**Abstract**

We aim to understand the structure and stability of the backbone tailored Watson-Crick base pairs, Guanine-Cytosine (GC), Adenine-Thymine (AT) and Adenine-Uracil (AU) by incorporating N-(2-aminoethyl) glycine units (linked by amide bonds) at the purine and pyrimidine sites of the nucleobases. Density functional theory (DFT) is employed in which B3LYP/6-311++G∗∗ level of theory has been used to optimize all the structures. The peptide attached base pairs are compared with the natural deoxyribose nucleic acid (DNA)/ribonucleic acid (RNA) base pairs and the calculations are carried out in both the gas and solution phases. The structural propensities of the optimized base pairs are analyzed using base pair geometries, hydrogen bond distances and stabilization energies and, compared with the standard reference data. The structural parameters were found to correlate well with the available data. The addition of peptide chain at the back bone of the DNA/RNA base pairs results only with a minimal distortion and hence does not alter the structural configuration of the base pairs. Also enhanced stability of the base pairs is spotted while adding peptidic chain at the purine site rather than the pyrimidine site of the nucleobases. The stability of the complexes is further interpreted by considering the hydrogen bonded N–H stretching frequencies of the respective base pairs. The discrimination in the interaction energies observed in both gas and solution phases are resulted due to the existence of distinct lowest unoccupied molecular orbitals (LUMO) in the solution phase. The reactivity of the base pairs is also analyzed through the in-depth examinations on the highest occupied molecular orbital (HOMO)-LUMO orbitals.