

s9.m1.o1 **Hydrogen Bonding in the Last Quarter of the Century: New Methods, New Results, New Ideas.** G. Gilli*, Th. Steiner. *Chemistry Department and Centro di Strutturistica Diffattometrica, Ferrara University, Via Borsari 46, I-44100 Ferrara, Italy; Institut für Kristallographie, Freie Universität Berlin, Takustr. 6, D-14195 Berlin, Germany.* ggilli.chim@unife.it – steiner@chemie.fu-berlin.de

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The last few decades have registered an unprecedented evolution of new experimental and computational techniques for the study of this rather mysterious phenomenon called hydrogen bond. This is deeply modifying our old views on the matter, though often in a rather confused way because of the difficulties in handling such a profusion of new and heterogeneous findings. It seems the very moment for attempting novel unified and unifying approaches to H-bond theory or, at least, for summarizing the new results and getting rid of a number of old biases incompatible with the new ascertained facts. The present lecture intends to give a first contribution to this difficult but intriguing subject by addressing a number of selected H-bond topics¹⁻⁴:

- 1. H-Bond Energies.** Both experimental and theoretical methods have terribly extended H-bond energy ranges. Present theories must deal with O–H...O bonds whose energies range continuously from 0 to 32 kcal mol⁻¹ (45 kcal mol⁻¹ for F–H...F).
- 2. Electrostaticity and Covalency.** The idea of a purely electrostatic H-bond is declining. Increasing evidence is being collected that weak electrostatic bonds grow more and more covalent with their increasing strength, till becoming true three-centre-four-electron covalent bonds.
- 3. Electronegativities and Relative Proton Affinities (PA).** Increasing evidence has been put forward that the strength of the X–H...Y bond is determined, besides the average (X,Y) electronegativity, by the PA difference (Δ PA) between X and Y, the H-bond energy reaching a maximum for Δ PA = 0.
- 4. Strong HBond Chemical Leit-Motivs.** High electronegativities and small Δ PA's are not enough to produce strong H-bonds that must be associated with a limited number of chemical leit-motivs, such as $[X-H...Y]^+$, $[X-H...Y]$, $[^+X-H...Y]$ and patterns of σ - and π -cooperativity.
- 5. Contiguity of All Shared-Proton Interactions.** There are increasing theoretical indications of a contiguity of properties between traditional H-bonds, weak C–H...O and C–H...N bond, and a number of non-conventional interactions, such as π -acceptors or dihydrogen bonds. The only discriminant among shared-proton interactions remains the difference between three-centre-four-electron (any H-bond) and three-centre-two-electron bonds (boranes and agostic interactions).

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[4] Gilli, G.; Gilli, P. *J. Mol. Struct.* (2000), in press.

s9.m1.o2 **Energetic properties of the hydrogen bond interaction: a straight representation in terms of the electron density distribution.** E. Espinosa^{1,2} E. Molins² and C. Lecomte³. ¹LIMSAG, Faculté des Sciences, Université de Bourgogne, 6 bd Gabriel, 21100 Dijon, France. ²Institut de Ciència de Materials de Barcelona (CSIC). Campus de la UAB, 08193 Cerdanyola (Barcelona), Spain. ³LCM3B, UPRESA CNRS 7036, Université Henri Poincaré, Nancy 1, BP 239, 54506 Vandoeuvre-lès-Nancy CEDEX, France. E-mail: enrique.espinosa@u-bourgogne.fr.

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Interatomic interactions such as hydrogen bonds (HB's) can be adequately described and classified by the topological properties of the electron density $\rho(\mathbf{r})$ at the (3,-1) critical points \mathbf{r}_{CP} , where the gradients of $\rho(\mathbf{r})$ vanish.¹ We have analysed^{2,3} the topological properties of $\rho(\mathbf{r})$ at the intermolecular critical points of 83 experimentally observed HB's $[X-H...O]$ (X = C, N, O) on a large set of compounds, obtained from accurate X-ray diffraction experiments. In spite of different models, methods and experimental conditions employed to obtain the topological properties of $\rho(\mathbf{r})$, we show that, for closed-shell interactions, the kinetic energy density $G(\mathbf{r}_{CP})$ and the potential energy density $V(\mathbf{r}_{CP})$ at the critical point, depend exponentially on the H...O distance. We point out the positive correlation found between the $V(\mathbf{r}_{CP})$ and the HB energy when their functionalities against the H...O distance are compared. We have also observed⁴ that the positive and the negative curvatures of $\rho(\mathbf{r})$ at the H...O critical point exhibit linear relationships against, respectively, $G(\mathbf{r}_{CP})$ and $V(\mathbf{r}_{CP})$. The proportional behaviours found between those quantities show that the strength of the hydrogen bond interaction can be indistinctly interpreted in terms of any of them. The functionality of the total electron energy density (E) against the interatomic distance, at the (3,-1) critical point of the H...O interaction, has been obtained through the corresponding experimental functionalities retrieved for the local electron kinetic (G^{CP}) and potential (V^{CP}) energy densities ($E^{CP} = G^{CP} + V^{CP}$) for the same set of 83 HB's. The E^{CP} function, which describes the interaction of those electrons in the system, has been recently related⁵ to the H...O interaction potential. The proposed potential has been successfully checked against several physical and chemical properties.

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