

B3 - Non-Ambient Conditions

B3 - O1

THE CRYSTAL STRUCTURE OF AROMATIC MOLECULES UNDER HIGH PRESSURE

M. Oehzelt¹, G. Heimel¹, A. Aichholzer¹, P. Puschnig², K. Hummer², C. Ambrosch-Draxl²,
M. Hanfland³, F. Porsch⁴, A. Nakayama⁵, R. Resel¹

¹Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

²Department for Physics - Theoretical Physics, University of Graz, Universitätsplatz 5, A-8010 Graz, Austria

³European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France

⁴Institute of Mineralogy and Petrology, University of Bonn, Poppelsdorfer Schloß, D-53115 Bonn, Germany

⁵Reserach Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

In the last three decades, π -conjugated hydrocarbon materials have attracted a lot of attention. In particular, organic polymers seem to be promising candidates for low-cost, easy-processing materials for electro-optical and electronic applications. Significant insight into many properties of these materials can often be gained by studying a single, isolated molecule (e.g. in solution). Nevertheless, for transport phenomena determining the performance of (opto)electronic devices, intermolecular interaction in terms of wavefunction overlap and low frequency (external) phonons will play a crucial role. Moreover, important optical features such as the luminescence quantum yield in the solid state can drastically differ from that of single molecules. Last but not least, the strong anisotropy of the conductivity and the dielectric function often found in crystals of short polycyclic organic molecules is closely related to the specific way of molecular packing. Hence, a detailed understanding of the crystal structure and the arrangement of the molecules relative to each other is a prerequisite for understanding important bulk and thin film properties in this classes of materials.

A deeper insight into the nature of the intermolecular interactions and the packing forces acting between the molecules can be gained by modulating the intermolecular distances. Applying pressure to the sample is a 'clean' way to tune the degree of intermolecular interaction. There are essentially two different kinds of atom-atom interaction in molecular crystals. On one hand there are strong, covalent intramolecular bonds and, on the other hand, there are weak, van der Waals-type forces acting between separate molecules. This fact justifies to regard the molecules as rigid. Applying pressure brings the whole molecular units closer together and/or changes their arrangement relative to each other.

This work is a summary of measurements performed over several years. The samples for all measurements were crystalline powders. The considered materials are the oligo-acenes (anthracene - $C_{14}H_{10}$, tetracene - $C_{18}H_{12}$, pentacene - $C_{22}H_{14}$), the oligo-phenylenes (from biphenyl - $C_{12}H_{10}$ to hexaphenyl - $C_{36}H_{26}$), fluorene - $C_{13}H_{10}$, and perylene - $C_{20}H_{12}$. Anthracene was measured at the photon factory BL18C (Tsukuba, Japan)[1,2], the whole series of

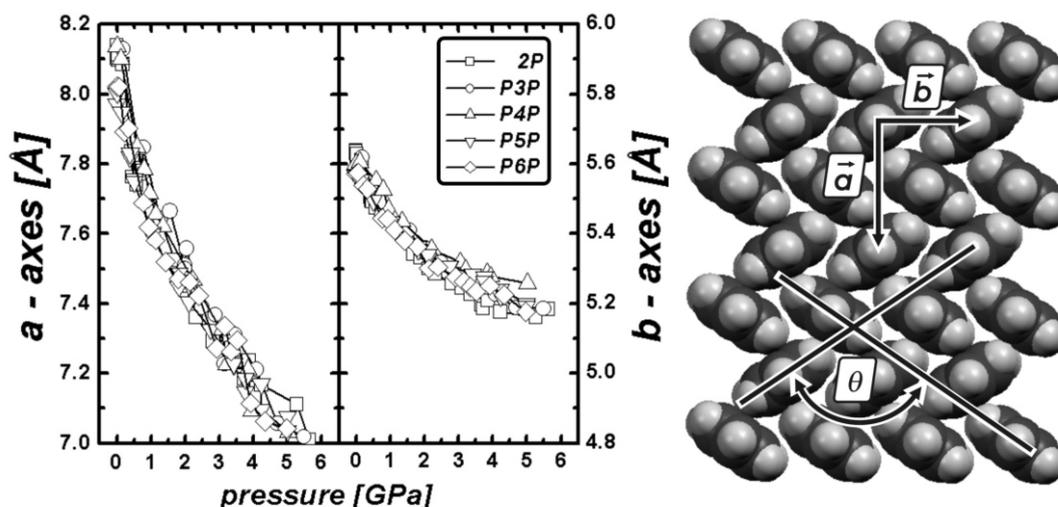


Figure 1: Lattice parameter a (left panel) and b (right panel) of the oligo(*para*)-phenylenes containing two to six phenyl rings as a function of hydrostatic pressure. The lattice parameters of all oligomers have the same length at ambient conditions and show the same pressure dependence. The left and right y axis cover the same range (1.2 Å). Note that the lattice constant a is reduced approximately twice as much as the lattice constant b in this pressure region. The pictogram on the right side shows a projection of the crystal structure of the oligo(*para*)-phenylenes visualizing the two lattice parameters a , b and the herring bone angle θ .

