RESONANCE-ASSISTED HYDROGEN-BRIDGED RINGS—PARALLEL ALIGNMENT IN CRYSTAL STRUCTURES AND SIGNIFICANT NONCOVALENT ATTRACTION

Jelena P. Blagojević Filipović [1], Snežana D. Zarić [2]

[1] *Innovation Centre of the Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia*
[2] *Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia **

**szaric@chem.bg.ac.rs*

Abstract

Resonance-assisted hydrogen-bridged rings (RAHB) are promising structures in material design due to synergistic effects between hydrogen bonding and resonance. We investigated mutual contacts between RAHB ring structures deposited in the Cambridge Structural Database (CSD), as well as contacts between RAHB rings and C_6-aromatic fragments. Stacking interactions in crystal structures are identified by parallel alignment of interacting fragments and a characteristic distance between the planes of the interacting fragments, which is between 3.0 and 4.0 Å. The existence of stacking interactions is then confirmed by quantum chemical calculations of interaction energies at dimer model systems. Namely, more than 90% of mutual RAHB/RAHB contacts found in the CSD are parallel and anti oriented. A smaller part of RAHB/C_6-aromatic contacts (around 60%) is in parallel orientation. Both RAHB/RAHB and RAHB/C_6-aromatic contacts typically form parallel layers at a specific distance (between 3.0 and 4.0 Å), which distinguishes them from benzene/benzene parallel contacts found in the CSD, where layers are not formed. The most abundant RAHB ring types found in the CSD are used as model systems for quantum chemical calculations of interaction energies. Malonaldehyde ($H_4C_3O_2$), its mononitrigen analogue (H_5C_3NO) and dinitrogen analogue ($H_4C_2N_2O$) are used as model systems for RAHB rings, while benzene molecule is used as a model system for a C_6-aromatic fragment. RAHB/RAHB interactions can be quite strong (up to -4.7 kcal/mol in case of H_5C_3NO/H_5C_3NO dimer). RAHB/benzene interactions are generally weaker (up to -3.5 kcal/mol in case of $H_4C_3O_2$/benzene dimer), but they can be also stronger than the corresponding RAHB/RAHB interactions, depending on the system. Both RAHB/RAHB and RAHB/benzene interactions are stronger than benzene/benzene stacking interactions (-2.7 kcal/mol). Stacking interactions can remain strong in some systems even when placed to large horizontal displacements. For example, benzene/benzene stacking preserves 70% of its maximum strength upon shifting to the displacement of 5.0 Å. Stacking interactions of RAHB rings can, in some cases, preserve similar portion of their strength (around 70%) at large displacements.

Key words: *RAHB rings, stacking interactions, CSD*