



Collaboration with Hans-Beat Bürgi: crystallography at Bern and Lausanne

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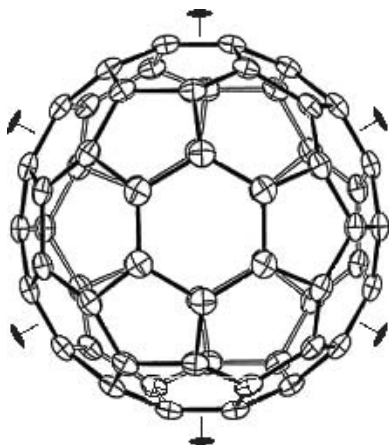
A personal recollection of scientific developments by Hans-Beat Bürgi and fellow crystallographers in Switzerland is given.

1. Crystallography in Western Switzerland

Hans-Beat Bürgi and I both studied at ETH Zürich, and we both became crystallographers, but the curricula we followed were vastly different. Hans-Beat studied chemistry, and as a graduate student of J. D. Dunitz specialized in the then modern chemical crystallography and crystal structure determination as developed in Britain and the English-speaking world. I was a student of Fritz H. Laves in the Department of Earth Sciences. Laves was the successor, and a former student, of Paul Niggli. In the tradition of this towering scientist, his Institute of Crystallography comprised a very diverse crowd of people with interests ranging from mathematical group theory to field work in mineralogy and petrography, looking for example at feldspars, quartz, clay and alloys, using for example X-ray and neutron diffraction, electron microscopy, crystal optics, nuclear quadrupole resonance spectroscopy and IR spectroscopy, but the then modern crystallographic structure determination was not a major concern. Hans-Beat is my junior by six years. Therefore, I had no contact with him as a student. When he became a graduate student with Jack Dunitz, I had moved to the United States and was learning as a post-doc the technique and art of crystal structure determination.

We both became professors of Crystallography. I became a member of the Physics Department of the University of Lausanne heading a newly created Institute of Crystallography without an explicit obligation as to the type of research to be pursued. Hans-Beat became professor at the Chemistry Department of the University of Bern charged with installing a new research group in Chemical Crystallography. A few years earlier, the University of Geneva had appointed Erwin Parthé to organize an interdepartmental crystallography institute to serve all the needs of chemists, physicists and mineralogists requiring X-ray diffraction. Thus, I was surrounded by very capable scientists and friends, notably Howard Flack in Geneva about 60 km to the southwest and Hans-Beat in Bern about 110 km to the northeast of Lausanne.

Hans-Beat usually started collaborations by phone call or e-mail, telling me that he wished to be introduced to a research topic he believed I knew something about. (Not that he ever needed much instruction.) In the mid-1980s, it was the determination of electron densities by X-ray diffraction. This topic



changed into studies of thermal motion. The thermal motions became an important part of fullerene research. Finally, we became interested in OD-polytypes. The collaboration with Hans-Beat was not only a pleasure and fruitful, it was also hard work. After an hour of discussing on the telephone, I usually became impatient, but Hans-Beat went on and on discussing, saying that not everything was clear yet. Relief came only when he said that he was becoming hypoglycemic and needed to eat. Note that cell phones were not yet a usual means of communication and hunger could interrupt a conversation.

2. From charge density to thermal motion

At the time Hans-Beat became interested in electron densities, I was just about ready to abandon that topic. I had a rather negative opinion on the accuracy of 'accurate electron densities' and had become convinced that models needed to be developed with parameters to be fitted to the raw intensities from diffraction measurements and to other observations such as crystal shape, instead of to structure amplitudes derived by procedures called 'data reduction'. Hans-Beat's request stopped these technical considerations. He proposed to study a small rigid molecule, boron nitrilotriacetate, $C_6H_6BNO_6$ (NTA-B; Moeckli *et al.*, 1988). This molecule shows six different types of bonds (C–C, B–N, C–N, B–O, C–O and C=O) with different polarities. The molecular symmetry $3m$ is non-crystallographic and provides a useful test of the accuracy of the resulting charge density. The structure is non-centrosymmetric, space group $Pn2_1a$. However, the diffraction data measured with Mo radiation at 100 K by Jürg Hauser in Hans-Beat's laboratory were of excellent quality. Despite the very small dispersion terms of the scattering factors, they seemed to suggest the polar direction of the structure. Charge density refinements converged close to the non-crystallographic molecular symmetry $3m$ and the displacement parameters agreed well with the rigid-body TLS formalism. This work was a classical electron density determination resulting in density maps that agreed reasonably well with calculated maps, and the accuracy appeared to be more acceptable than I usually expected for electron densities. Bond polarities were discussed for the six different bonding regions.

Studies of charge densities and of thermal motion are very much related: effects of the one must be properly accounted for in studies of the other. In light-atom structures such as NTA-B at 100 K, the usual harmonic approximation of thermal motion may be adequate; in heavy-atom structures at room temperature, the effects of thermal motion may be dominant. I chose to study K_2PtCl_6 because in the literature, difference electron densities from this compound were attributed to bonding effects. This project became an extended collaboration employing single-crystal and powder neutron diffraction and single-crystal X-ray diffraction at temperatures between 8 K and 380 K. I asked Hans-Beat for help in the proper interpretation of these nine different datasets. We concluded that no bonding electron density could be

observed, and the project became an in-depth study of harmonic and anharmonic thermal motion (Schefer *et al.*, 1998).