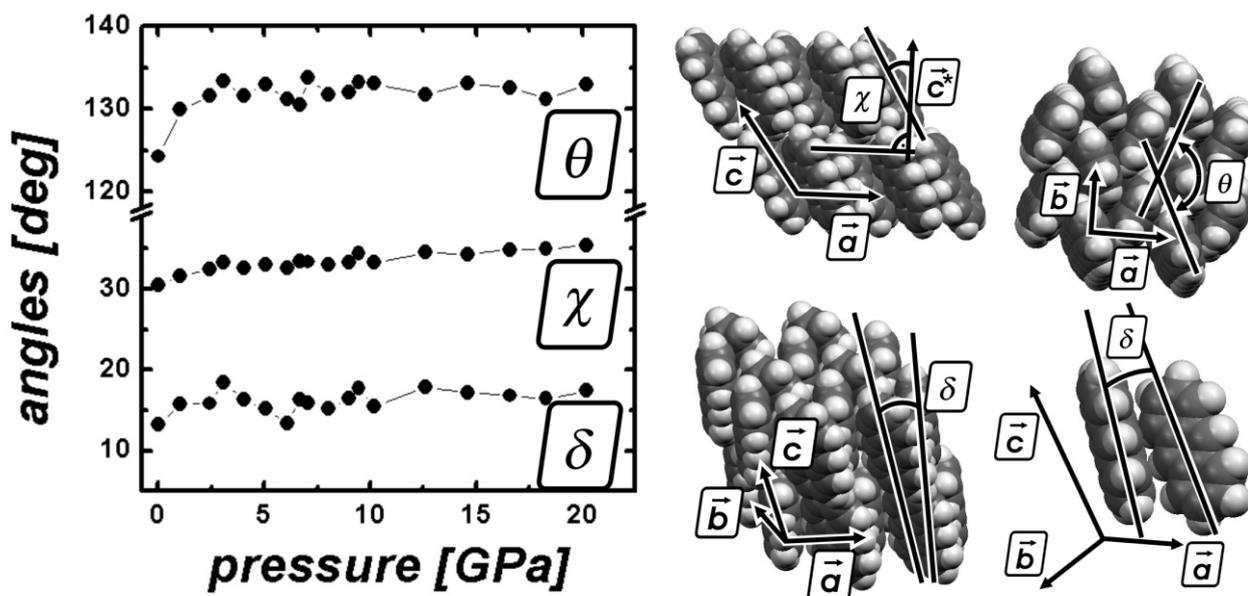


Figure 2: Rearrangement of the anthracene molecules under pressure visualized by the angles θ and χ . θ is the herringbone angle and defined as the angle between the molecular planes of the two translationally inequivalent molecules. The setting angle between the long molecular axis and the c^* axis is denoted by χ , whereas the tilt angle between the two long molecular axes of translational inequivalent molecules is given by δ .

oligo-acenes and oligo-phenylenes at HasyLab BL F3 (Hamburg, Germany)[3,4], fluorene and perylene at ESRF ID 9 (Grenoble, France) [work in progress]. All experiments, except at the HasyLab BL F3 which is an energy dispersive x-ray diffraction (EDXD) beam line, are done on angle dispersive x-ray diffraction (ADXDX) beam lines. The advantage of ADXD over EDXD is the amount of information that can be drawn from the diffraction data. In case of ADXD, the diffraction data could be refined with the Rietveld method and in addition to the change of the lattice constants, the rearrangement of the molecules (considered as rigid bodies) within the unit cell could be determined. Pressures up to 22 GPa were applied using diamond anvil cells (DAC).

