Supramolecular Covalence in Bifurcated Chalcogen Bonding

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Abstract

Chalcogen bond belongs to the class of supramolecular interactions that are generally classified as non-covalent. However, recent studies have demonstrated that many of these formally non-covalent interactions are stabilized by a significant covalent component. Hence the use of electrostatic potential (ESP) map and maximum value of surface potential ($V_{S,max}$) to predict the strength of these interactions is somewhat questionable. Herein we demonstrate that the electrostatic parameters are useful for estimating the long-range electrostatic component of the interaction but fail to characterize the short-range electrostatics that accompanies the significant orbital interactions and electron sharing between the interacting systems. The electrostatic potential, because of its static nature, cannot account for the polarizabilities of individual fragments and the propensity of interacting systems to the electron sharing. It is shown for our supramolecular systems of a general structure $[MX_6]^{2-}$:YX_2 (where M = Se or Pt, X = halogen, Y = chalcogen) – related to the experimentally observed arrangement featuring a bifurcated chalcogen bonding – that the characteristics of the ESPs fail to predict correct order of the binding energies in a series of compounds. Instead, polarizabilities of individual fragments attached to the chalcogen atom and supramolecular orbital interactions govern the trends in the binding energies. The substituent effects on the binding energy and supramolecular electron sharing are consistently identified by an arsenal of theoretical methods ranging from approaches based on the quantum chemical topology (QTAIM, IQA) to analytical tools based on the localized molecular orbitals (EDA-NOCV, NBO). It is demonstrated that the chalcogen bonding investigated in this work is driven by the orbital interactions with significant electron sharing, which can be classified as the *supramolecular covalence*.