Anion-π and Halogen Bonding:

Unconventional Intermolecular Interactions at Work

Sergiy V. Rosokha, *Department of Chemistry, Ball State University*

Anion-π bonding can be broadly defined as an attraction of anions to electron-deficient π-systems. Halogen bonding is an attraction between electrophilic halogen atoms and electron reach centers. Both these supramolecular bondings seems counter-intuitive, and the experimental proofs and theoretical validations of their existence were established only during the last two decades. The latest works demonstrated a significant role of such interactions in biological and chemical systems, as well as their considerable potential for crystal engineering of solid-state materials, molecular recognition, anion transport, catalysis, rational drug design, etc. Most commonly, these unconventional interactions are related to the attraction of electron-rich species to the areas of the positive potentials on the surfaces of covalently-bonded halogen atoms or aromatic/olefinic molecules (referred to as σ-holes and π-holes, respectively). We have demonstrated that molecular-orbital (charge-transfer) interactions are also vital for the formation of halogen-bonded and anion-π complexes. The increase of their contribution results in the gradual transformation of the weak intermolecular interactions into fully developed covalent bonds. Besides affecting structures, thermodynamics and spectral properties of the halogen-bonded and anion-π complexes, the weakly-covalent components substantially lower barriers for the electron transfer and subsequent chemical transformation of the interacting species.