ESRF	**Experiment title:** **Picosecond time-resolved Laue diffraction on organic and inorganic pigments and chromophors**	**Experiment number**: CH1911
Beamline: ID09B	**Date of experiment**: from: **23 July 2005** to: **27 July 2005**	**Date of report**: 15/08/2006
Shifts: 12	**Local contact(s)**: Dr. Q. Kong	*Received at ESRF:*

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Report:

Recently we have started a series of studying and characterising photo-induced chemical reactions in organic single crystals [1-5], namely [2+2] photodimerisation processes based on the topochemical principle. Here it is of particular interest to understand how during the photodimerisation order and periodicity of the crystal lattice changes, respectively remains. From a methodological point of view it is of interest to investigate which kind of experimental approach is of most use for monitoring such processes and determining the structure of eventually populated intermediates.

In the present experiment No **CH-1911** we specifically studied mono- and polychromatic data evaluation strategies for determining possible intermediates during the photodimerisation of 2-benzyl-5-benzylidene-cyclopentanone (BBCP). BBCP is known to photo-transform homogeneously.

In Figure1a the high-resolution (0.2 A) monochromatic structure refinement results for the monomer (R = 1.4 %) and dimer structure (R = 2.3 %) are shown which were on the border of been usable for electron density studies. These experiments were based on 36000 collected Bragg diffraction peaks at D3 of Hasylab/DESY, Hamburg. At ID09, in monochromatic mode, the same quality crystals were used in order to collect about 5000 Bragg diffraction peaks, which resulted in the ORTEP structure plots presented in Figure1b, with R values of about R = 5-7 %. The monochromatic time-resolved data were used to refine the structure of the intermediate, found in the "time-scan" of figure 2. Its structure, which is of high pi-character, is visualised in figure 3, the reaction pathway of the [2+2] photodimerisation of BBCP, which is a result of this reported study. The experimental results are supported by quantumchemical simulation of the dimerisation prcoess in the crystal lattice (B3LYP / 6-31G-d** basis set). Please note, that D3 is equipped with a 4-circle diffractometer, ID09 not, which explains the differences in the number of collected diffraction peaks.

Probably the population of this intermediate with extended pi-character has such a stabilising influence on the crystal lattice, that the reaction can proceed homogeneously and not heterogeneously. Unfortunatelly the resolution of the collected Laue data (R=15 %) were not of such a good quality that they allowed to work on the structural refinement of intermediates (probably also since we had to "speed up" the data acquisition time

due to running out of beamtime….). Therefore we think how we can improve these at least promissing results in future.

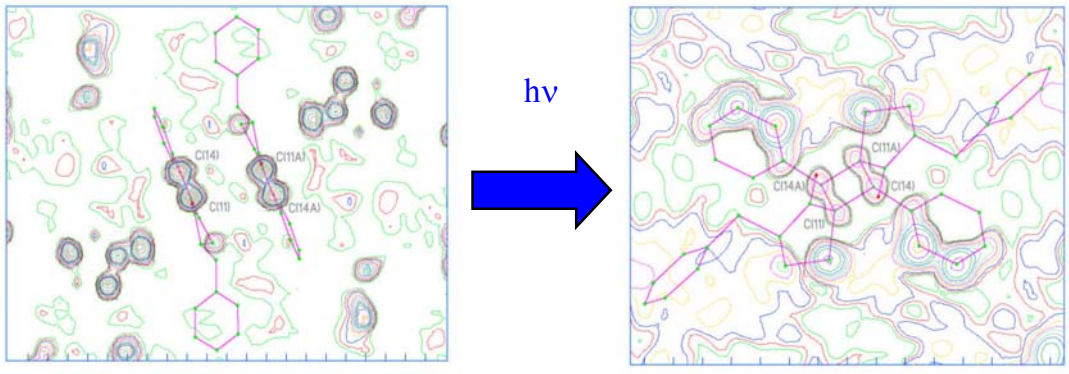

Figure 1a: Left: High resolution (0.2 A) electron density study of the BBCP monomer structure (R= 1.4 %). Right: High resolution (0.2 A) electron density study of the BBCP dimer structure (R= 2.3 %).

