

## The origin of RAHB in hydrogen bonds (HB): which are the main effects?

Among all the types of H-bonds the strongest known are those assisted by additional effects, e.g., resonance assisted or charge assisted H-bonds. Since Gilli et al.<sup>[1]</sup> introduced in 1989 the concept of resonance-assisted hydrogen bonds (RAHBs) it has become one of the most frequently used concepts in structural chemistry. Usually RAHBs are classified as  $\pi$ -conjugated ring or chain motives, for which changes in geometrical or electronic properties are observed, i.e., elongation of formally double bonds and shortening of formally single bonds accompanied by suitable changes in critical points corresponding to these bonds, together with elongation of the X-H (X = proton donor) bond and shortening of the XH $\cdots$ Y (Y = proton acceptor) bond within H-bridge.

This RAHB effect was stated by Gilli in DNA base-pair and corroborated by Fonseca Guerra et al. using the energy decomposition analysis (EDA) scheme in the framework of the Kohn-Sham MO model. Although RAHB is usually linked with the presence of  $\pi$  electrons, the aim of this talk will be to analyze the origin of this extra stabilization, as some of our previous calculations show that double bonds, and consequently  $\pi$ -electrons, may not be the main reason of this RAHB. Not far from these observations, some authors<sup>[2]</sup> have been working in similar hypothesis. According to it, the primary effect causing this extra stabilization is the  $\sigma$ -skeleton, more than the  $\pi$  electrons.

One of the most important biological systems that is based on hydrogen bonds and show double bonds as part of its structure is DNA, so some small compounds similar to it will be used. Calculations will be performed with and without  $\pi$  electrons in order to know the real influence of them in the RAHB. By considering the results obtained thanks to the fragment analysis and by using ADF (Amsterdam Density Functional), we will be able to know which characteristics could play an important role in this RAHB. Previous studies have been performed within Dr. Fonseca Guerra group, helping to clarify the hypothesis to be studied.<sup>[3]</sup>

[1] (a) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023; (b) Gilli, G.; Bertolasi, V. in: Z. Rappoport (Ed.), *The Chemistry of Enols*, Wiley, Chichester, **1990**, p. 713 (Chapter 13).

[2] (a) Sanz, P; M3, O; Y3nez, M; Elguero, J. *Chem. Phys. Chem.* **2007**, *8*, 1950. (b) Sanz, P; M3, O; Y3nez, M; Elguero, J. *J. Phys. Chem. A* **2007**, *11*, 3585. (c) Sanz, P.; M3, O.; Y3nez, M.; Elguero, J. *Chem. Eur. J.* **2008**, *14*, 4225.

[3] C3lia Fonseca Guerra, F. Matthias Bickelhaupt, Jaap G. Snijders and Evert Jan Baerends. *Chem. Eur. J.* **1999**, *5*, No. 12, 3581.