Molecular Crystals and Solid State Chemistry

Molecular Crystals. By *J. D. Wright*. Cambridge University Press, Cambridge 1987. VIII, 178 pp., bound, £ 32.50.—ISBN 0-542-26460

Twenty years ago the three volumes entitled "Physics and Chemistry of the Organic Solid State", edited by *Fox, Labes* and *Weissberger* and published between 1963 and 1967 provided an excellent introduction to the subject, which was then covered by some 30 authors in 26 chapters, encompassing more than 2300 pages. The series was as successful as such books can be, and many of the chapters are still well worth reading. Since then the subject has grown enormously; some of the then existing areas have been developed beyond anything that could have been foreseen: crystal growth, the effect of solvents and impurities on crystal morphology, organic solid-state reactions, to name only a few. At the same time important new areas have been added: force field calculations and lattice dynamics (made possible by computer developments), organic metals and superconductors, second-harmonic generators, the study of molecular motion in crystals by solid-state NMR as well as diffraction methods. Also, since the mid-60s the number of molecular crystal structures available, so to say, for detailed scrutiny has increased from around 2000 to more than 70000.

As Dr. *Wright* correctly points out in his preface, there is a serious gap in the teaching of this subject in that most of the current solid-state chemistry and physics textbooks scarcely mention molecular crystals. There are excellent advanced texts covering limited areas, but apart from their specialized coverage they tend to be difficult for newcomers.

In this book, Dr. *Wright* has made a brave attempt to cover the whole subject, single-handed, in less than 180 pages. There are short chapters on purification and crystal growth (10 pages), intermolecular forces (9 pages), crystal structures (12 pages), impurities and defects (24 pages), molecular motion in crystals (22 pages), optical properties of molecular crystals (20 pages), chemical reactions in molecular crystals (23 pages), and, finally, electrical properties (the pièce de résistance with 46 pages). The author whisks us briskly through all these topics, in one door, out of another, and it is all a little like being taken on a ten-minute tour of the Louvre. Thus the book does provide an overall impression of the richness and variety of the subject matter. There are many illuminating explanations and comments, as well as a few slips and other mishaps, but the pace is so breathtaking that they do not really matter. On almost every topic, the beginner is likely to be dazed as much as enlightened, and the research worker will find the treatment far too superficial for his needs.

As an example, take the chapter on crystal structures. Dr. *Wright* considers a few very simple structures out of the 70000 available and has some sensible things to say about them. But he gives the impression that a classification of molecular crystal structures into three groups (non-polar molecules, molecules with polar substituents, and intermolecular donor-acceptor or charge-transfer complexes) provides genuine insight into the complexity of this enormously intricate subject. Such a classification could at best serve as a basis for defining three special types of interaction that could be invoked in the discussion of crystal structures, but in the vast majority of actual structures all three types of interaction come into play. We are still very far from an understanding of why particular molecules crystallize as they do. We may understand the general principles, but there are far too many details. It is true that when energy calculations based on fairly simple types of force field are made for an *observed crystal structure*, they usually produce an energy minimum at or close to the structure in question, but they give no hint of what other molecular arrangements may be possible. Nearly all the structures discussed here are built from planar aromatic molecules, a very small sample of the real, messy world. More stereodiagrams (I found only one) would have helped the reader, in this chapter and in others, to visualize the three-dimensional packing of the molecules.

In my opinion, Dr. *Wright* has undertaken a hopeless task in his effort to provide an elementary textbook on molecular crystals in such a short book. Perhaps it is the publishers who are to be blamed for imposing this limitation (as well as for the price, which will surely drive much of the prospective readership to the photocopier). Solid-state NMR in less than five pages! Lattice dynamics in three! It is difficult to see how a student can benefit from such superficial coverage. Many of the topics that are compressed here into a few pages would take an entire book to do them justice. His publishers should encourage him to expand one or two of his chapters into such a book. That would be a really worthwhile venture!

Organic Solid State Chemistry. Edited by *G. R. Desiraju*. Elsevier Science Publishers, Amsterdam 1987. xx, 550 pp., hard cover, Hfl 360.00.—ISBN 0-444-42844-5

