

***Molecular recognition in DNA: the Role of Aromaticity, Hybridization,  
Electrostatics and Covalence***

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Abstract: Quantum chemical studies show that neither aromaticity nor other  $\pi$  assistance are responsible for the enhanced stability of the hydrogen bonds in adenine-thymine (AT). This follows from extensive bonding analyses of AT and smaller analogs thereof, based on dispersion-corrected density functional theory. Removing the aromatic rings of either A or T has no effect on the Watson-Crick bond strength. Only when the smaller mimics become saturated, that is, when the hydrogen-bond acceptor and donor groups go from  $sp^2$  to  $sp^3$ , the stability of the resulting model complexes suddenly drops. Bonding analyses based on quantitative Kohn-Sham molecular orbital theory, a corresponding energy decomposition analyses (EDA) and Voronoi Deformation Density (VDD) Analysis show that the stronger hydrogen bonds in the unsaturated model complexes and in AT stems from stronger electrostatic interaction as well as enhanced donor-acceptor interactions in the sigma-electron system, with the covalency being responsible for shortening the hydrogen bonds in these dimers.