Book Reviews

Interpretative Study

Organic Chemical Crystallography. A. I. Kitaigorodskii (translated from the Russian). Consultants Bureau, New York, 1961. x + 541 pp. Illus. $17.50.

Here is a book like a breath of fresh air; it is not a textbook, nor does it embellish a shopworn theme. Rather it devotes itself to a thesis and to documenting the evidence for that thesis; and it complements many books devoted primarily to the crystal chemistry of inorganic substances, for it is concerned solely with organic substances. More exactly, the author seeks to understand why a given organic molecule, when crystallizing with other molecules of the same kind, selects that particular packing arrangement which crystal-structure analysis reveals. After much study Kitaigorodskii convinced himself that there was a relatively simple theme here. He states this early in the preface; then in the body of the book he presents, first, a theoretical basis for the theme, and second, a substantiation of it by the use of well-arranged data.

The theme is touched off by this remark: "organic crystals are always so constituted that the projections in one molecule enter the hollows in another." This implies that molecules tend to assume as close packing as possible, this arrangement giving rise to the least free energy, primarily because molecules hold together by means of surface forces. Crystals in which the molecules are held together by hydrogen bonding are, of course, not included here.

The book contains only five chapters. In the first chapter, "The molecule," the discussion is centered on the molecule as a building unit, especially in its dimensional and symmetrical aspects. The internal structure of the molecule is established by the bond lengths and bond angles, but the external geometry, or packing shape, is determined by van der Waals' radii, here called "intermolecular radii." Molecular symmetry is the point-group symmetry of the molecule. (Figure 18 shows a molecule said to have symmetry *mm*, but it appears to have symmetry $\bar{4}m2$.)

"The elements of lattice theory" (meaning space-group symmetry) is only an introduction to the topic. The crystallographer already knows the material, and the uninitiated will not find here an understandable development of space groups. Either the chapter should have been written differently or it should have been omitted.

Chapter 3, "Theory of close packing of molecules," is the heart of the book. Unfortunately this important chapter is presented in Kitaigorodskii's private nomenclature for line groups and plane groups. The author will certainly lose many who would have become his disciples if he had used international symbols. The reader, if he is willing to grant that the author knows what he is doing, will find the conclusions that result from this important study in a limited number of tabulations and will have to translate only these tabulations into standard symbols. The gist of the chapter is that certain plane symmetries permit a molecule to touch six others in its layer, and thus to assume a "molecular coordination number" of six; other plane symmetries prohibit this.

This and attendant considerations permit a survey of the space groups for suitable candidates for packing molecules in organic crystals in which a molecular coordination number of 10 to 14 is ordinarily achieved. It develops that a molecule abhors space groups with mirror symmetry, unless that molecule itself has one or more mirrors. Some of Nowacki's data on the distribution of organic crystals over the space groups are not in harmony with Kitaigorodskii's results, but it appears that some of these data are from old determinations which have since been proven incorrect.

A packing coefficient, k, can be defined as the ratio of the sum of the volumes of the molecules in a cell to the volume of the cell. (This is not the same as Fairbairn's "packing index," in which the volumes occupied by the atoms are controlled by bonding radii.) This varies from 0.6 to 0.8 for aromatics, and much smaller numbers are unknown.

This part of the book covers only 112 pages. The remaining chapters—chapter 4, "Application of close-packing theory to organic crystals," and chapter 5, "Crystal structure descriptions for organic compounds"—are devoted to a critical and systematic description of the structures of organic crystals. This mass of data substantiates the author's theory.

The book appears to be printed by offset from excellent typing, with justified margins. The lack of italics is noticeable and causes awkwardness in some sentences. There are no bibliographies, and the few citations are chiefly footnotes to descriptions.

In his book, *The Theory of Crystal Structure Analysis*, Kitaigorodskii proved he was a master of crystal-structure analysis. The present (but older) book shows that he is also a leader in interpreting the results of such studies. All crystallographers, particularly those steeped mostly in inorganic crystal chemistry, will profit from reading this original work.

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Factual Descriptions

Larousse Encyclopedia of Geography. vol. 1, *Europe*. Pierre Deffontaines, Ed. Prometheus Press, New York, 1961. 450 pp. Illus. + maps. $17.50.

Rarely are such delicious geographic descriptions aimed at university audiences. Each chapter describes a political state in artful and knowledgeable manner. That the volume is a translation from the French is barely perceptible, except when suspiciously precise distances, such as 164 feet, are used where, in the original, the equivalent