This book is a collection of 14 review articles that describe developments in solid state chemistry during the last two decades. First a description of the contents: The book opens with five chapters on "Organic solid state reactions: topochemistry and mechanism". The reactions discussed are mainly photochemical intramolecular hydrogen abstractions *(Scheffer)* and [2+2] additions *(Theocharis* and *Jones,* and *Hasegawa),* there is a chapter on the prediction of reactivity using geometric criteria *(Kearsley)* and one on phonon spectroscopy *(Prasad).* The middle section consists of four chapters on the theme "Some stereochemical questions: pure and applied chemistry". *J. M. Thomas* and *Harris* discuss experimental and computational techniques for studying the structure and properties of molecules embedded within solid hosts. This is followed by a long, informative chapter on clathrates *(Tsoucaris)* and one on the structural complexities of phenols and their expression in different types of solid state reactivity *(Perrin, Lamartine, Perrin,* and *Thozet).* A chapter by *Paul* and *Curtin* on gas-solid reactions and polar crystals concludes this section. The five chapters of the final section entitled "Intermolecular interactions: from crystallography to chemical physics" form what is perhaps the most interesting part of the book. *Rao* summarizes what is known about phase changes in molecular crystals, *Gavezzotti* and *Simonetta* discuss the nature and magnitude of molecular motions in solids, and *Ramdas* and *N. W. Thomas* take up again the problem of modeling the packing energy in terms of inter- and intramolecular interactions. *Bernstein* provides a wealth of examples of conformational polymorphism—structural relationships that a physicist would describe as phase transformations, a chemist as conformational isomerizations—and finally *Desiraju* takes up the question of why some planar chloro aromatic molecules crystallize with a 4 Å translation and others not.

In a way, this book is a tribute to the memory of *G. M. J. Schmidt* and *A. I. Kitaigorodskii*, who did so much to pioneer the systematic study of organic chemical crystallography and whose names are mentioned in nearly every chapter. For the non-specialist the book provides a useful survey of current research in a complex, rapidly developing field, and also the experienced researcher in solid-state organic chemistry will find many fascinating snippets of information even in his own speciality besides an introduction to less familiar areas.

Yet I do not think the editor has succeeded in the attempt to produce "a reference work for specialists and non-specialists alike". As in many other multi-authored books, there is a sad lack of coordination among the various chapters. There seems to have been little agreement about the level of knowledge to be taken for granted in the imaginary reader; in one chapter, for example, this shadowy person knows all about the Metropolis algorithm but needs to be reminded that inversion of the cyclohexane ring interchanges axial and equatorial substituents. A work of reference needs a better index than the one provided. The end result is not much more than a collection of disconnected essays. Even visually, the book makes a disjointed impression as it was obviously prepared from camera-ready copy with a noticeable lack of agreement even about such matters as the choice of fonts, styles, literature citations, etc.

There are advantages to a type-set book. If this one had been type-set it could have benefited from the services of a copy editor, who would have corrected most of the spelling mistakes and noticed, for example, that Figures 10 and 11 of Chapter 2 are not mentioned in the text, besides other minor blemishes, such as, in one place, 10^{16} s (for 10^{-16} s). Moreover, the authors themselves would have had a second chance to correct undetected errors and mishaps at the galley proof stage. All this costs time and money, it must be assumed. The advantages of making a book from camera-ready copy would then, one might suppose, be cheapness and speed of publication. But there is no evidence that this volume was produced with any remarkable alacrity, and the price of 360 Hfl is certainly not cheap but rather seems outrageously expensive for a book produced from camera-ready copy.

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Zeolites

Synthesis of High-Silica Aluminosilicate Zeolites. By *P. A. Jacobs* and *J. A. Martens.* Elsevier, Amsterdam 1987. xvi, 390 pp., bound, Hfl 280.00.—ISBN 0-444-42814-3

For about 15 years high-silica zeolites have been attracting much interest. Meanwhile, they have become important especially as catalysts for petrochemical processes, although their application potential is not limited to this field. The variety of possible applications can be demonstrated with the best-known example of this class of compounds, the zeolite ZSM-5.

The intense research activity, especially on the synthesis of high-silica zeolites, is documented by a large number of publications, a very important fraction of which is patent literature. The great variety of zeolites makes it difficult, even for the expert, to keep up with the literature. Who, for instance, is familiar with the classification of the zeolite ZETA-1?

Therefore, it was time for a comprehensive account, such as the one *P. A. Jacobs* and *J. A. Martens* now present as volume 33 of the series "Studies in Surface Science and Catalysis". The authors restrict their topic to zeolites which can be synthesized directly as high-silica zeolites, and which have potential uses as shape-selective catalysts. They exclude zeolites that can be obtained by isomorphic replacement of aluminum lattice atoms by other elements. There may be some controversy about this restrictive interpretation of the term "high-silica zeolites", but not about the great usefulness of this monograph, in spite of the mentioned limitations.

The first part ("experimental", 40 pages) gives detailed and tested recipes for the preparation of 14 high-silica zeolites. The resulting materials are characterized by X-ray diffraction, electron microscopy, and IR spectroscopy. These instructions will be welcomed, and not only by newcomers.

The much larger second part of the book is devoted to zeolites having the structures MFI (ZSM-5), MEL (ZSM-11), TON, MTT, MTW, and FER (ferrierite). In addition