



The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory (International Union of Crystallography Monographs on Crystallography)

Gastone Gilli, Paola Gilli

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Hydrogen bond (H-bond) effects are known: it makes sea water liquid, joins cellulose microfibrils in trees, shapes DNA into genes and polypeptide chains into wool, hair, muscles or enzymes. Its true nature is less known and we may still wonder why O-H...O bond energies range from less than 1 to more than 30 kcal/mol without apparent reason. This H-bond puzzle is re-examined here from its very beginning on the ground of an inclusive compilation of experimental H-bond energies and geometries.

New concepts emerge from this analysis: new classes of systematically strong H-bonds (CAHBs and RAHBs: charge- and resonance-assisted H-bonds); full H-bond classification in six classes (the six chemical leitmotifs); and assessment of the covalent nature of strong H-bonds. This leads to three distinct but inter-consistent models able to rationalize the H-bond and predict its strength, based on classical VB theory, matching of donor-acceptor acid-base parameters (PA or pKa), or shape of the H-bond proton-transfer pathway.

Applications survey a number of systems where strong H-bonds play an important functional role, namely drug-receptor binding, enzymatic catalysis, ion-transport through cell membranes, crystal design and molecular mechanisms of functional materials.

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