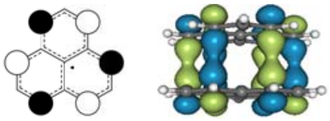
π–π stacking is different from pancake bonding: interpretations with molecular and solid state examples

Miklos Kertesz

Chemistry Department and Institute for Soft Matter, Georgetown University, Washington, D.C., 20057-1227, USA (kertesz@georgetown.edu)

In highly conducting charge transfer salts of the TCNQ-type and in the more recent neutral radical conductors and in many other organic crystals neighboring radicals display uniquely short contacts due to the overlap of the singly occupied molecular orbitals, SOMOs. These unusual intermolecular bonds occur between (1) conjugated molecules or ions with delocalized π-electrons, and are further characterized by (2) good face to face π–π stacking overlap with (3) shorter than van der Waals (vdW) contact distances. These aggregates differ qualitatively from ordinary π–π stacking such as found between DNA base pairs that occur between closed shell systems and should therefore not be considered a type of vdW interaction.



This intermolecular interaction (termed "pancake bonding" after Mulliken-Person) has further characteristics: (4) the binding energy associated with it can be significantly larger than typical vdW interactions, (5) intermolecular orbital overlap is important and dictates preferred relative packing by maximizing SOMO-SOMO overlap, (6) there are low-lying triplet and singlet excited states. The problem is theoretically challenging because the multireference (diradicaloid) character of the ground state is coupled with significant dispersion interactions that require the inclusion of a large number of configurations. We discuss the application of wave function methods (MR-AQCC) and various density functional theory (DFT) approaches that include long-rage or dispersion terms and vdW-DFT. We explore the limits of pancake bonding: which might be the strongest/shortest pancake bond?

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