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Exploring Novel Halogen Bonding Motifs: Birds, π-Systems, and Anionic Complexes

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We have recently studied unconventional halogen-bonded structures using electronic structure calculations. The projects I will discuss in my presentation include:

- The halogenabenzene bird: Halogen-substituted benzenes have received ample attention in the literature. Conversely, benzene structures where a carbon is replaced by a halogen, dubbed halogenabenzenes have received much less attention. Rawashdeh et al.[1] dubbed this structure "bird" because of the similarity with a flying bird (see Figure 1). The bird structure is unusual in the sense that the iodine is bonded to two carbon atoms. We investigated the ability of the bird-like halogenabenzene molecule, referred to as X-bird (X= Cl to At), to form halogen-bonded complexes with the nucleophiles H_2O and NH_3 using double-hybrid density functional theory.[2]
- Halogen bonds to aromatic systems: Whereas hydrogen bonding to π-systems (where the source of electrons is an aromatic system) has been well studied, studies of halogen bonding to π-systems are much sparser. Our group has looked at interactions of small halogen bond donors to aromatic systems including benzene, naphthalene, coronene and Buckminster fullerene.
- Anti-electrostatic halogen bonding: Halogen-bonding interactions normally include cationic or neutral donors. However, recently researchers have observed experimentally a series of halogen-bonded complexes where both constituents are anions.[3,4] We have studied these unusual complexes computationally to provide more information on such systems.

Figure 1. The haogenabenzene bird

References:
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