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Editorial

σ- and π-Hole Interactions

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Supramolecular chemistry is a very active research field that was initiated in the last century [1–4]. It was defined as *chemistry beyond the molecule*, and the word *supermolecule* was invented by Lehn [3]. The *chemistry beyond the molecule* refers to organized entities of higher complexity resulting from the association of molecules that are held together by noncovalent interactions [5]. The organized supramolecular entities are built by the formation of various noncovalent forces, which are frequently working synergistically in the same supramolecular assembly. Therefore, precise control of the noncovalent interactions is needed to succeed in this field, as exemplified by many regulation processes in nature.

A deep understanding of noncovalent interactions is necessary to advance in many fields, especially in crystal growth and crystal engineering [6]. Theoreticians have demonstrated that the distribution of the electron density around covalently bonded atoms is not isotropic, revealing that the use of point charges to define the properties of an atom (electron-rich or electron-poor) is not valid [7]. That is, a single atom presents regions of higher and lower electron density, where the electrostatic potential can be negative and positive, respectively, in some cases. The positive area is usually defined as a σ- or π-hole, depending on its location. These holes of electron density are responsible for the formation of attractive interactions with any electron-rich site (anion, Lewis base, π-system, etc.). The halogen bond can be considered as the prototypical example of σ-hole interaction [8]. After the emergence of the halogen bond, the interest in σ- and π-hole interactions embracing elements of groups 12–16 [9–13] and 18 [14–17] of the Periodic Table has grown exponentially. Halogen and chalcogen bonding interactions have already been defined by the IUPAC [18,19]. They are well-recognized interactions that are used regularly by the scientific community in crystal engineering, supramolecular chemistry, and catalysis [20]. However, more experimental and theoretical work is probably needed to extend such a statement to the elements of groups 12–15, acting as Lewis acids.

This issue gathers nine excellent contributions. In reference [21], Alkorta et al. combined theoretical calculations and a search in the Cambridge Structural Database (CSD) to investigate the interaction of dinuclear Ag(I) pyrazolates with Lewis bases, as examples of regium bonding [22]. They studied the effect of the substituents and ligands on the aromaticity and found an interesting relationship between the intramolecular Ag–Ag distance and stability.

In reference [23], Varadwaj et al. studied theoretically the CH_3Cl molecule and its complexes with ten Lewis bases to demonstrate that CH_3Cl is a genuine halogen bond donor. They have evidenced that the electronic charge density distribution around the Cl is anisotropic. The negative belt is able to participate in halogen, chalcogen, or hydrogen bonding interactions. Moreover, they show that the positive σ-hole on the Cl atom in CH_3Cl is not induced by the electric field of the interacting species, as previously suggested in the literature. Instead, it is an inherent property of chlorine in this molecule.

In reference [24], Belmont-Sanchez et al. reported the synthesis and X-ray characterization of several out-of-sphere cadmium complexes with 2,6-diaminopurine. The crystal packing of these compounds is mostly dominated by H-bonds, which were analyzed by using DFT calculations.

Interestingly, the results were in clear contrast with those previously reported for similar complexes with adenine instead of 2,6-diaminopurine [25]. The factors contributing to such differences are discussed and rationalized on the basis of the additional exocyclic 2-amino group in 2,6-diaminopurine compared to adenine.

In reference [26], Kletsov et al. synthesized and X-ray characterized four *N*-substituted 1,3,5-triazinanes and focused on the crucial role of C–H···π and C–H···O H-bonding interactions determining their solid-state architecture. Quite remarkable is the fact that the XRD analysis demonstrated an unprecedented feature of the crystalline structure. That is, the symmetrically substituted 1,3,5-triazacyclohexanes have two chemically identical sulfonamide *N*-atoms in different sp^2 and sp^3 hybridizations.

In reference [27], Zhang et al. reported the synthesis and X-ray characterization of a cocrystal formed by hexamethylbenzene (HMB) combined with 1,3-diiodotetrafluorobenzene (1,3-DITFB) founding an unexpected sandwiched-layer structure. The formation of the alternating layer was further studied using DFT calculations showing that dispersion forces are very important in the formation of the HMB layer. In contrast, the formation of the 1,3-DITFB layer is induced by weak but cooperative C–I···F halogen bonds.

In reference [28], Yannacone et al. studied the nature of π-hole interaction in several fluorinated aromatic systems focusing on the effect of the substituents and the presence/absence of heteroatoms in the arene on the strength of the π-hole interaction. Moreover, the authors have also analyzed cooperativity effects with other interactions like hydrogen bonding.

In reference [29], Novoa-Ramírez et al. have used thirteen ligands (*N*,*N*′-bis(5-R-salicylidene)ethylenediamine (where R = MeO, Me, OH, H, Cl, Br, NO_2) and (*N*,*N*′-bis(5-R-salicylidene)-1,2-phenylenediamine (where R = MeO, Me, OH, H, Cl, Br) to synthesize and X-ray characterize thirteen nickel complexes. By using Hirshfeld surface analysis, they showed that their packaging was favored by C···H/H···C interactions, C–H···O hydrogen, and π-stacking interactions.

This Special Issue also includes two reviews, one written by Tiekink [30], who elegantly describes the results of a survey of X-ray structures of main group element compounds (M = Sn, Pb As, Sb, Bi and Te) exhibiting intermolecular M···Se noncovalent interactions. The second review written by Alkorta, Elguero, and I [31], provides a consistent description of noncovalent interactions, covering most groups of the Periodic Table. The interactions are described and discussed using their trivial names. That is, apart from hydrogen bonds, the following noncovalent interactions are described: alkali, alkaline earth, regium, spodium, triel, tetrel, pnictogen, chalcogen, halogen, and aerogen, thus covering a wide range of interactions. In this review, the possibility of extending the Cahn-Ingold-Prelog priority rules to noncovalent interactions is suggested.

In summary, this Special Issue gathers an interesting group of manuscripts devoted to the study of several types of σ- and π-hole noncovalent interactions and their importance in the solid-state of different compounds, including biologically relevant ones like diaminopurines, good halogen bond donors like 1,3-diiodotetrafluorobenzene, and several theoretical investigations devoted to π-hole interactions in arenes and regium bonds in Ag(I) derivatives. Moreover, two excellent and comprehensive reviews are published in this collection with the latest advances in noncovalent interactions that I believe make this Special Issue even more special.

To finish, I wish to thank all authors who have submitted their excellent papers to this Special Issue and also the reviewers who carefully read them, providing constructive and helpful suggestions and corrections on all manuscripts. I am especially thankful to the editorial staff at Crystals for their incredibly fast and professional work, dealing with all manuscripts and the selection of suitable referees.

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