Personal Reminiscences

ISAMU NITTA

When I was a student of chemistry in the University of Tokyo, I had a vague ambition to devote myself in future to the question of how far one could go into the phenomenon of life from the standpoint of chemistry. Thus I had no presentiment that I should be later engaged in research and education in X-ray crystallography and crystal chemistry. However, this actually came about when M. Katayama, one of my teachers, recommended me to S. Nishikawa to work under him in the field of X-ray crystal analysis. This was in 1923, the year of my graduation from the University. After that I worked for about ten years in his laboratory in the Institute of Physical and Chemical Research, Tokyo, occupying myself primarily with the analysis of organic crystals. From the beginning I thought it quite significant to make any contribution to the confirmation of stereochemistry by such a direct physical method as X-ray diffraction analysis. With such expectation it was inspiring to me to learn from Nishikawa the experimental techniques of crystal analysis using Laue photographs and an ionization spectrometer, though it was not very easy for me to throw myself suddenly from chemistry into physics. It was very fortunate that in my undergraduate course I had attended the lectures of Professor Nagaoka on the Maxwellian theory of electricity and magnetism, and also those of Professor Nakamura on the classical theories of crystal structure and space groups. This greatly facilitated the access to X-ray analysis for the chemistry student I was. The three earliest classical books on X-ray crystallography, namely *X-rays and Crystal Structure* by W. H. and W. L. Bragg, *Kristalle und Röntgenstrahlen* by P. P. Ewald, and *The Structure of Crystals* by R. W. G. Wyckoff, rendered great help to me as they did to all others of that time.

My first paper, which appeared in 1926, was on the crystal structure of iodoform,[1] a substance I chose in an attempt to prove the tetrahedral nature of the carbon atom. The atomic parameters, x and y, for the iodine atoms in this hexagonal crystal ($P6_3$) could be determined exclusively from the qualitative comparison of intensity inequalities for pairs of reflections such as hkl and khl. Although I could of course not find the positions of hydrogen and carbon atoms owing to the overwhelmingly strong scattering power of iodine, the probability of the tetrahedral nature of the carbon atom could be seen in the structure. Only the hexagonal unipolar space group did not appear to conform with the observed bipolar external form of the crystal. I became gradually aware that this might be due to the orientational disorder of the molecular axes along the hexagonal axis. In my early period I was convinced that one should begin with the simplest compounds of organic chemistry; i.e., with methane derivatives and those containing only one carbon atom. Such a thought was due to youthful overvaluation of logic and lack of experimental experience, and it made it difficult for me to find, in that period of development, suitable crystals for analysis.

My second paper, which appeared in the same year, was on the crystal structure of pentaerythritol,[2] and contained some comments on the previous investigations of the same crystal by other authors. One of the unfortunate conclusions of these authors was due to the inappropriate description of the unipolar, tetragonal symmetry of the crystal given in Groth's *Chemische Krystallographie*. By observing carefully the crystal growth of pentaerythritol from aqueous solution, I realized that crystals frequently grow with their tetragonal axes hanging perpendicular from the surface of the solution, so that the crystals appeared as if they had unipolar, tetragonal axes. Bearing this in mind I chose the space group $I\bar{4}$, which enabled the central carbon atom of the molecule to conform with the tetrahedral distribution of the valence bonds.

From 1928 to 1931 I was sent abroad for further study by the Institute of Physical and Chemical Research. I first visited Professor Coster at the Physical Laboratory, University of Groningen, and stayed there more than one year in the hope that I might learn something about X-ray spectroscopy, which would be of chemical significance in the problems of the structure of atoms and of the nature of chemical bonds. When I first met Coster, he proposed that I carry out an experiment proving the non-validity of Friedel's law using zincblende, a surprising coincidence, because such an experiment had just been finished by my teacher, Professor Nishikawa, and my colleague, Matsukawa, by the time I left Japan. Without repeating such an experiment, I tried to see if the effect reported by Bergen Davis, namely the Raman effect in the X-ray region, was a real one, and came to the conclusion experimentally that such an effect did not exist, although a negative proof is always very difficult.

After studying further the problem of multiplicity in the M series of rare-earth elements, I then visited professor Ewald at the Institut für theoretische Physik, Technische Hochschule in Stuttgart, with a hope of learning a bit of crystal lattice optics, which Ewald had developed in its full elegance in 1916. My visit was motivated by the deep impression I had when I read Ewald's book mentioned above and the classical paper by W. L. Bragg in 1924 on the refractive indices of calcite and aragonite. I thought that the general theory of Ewald might be of use in the course of X-ray crystal analysis of molecular crystals, such as organic. Indeed, Ewald's theory was very difficult for me to master, but the personal contact with him during my stay there was a great addition to my later life. In this period of my stay in foreign countries I saw many eminent men, of science in general and of the special field of X-ray crystallography, during personal visits, at university colloquia and at public lectures. These contacts acted as an incessant source of scientific encouragement for me.

In 1933 I was called to a professorship of physical chemistry in the Department of Chemistry, Osaka University, which was newly established. I was quite fortunate to have a collaborator in X-ray crystallography as good as Tokunosuké Watanabé, with whom I have worked more than a quarter of a century. From my experience up to that time, I thought it very significant for me, as a chemist, to try as far as possible to mediate between physics and chemistry in university education. As for X-ray crystallography, I felt it to be my duty to popularize among organic chemists the X-ray method for determining molecular structure, not as a method of physics, but as one of organic chemistry, although this method was not so far developed at that time. Our first contribution from the laboratory was the crystal analysis of cubic barium dicalcium propionate published in 1935.[3] In this crystal we had to make the propionate group possess digonal symmetry. Thus we were led to assume a rotational or orientational disorder so as to furnish the group with a statistical digonal character. I then came back again to pentaerythritol and in 1937 with Watanabé carried out two-dimensional Fourier syntheses of the electron density in this crystal,[4] quite independently of the similar work by Llewellyn, Cox and Goodwin. This was the first two-dimensional Fourier synthesis in Japan, and this was also the first hydrogen-bonded structure found in Japan. The anisotropy of thermal expansion of pentaerythritol in this low temperature tetragonal phase was then determined by means of X-ray diffraction, and the result showed the characteristic features of the crystal structure of hydrogen-bonded layers. Further X-ray investigation revealed that the transformation of pentaerythritol at about 190°C from tetragonal to cubic was of a most complicated type, composed from the onset of intramolecular rotations and of orientational disordering of the molecule as a whole.[5] These various findings stimulated us to further studies: investigations of thermodynamical, electrical and optical properties of pentaerythritol in both phases,[6] X-ray and crystal-chemical studies of orientational and rotational disorder in molecular crystals,[7] X-ray analysis of organic as well as inorganic hydrogen-bonded crystals, etc. At all times I have been very fortunate to have had many good students who have worked with me on these and various other projects and to whom I am indebted for their devoted collaboration.

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Next Section