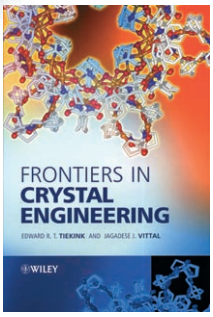
Frontiers in Crystal Engineering



Edited by *Edward R. T. Tiekink* and *Jagadese Vittal*. John Wiley & Sons, Hoboken 2006. 346 pp., hardcover € 169.00.—ISBN 0-470-02258-2

The term "crystal engineering" was coined as long ago as the 1950s, and was defined by G. R. Desiraju in 1989 as "the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties".[1] As it turns out, and as one also finds on reading this book, there are fundamentally different views about what is meant by the "design" of crystal structures or solid-state compounds: whereas many of the authors describe targeted synthesis and design of crystal structures, others confirm that the results are usually based on the principles of "trial and error" or "mix and hope" (p. 268). Whether it is actually possible to apply "design" in chemical (solid-state) synthesis was recently called into question in an essay by M. Jansen and J. C. Schön.[2]

The book *Frontiers in Crystal Engineering* now tries to show where the frontiers actually are, in other words, to identify the limitations that govern the extent to which one can rationally design and control the packing in the crystal, which certainly affects the properties of the material. In 12 articles, 24 authors—including the names of internationally known scientists such as Desiraju, Kitagawa, and Zaworotko,[3] to mention only a few—report research on specific compounds in which the crystal structures are determined not only by covalent and coordinative bonding but also by additional, often weak, interactions.

The structures described include such different types as zwitterionic cobaltacene derivatives prepared under mechanochemical synthetic conditions, pharmaceutical cocrystalline compounds (which often have better crystallization properties than the corresponding pure compounds), compounds in which molecules of the starting materials are fixed by hydrogen bonds in positions that facilitate photochemical cycloadditions, networks with mutual interpenetration, and chiral networks with amino acid derivatives as bridging ligands. Using these as examples, the authors describe in detail how even weak interactions can have a cumulative effect in determining the crystal structure. As well as hydrogen bonding and interactions between aromatic ring systems ("π stacking"), the effects of C–H···π interactions and secondary interactions between atoms of heavy Main Group elements are analyzed. Bonding interactions of halogen atoms in organic molecules and of carbonyl groups with aromatic π systems are treated only briefly and without giving numerical data (pp. 102, 309), even though it is now accepted that significant attractive forces also occur between atoms with negative partial charge and the positive region of an electron-deficient aromatic π system. Such noncovalent bonds are, of course, weak; nevertheless, careful analyses of the crystal structures confirm that the sum of their actions can have a significant influence on the structure, which was often not recognized in the past, or at least not taken into account. Even intermolecular Br···Br or Br···N interactions (p. 99), which involve interatomic distances in the van der Waals range (3.6–4.0 Å and 3.6 Å, respectively) are considered as possibly influencing structure (while in crystalline Br_2, intermolecular Br···Br distances as short as 3.31 Å occur). In such cases, there is clearly a difficulty in unambiguously identifying effects caused by very weak bonding interactions and distinguishing them from random variations in arrangement. However, one can have doubts about the significance of metallophilic interactions between d^{10} Cu^+ ions with Cu···Cu distances of 2.7–3.0 Å (p. 248).

The last chapter discusses the proposition that, in addition to supramolecular interactions, kinetic effects also play a role in the formation of the three-dimensional packing arrangement in the crystal. Since there are chemical equilibria in the solution, this often leads to the formation of compounds and structures that crystallize most easily or rapidly under the existing crystallization conditions.

The book deals with a highly topical subject, as is shown by the current rapid increase in the numbers of publications and research projects in the area of polymeric coordination compounds and metalloorganic frameworks (MOFs). As a consequence of their lattice structures, which form according to the (more or less controllable) principles described in the book, these materials have interesting present or potential applications in the areas of adsorption, storage of gases, sensors, and catalysis.

The articles contain a few small errors and inaccuracies. The structures that are discussed are illustrated by many helpful figures that explain the principles involved. Although these are (unfortunately) only printed in black-and-white, they mainly succeed in clearly showing even complicated structures (such as S. R. Batten's interprenetating networks) and making them understandable. However, in some of the chapters a few of the figures suffer from poor resolution (pp. 34, 40) or fuzziness (p. 85), or show strange hatching patterns (p. 113). If authors' names had been included in the list of contents, it would have made it easier to search for particular topics and types of compounds.

