Aim of the beamtime was the real-time investigation of the structural dynamics of organic molecular switching devices in the solid state. We have studied α-styrylpyrylium(TFMS), 9-anthracenecarboxylic acid and 2,5-distyrylpyrazine.

Our photo-crystallographic studies reveal that α-styrylpyrylium(TFMS) is indeed a photo-activated molecular switcher, which can be switched between monomer and dimer state by light and heat (Figure 1).

In the case of 9-anthracenecarboxylic acid (9-CA) – and contrary to the reported studies [2, 3] – a topotactical switching could not be confirmed by our photo-crystallographic studies. 9-anthracenecarboxylic acid photo-dimerises – no doubt – but the formed dimer phase is not only of metastable character but also without any pronounced crystal periodicity (no real single crystal / single crystal transformation). At temperatures below 250 K, the metastable dimer “phase” forms within 2 hours of illumination. It is detectable as the light-induced occurrence of diffuse planes in the diffraction patterns. For the photo-crystallographic experiment, the low-power laser beam has been coupled into the goniometer with a Schwarzschild objective. The optical excitation conditions have been chosen in such a way that – based on our spectroscopic studies - they were far away from photo-destruction processes – and that the predicted overall transformation times to 100 % dimer state should be on the 5-6 hours time scale.

In the case of 9-anthracenecarboxylic acid one striking characteristic is the coupled kinetics of excimer formation – which is the activated complex possibly leading to the dimer product – and the proton transfer through the carboxy chain. Temperature-dependent crystallographic studies (monomer: R1 = 6.5 %, 20000 Bragg diffractions, GooF= 1.65, resolution to d = 0.6 Å) show that 9-anthracenecarboxylic acid undergoes at least two-phase transitions – one structural ones at 190 K (Figure 3) and one optical ones at 150 K (not shown). The evaluation of the crystallographic data (Figure 3) suggest for the structural phase transition (2nd order) a rearrangement of the anthracene moieties towards each other – which leads to a shortening in the c-axis of 9-CA crystals. The
rearrangement of the anthracene moieties sterically supports the dimerisation reaction – however not to such an extend that the dimerisation reaction could proceed through the entire crystal homogeneously! We have monitored dimer-formation and within the diffraction pattern signatures of disorder have been reproducibly detected – however, a clear and pronounced singe crystal to single crystal transformation as it could be investigated in the case of α-styrylpyrylium(TFMS) [3] or benzylidene-cyclopentanone [4] has not be observed.

The optical 150 K phase transitions is not caused by a refinable structural rearrangement – due to the monotonic shortening of the unit cell axis in 9-CA upon cooling, the carboxy groups start to interact more strongly with each other, enhancing proton transfer activity and quenching of the excimer channel [5].

Currently we are making a detailed analysis of the detected diffuse planes in 9-CA which arise upon illumination beyond 190 K and which we assign to the dimer phase. In order to complete the physico-chemical characterisation of crystalline 9-CA, we need to study the kinetic effects of the proton transfer in more detail.

In sum, the experiment again proofs the power of photo-crystallography for investigating photoreactions in the solid state. In contrast to some spectroscopic methods, the crystallographic experiments reveal the possibility for studying periodic order and disorder processes. Therefore, it is the method of choice for cataloguing solid-state chemical reactions into the group of crystal-remaining reactions and periodicity-destroying reactions. This of course has a huge impact on the product quantum yields of a photoreaction – and more important on its stereo-selective purity. Our extended DORIS studies in this field have left to an extended knowledge of substances and compounds in this field.