3. Fullerenes

The next collaboration with Hans-Beat was on Buckminsterfullerene, C_{60} . J. A. Ibers had published the crystal structure of C_{60} from twinned-crystal X-ray diffraction data at 110 K (Liu *et al.*, 1991), but the spread in the lengths of chemically equivalent bonds and the atomic displacement parameters suggested deficiencies in the model. Hans-Beat suspected that the molecules are disordered, adopting two orientations, but lacked the program to refine a disordered model with a reasonable number of parameters. In Lausanne, we had been developing at this time a least-squares program with many restraints not only on distances and angles but also on displacement parameters, believing that it made little sense to prescribe interatomic distances without prescribing also a bond restrained to a specific length to be vibrationally rigid, *i.e.* the r.m.s displacements of the atoms along the bond being equal (Hirshfeld, 1976). Thus, we were able to refine the structure of C_{60} with very few effective parameters describing a molecule with exact symmetry $m\bar{3}5$ undergoing rigid-body TLS motion. Using Ibers' data, the orientationally disordered structure refined easily to credible results. Ibers sent us also X-ray data sets obtained at 153 K and 200 K permitting us to study the twinning, disorder and thermal motion as functions of temperature (Bürgi *et al.*, 1992*a,b*). Subsequently, Hans-Beat found in the literature several structures containing fullerenes, C_{60} or C_{70} , that we re-refined with our software, some of them on the published diffraction data and others on our own data. Out of the seven resulting publications, the one on the structure of $(HQ)_3C_{60}$ (HQ is hydroquinone $C_6H_6O_2$) serves as an example. HQ forms a three-dimensional hydrogen-bonded clathrate structure, the C_{60} molecules occupy the voids (symmetry $\bar{3}m$) and are orientationally disordered (Ermer, 1991). In the original work, the positions of the partial C atoms on the C_{60} sphere could not be determined. This problem was easily solved by trial and error, by choosing and refining diverse orientations with different site symmetries of rigid C_{60} and the molecular symmetry restrained to $m\bar{3}5$. A very good fit with the observed structure amplitudes was found for site symmetry $2/m$, thus for a threefold disorder with 180 partial atoms on the C_{60} sphere. We studied the disorder and rigid-body thermal displacements with X-ray data at the four temperatures: 100, 200, 293 and 373 K (Blanc *et al.*, 2000). Refinement of an ordered threefold twinned structure gave results inferior to the disorder model. Thus, the orientations of neighbouring C_{60} molecules appear to be uncorrelated.

4. OD polytypes

The next collaboration with Hans-Beat was in the field of disordered layer structures and order–disorder theory (OD polytypes, Dornberger-Schiff, 1982). Such structures are built

from layers that are perfectly periodic in two dimensions, but the stacking of these layers in the third dimension lacks translational symmetry. Diffraction pictures from such structures show in general sharp reflections (family reflections independent of the disorder), and rods of diffuse intensities perpendicular to the layers. The disorder being one-dimensional, it can be quantitatively described by Markov chains with a very limited set of probabilities for layer sequences, suggesting the distance of interactions between layers. Normal ordered structures usually do not yield such information. OD theory also often explains the occurrence of crystals twinned by stacking faults. A well known example is the family of densest sphere packings and the occurrence of (111) twins in the cubic closest packing (ccp). Hans-Beat asked me to look at the disordered structure of the cyclohexatriene-like molecule tris(bicyclo[2.1.1]hexeno)benzene (Bürgi *et al.*, 1995). The structure is a very attractive OD polytype that turns out to be mathematically similar to the densest sphere packings. It has three maximum-degree-of-order (MDO) structures; domains of all three of them appear to be present in the crystals (Bürgi *et al.*, 2005). The diffuse intensities could be calculated quantitatively in closed mathematical form. However, the fit with the observations was only qualitative. Maybe the OD model of perfectly flat identical layers is not quite adequate. Ordered monoclinic OD-twinned MDO crystals show molecules that are slightly rotated out of the layer plane (Birkedal *et al.*, 2003). In the disordered stack, layers may deform slightly depending on their nearest neighbours.

5. Swiss–Norwegian Beamline

When the European Synchrotron Radiation Facility (ESRF) at Grenoble, France, was planned in the late 1980s, Gervais Chapuis of the University of Lausanne realized that structure research by X-ray diffraction did not figure very prominently in the plans. He therefore organized a Collaborating Research Group to build a beamline dedicated to crystallography. We soon brought the Norwegian crystallographers on board and created the consortium Swiss–Norwegian Beamlines (SNBL)

in the early 1990s. The beamline was built with H. P. Weber as chairman of the board and P. Pattison as beamline scientist. It still exists today. Currently it offers services in high-resolution single-crystal diffractometry, large-area diffraction imaging, high-resolution powder diffractometry and EXAFS spectroscopy. Many political problems had to be solved: the three countries Switzerland, Norway and France have quite different funding mechanisms and laws. During my term as chairman of the Swiss Users Group, the Norwegian partners demanded a legally sound new contract and mandated a Norwegian lawyer while the Swiss funding agency would not cover fees of lawyers. Hans-Beat's help with such problems was invaluable. I do not present in this article a history of SNBL, I just highlight Hans-Beat's merits in keeping SNBL running.

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