MS37. Molecular crystalline processes at ambient and non-ambient conditions

Chairs: Elena Boldyreva, Gareth Lloyd

MS37-P1 Thermostability of the chromomorph dimethyl3,6-dichloro-2,5-dihydroxyterephthalate

Philip Miguel Kofoed[1], Anna Hoser[2], Anders Madsen[2]

1. Nano-Science Center, University of Copenhagen
2. Department of Chemistry, University of Chopenhagen

email: vrj813@alumni.ku.dk

A century ago Hantzsch[1] observed that dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (MCHTEP) exhibited chromomorphism, upon heating yellow single crystals (Y) to 430K they entered a solid state phase transformation and change into white crystals (W). Later a third light yellow (LY) form was discovered by Yang, Richardson & Dunitz[2] a light yellow (LY). By a multi-temperature study they investigated how the structural differences between the different polymorphs could lead to colour change and phase transformation. Especially the thermal parameters were probed as a function of temperatures. With this information they formulated a model of the thermostability of the three known forms based on vibrational energies and entropies. In the publication by Yang et al. they concludingly write the following statement: *Why has our intuition led us astray in expecting that the crystals with the larger atomic ADP's should have the greater entropy? … The problem is left to the theoreticians.*

We investigate the system once more by introducing modern periodic ab-initio calculations as well as making a diffraction study of the system at approximately 10K. The ab-initio calculations in combination with the multi-temperature diffraction measurements allow us to assess the vibrational contribution to crystal stability in much more detail than previously done. This will be evaluated by calculation of cohesive energies with Crystal09[3,4] and comparison with other energy calculations programs like Pixel[5,6]. From Crystal09 we additionally derive lattice-dynamical information, and use this information to perform a normal mode refinement to obtain the vibrational energies and entropies[7], and thereby explain the phase transformations in this interesting chromomorphic system.

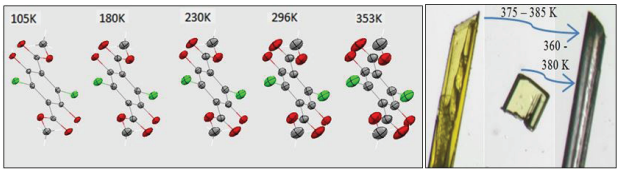

Figure 1. To the left 5 structures of Y with displayed ADPs in temperature steps 105K, 180K, 230K, 296K and 353K.The right image is of the three different coloured polymorphs from left yellow, light yellow and White and with their phase transition temperatures.

Keywords: Polymorphism, thermostability, ab-initio, chromomorphism, phase transition