# Does a Stacked DNA Base Pair Hydrate Better than a Hydrogen-Bonded One?: An ab Initio Study

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A systematic comparative study has been carried out on the explicit hydration of the cytosine base (C), cytosine−cytosine hydrogen-bonded (H-bonded) base pair (CC) and cytosine−cytosine stacked dimer (C/C). An electrostatics-based model, electrostatic potential for intermolecular complexation (EPIC) has been used to generate initial geometries of the hydrated complexes for ab initio calculations. For this purpose, first the topography of the molecular electrostatic potential (MESP) for C, CC and C/C is explored. Several geometries of the complexes, C...$(H_2O)_n$, CC...$(H_2O)_n$ and C/C...$(H_2O)_n$ ($n$ = 1, 2 and 3) are investigated with EPIC followed by constrained optimization at the HF/6-31G** level. Further, single point (SP) energy calculations have been performed at the MP2/6-31G** level to assess the role of electron correlation contribution in the hydration process. This study reveals that C/C stacked dimer hydrates better than the hydrogen-bonded (H-bonded) CC pair. Energetics of these systems show a clear-cut additional stability of 1 to 2.5 kcal/mol at the HF/6-31G** level and more than 3 kcal/mol at the MP2/6-31G**//HF/6-31G** level for C/C...$3H_2O$ complex as compared to CC...$3H_2O$. The present study thus confirms that the stacked base pair hydrates better than the corresponding H-bonded base pair.