

**TOWARDS AN UNDERSTANDING OF RADIATION DAMAGE -  
REPORT FROM THE SECOND INTERNATIONAL WORKSHOP**

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Optimising the potential of wiggler and undulator radiation for macromolecular crystallography at third generation synchrotrons requires that the problem of radiation damage to cryocooled crystals be addressed. In the past there has been little systematic or statistically significant research in this area. The experiments are difficult to design and interpret due to the number of variables involved, and they require beamtime on the most intense PX beamlines available: the very beamlines which are much in demand for solving structures. In June 1999, a Workshop was held at the ESRF in Grenoble to collect together and discuss what was known about radiation damage to macromolecular crystals, and a plan was formulated on how that knowledge could move forward. A second workshop was held at the APS in Chicago in December 2001. The specific topics discussed at the Workshop included: Mechanisms of radiation damage. Experience of data collection at very high intensities. Radiation damage at specific sites in a protein. Effect of radiation damage on structure determination by MAD and SAD. Modelling studies of putative heating effects at high intensities. Experience of use of helium for cryo-cooling. Assessment of the onset of increasing degrees of radiation damage as a function of dose and dose rate. A summary of the salient points of discussion and possible future directions will be presented.

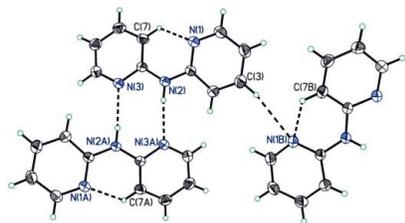
**Keywords:** PROTEIN SYNCHROTRON RADIATION DAMAGE

**EXPERIMENTAL AND THEORETICAL CHARGE DENSITY  
DISTRIBUTION OF DIPYRIDYLAMINE (HDPa)**

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Electron density distribution of dipyridylamine (Hdpa) is studied by single X-ray diffraction method at 120K. A dimeric molecular structure *via* two intermolecular N-H...N hydrogen bonds is determined with a *syn-anti* conformation of Hdpa molecule *via* an intra-molecular N...H-C hydrogen bond. Bond characterization is made in terms of deformation density, topological analysis of total electron density based on multipole model and molecular orbital (DFT) calculation. The agreement between experiment and theory is good. The bond characterization is made through topological properties associated with bond critical point (BCP). The experimental result is in a good agreement with the theoretical one. The topological properties of bond critical points at C-C, C-N, N-H and C-H bonds are reasonable and reveal a covalent bond character with the high  $\rho_b$ , negative  $\nabla^2\rho_b$  and negative total energy density  $H_b$  values. A low  $\rho_b$  and positive  $\nabla^2\rho_b$  of bond critical points at N...H bonds reveal a closed-shell interaction for N...H-C and N-H...N hydrogen bonds. The  $\pi$ -bond feature of the pyridine ring is also performed by bond ellipticity ( $\epsilon$ ) and fermi-hole distribution.



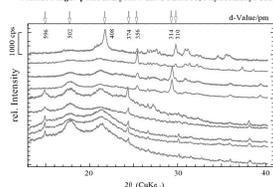
**PRINCIPLES OF BIOMINERALISATION: SILICA IN THE  
MESOSCOPIC STRUCTURE OF THE BIOCOMPOSITS POACEA  
PLANT, BAMBOO PHYLLOSTACHUS EDULIS**

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Plants of the Poacea-Group show a considerable concentration of silicon and other alkali-/alkaline earth elements as detected by EDX-Element mapping. Thermo-analyses data of the bamboo species *phyllostachys edulis* show a constant plateau of mass of 1-12% upon linear heating to 400°C in air. The concentration of silica varies due to the position of the plant in the field and seasons, i.e. nutriment and threshold properties. With the d-spacing of 596, 502, 414 and 374 pm from the WAXS-Experiment there is information available on the structure of the native bamboo material, but the interpretation is poor so far because we miss valuable models concerning the mesoscopic structure so far. SEM shows that the silica preserves the cell morphology in the biocomposit after heating to 400°C. The WAXS-fingerprint of the native bamboo sample changes significantly at temperatures beyond 400°C. At 900°C the main peak of the silica phase Tridymite ( $d = 408$  pm) shows up due to recrystallization of silica, which is mainly amorphous at low temperatures 20-400°C. The MAS-NMR data on the native bamboo samples verify mainly threefold and fourfold coordination of the <sup>29</sup>Si-Atoms in the silica matrix. We will discuss our 'Schindel-model' of the given structural data with respect to the distinct mechanical properties of the bamboo biocomposit material which amounts to values of 13.000-16.000 Pa mm<sup>2</sup> in the tensile and bending strength. The aim of research is to produce a new generation of materials from biomass and silica employing a silica protein template in the biomimetic syntheses.

WAXS: Finger-print analysis: Native bamboo, Phyllostachys edulis



**Keywords:** BIOMINERALISATION SILICA BAMBOO

**STRUCTURAL CHANGE DURING PHASE TRANSITION OF THE  
PENTACOORDINATE HYPERVALENT BORON COMPOUND  
(10-B-5)**

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The structure analysis of the pentacoordinated boron compound bearing 1,8-dimethoxyanthracene and dithiocatecholato ligands at 300 K revealed that dithiocatecholato ligand was located on the crystallographic mirror plane of the space group of *Pnma* and perpendicular to the anthracene moiety. The B-O distance is 2.433 Å. At 120 K, the space group changed to *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* and the molecules deviated from the mirror symmetry by 5 degrees. The distances of the B-O bonds are 2.422 and 2.459 Å. Temperature-dependent structure analyses were performed every 2 K from 220 to 200 K and every 10 or 5 K from 300 to 220 K and 200 to 120 K. The variation of intensities of extinctions resulting from glide planes showed that the transition occurred at 203 K. Discontinuity of the cell constants was not observed during the phase transition, but the small inflection point was shown at 210 K. Large thermal displacements observed at the end parts of the molecules at high-temperature range showed slight disordered state with mirror symmetry. Following the thermal expansion along the c axis, the catecholato moieties begin to librate even from 120 K and become disordered at 203 K.

Intermolecular energies were calculated using simple force field potentials for the neighboring molecular pairs at each temperature. The energy barrier between ordered and disordered structures at the transition point was estimated about 1 kJ/mol. This value indicates that the energy of the inversion of the molecular moiety is very small.

**Keywords:** PHASE TRANSITION TEMPERATURE RESOLVED ANALYSIS HYPERVALENT BORON COMPOUND