



	Experiment title: Exploring X-ray linear dichroism in p-bromobenzamide	Experiment number: MI-593
Beam line: BM1A	Date of experiment: from: 20.11.2002 to: 24.11.2002	Date of report: 5 Feb 2003
Shifts: 12	Local contact(s): S Capelli	<i>Received at ESRF:</i>
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Report:

The intensity of X-ray fluorescence produced by single crystals when illuminated by linearly polarized synchrotron radiation can reveal a striking anisotropy when the incident photon energy is close to an absorption edge. This angular dependence is a consequence of X-ray linear dichroism, which implies that the absorption cross-section depends upon the polarization of the incident X-ray beam. Since the radiation on a ESRF bending magnet beamline shows a high degree of linear polarization in the orbital plane, it provides an ideal source for investigating X-ray dichroism. The aim of this experiment was to select a suitable compound containing an atom with an absorption edge in the X-ray region around 10 – 20 keV, and to measure the anisotropy of the fluorescence signal as a function of orientation of the crystal axes relative to the incident beam. Since strong linear dichroism has already been observed at the bromine K-edge in several compounds, we selected p-bromobenzamide ($\text{BrC}_6\text{H}_4\text{CONH}_2$) as a candidate material. This compound is known to crystallize in two polymorphic forms (P-1 and P_{21/a}). In the triclinic form, all Br-C bonds are parallel, and we can therefore expect the anisotropy of the fluorescence signal to be large. Since this compound is available commercially and easy to crystallize, it could also be a good material for the manufacture of a highly efficient dichromic analyzer or polarization filter (as suggest by Collins et al J Phys C14,2002, 123-134 using a dibromoalkane/urea inclusion compound). Therefore we decided to proceed with the selection and structural characterization of a suitable single crystal of p-bromobenzamide, followed by the

collection of spectra of the K-shell fluorescence signal as a function of incident photon energy and crystal orientation.

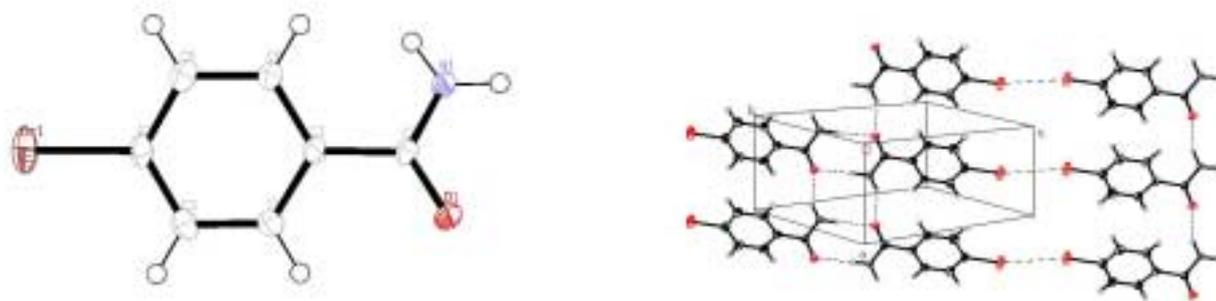


Fig 1 Molecular structure and crystal packing of *p*-bromobenzamide (triclinic form)

A room temperature diffraction data set on a single crystal of *p*-bromobenzamide was collected using the MAR345 image plate detector on BM1A. The data was processed and the structure solved and refined using Shelx. The refined cell parameters and atomic coordinates are in good agreement with the literature values (Ref BBEZAM in the Cambridge Structural Database) for the triclinic form. The crystal was then transferred to the KM6 multi-axis diffractometer on BM1A and the orientation matrix determined. A scintillation counter (Bede Enhanced Dynamic Range) was mounted in the orbital plane of the synchrotron and at 90° to the incident beam, in order to observe the fluorescence intensity with the minimum of background from scattered radiation. The crystal could then be aligned with the Br-C bond axis at various orientations relative to the polarization vector of the incident beam. A series of spectra were then collected over an energy range of 200eV around the Br K-edge (13.474 keV). Spectral data were collected for a total of about 50 different crystal orientations, allowing us to map out the 3-dimensional distribution of the fluorescence signal. As expected, the K-shell fluorescence of *p*-bromobenzamide displayed a dramatic anisotropy, with a very pronounced white line and strong angular dependence in the near-edge XANES structure. Examples of the spectra are shown in Fig 2a, together with the energy dependence of the anomalous scattering factor in Fig 2b derived from the fluorescence data by Kramers-Kronig inversion.

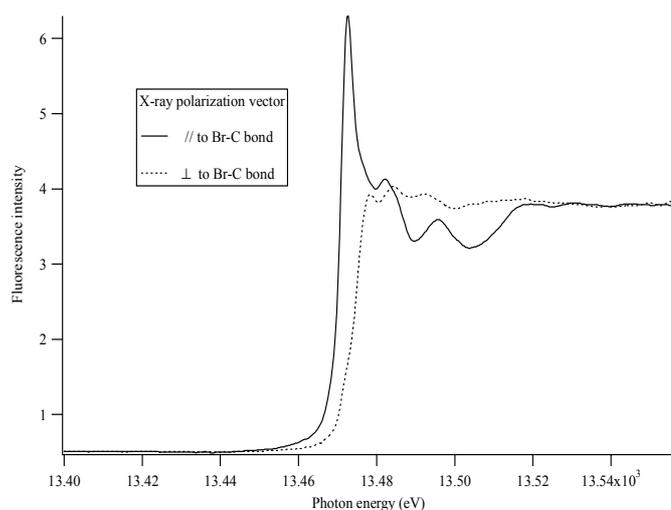


Fig 2a
Examples of fluorescence intensity measured as a function of incident beam energy for two different crystal orientations.

