σ-Hole Interactions: An Umbrella Encompassing Group IV, Pnicogens, Chalcogens and Halogens

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A σ-hole bond is a noncovalent interaction between a covalently-bonded atom of Groups IV–VII and a negative site, e.g. a lone pair of a Lewis base, a π-region of an unsaturated system or an anion [1]. It involves a region of positive electrostatic potential, labeled a σ-hole, on the extension of one of the covalent bonds to the Group IV – VII atom. The σ-hole is due to the anisotropy of the atom's charge distribution that is the result of covalent σ bond formation. Halogen bonding [2] is a subset of σ-hole interactions, and is increasingly being recognized for numerous innovative applications in crystal engineering [3] and pharmaceutical [4] applications. The features and properties of σ-hole bonds can be fully explained in terms of electrostatics and polarization plus dispersion [1,5,6]. The strengths of the interactions generally correlate well with the magnitudes of the positive and negative electrostatic potentials of the σ-hole and the negative site. In certain instances, however, polarizabilities must be taken into account explicitly, as the polarization of the negative site reaches a level that can be viewed as a degree of dative sharing of electronic charge (coordinate covalence) [7]. This presentation will provide an overview of σ-hole interactions.

References

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