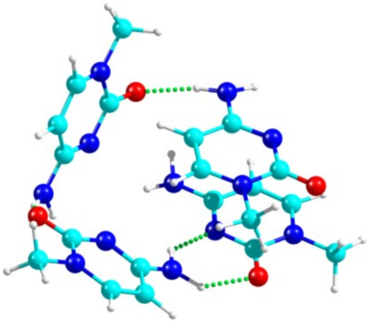
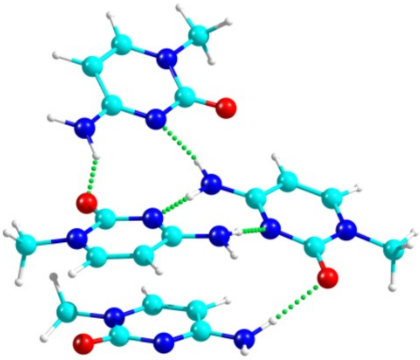


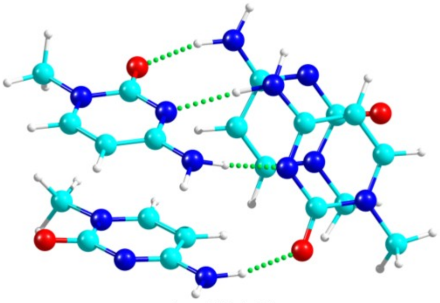
1m-kkkk8
[15.86]



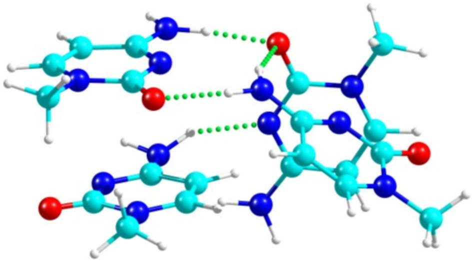
1m-kkkk9
[16.19]



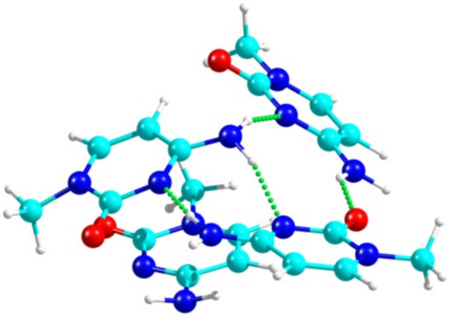
1m-kkkk10
[16.81]



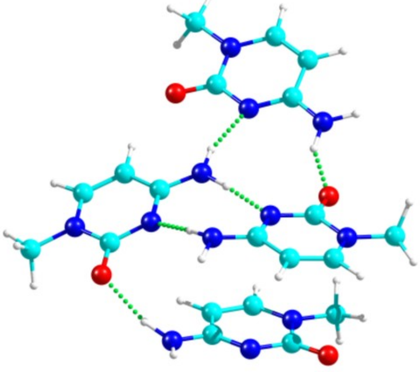
1m-kkkk11
[16.92]



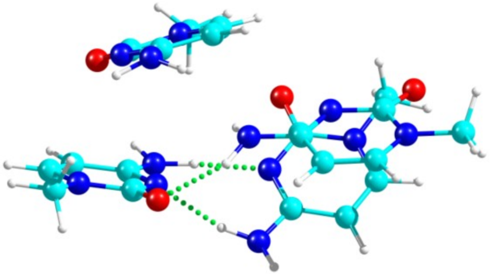
1m-kkkk12
[17.53]



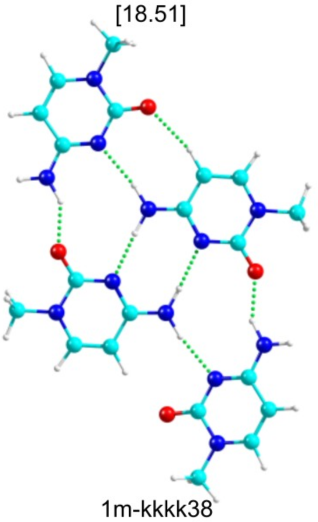
1m-kkkk13
[18.29]



1m-kkkk14
[18.51]



1m-kkkk15
[19.60]



1m-kkkk38
[26.97]

Figure S35. Relative Gibbs free energy of the computed kkkk 1-methylcytosine tetramers. The dark blue traces correspond to stacking structures.

