Understanding σ- and π-hole centered interactions in crystals from electron density analysis

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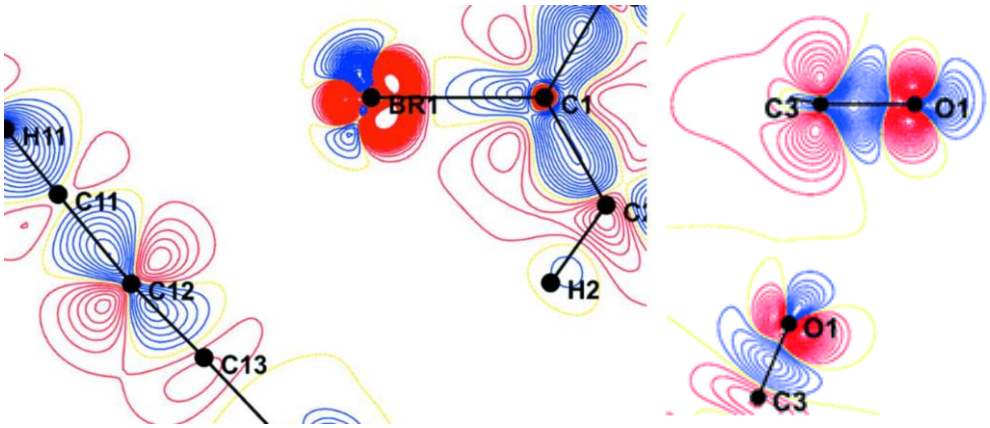
The last decade has witnessed significant growth in our understanding on intermolecular interactions [1]. Experimental and computational approaches have resulted in obtaining quantitative insights into the underlying nature of different interactions [2]. Non-covalent interactions involving halogens have attracted significant attention. Interactions involving the heavier halogen bromine are ubiquitous and hence an investigation into the electronic features of such interactions is of interest. The existence of the σ- hole in bromine-centered interactions have been quantitatively investigated via high resolution electron density analysis in crystals of an ebselen derivative (**I**). It has been observed that in addition to formation of σ-hole centered linear interaction involving bromine, the lone pairs on bromine also interact with the electron deficient region on the π-ring (**Fig. 1a**) [3]. Thus bromine is associated with both electron donor and acceptor characteristics. Furthermore, this approach has also been utilized to understand carbon-centered π-hole directed O=C...O=C interactions in crystalline fluoroanil (**II**) and chloranil [4]. The topological characteristics in terms of the MESP, and the electronic features of the interacting atoms will be discussed (**Fig. 1b**). Such studies establish the subtle yet pivotal role of weak intermolecular interactions in the crystal packing of organic molecules.



(a) (b)

Figure 1.(a) 2D experimental deformation density depicting bromine centered interaction at the ±**0.05eÅ**$^{-3}$ level in (I). (b) 2D experimental deformation density denoting C...O contact at the ±**0.05eÅ**$^{-3}$ level in (II). Red region denotes charge depletion and blue denotes charge concentration.

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