Stacking Interactions of Resonance-Assisted Hydrogen-Bridged (RAHB) Rings; Significant Attraction at Large Displacements

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Some systems that form stacking interactions conserve large portion of their strength upon shifting to large horizontal displacements, which might have implications on molecular recognition.[1] The possibility of RAHB/RAHB and RAHB/C_6-aromatic systems to form stacking at large horizontal displacements is studied in this work. Large part of parallel RAHB/RAHB and RAHB/C_6-aromatic contacts found in the Cambridge Structural Database (CSD) are classified as large offset stacking (44% and 47%, respectively).[2] Crystal structures of both RAHB/RAHB and RAHB/C_6-aromatic systems are organized into parallel layers, unlike benzene crystal structures. Quantum chemical calculations show that the contacts at large offsets found in the CSD are not just the consequence of crystal packing. The calculated potential energy curves reveal the existence of certain stabilizations at large offsets (plateaus and even shallow minima). The large offset stacking interaction energies can be significant even at interplane separations typical for stacking (3.0-4.0 Å), or slightly smaller (Figure 1). In some systems, up to 66% of the strongest calculated interaction energy can be preserved upon shifting to large offsets.[2]

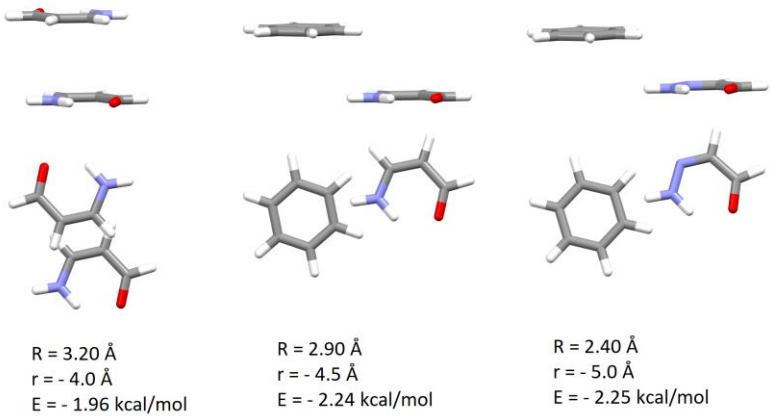

Figure 1. Some examples of the RAHB/RAHB and RAHB/C_6-aromatic stacking at large horizontal displacements; R-interplane separation; r-horizontal displacement; E-interaction energy

References

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