Solving a structure as a goal vs. solving a structure as a tool. Learning crystallography along evolving times

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My education in crystallography started in 1993 at the Laboratorio de Cristalografía (where I still work) when I filled up a temporary research assistant position for undergrads. I had a family-induced informal background in mineralogy and I was a computer fan so the Crystallography Lab. was kind of calling. I knew very little of the discipline I was diving into, though, at that time. My first task was to help the group leader Prof. R. Mariezcurrena, adapt some FORTRAN programs running on an old PDP11 computer to make a Hilger-Watts single-crystal diffractometer perform some automatic operations. Some knowledge of BASIC programming language and a lot of FORTRAN Manual reading allowed me to quickly get engaged with the task while learning X-ray diffraction applications and crystallography basics. When not typing code I was using X-ray cameras with film (including loading and developing in the darkroom) for powder diffraction (Debye-Scherrer) and single-crystal analysis (Weissenberg and Precession). In less than a year I was collecting and analyzing powder data all by myself; measuring 2θ angles, calculating d-spacings, and comparing with the JCPDS files for phase identification by hand. During that period I was also responsible for recrystallizing powders coming from some colleagues that were just done with their studies and would profit from an additional paper if the structure could be published (kind of scientific RRR).

The single-crystal diffractometer and cameras never gave a useful dataset, however, I had fully engaged already with crystallography, after attending two international schools in Sept. and Dec. 1994. At the end of that year, a co-worker brought a dataset of one of that recycled crystals from abroad and my boss announced we had obtained funding to buy a new automatic single-crystal diffractometer. My excitement of those days changed my interaction with the discipline forever.

The first structure I fully solved and refined, while graduating in Chemistry, was that of a furosemide derivative, a molecule with no chiral atoms crystallized in the triclinic P-1 space group.[1] Using the first PC (Intel 80486) on MS-DOS the structure determination run would take an hour in SHELXS86[2] and each least-squares refinement cycle 3-5 minutes in SHELXL93.[3] A couple of extra datasets were obtained by the group during 1995/1996 and soon the diffractometer started producing one or two datasets/month so I started to get hands-on experience with structure completion and refinement that ended up in publications.[4] Looking for the hexagonal and pentagonal rings in the furosemide-derivative molecule (Fig 1) was easy in a printout of SHELXL-93 output but for some other compounds I got to analyze, there were no such rings, so I slowly got used to typical C-C, C-O/N bond distances and angles in order to complete structural models. After submitting my first manuscript to Acta Cryst. C by mail in 1996 I recall receiving comments from referees pointing to the evident intermolecular hydrogen bonds I had missed in the packing description. At that point, it became evident I needed to dive into symmetry, not only to fill up the SYMM command in SHELX but for building packing diagrams, understanding, and using #NNN codes in XPMA (ZORTEP [5]). The available International Tables for Crystallography Vol A (1956 edition) had only the standard setting of P21/c S.G. so transforming symmetry operations to P21/n setting was another of the challenges. Eventually, by 1999, reading the PLATON [6] output to look for interesting features and eventually publishing crystal structures in Acta C or metal-organic/organic chemistry journals was a routine task for an all-confident me. However, while finishing my Masters in Chemistry degree, I had the humbling experience of Marshing myself with a structure solved in Cc S.G. that turned out to be Fdd2.[7]

At that time solving a structure and publishing was my scientific goal. However, the availability of crystal structures was changing the minds of scientists and using the crystal structures to do further science was becoming the goal. I moved to perovskites for my Ph.D. studies, embracing the study of structure-property relations with neutrons, synchrotron X-rays, and Rietveld analysis of powder data. I think my early years of typing code, developing film, measuring diffraction lines on the backlit screen, etc. prepared me in the best possible way for today, where teaching and analyzing structures from single crystal or powder data are part of my daily routine.

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