

Origin of Anion/ π Interactions involving *N*-heterocycles

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Anion/ π interactions, which are traditionally defined as the attractive interactions between anions and the faces of “ π -acidic” aromatic rings, have emerged as a potentially powerful tool for supramolecular chemistry. Despite growing interest in these non-covalent interactions, there is not yet a satisfactory understanding of their origin. Often, anion/ π interactions involving *N*-heterocyclic rings are attributed to the depletion of the π -electron-density of these arenes. We have developed a physical model of the attractive non-covalent interactions between anions and *N*-heterocyclic azines based on results from symmetry-adapted perturbation theory. By decomposing the electrostatic interactions into σ - and π -contributions, we showed that the enhanced binding of anions by azines, compared to benzene, is due primarily to changes in electrostatic interactions involving the σ -system. Moreover, electrostatic interactions of anions with the aromatic π -electrons are actually slightly more repulsive for π -acidic azines than for benzene. This adds to our growing body of work showing that, in contrast to prevailing views in the literature, the strength of non-covalent interactions involving aromatic rings has little to do with variations in the aryl π -electron system.