Ph. D. Open Seminar

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Title of Seminar: Experimental and computational methods towards a quantitative understanding of σ and π hole directed intermolecular interactions

Date: 14th May 2018 **Time:** 10:00 AM **Venue:** AB-II-401

Abstract

Intermolecular interactions play an important role in both chemical and biological systems due to their cooperative nature[1a]. While hydrogen bonds[1b] remains one of the most studied interaction, the focus has now shifted to other categories of intermolecular interactions. The origin of these new categories of interactions lies in the fact that during the formation of a covalent bond, the electron density of the interacting atoms gets redistributed anisotropically depending on the electronic environment. This can lead to the presence of a positive electrostatic region on the surface of the atom, opposite to the covalent bond, known as σ-hole[1c]. Similarly, when an electrostatic positive region is present perpendicular to the σ-framework above the π-region, it is known as π-hole[1d]. Interaction between this σ-hole or π-hole element with a negative site, for example, the lone pair of a Lewis base, is known as σ-hole interaction or π-hole interaction, respectively[1c,d]. Depending on the atom on which this σ-hole or π-hole is present, these interactions are termed as Tetrel bonds (Group 14), Pnicogen Bonds (Group 15), Chalcogen Bonds (Group 16) or Halogen Bonds (Group 17)[1e].

In the current work, *ab initio* studies have been performed on gas phase neutral complexes to understand the nature and characteristics of σ-hole directed pnicogen and chalcogen bonds[2a-d]. In addition to this, detailed computational (energy calculations, topological analysis) and crystallographic investigation was carried out to understand the features of C=S···S=C intermolecular bonds in the crystal structures of organic solids[3]. We have also performed high resolution X-ray charge density experiments, the electron density being fitted to the multipolar model[1f] to unravel the dual σ-hole/π-hole bonding feature of a unique Br···π interaction present in 2-(2-bromophenyl)benzo[d][1,2]selenazol-3(2H)-one[4]. High resolution X-ray diffraction experiments were also carried out to unravel the characteristics of O=C···O=C π-hole tetrel bonds[5] in Fluoranil and Chloranil. In addition to this, theoretical charge density calculations, in addition to analysis of energy frameworks were performed to account for electron mobility features observed in fluoro substituted Tetracyanoquinodimethane (F_x –TCNQ; x = 0, 2, 4) family of molecules wherein the crystal structures are stabilized via intramolecular N≡C(π-hole)···F(*lp*) tetrel bonds[6].

References

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