Evaluating the role of σ and π holes in molecular crystals in directing intermolecular interactions: An experimental charge density approach

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A noncovalent interaction between a covalently-bonded atom of Groups IV–VII and a negative site (a lone pair of a Lewis base or an anion) is a σ-hole bond[1]. σ-holes are formed due to the anisotropy of the atom's charge distribution resulting in a region of positive electrostatic potential on the extension of one of the covalent bonds while π holes describe similar positive regions perpendicular to a portion of the molecular framework. Interactions such as Halogen bonding[2], chalcogen bonding[3], pnicogen bonding[4] and carbon (tetral) bonding[5] use the anisotropy in charge distribution as a key ingredient to form contacts which are less than the sum of the van der Walls radii of the participating atoms and experimental charge density analysis based on multipole modelling (XD) is ideally suited for a quantitative exploration. The relevance of the participation of σ and π holes[6] in the context of bonding has been examined in terms of QTAIM analysis followed by comparison with periodic theory calculations based on CRYSTAL14. The application potential of the findings to further understanding of bond theory will be highlighted.

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