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Crystallography and Chemistry: An Ongoing Engagement

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Crystallography is as old as chemistry itself. As an intellectual endeavour, it is practically without equal, such that Johann Wolfgang von Goethe, who was also interested in mineralogy, said almost regretfully, if a little disparagingly "Seen as a science, crystallography is an altogether unusual case. It is not productive; it is just itself, not giving rise to anything else, more especially now that a number of isomorphic bodies have been found which turn out to be quite distinct according to their content. As it really is not possible to apply crystallography in any way, it has developed largely as something self-contained. It gives the mind a certain limited satisfaction and is so manifold in its detail that it can be called inexhaustible; which is the reason why it keeps a lasting and decisive hold on outstanding people." One is tempted to ask whether inexhaustible detail can really exert an endless fascination over outstanding people. In any case, Goethe continues to emphasize the introverted nature of the subject when he says "Crystallography has something of the monk and the confirmed bachelor about it and it is therefore sufficient unto itself. It has no practical influence in a living context for its most precious products, crystalline gems, first have to be cut and polished before we can use them to adorn our womenfolk." In contrast, his attitude to chemistry is more generous as he states "The opposite can be said of chemistry, which can be applied in the most extensive way and proves to be of the most unlimited influence on life."[**] The contrast between crystal statics and chemical dynamics continues to pervade and persist in the consciousness of chemists, even though crystallography and chemistry have merged in many contexts and are almost indistinguishable today.

We have indeed traveled in the 200 years since Goethe, and especially so during the last century since the discovery by Max von Laue of diffraction by crystals and the development of methods to determine the internal structure of matter. The ability to image the structure of matter at an atomic and molecular level has had deep-seated consequences in chemistry and biology. In the context of *Angewandte Chemie*, it is pertinent to discuss the relationship that crystallography has had with chemistry. Lawrence Bragg was criticized early in his career of trying to reduce chemistry to geometry. Linus Pauling showed time and again, that chemical considerations could simplify the process of crystal structure determination. This was especially relevant in his time, when the determination of crystal structures of "small molecules" was in itself a nontrivial task. In general however, crystallography was derided as a "tool" of no research significance, and organic chemists, mostly between 1960 and 1990, would often ask rhetorically as to the relevance of the structure of a molecule in the crystal in the context of its solution chemistry. Much of this mercifully came to an end with the advent of organometallic chemistry and the appearance of a large number of compounds whose complex internal molecular structures could not be determined in solution; notably NMR spectroscopy was not an effective structure-determining "tool" for this category of compound. The crystal structure often was the only structure one had. Still, crystallographers were not intimidated by chemists altogether—Jack Dunitz described the manner of structure determination by chemists and crystallographers as trying to locate furniture in a darkened room. He claimed that a chemist will find the furniture by stumbling around in the darkness and bumping into each and every piece but that a crystallographer need just turn the lights on and see the arrangement at once!

Crystallographers and chemists have had more serious exchanges: 1) what is the "real" structure of a molecule, real at least in a chemical context; is it the "not so accurate" structure that is obtained in an X-ray diffraction experiment that shows electron density or the "more accurate" structure that one obtains by neutron diffraction? 2) Which is the "more meaningful" molecular structure, the one obtained with the most sophisticated X-ray diffraction experiment, or the one obtained with the most sophisticated state-of-the-

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[**] The original citations are from *Maxims and Reflections*, a collection of quotes that was published posthumously in 1833.

art computation, if these structures are different? 3) Can one establish direct connections between molecular structure and crystal structure and therefore predict crystal structures from molecular structures? 4) How many crystal structures can a molecule have, or does polymorphism have no upper limit if one varies the crystallization conditions sufficiently, including computer simulations? One can go on; distance-resolved crystallography is now supplemented by time-resolved crystallography so that crystallographers can enter the domains of dynamics—an area that they were traditionally excluded from. Chemistry today is an interplay of synthesis, structure, and dynamics. Crystallography dominates structural chemistry, but it has also made significant inroads into synthesis, as for example in crystal engineering, and into dynamics. One cannot conceive of modern chemistry without crystallography.

