

The nature of the hydrogen bond in DNA base pairs.

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The view that the hydrogen bonds in Watson-Crick adenine–thymine (AT) and guanine–cytosine (GC) base pairs are in essence electrostatic interactions with substantial resonance assistance from the π electrons is questioned. Our investigation is based on a state-of-the-art density functional theoretical (DFT) approach (BP86/TZ2P) that has been shown to properly reproduce experimental data. Through a quantitative decomposition of the hydrogen bond energy into its various physical terms, we demonstrate that, contrary to the widespread belief, donor-acceptor orbital interactions (i.e. , charge transfer) in σ symmetry between N or O lone pairs on one base and N–H σ^* -acceptor orbitals on the other base do provide a substantial bonding contribution which is, in fact, of the same order of magnitude as the electrostatic interaction term. The overall orbital interactions are reinforced by a small π component which stems from polarization in the π -electron system of the individual bases. This π component is, however, one order of magnitude smaller than the σ term. Furthermore, we have investigated the synergism in a base pair between charge transfer from one base to the other through one hydrogen bond and in the opposite direction through another hydrogen bond, as well as the cooperative effect between the donor-acceptor interactions in the σ - and polarization in the π -electron system. The possibility of C–H...O hydrogen bonding in AT is also examined. In the course of these analyses, we introduce an extension of the Voronoi deformation density (VDD) method which monitors the redistribution of the σ - and π -electron densities individually out of ($\Delta Q > 0$) or into ($\Delta Q < 0$) the Voronoi cell of an atom upon formation of the base pair from the separate bases.

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