

Exploring the Hydrogen Bond Enhanced Halogen Bond

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The hydrogen bond enhanced halogen bond (HBeXB) is a newly discovered synergistic relationship between hydrogen bonds (HBs) and halogen bonds (XBs). The HBeXB represents a unique method of tuning a XB by positioning a HB donor(s) proximal to the electron-rich belt of a XB donor. The HB further polarizes the electron density of the XB donor, making the XB stronger. This relationship was simultaneously demonstrated in our supramolecular chemistry group¹ and a biochemistry group², highlighting the far-reaching and diverse impact of the HBeXB.

Our seminal investigation also demonstrated the HBeXB as a tactic to engender molecular preorganization. The preorganization effects of our bidentate system precluded our ability to isolate and quantify XB augmentation afforded by an intramolecular HB. This has motivated us to develop a model system to isolate and measure XB enhancement by an intramolecular HB for the first time. Crystal structures, solution studies, and computations of both neutral and charge-assisted HBeXB donors will be presented.

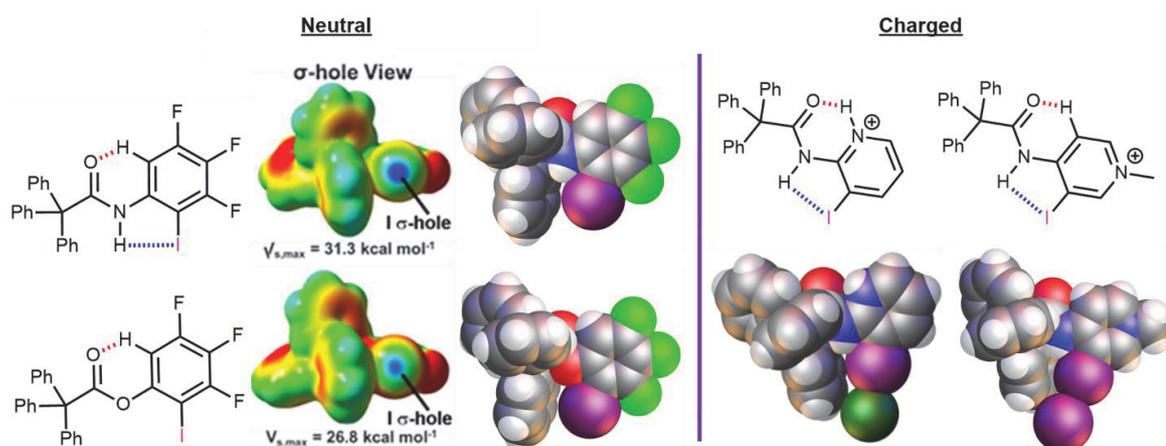


Figure 1. Crystal structures and molecular electrostatic surface potential maps (isodensity = 0.001au) of neutral compounds highlighting that intramolecular HBing enhances the σ -hole (blue circle) $V_{s,max}$ by 4.5 kcal/mol compared to isostructural control (left). Representative examples and crystal structures of charge-assisted HBeXB compounds (right)

References

¹ Riel, A. M. S.†; **Decato, D. A.†**; Sun, J.; Massena, C.J.; Jessop, M.J.; and Berryman, O.B., Chem. Sci. 2018, 9, 5828–5836.

² Carlsson, A. C.; Scholfield, M. R.; Rowe, R. K.; Ford, M. C.; Alexander, A. T.; Mehl, R. A.; and Ho, P. S.; Biochemistry. 2018, 57, 4135–414.