Close contacts involving carbon and antimony: Tetrel bonded and pnictogen bonded systems by design

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In this communication we will describe the packing of some homomeric and heteromeric crystals wherein the composition and architecture is affected and/or determined by attractive interactions involving carbon and antimony atoms as electrophilic sites.
Molecular modelling predicts that region(s) of depleted electron density are typically present on an atom opposite to the covalent bond(s) it is involved in. This is true for any element belonging to groups 14-18 of the periodic table [1] and the electrostatic potential at the depleted region(s) becomes positive when the atom is covalently bonded to strongly electron withdrawing residues [2]. We thus expected that the depleted regions on fluorinated carbon and antimony moieties might be positive enough to enable for the formation of attractive interactions with lone pair possessing atoms. We also expected that the resulting bonds might be strong enough to determine the crystal composition and architecture. Here we describe that various 5,5-difluorobarbituric derivatives form adducts were F–C···O=C intermolecular contacts can be as short as 90% of the sum of carbon and oxygen van der Waals radii. The C···O supramolecular synthon in these derivatives is robust enough to be observed also in 5,5-dichloro and 5,5-dibromo analogues, namely when halogens less electron withdrawing than fluorine are present (Fig. 1). As to fluorinated antimony derivatives, we report, for instance, that the tendency of antimony trifluoride to attractively interact with lone pair possessing atoms is so strong that in the tetrameric adducts formed on self-assembly with *p*-dipyridyl dioxide, two antimony atom gives two F–Sb···O close contacts with two different dioxide molecules.
The described interactions are typically named tetrel bond and pnictogen bond [3], respectively. The reported results shown how their understanding is developed enough to enable for their successful use in the design of the intermolecular interactions of crystal lattices. The described structure may also suggest that tetrel bond and pnictogen bond are robust enough to become new, useful and general tools in crystal engineering.

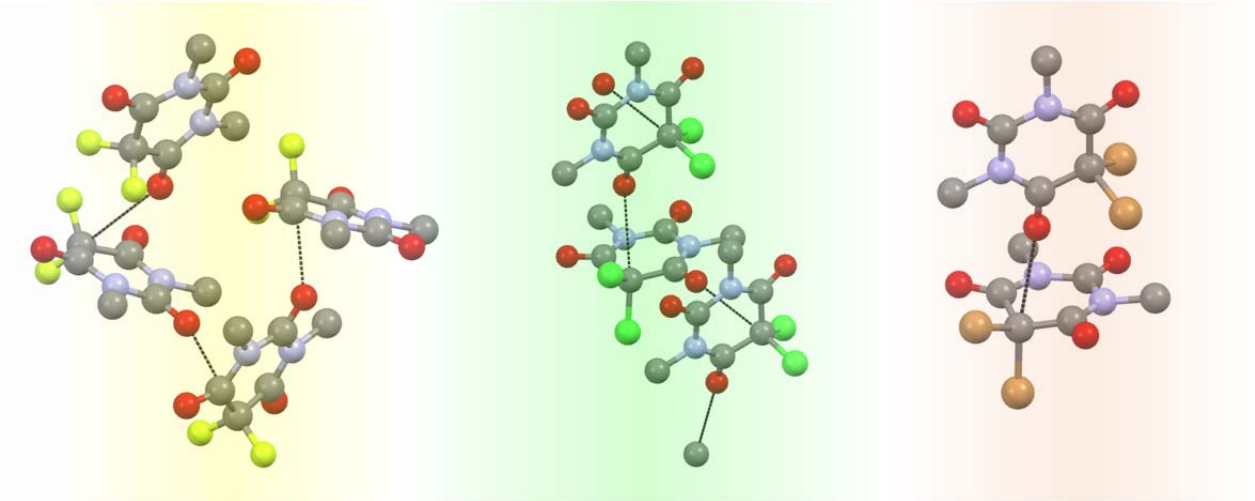

Fig. 1 Adducts present in crystals of 5,5-difluoro- (left), 5,5-dichloro- (mid), and 5,5-dibromo-N,N'-dimethylbarbituric acid (right); F–C···O=C tetrel bonds are dashed black lines.

[1] Murray, J. S. *et al.* (2017) *Faraday Discuss.* **203**, 113–130.

[2] Scilabra, P. *et al.* (2017) *J. Fluorine Chem.* **203**, 62–74.

[3] Cavallo, G. *et al.* (2014) *Cryst. Growth Des.* **14**, 2697−2702.