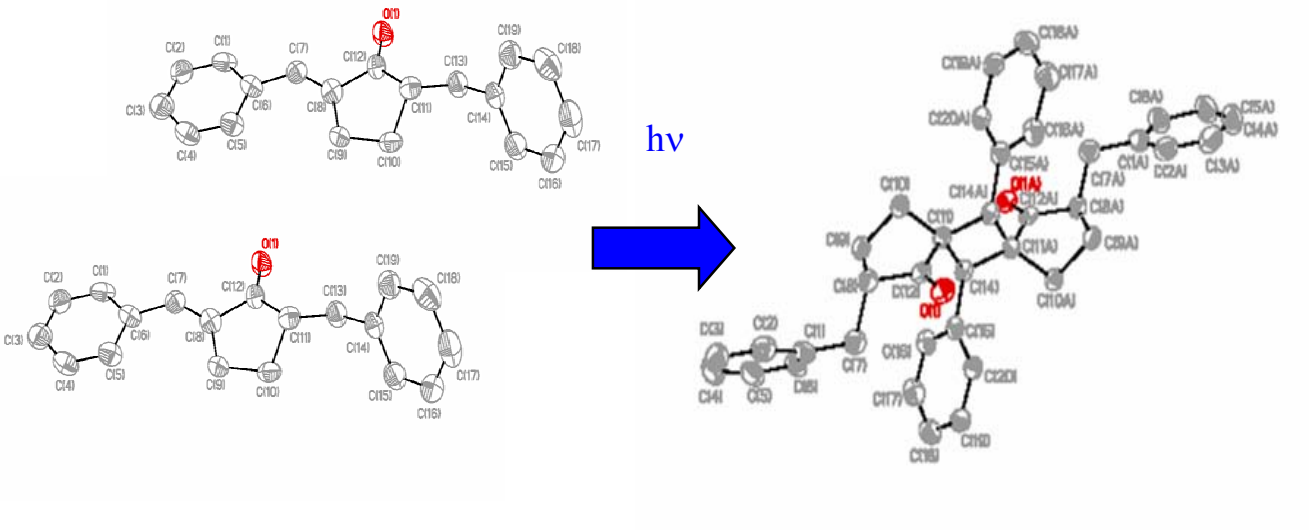

Figure 1b: Left: Ortep plot resulting from TR-XRD studies on BBCP at ID09 B (R = 6-8 %). Left: monomer, right: dimer structure.

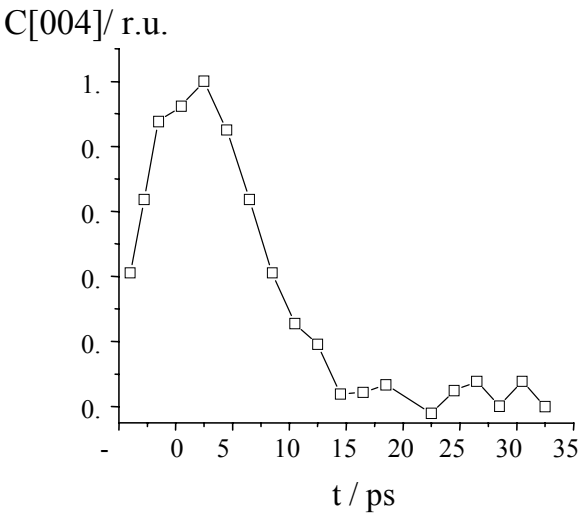

Figure 2: Intensity correlation function C(t) of the [004] Bragg diffraction peak as a function of time.

