

**[s9.m2.p5] Effect of Tailor-Made Additives on Benzil Crystal Growth: Real-Time Imaging by Atomic Force Microscopy and Habit Modification Analysis.** G. Calabrese<sup>a</sup>, M. Moret,<sup>a,b</sup> a) *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy;* b) *Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, 20125 Milano, Italy.*  
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Atomic force microscopy (AFM) was used in situ to study benzil (1,2-diphenylethanedione) crystal growth in the presence of tailor-made additives. The {100} and {001} faces were observed while growing from water/ethanol supersaturated solutions. Several additive molecules having a *phenyl-carbonyl* moiety were selected as potential tailor-made additives. 4,4'-dimethoxybenzil, 4-methoxybenzil and methyl phenylglyoxylate were tested in growth experiments. As expected, 4,4'-dimethoxybenzil did not produce noticeable effects on the crystal habit owing to its «wrong» molecular architecture which prevents incorporation into the host benzil lattice. On the contrary, 4-methoxybenzil is a strong habit modifier, being able to interact with the {100} faces. Interestingly, methyl phenylglyoxylate, also comprising the correct C<sub>6</sub>H<sub>5</sub>COR moiety, did not produce any significant effects on benzil crystals. Using AFM, we analyzed the changes in surface micromorphology induced by 4-methoxybenzil molecules on advancing steps for the {100} and {001} surfaces. Evolution of micromorphology with time showed that at low supersaturations layers grow by step flow of preexisting steps by the addition of growth units at the step edges. During growth, the presence of 4-methoxybenzil molecules at concentrations 0.01-0.06 mol/mol produced on {100} significant changes in the step morphology and growth rates. The additive molecules were indeed able to pin the growing front at the terraces, causing the step edges to become jagged; upon reaching a critical additive concentration crystal growth was entirely blocked. Concurrently, on a macroscopic scale strong habit modifications were observed, producing thin {001} needles.

**[s9.m2.p6] Thermally Induced Solid to Solid Reaction of 2,4-Dinitrophenylhydrazine with Aromatic Aldehydes.** Z. Urbanczyk-Lipkowska. *Institute of Organic Chemistry, Polish Academy of Sciences, 01-224, Warsaw, Poland, e-mail: ocryst@icho.edu.pl*  
Key words: thermal reaction, non-solvent.

Efficient, thermally induced solid state reaction between powdered 2,4-dinitrophenylhydrazine and benzaldehydes substituted with electron donating groups [OMe, N(Me)<sub>2</sub>, OH] was performed, yielding hydrazones. The reaction products obtained by heating substrates in glass ampoules up to 250 °C and up to 80 °C in the open air were compared. The reaction progress was monitored by FT-IR and X-ray powder diffraction. Single crystal structures of substrates and reaction products were solved or known from the literature. Knowledge of single crystal structures allowed identification of structural changes detected in X-ray powder spectra during the course of the reaction on heating reacting mixture. According to these, disruption of the aldehyde's crystal lattice, often induced by sublimation at temperatures below their melting points, was followed by partial desolvation of 2,4-dinitrophenylhydrazine in the melt and then product formation. This correlates with low melting points of aromatic aldehydes. The same *E*-isomer was formed predominately in both reaction media. In most cases, polar hydrazone molecules crystallised in centrosymmetric space groups forming planar layers perpendicular to the shortest axis. Planes were formed due to hydrogen bonds formation involving NO<sub>2</sub>, NH and =CH residues. Due to efficient overlapping of  $\pi$ -electron rich and deficient rings the above solids are characterised by high density and melting points (>250° C). In the case of compounds bearing *o*, *m*, *p*-hydroxy groups different crystal forms are observed. Packing patterns were rationalised on the basis of partial charges, calculated dipol moments and intra- vs. intermolecular interactions of the molecules.