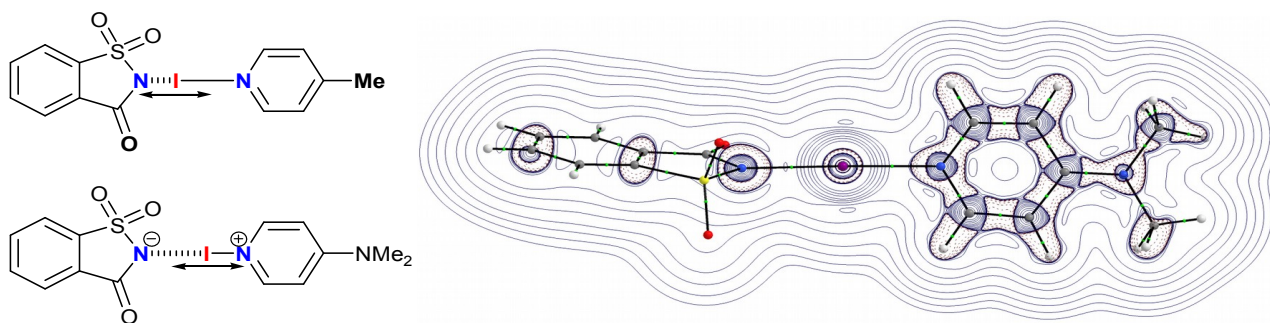


## Cocrystal or Salt: Solid State-Controlled Iodine Shift in Crystalline Halogen-Bonded Systems

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The distinction between co-crystals and salts is currently investigated in hydrogen-bonded systems as  $A-H\cdots B \rightleftharpoons [A]^{-}\cdots[H-B]^{+}$ , where the position of the hydrogen atom actually defines the ionicity of the complex [1]. The same distinction, but in halogen-bonded systems [2], is addressed here, in complexes formed out of N-iodoimide derivatives as halogen bond donors, and pyridines as halogen-bond acceptors, anticipating that the position of the iodine in  $A-I\cdots B \rightleftharpoons [A]^{-}\cdots[I-B]^{+}$  systems will also define their degree of ionicity. We show that the crystalline halogen-bonded complexes of N-iodosuccinimide (NIS) with pyridine, 4-methylpyridine and 4-dimethylaminopyridine can be described as "close-to-neutral" cocrystals while the crystalline halogen-bonded complex of N-iodosaccharin (NISac) [3] with 4-dimethylaminopyridine adopts a "close-to-ionic" structure. Theoretical calculations were performed (i) in gas phase on isolated  $NIS\cdots Py-NMe_2$  and  $NISac\cdots Py-NMe_2$  complexes, and (ii) on the periodic crystal phases, and combined with the topological analysis of the electron density distribution [4]. The strong influence of the crystalline environment on the iodine position is demonstrated by using plane wave DFT periodic calculations on optimized  $NIS\cdots Py-NMe_2$  and  $NISac\cdots Py-NMe_2$  structures, as well as by applying the plane wave basis set formalism to a hypothetical solid where the halogen-bonded complexes are pushed apart from each other within a periodic system.



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