

The Nature of the HB. 3. Towards a Comprehensive HB Theory

Paola Gilli, Valerio Bertolasi, Valeria Ferretti, Gastone Gilli,
Chemistry Department and Centre for Structural Diffractionometry,
University of Ferrara, Ferrara, Italy. E-mail: paola.gilli@unife.it

Communications 1 and 2 have shown that the *empirical laws* governing HB strength can be reduced to two main points: (i) The PA/pK_a Equalization Principle; and (ii) The Six Chemical Leitmotifs. Much more difficult is the formulation of a *HB theory*, that is a complete explanation of the two empirical laws in terms of basic chemical bonding theory. Our method relies on what we have called "*The Transition-State HB Theory*" according to which any X-H...Y bond can be considered as a proton-transfer (PT) reaction X-H...Y ↔ X...H...Y ↔ X...H-Y which is bimolecular in both directions, proceeds *via* the X...H...Y transition state (the activated complex) and differs from ordinary reactions only because reactants and products are pre-bound by the HB, so that rather small PT-barriers are to be expected. This method is applied to the study of O-H...O and N-H...O/O-H...N RAHBs by quantum-mechanical DFT emulation with full geometry optimization of the three stationary points or of the complete PT-pathway profile. Analysis of the data was performed, in a VB logic frame, by the Marcus rate-equilibrium relationships, extrathermodynamic LFER Hammett parameters and avoided crossing (state correlation) diagrams. Results show that HB strength, single or double-well shape of the PT-pathway and height of the PT-barriers are completely determined, for any R₁X-H...YR₂ HB, by the ability of the R₁ and R₂ substituents to achieve the condition of PA/pK_a matching between the HB donor and acceptor molecules. The theory is used to interpret accurate variable-temperature X-ray crystallographic data.

Keywords: hydrogen bond theory, proton transfer, variable-temperature x-ray crystallography