

MS30-P02**Cooperativity of halogen bonds – enhancing halogen bond donating ability of halogenated pyridines through halogen bonding with *N*-haloimides**Vladimir Stilinović¹, Dominik Cinčić¹¹. University of Zagreb, Faculty of science, Department of chemistry, Zagreb, Croatiaemail: vstilinovic@chem.pmf.hr

N-halogenated imides, common halogenating agents in organic synthesis, have recently been marked as extremely strong halogen donors. [1], [2], [3] In previous studies we have demonstrated that *N*-halogenated succinimides form extremely short XBs with halogen bond energies between 20 and 60 kJ mol⁻¹, depending on the pyridine basicity and the halogen atom.[2] In light of rather high bond energies, it seemed possible for such halogen bonds to have a significant effect on the electron structure of both donor and the acceptor molecules, which in turn might be expected to affect the ability of the molecules to form additional intermolecular bonds in general and halogen bonds in particular. To test this supposition, we have prepared a series of cocrystals of *N*-haloimides (*N*-iodo- and *N*-bromosuccinimide, *N*-iodo- and *N*-bromosaccharin and *N*-bromophthalimide) with halogenated pyridine derivatives, thus introducing the possibility of a secondary halogen bond with halogenated pyridines as donors and imide oxygen atoms as potential acceptors.

In all the obtained crystal structures the expected halogen bond between the *N*-haloimide halogen and pyridine nitrogen was found to be present. However, the occurrence of a secondary halogen bond (as well as its geometry when it is present) was found to depend on both the halogen atom of the pyridine, but also the halogen bond donor ability of the *N*-haloimide. While secondary I...O contacts were present in all cocrystals of iodopyridines, the equivalent Br...O contacts with bromopyridines were generally found only in cocrystals with *N*-iodoimides (stronger halogen donors), due to a larger polarization of the bromopyridine by a stronger primary halogen bond. This difference in polarisation has been verified through the molecular electrostatic potential calculations which have shown that the maximal positive potential in the σ -hole of the bromine of a 3-bromopyridine involved in a strong halogen bond (with *N*-iodosuccinimide as halogen donor) is markedly higher than that in the free 3-bromopyridine or in 3-bromopyridine involved in a weaker halogen bond (with *N*-bromosuccinimide), and approaches the value for bromine in protonated 3-bromopyridinium cation. This strongly reflects on the structures of the cocrystals with no secondary Br...O contacts in the structure of 3-bromopyridine-*N*-bromosuccinimide cocrystal, Br...O halogen bonds of ca. 3.11 Å in 3-bromopyridine-*N*-iodosuccinimide cocrystal and ca. 3.01 Å in ionic 3-bromopyridinium saccharinate which is isostructural with the *N*-iodosuccinimide cocrystal. The obtained results demonstrate that when several (inequivalent) halogen bonds are to be employed in engineering a crystal, their cooperativity (more generally, interdependency) must be taken into account.

References:

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- [1] Raatikainen, K. & Rissanen, K, (2011) CrystEngComm, 13, 6972-6977.
 [2] Stilinović, V. et al. (2017). Chem. – Eur. J., 23, 5244-5257.
 [3] Eraković, M., et al., (2018) Cryst. Growth Des., 18, 1182–1190.
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