

# Supramolecular Complexes Based on Very Strong Halogen Bonds

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In the last 15 years growing attention has been focused to halogen bonding (XB)<sup>1</sup> stimulated by its intriguing properties, such as strong directionality, specificity and strength comparable to hydrogen bonding (HB).[2] Recently, we have applied this “long lost brother” of hydrogen bonding[3] to very strong (OC)<sub>2</sub>N-I•••N halogen bonds using *N*-iodosuccinimide (NIS) as the XB donor and hexamethylenetetramine (HMTA) as the XB acceptor,[4-5] where the iodine at the N atom is strongly polarized by the two electron withdrawing carbonyl groups. Inspired by the strong N-I polarization in NIS, and in an endeavour to polarize the N-I bond even further, an analogue *N*-iodosaccharin (NISac) was used as an alternative XB donor. Using pyridine *N*-oxides as the XB acceptor led to a new  $\bar{\text{N}}\text{-X}^+\cdots\bar{\text{O}}\text{-N}^+$  paradigm for halogen bonding[6] and have yielded extremely strong halogen bonded complexes with very high association constants characterized in either CDCl<sub>3</sub> or acetone-d<sub>6</sub> solution by <sup>1</sup>H NMR titrations and in the solid-state by single crystal X-ray analysis. The obtained halogen bond interactions, R<sub>XB</sub>, in the solid-state are found to be in the order of strong hydrogen bonds, *viz.* R<sub>XB</sub> ≈ R<sub>HB</sub>. The robustness of the  $\bar{\text{N}}\text{-X}^+\cdots\bar{\text{O}}\text{-N}^+$  XB motif is evident in the X-ray structure of the XB complex of **NIS**, where besides the XB formation the co-crystallized water molecule bridges two NIS complexes generating a dimeric assembly held together with concerted XB and HB interactions as shown in figure below. The carbonyl oxygen atoms act as weak HB acceptors indicating tolerance of the XB complex even under moist conditions. Most recently we have managed to create an extremely robust molecular capsules with the help of [N•••I<sup>+</sup>•••N] halogen bonds.[7]

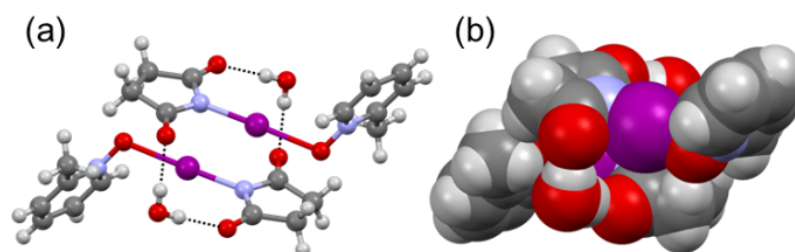


Figure 1. X-ray structure of a dimeric XB complex.

## References

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