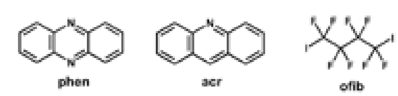
REACTIONS IN THE SOLID STATE: A SAFER, MORE ENVIRONMENTAL APPROACH TO CHEMISTRY

Making chemistry safer and more environmentally-friendly, while improving efficiency and speed, is a fascinating challenge being tackled by the Tomislav Friščić group at McGill University. A number of advantages are gained by performing chemical reactions in the solid state instead of using traditional solvents. Eliminating the use of solvents greatly reduces toxic waste streams while enabling access to novel reactions, materials, and molecules. So how does this "Chemistry 2.0" work? "Thinking about reactions between solids means you must forget most things you know about chemistry and focus on surface, particle size, rheology, and nucleation effects," says Friščić. Their latest paper published in Crystal Growth & Design (2018, 18 (4), 2387–2396) studies the bench stability of halogen-bonded cocrystals that are synthesized via mechanical milling, using a 10ml stainless steel jar that contains 7mm stainless steel balls. The milling is done for 15 minutes during which time the grinding action of the balls with a small amount of liquid (known as liquid-assisted-grinding or LAG) causes the reaction to occur. Halogen-bonded cocrystals involving the volatile halogen bond donor octafluoro-1,4-diiodobutane (ofib), with phenazine (phen) and acridine (acr) as acceptors are then synthesized. These types of materials are of interest, as halogen bonds have found use as building blocks for creating novel molecular solids and functional materials in crystal engineering.

Igor Huskić, Graduate Student from the Tomislav Friščić group at McGill University, uses X-ray Diffraction and Rietveld analysis to understand solid-state reactivity mechanisms and kinetics.



These cocrystals are the first examples of acridine or phenazine combined with an aliphatic halogen bond donor and bench stability studies help provide further insight into halogen bond-driven cocrystallization as a route to stabilize volatile compounds in the solid state.

Crystal engineering by cocrystal formation is often focused on structural analysis and the development of more efficient designs and routes for synthesis. The overall stability of cocrystals is still not well understood. "This is surprising, as understanding and manipulating cocrystal stability are central to development of pharmaceutically relevant materials with improved solubility and in the design of materials for the capture of volatile compounds," says Friščić.

Cocrystal stability and characterization of the solid-state reactivity and phase transformations of these materials can be studied using Powder X-ray Diffraction.

As pioneers in this field, the group has to sometimes create novel equipment. Graduate student Igor Huskić developed a home-made environmental cell which can be placed inside their PROTO AXRD Benchtop X-ray diffractometer. The cell can be used to modify the atmosphere around the sample. Conducting real-time studies of solid-state reactivity and phase transformations within the environmental cell, is a central point of Huskić's doctoral work.

Other not yet published work in his doctorate also shows how the environmental cell can be used for monitoring transformations of microporous metal-organic frameworks (MOFs) under different environmental conditions, as well as for development of solvent-free, clean transformations for extraction of rare elements from minerals under high humidity conditions.

Some of these novel materials can be evaluated for new ways to sequestrate CO_2, store gases or extract critical elements.