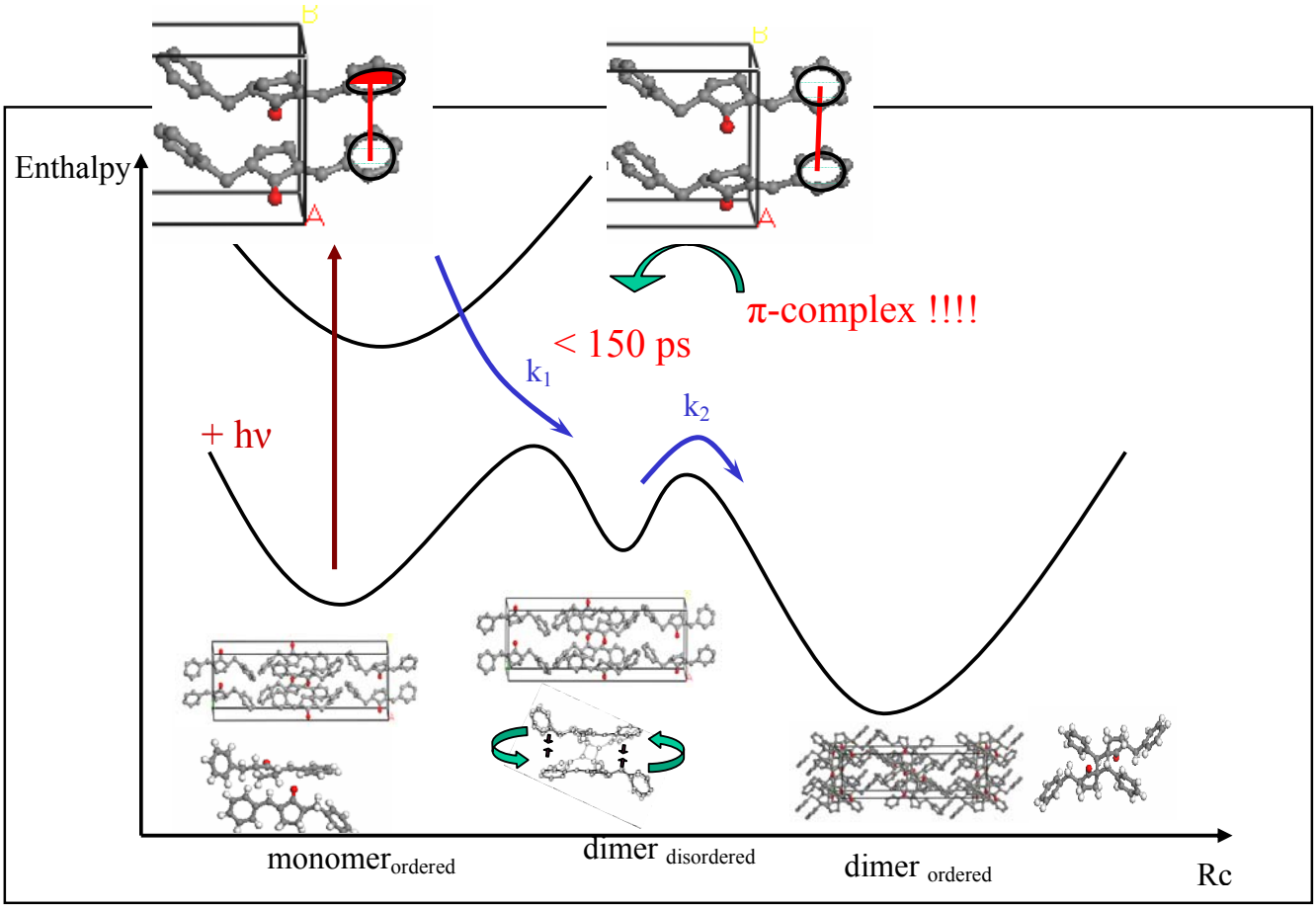

Figure 3: Structural reaction pathway of the [2+2] photodimerisation of BBCP based on the evaluation of the 100 ps resolved TR-XRD experiments. For the first time it could be shown, that this type of reactions has to go via a the lattice stabilising pi-complex and its structure could be solved [6].

References

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