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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 H₂O and NH₃ 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:

- [1] Rawashdeh, A.M. Chakkingal Parambil, P., Zeng, T. and Hoffmann, R. J. Am. Chem. Soc. **2017**, *139*, 7124-7129
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- [4] Loy, C., Holthoff, J.M., Weiss, R., Huber, S.M., Rosokha, S.V. Chem. Sci. **2021**, *12*, 8246-8251.