The International Union of Crystallography (IUCr) was founded in 1948 and today, 51 countries adhere to it, through three Regional Associates (American, Asian and European) and 41 National Associates. The IUCr publishes very high quality crystallographic research in eight journals, and a ninth one, called simply *IUCrJ*, will be launched in 2014 to coincide with the International Year of Crystallography. The IUCr, as a depository of crystallographic standards, also acts as an editor and publisher of the International Tables of Crystallography, thus facilitating standardization of methods, units, nomenclature, and symbols. Additionally, the IUCr promotes international cooperation in crystallography and coordinates the relationship of crystallography to other sciences.

The International Year of Crystallography 2014 (IYCr2014) was declared by the United Nations to commemorate the centennial of X-ray diffraction by crystals. The IUCr has partnered with UNESCO to implement IYCr2014. The declared goals of IYCr are to disseminate the fundamental role of crystallography for the development of chemistry, mineralogy, physics, biology, medicine, materials science, geosciences, and to emphasize role of the results from crystallographic research in everyday life to students and scientists. To render these lofty goals into practical execution, many activities have been planned across the world, including this special issue of *Angewandte Chemie*.

The opening ceremony of IYCr2014 will be held at the UNESCO headquarters in Paris on 20th and 21st January, 2014. About 2000 participants are expected to attend, including ambassadors and representatives of governments of member countries to UNESCO, as well as crystallographers from all over the world and delegations from other international scientific and educational societies. The event will use science to bring nations together and ignite new collaborations.

The IUCr and UNESCO have drawn up an ambitious plan for open laboratories and summit meetings in Asia, Africa, and South America in the context of IYCr2014. These open labs are being planned with major equipment makers. New installations of crystallographic instrumentation will be made in Ivory Coast and Uruguay to serve as research hubs, hosting students and researchers from neighboring countries. Otherwise, these open labs will function where an X-ray diffractometer is already operational. Parallel to this initiative, some workshops and tutorials will be held in the factories of the diffractometer manufacturer companies, thus also opening job opportunities to participants from developing countries.

Three summit meetings will bring together scientists, administrators, and policy makers in using a common crystallographic theme. The first in Campinas, Brazil, on the crystallography of (mainly biological) macromolecules, will focus on South and Central America. The second summit in Karachi, Pakistan, aims to bring together a similar group from China, India, and Pakistan under the umbrella of chemical crystallography and pharmaceutical sciences. The third meeting is scheduled in Bloemfontein, South Africa, as an adjunct to a workshop on powder diffraction and hopes to bring together government representatives from many countries in Sub-Saharan Africa and North Africa. There is a real necessity for scientists to think beyond political and other borders. Therefore these summits, which will be attended by scientists in academia and industry, and by science administrators, are planned between countries that have hitherto been divided on the basis of geography, ethnicity, religion, or politics. The meetings will focus on high-level science, also highlighting the difficulties and problems of conducting competitive scientific research in different parts of the developing world.

The IUCr has strong experience in conducting programs in developing regions. The IUCr Initiative in Africa dates back to 1999 and provides faculty and students with training in crystallography teaching and research methods. Thanks to the collaboration with UNESCO and The World Academy of Science for the Advancement of Science in Developing Countries (TWAS), the IUCr will now extend the Initiative in Africa into the open lab project and also target South America. Its aim is to make science more broad-based and energize youth in parts of the world that have remained underdeveloped for too long.

In changing times, there is a need for scientists to look beyond their laboratories, students, and research projects, to the larger business of making science more relevant and meaningful to society at large. I am happy to note that *Angewandte Chemie* has brought out this special issue to support the ongoing engagement between crystallography and chemistry.