In case of these soft organic materials it is of major importance to guarantee appropriate hydrostatic conditions. For example anthracene undergoes a phase transition if it is not isotropically compressed [5], but it does not show a crystallographic phase transition up to at least 22 GPa under hydrostatic conditions. In the case of fluorene we observe a phase transition at 3.5 GPa under hydrostatic conditions [paper in preparation]. The structure remains in the orthorhombic space group but the angle of the herringbone pattern (see figures 1, 2) decreases significantly and an almost π -stacked regime is formed. The herringbone angle changes from around 120° to around 60° during the transition, while any compression in a non-hydrostatic environment results in a phase transition at even lower pressures.

Figure 1 shows the summary of changes in the ab -plane of the oligo-phenylenes obtained by EDXD measurements. Note that the lattice constant a changes twice as much as the lattice constant b . This behaviour results in an effective

rotation of the molecules to higher herringbone angles which is similar for all oligo-phenylenes. The same behaviour of a changing twice as much as b is shown in the oligoacenes. ADXD measurements of anthracene reveal more details in the changing of the molecular packing. The rearrangement of the molecules under pressure has a high impact on the band structure as well as on the optical properties [4,6]. For example a redshift and a broadening of the optical transition under pressure is observed, which has a purely intermolecular origin.

Acknowledgement

This research project is supported by the Austrian Science Fund (Project No. P15626-PHY). M.O. also likes to acknowledge the Austrian Research Society (ÖFG).

- [1] M. Oehzelt, R. Resel, A. Nakayama, *Phys. Rev. B* 66 (2002) 174104.
- [2] M. Oehzelt, G. Heimel, R. Resel, P. Puschnig, K. Hummer, C. Ambrosch-Draxl, K. Takemura, A. Nakayama, *J. Chem. Phys.* 119 (2003) 1078.
- [3] G. Heimel, P. Puschnig, M. Oehzelt, K. Hummer, B. Koppelhuber-Bitschnau, F. Porsch, C. Ambrosch-Draxl, R. Resel, *J. Phys.: Condens. Matter* 15 (2003) 3375.
- [4] P. Puschnig, K. Hummer, C. Ambrosch-Draxl, G. Heimel, M. Oehzelt, R. Resel, *Phys. Rev. B* 67 (2003) 235321.
- [5] R. Resel, M. Oehzelt, K. Shimizu, A. Nakayama, K. Takemura, *Solid State Comm.* 129 (2004) 103.
- [6] K. Hummer, P. Puschnig, C. Ambrosch-Draxl, *Phys. Rev. B* 67 (2003) 184105; *Phys. Rev. Lett.* 92 (2004) 147402.

HIGH TEMPERATURE BORATE CRYSTAL CHEMISTRY

S. Filatov¹, R. Bubnova²

¹Dept. of Crystallography, St. Petersburg State University, University Emb. 7/9, St. Petersburg 199034, Russia

²Institute of the Silicate Chemistry of Russ. Acad. of Sci., Ul. Odoevskogo, 24/2, St. Petersburg 199155, Russia

Thermal expansion of more than 40 borates has been investigated by powder X-ray diffraction and 30 of them demonstrate greatly anisotropic thermal expansion ($\alpha_{\max}/\alpha_{\min} \approx 5$), moreover, about 20 of them show negative linear thermal expansion. The average linear coefficient of thermal expansion is about $25 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ over 40 borates [1].

Role cations. When the borate thermal expansion coefficients are compared with chemical composition it is apparent that the average linear coefficient of thermal expansion rises with cation size increasing and cation valence decreasing.

High-temperature crystal structure investigation. To understand the sharply anisotropic character of borate thermal expansion we have studied crystal structures of some borates ($\text{-CsB}_5\text{O}_8$, $\text{-Na}_2\text{B}_8\text{O}_{13}$ [2], LiB_3O_5 and $\text{Bi}_4\text{B}_2\text{O}_9$) using single crystal high-temperature X-ray diffraction method. The main result is that boron-oxygen tetrahedra and triangles and rigid groups consisting of these B-O polyhedra do not change practically their configuration on heating but they can be turned of each other [1,2].

Role B-O-anions. The thermal structural behaviour of rigid groups provides an explanation of anisotropical character of thermal expansion for most borates. The B-O rigid groups do not essentially change their configuration on heating but they can be rotated relative to each other as hinges. In this case a large expansion along some directions is coupled with a contraction along others as it occurs in chain, layer and framework pentaborates. It is notable that existing of screw 2_1 -chains of rigid B-O groups leads to greatly anisotropic thermal expansion of borates under study whereas insignificant influence of the B-O anion dimensionality on anisotropy of thermal expansion is revealed. As example all of the B-O anions in pentaborate structures (Figure) contain the same chains of the pentaborate groups extended along the 2_1 screw axis and all of them have the same maximum coefficient of thermal expansion along chains equal to about $60 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ and negative one in the perpendicular direction equal to about $-5 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$.