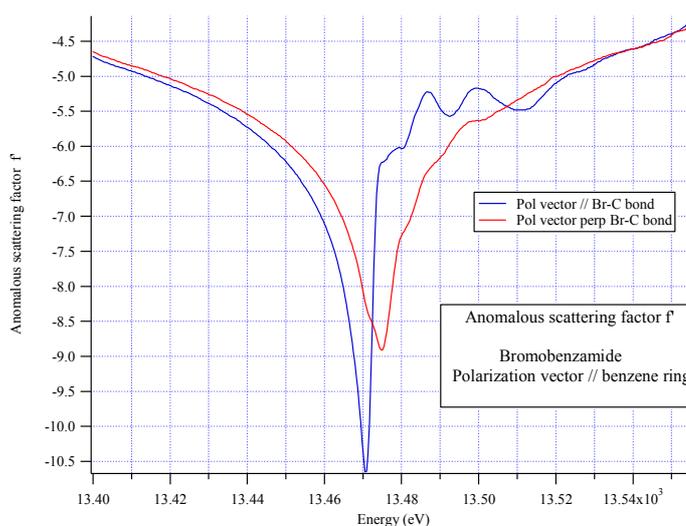


Fig 2b
Anomalous scattering factor f' derived from the fluorescence intensities by Kramers-Kronig inversion

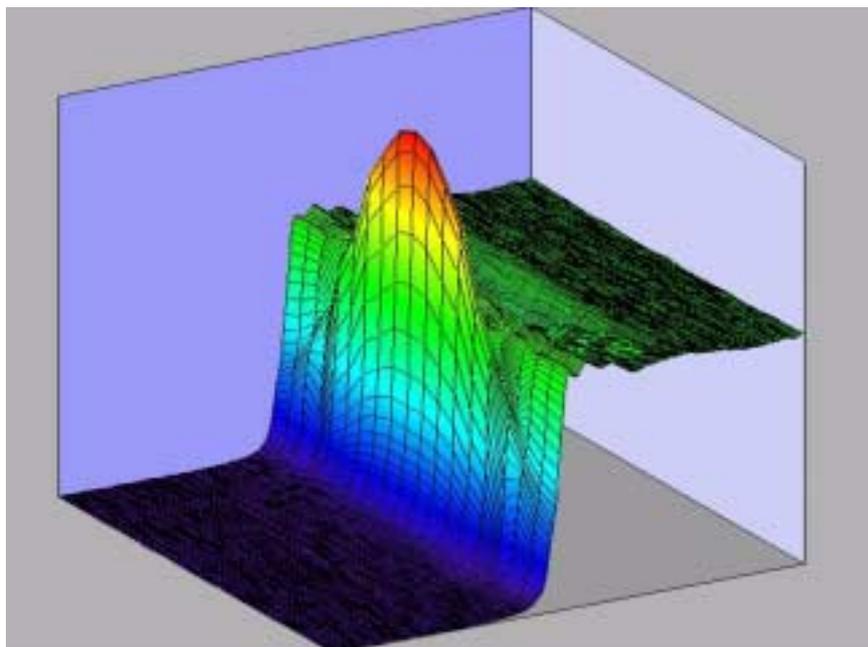


Fig 3
The angular dependence of the anomalous scattering factor f'' for p-bromobenzamide derived from the observed K-shell fluorescence intensity.

In Fig 3 we show the angular distribution of the fluorescence signal from p-bromobenzamide as a function of energy and crystal orientation relative to the incident beam polarization vector. The spectra range is 140 eV, centred at the absorption edge 13.474 keV. In the case of the spectra shown in Fig 3, the crystal has been aligned with the polarization vector always in the plane of the aromatic ring. The strong white line corresponds to the polarization vector parallel to the Br-C bond axis. The angular variation of the intensity of the white line (more properly called a *shape resonance*) follows the well-known $\cos^2\gamma$ dependence, where γ is the angle between the photon \mathbf{E} vector and the symmetry axis \mathbf{M} of the Br-C bond.

In conclusion, we have characterized the molecular and crystal structure of a molecule which displays pronounced X-ray linear dichroism. The angular dependence of the dichroism has been measured over a fine mesh of crystal orientations relative to the incident polarization vector. It is apparent from these results that p-bromobenzamide would make an ideal material for the construction of an X-ray polarizer, although the available beamtime was not sufficient to allow us to measure the *principal transmittance ratio* for this device. The calculation of the tensor properties of the anomalous scattering factor f'' for this molecular and crystal structure is in progress. The experimental results presented above confirm that this compound will provide an excellent model system for evaluating the quality of such calculations.

