



	Experiment title: Photocrystallography – Probing the excited state in crystals	Experiment number: 01-02-602
Beamline: BM1A	Date of experiment: from: 12.03.2003 to: 14.03.2003	Date of report: 3 June 2003
Shifts: 6	Local contact(s): P Pattison	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): G Chapuis , F Arod and M Chergui, Section de Physique, Université de Lausanne, CH-1015 Lausanne, Switzerland P Pattison, SNBL/ESRF, BP 220, F-38043 Grenoble, France		

Report:

This is the first interim report on long-term proposal 01-02-602. We have begun the selection of suitable photosensitive systems, using both single crystal and powder techniques to characterize the crystallographic properties of the chosen compounds. We are concentrating on two types of photoinduced chemical reactions, *proton transfer* and *dimerization*.

Photoinduced proton transfer

When transparent crystals of 2-(2',4'-dinitrobenzyl)pyridine, $C_{12}H_9N_3O_4$ (DNBP), are irradiated with optical photons, a colour change to deep blue occurs. The lifetime of this excited form is several hours in the crystal, but can be seconds or less in various solvents. This photochromic reaction is known from spectroscopic studies to be the result of photoinduced proton transfer. We have measured optical absorption spectra of single crystals of DNBP, and the results are consistent with recent studies of DNBP grown on polymer substrates and earlier bulk measurements. Single crystal diffraction measurements were carried out on BM1A. The data were collected at cryogenic temperatures in order to obtain the best possible data quality ($R_{int} = 0.027$ for 2060 unique reflections measured to a resolution of $d = 0.80\text{\AA}$), and because it is known that

low temperatures leads to an increase in the population of excited state molecules in the crystal. Preliminary analysis revealed no dramatic differences between the diffraction data collected before and after irradiation using a Hg lamp with a 365nm filter. A more detailed analysis of the data is now in progress. It is known in experiments of this type that incident light can be strongly self-absorbed by a thin transformed layer at the surface, thus preventing transformation of the bulk of the crystal. We therefore intend to repeat these experiments in our next period of beamtime on this long-term proposal using different filters in order to reduce self-absorption effects. Because we have been able to obtain high-quality diffraction data, and since the crystal could survive after intense optical irradiation without losing its diffraction quality, we are confident that DNBP will provide a suitable target system to develop synchrotron diffraction techniques for investigating structural and electron density changes resulting from photoinduced proton transfer reactions in crystals.

Photoinduced dimerization

One of the first solid-state photochemical reactions ever investigated was the dimerization of cinnamic acid (a derivative of phenylalanine). The vast majority of dimerization reactions of this type are non-topotactical i.e. the change in molecular geometry is so drastic that the crystals disintegrate. In exceptional cases, it has been claimed that large molecular movements are possible, without destroying the long-range crystal order. We have chosen to investigate the phenomenon of photoinduced dimerization using crystallographic methods, because the paradigm of single-crystal to single crystal topotactic reactions is still in dispute. Even in the classic case of α -cinnamic acid, there is disagreement about the published structure of the dimer). The reactions are irreversible, which allows us to achieve a significant transformed population. Furthermore, it is possible to study the influence of molecular environment and crystal packing in a controlled fashion by following the dimerization in cinnamic acid (CA) itself and in some of its many derivatives, such as ethoxy-CA, methoxy-CA, and chloro-CA. The very different rates of photoreaction in the various derivatives imply that the details of the intermolecular molecular interactions play an important role in determining the photochemical reactivity.

We began our investigation by using high-resolution powder diffraction at SNBL (see report for proposal CH-1325). In each case, the sample was contained in a 1mm capillary and irradiated with the Hg lamp using a 365nm filter. We have collected powder diffraction data on samples of α -cinnamic acid (α -CA), α -ethoxy-CA, α -methoxy-CA, β -chloro-CA before and after optical irradiation. The technique of powder diffraction is an excellent way of allowing us to characterize the solid-state photoreactivity of cinnamic acid and some of its derivatives as a prelude to single crystal measurements. In a follow-up experiment on proposal 01-02-602, we have collected single crystal synchrotron data at BM1A on α -CA and α -ethoxy-CA before and after optical irradiation. Interpretation of the data collected on α -CA was complicated by the unexpected discovery of a new polymorphic form with 3 molecules in the asymmetric unit. A short structural report on this new crystal form of cinnamic acid is in preparation. In the case of α -ethoxy-CA, the photo-transformation occurred with unexpected force and speed, resulting in the destruction of several crystals.