The highly anisotropic character of expansion of the structures based on finite complexes, e. g. $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4]8\text{H}_2\text{O}$ borax, may be rather caused by shear deformations.

Conclusion. To summarize, most borates demonstrate highly anisotropic character and great magnitude of thermal expansion: the average linear or volume coefficient of thermal expansion depends on size and valence of cation, whereas thermal behaviour of rigid BO groups dictates an anisotropy of thermal expansion.

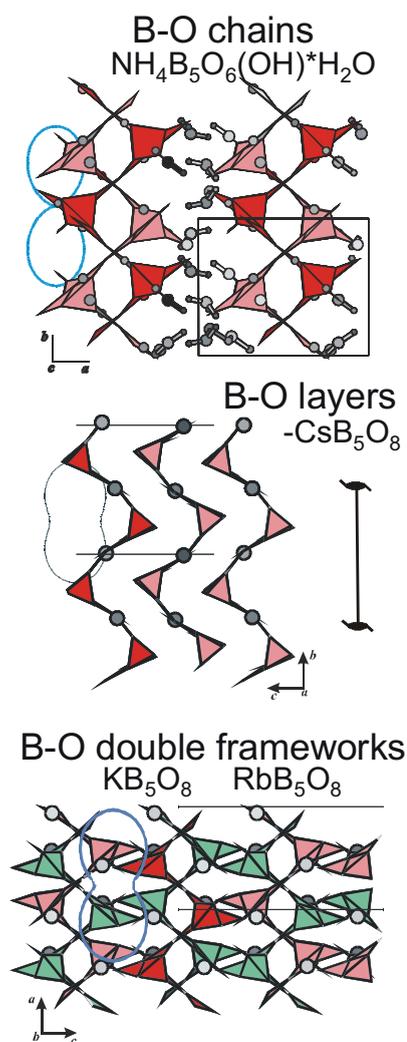


Figure. Hinge thermal expansion of pentaborates of 1-, 2- and 3-dimensionality

The research has been supported by RFBR (project # 02-03-32842).

1. S.K.Filatov, R.S.Bubnova, *Phys. Chem. Glasses* 41 (2000) 216.
2. R.S. Bubnova, Yu.F. Shepelev, N.A. Sennova, S.K. Filatov, *Z. Krist.* 217 (2002) 444.



B3 - O3

CRYSTAL STRUCTURES OF AND TOPOLOGICAL ASPECTS ON THE HIGH TEMPERATURE PHASES AND THE DECOMPOSITION PRODUCTS OF $M_2C_2O_4$ M = [K, RB, CS]

Robert E. Dinnebier¹, Sascha Vensky¹, Martin Jansen¹, Jonathan Hanson²

¹Max-Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

²Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

The high temperature phases of the higher homologues of the alkali oxalates $M_2C_2O_4$ M=[K, Rb, Cs] and their decomposition products M_2CO_3 were investigated using *fast* angle dispersive X-ray powder diffraction with an image plate detector and DTA/DSC measurements. The following phases in order of decreasing temperature have been observed and crystallographically characterized. A (*) denotes a previously unknown modification: $-K_2[C_2O_4]^*$, $-Rb_2[C_2O_4]^*$ (Fig. 1), $-Cs_2[C_2O_4]^*$, $-K_2[CO_3]$, $-Rb_2[CO_3]^*$ (Fig. 1), $-Cs_2[CO_3]^*$: $P6_3/mmc$; $-K_2[C_2O_4]^*$, $-Rb_2[C_2O_4]^*$ (Fig. 1), $-Cs_2[C_2O_4]^*$, $-Rb_2[CO_3]^*$ (Fig. 1), $-Cs_2[CO_3]^*$: $Pnma$; $-K_2[CO_3]$: $C2/c$; $-K_2[C_2O_4]$, $-Rb_2[C_2O_4]$ (Fig. 1), \check{a} - $Cs_2[C_2O_4]$, $-K_2[CO_3]$, $-Rb_2[CO_3]$ (Fig. 1), $-Cs_2[CO_3]$: $P2_1/c$; $-K_2[C_2O_4]$, $-Rb_2[C_2O_4]$ (Fig. 1): $Pbam$.

