Filling in the hole: The Influence of Adjacent Anionic Centers on Sigma Holes

DeVante Gordon and Kelling J. Donald,
Department of Chemistry, Gottwald Center for the Sciences, University of Richmond

Halogen bonding is a form of weak non-covalent interaction. It involves the alignment of a base (Y) with a region of positive electrostatic potential, sigma hole, on the surface of a halogen atom (X) that is bonded to an electron withdrawing group, R (Y---X—R). The sigma hole forms on the outside of X in the X-R bond, along the X-R bond axis. Numerous applications and potential roles of halogen bonding have been revealed. These include evidence of a role in biochemistry and materials science, yet more work remains to be done to understand fundamental aspects of the phenomenon. Recently, Ugalde et al indicated that the size of the sigma hole may be significantly affected by the sign of charges on other species close to the halogen atom. Specifically, they showed that the presence of a negative ion close to the negative belt of the halide ion (perpendicular to the X—R bond) causes a sort of flooding of the sigma hole, which tends to diminish, if not overwhelm, the sigma hole, turning off the halogen bond. In this work we have constructed and examined the possible role of intra-molecular anionic sites adjacent to the halide site with sigma holes and assess in detail its influence on the presence and strength of the sigma hole.