Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

International review of science, physical chemistry series two. Vol. 11. **Chemical crystallography.** Edited by J. M. ROBERTSON. Pp. iv + 228. London: Butterworths, 1975. Price £13·45.

Nowadays, if scientists wish to outline the subject of what is called 'chemical crystallography', they will encounter a vast number of divergent topics which have been accumulated under this title since the early days of X-ray crystallography. Keeping this formidable problem in mind, a team of well known crystallographers, clustered around the editor J. M. Robertson, selected only six, deliberately different, topics by the aid of which they show convincingly the manifold applications of the methods and results of crystallography (mainly X-ray) in the solution of chemical problems. Fortunately, the authors did not introduce this work in the usual way by describing the methods of crystallography (crystal geometry, physics and optics, X-ray and neutron diffraction, *etc.*) which was, however, unavoidable in former works.

Chap. 1 (pp. 1–20) by J. C. Speakman summarizes the latest developments in the field of hydrogen bonding, based mainly on structure determinations by neutron diffraction. This survey of hydrogen bridges, starting with those found in the polymorphs of ice up to the queried existence of bifurcated hydrogen bonds, shows the great development in our knowledge, since the suggestion of Huggins advanced by Latimer and Rodebush, about what is perhaps the most curious chemical bond.

Chap. 2 (pp. 22–56). Accurate experimental intensities collected on automatic single-crystal (X-ray and neutron) diffractometers at low temperature and elaborated by powerful computers provide quite new perspectives for the accurate analysis of electron density (e.d.) surrounding the atoms in crystals. The substance of these e.d. calculations and measurements is presented with great skill by P. Coppens. First, the conditions of advanced structure refinement and the methods of experimental difference synthesis are discussed. Further parts of this chapter deal with (*a*) the calculation of theoretical difference densities by various quantum-chemical methods and their comparison with experiment, (*b*) the introduction of atomic asphericity in e.d. formalism and (*c*) the measurement of net atomic charge. It is encouraging to see how the improved e.d. measurements are going to reveal the much debated electron distribution in metal, ionic and covalent (single or multiple) bonds *etc.*, in order to give a better understanding of the chemical bond.

In Chap. 3 (pp. 57–79) one can find a fascinating description of how the chemical and molecular structure of approximately 30 sesquiterpenes, caryophyllene and related compounds (clovenes, humulenes) separated painstakingly from complicated oils of clove *etc.* have been determined and distinguished in joint, well organized work by organic chemists and X-ray crystallographers. Really, this chapter, as the author J. M. Robertson remarks, proves that 'Without chemistry, crystallographers would have no interesting structures to solve. Without crystallography, chemists would often be spending valuable time in trying to solve structures in a difficult way'.

In Chap. 4 (pp. 81–120), under the title *Non-bonded Interactions in Organic Molecules*, J. D. Dunitz and H. B. Bürgi discuss some solutions of the problems that have arisen from the failure of quantum chemistry to provide accurate molecular parameters (energy, geometry, electron density, vibrational and electronic transitions, *etc.*) even in the case of simple organic molecules. After a minimum of non-mathematical quantum mechanics they suggest the construction of a multidimensional energy surface, the Born–Oppenheimer (BO) surface, by using experimental data inferred from X-ray structure analysis, spectroscopic and other physico-chemical measurements, instead of attempting to apply the rather doubtful calculations of quantum mechanics. The application of molecular force-field calculations in the case of simple medium-size molecules (mainly cyclic hydrocarbons) convincingly shows that the results of the empirical and semi-empirical methods discussed can corroborate each other. It is shown that, for molecular crystals, even the phase problem can be solved with the help of information about cell parameters, space group, non-bonded contact distances and the approximate structure of the molecule, regarded for this purpose as being rigid.

In Chap. 5 (pp. 121–176), R. Mason and D. M. P. Mingos review a selected group of metal complexes under the title *Structural Organotransition-Metal Chemistry*. The structures of many dozens of these coordination compounds, known as powerful (or potential) catalysts in homogeneous and heterogeneous catalytic reactions, have been determined by X-ray diffraction and studied by spectroscopic methods over the past twenty years. The authors systematically demonstrate a hierarchy of polynuclear organotransition compounds from the simple mononuclear systems with unsaturated ligands (olefines, allenes, *etc.*) up to the rather sophisticated clusters of the substituted (with, for example, tertiary phosphines or carbocyclic ligands) metal–carbonyl complexes. In this framework the most important structural features (geometry, bonding, *etc.*) of these complexes are discussed.

Chap. 6 (pp. 177–216). The contribution of A. McL. Mathieson surveys the formidable number of structure analyses of alkaloids. The structures are discussed in ten groups according to their characteristic moiety or mother compound (*e.g.* indole, protopine, steroidal alkaloids, *etc.*). This section really helps those who wish to be informed about the structural chemistry of alkaloids.

Apart from minor shortcomings, the reviewer dares to say that these six basically divergent chapters, as *pars pro toto*, have rightly been given the title *Chemical Crystallography*. In order to make this clear, let the reviewer remark that the apparently synonymous term 'crystal chemistry' means, in principle, the chemistry of crystalline materials (inorganic, organic, *etc.*) discussed in terms of their different chemical

properties. No one should expect the same thing from a work which bears the title *Chemical Crystallography*. One could ask, of course, why other important topics in this field have been deliberately omitted. Instead of criticizing the selection of the topics discussed, the reviewer suggests that the editor consider the issue of further volumes under the same title covering other chemical problems solved by the tools of crystallography.

The reviewer is pleased to recommend this book to all researchers, teachers and students who are interested in the modern approach to structural chemistry.

A. KÁLMÁN

Central Research Institute for Chemistry
Hungarian Academy of Sciences
H-1525-Budapest, POB 17
Hungary