With respect to the center of gravity locations of the oxalate respectively carbonate dianions, the crystal structures of all known alkali-oxalates and -carbonates belong to the AlB_2 structure family, crystallizing either in the AlB_2 or in the Ni_2In structure type. Despite the different sizes of the carbonate- and oxalate dianions the high temperature phases of the alkali carbonates M_2CO_3 M=[K, Rb, Cs] show the same sequence crystal structures as the corresponding (isotypic) alkali oxalates. Topological aspects and order-disorder phenomena at elevated temperature are discussed. For data reduction and graphical visualization of large sets of powder patterns, a new software POWDER3D has been developed which is subject of another abstract.

Acknowledgments:

This work was supported by the MPG, the FCI and the BMBF

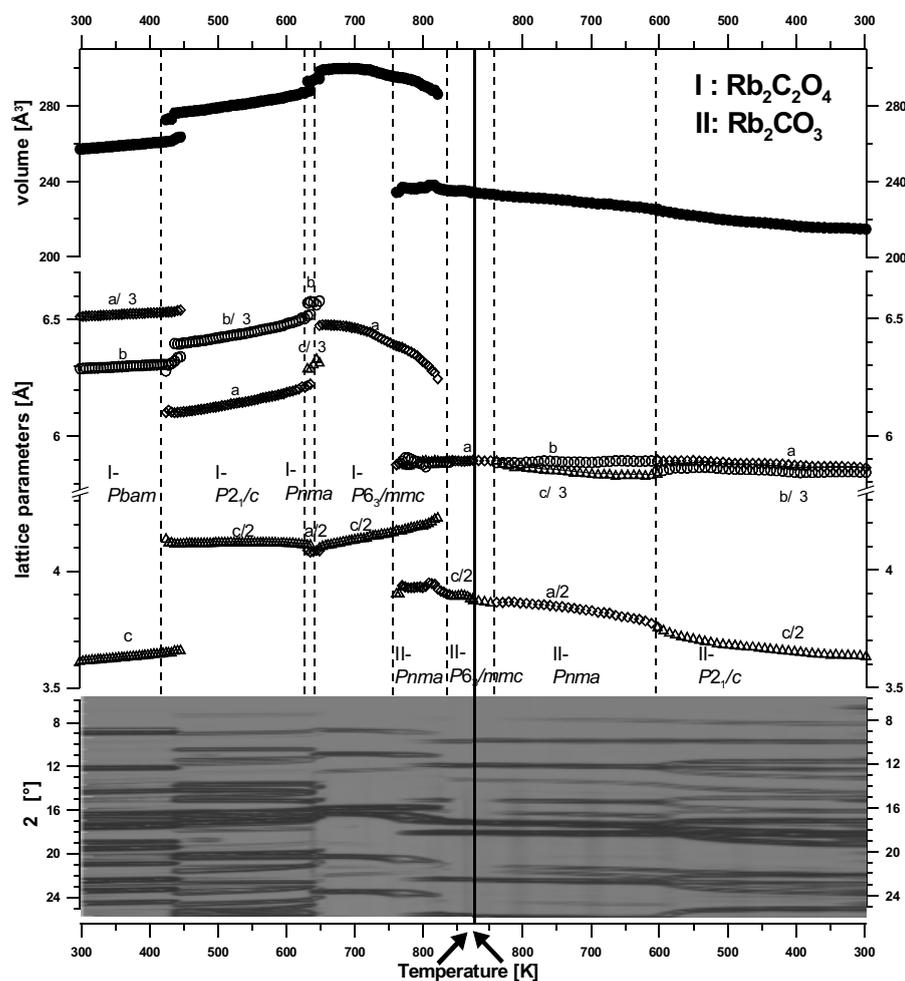


Figure 1

**B3 - O4**

EXPERIMENTAL EVALUATION OF THE TEMPERATURE ACCURACY OF THE OXFORD PHENIX CRYOSTAT

Martijn Fransen and John Vasterink

PANalytical, Almelo, The Netherlands

Recently, Oxford Cryosystems has introduced a closed-circle cryostat for X-ray powder diffraction applications. The absence of the need for continuous supply of new liquid Helium, makes X-ray powder diffraction experiments possible also for users having limited experience with cryogenic techniques.

Ease of use of a non-ambient device with a powder diffractometer is of course nice, but much more important is the accuracy of the temperature readouts. Modern non-ambient chambers perform quite well in this respect

and we were curious to see whether this was also the case for a cryostat.

There are two basic methods for determining the temperature accuracy:

- measure diffractograms over a large temperature range and calculate the lattice parameter change as a function of temperature,

- find material(s) with phase transition(s) at known temperature(s).

Both of these were used to test this non-ambient chamber.



PANalytical