ISXB4 4TH INTERNATIONAL SYMPOSIUM ON HALOGEN BONDING

Stacking interactions of resonance-assisted hydrogen-bridged (RAHB) rings - RAHB/RAHB and RAHB/C_6-aromatic systems

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Supramolecular arrangements of RAHB/RAHB and RAHB/C_6-aromatic contacts were studied by the Cambridge Structural Database (CSD) search, while interaction energies of these interactions were calculated on dimer model systems by using quantum-chemical methods. Parallel alignment contacts are quite dominant in the crystal structures of these species, since 91% of the RAHB/RAHB contacts, satisfying the search criteria [1], are parallel, while that preference is not so large in RAHB/C_6-aromatic contacts, since 59% of them are parallel [2]. Interplane separations of the parallel contacts of both systems are between 3.0 and 4.0 Å, which is a characteristic of stacking interactions. Examples of the RAHB/RAHB and RAHB/C_6-aromatic contacts are given in Figure 1.
Model systems for quantum chemical calculations are based on abundance in the crystal structures. Energy decomposition analysis is also performed by using Symmetry Adopted Perturbation Theory (SAPT) calculations. The strongest calculated RAHB/RAHB interaction is -4.7 kcal/mol. Electrostatic contribution is dominant or equal to the net dispersion (the sum of dispersion and exchange-repulsion terms). The strongest calculated RAHB/benzene interaction is -3.7 kcal/mol, but RAHB/benzene interactions can be stronger or weaker than the corresponding RAHB/RAHB interactions. Electrostatic term is dominant in all studied RAHB/benzene interactions.

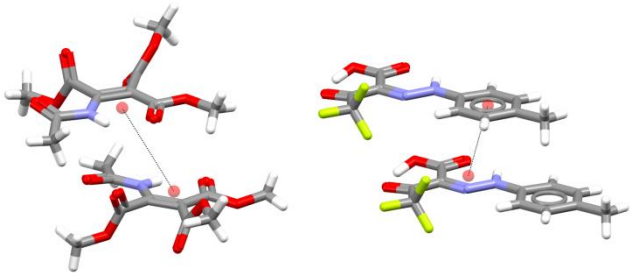

Figure 1: Examples of RAHB/RAHB (left) and RAHB/C_6-aromatic (right) interactions

References

1. J.P. Blagojević Filipović, M.B. Hall, S.D. Zarić, *Cryst. Growth Des. Stacking Interactions of Resonance-Assisted Hydrogen-Bridged Rings. A Systematic Study of Crystal Structures and Quantum-Chemical Calculations* **2019**, 19, 5619-5628.
2. J.P. Blagojević Filipović, M.B. Hall, S.D. Zarić, *Phys. Chem. Chem. Phys. Stacking interactions of resonance-assisted hydrogen-bridged rings and C_6-aromatic rings* **2020**, 22, 13721-13728.