Discovering in silico the uniqueness of hydrogen bonding

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ABSTRACT

Hydrogen bonds are omnipresent in biological and supramolecular chemistry. Nevertheless, they are still mostly represented in an oversimplified manner which is easy to use but often fails to explain or even qualitatively reproduce experimental findings. In my lecture, I present a state-of-the art physical model, based on quantitative molecular orbital theory, which enables a quantum-mechanically sound, yet intuitive approach to the interesting complexity of the hydrogen bond. The latter can be dissected into understandable contributions such as covalent bonding and Pauli repulsion between occupied orbitals. Complex and seemingly exotic phenomena are unraveled and explained in a unified manner: cooperativity in hydrogen bonds [1], variations in hydrogen bond lengths and energies due to steric repulsion, [2] legitimacy of the secondary electrostatic interaction model [3] and hydrogen bond donor capability of carboxamides, thioamides and selenoamides.[4]

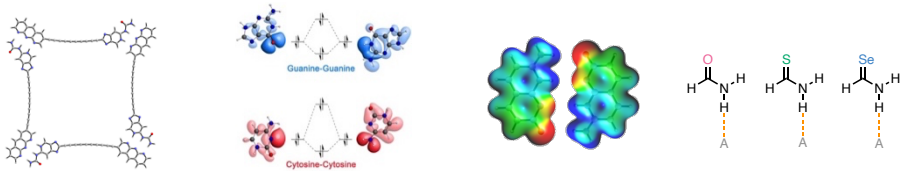

Figure 1: Different aspects of the nature of hydrogen-bonded systems.

References

[1] Almacellas, D. et al. Non-Innocent π Linkers Affect Cooperativity in Hydrogen-Bonded Macrocycles. *ChemistryEurope* **2024**, 2, e202300036

[2] van der Lubbe, S. C. C.; Fonseca Guerra, C. Hydrogen bond strength of CC and GG pairs is determined by steric repulsion. *Chem. Eur. J.* **2017**, *23*, 10249

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[4] Nieuwland, C.; Fonseca Guerra, C. How the Chalcogen Atom Size Dictates the Hydrogen-Bond Donor Capability of Carboxamides, Thioamides, and Selenoamides, *Chem. Eur. J.* **2022**, *28,* e202200755.