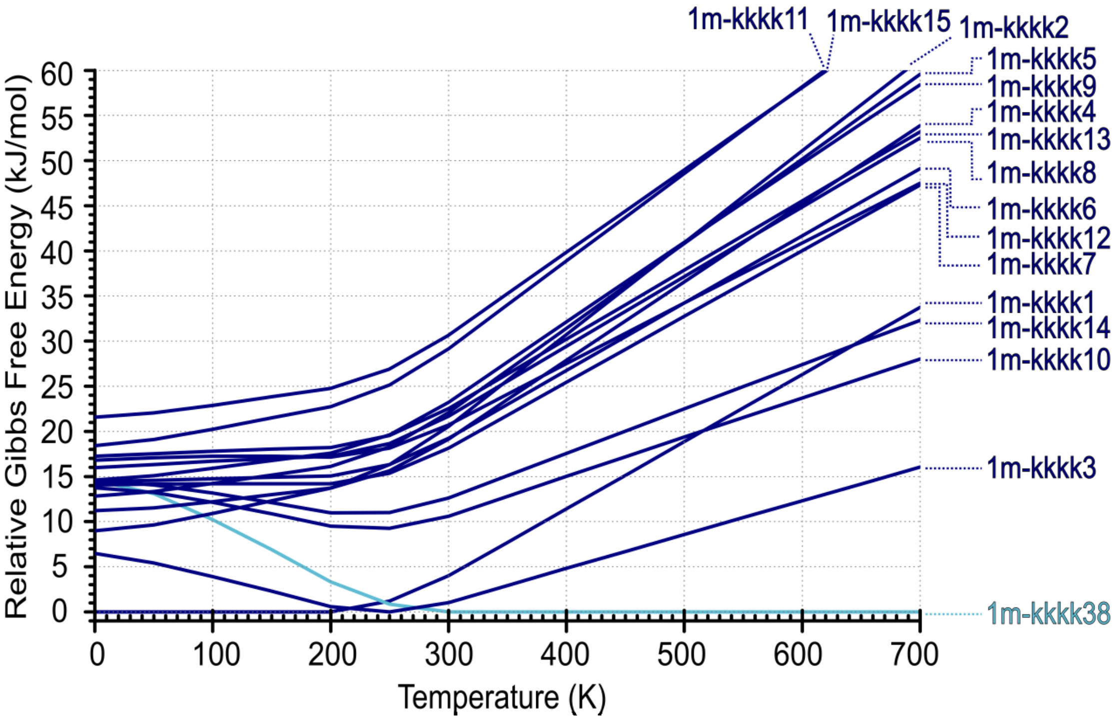


Figure S36. NCI plots of cytosine dimer's two most stable calculated structures. Blue areas represent strong hydrogen bonds, while green volumes represent attractive van der Waals interactions. Repulsive interactions appear as red areas (for example at the centre of the rings).

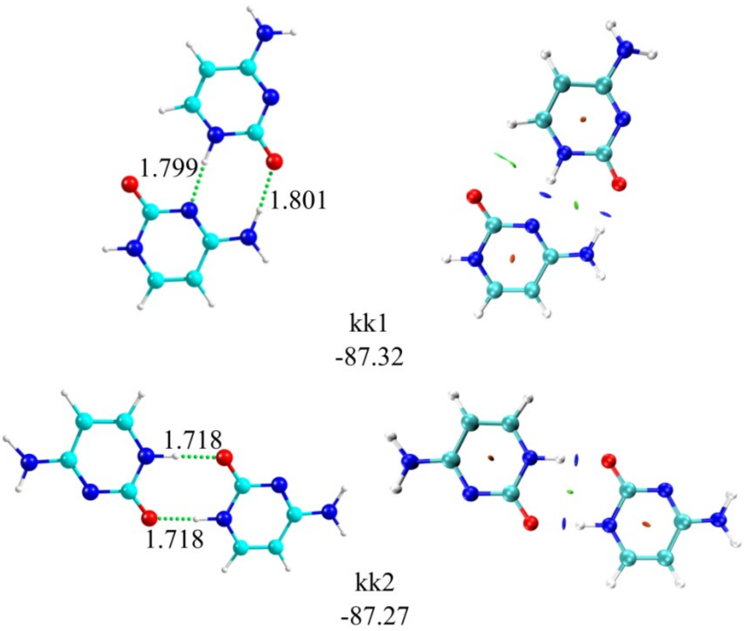


Figure S37. Relative Gibbs free energy of some selected calculated species of cytosine A) monomer; B) dimer; C) trimer; D) tetramer in the 0-700 K interval, assuming a non-equilibrium system with a rotational temperature around T = 4 K.

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