Where are the present frontiers of crystal engineering? In special cases it is possible to plan additional noncovalent interactions, for example, where dehydration reactions can occur in the solid state, or where the structure of ligands can be adjusted precisely so that donor and acceptor functions lead to hydrogen bonding. On the other hand, in most cases the existence of many different

contributions to the total bonding system in the crystal makes it still impossible to predict the structure that will result.

Frontiers in Crystal Engineering offers an interesting collection of individual reports about selected, mostly highly specialized, topics in the field, without claiming to cover all its aspects. Up to now, and for the immediately foreseeable future, it remains easier to understand the principles of crystal engineering for compounds that have been structurally characterized than to "design" crystal structures of complex compounds. Therefore, *Frontiers in Crystal Engineering* cannot provide a patent recipe for the targeted synthesis and crystallization of functional networks, but instead explains the many different influences on the crystal structures that are formed, and shows the importance of a thorough and sound interpretation of structural data.

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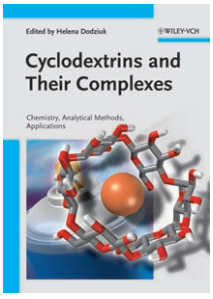
[1] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.
[2] M. Jansen, J. C. Schön, *Angew. Chem.* **2006**, *118*, 3484; *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 3406.
[3] *Crystal Engineering: The Design and Application of Functional Solids*, (Eds.: K. R. Seddon, M. J. Zaworotko), Kluwer Academic Publishers, Dordrecht, **1996**.

Cyclodextrins and Their Complexes



Chemistry, Analytical Methods, Applications. Edited by *Helena Dodziuk*. Wiley-VCH, Weinheim 2006. 489 pp., hardcover € 149.00.—ISBN 978-3-527-31280-1

The field of cyclodextrins has made tremendous advances in recent years. 10625 articles on cyclodextrins were published between 2001 and 2006 (data from Cyclolab website, http://www.cyclolab.hu) in various areas ranging from organic chemistry to pharmaceutical and analytical applications. The field is not only very large but also highly diversified and is expanding rapidly. Indeed, as claimed by the editor of this book, since 2005 more than 5.6 articles per day have been published on cyclodextrins. *Cyclodextrins and their Complexes* offers a fresh look, providing a broad survey of the field with numerous references. It can serve both as a textbook for scientists newly interested in the cyclodextrins field and as an advanced monograph.

This work is organized in 16 chapters with 36 contributing authors, and contains 489 pages. It assumes a basic knowledge of advances in cyclodextrins research. Most chapters are highly referenced to original research papers and review articles for further reading. However, the balance between different aspects does not accurately reflect their relative importance. The characterization of cyclodextrins and their inclusion complexes by different spectroscopic and physical-chemical methods is very well described and discussed. This part represents almost half of the book. The various applications of cyclodextrins and their derivatives in industry are also well covered. On the other hand, the chemistry of modified cyclodextrins, as well as separations by cyclodextrins, would have benefited from a more in-depth treatment. Various special aspects of cyclodextrins, such as polymers, catalysis, rotaxanes, and large-ring cyclodextrins, are covered in other chapters.

The introduction to the subject of cyclodextrins and modified cyclodextrins provides useful structural data to enable the reader to understand the properties and applications of these molecules. It is complemented by Chapter 13, which describes large-ring cyclodextrins, and their synthesis, properties, and applications.

The second chapter deals with the organic chemistry of cyclodextrins and modified cyclodextrins. The very useful selective mono-modification of cyclodextrins is well presented, followed by per-modification. Examples of modification at other positions are also described. The grafting of various moieties onto cyclodextrins (charged junctions, saccharides, peptides, metal ligands) is discussed with examples. However, amphiphilic derivatives are not discussed anywhere in this chapter, which is regrettable since these derivatives lead to many, often exciting, applications. Enzymatic modifications of cyclodextrins, which have been studied very thoroughly and are widely used, are given only a brief paragraph. The organic chemistry of cyclodextrins, a very large topic, is summarized here in a dense 30 pages, and is one of the less well treated areas of this book.

Chapters 3 and 12 focus on supramolecular polymers and rotaxanes, respectively. Chapter 3 explains, with examples, how polymers are formed when a hydrophobic moiety of a modified cyclodextrin becomes included in the cavity of another cyclodextrin. Analytical data are added to provide proof of their polymeric structures. In Chapter 12, rotaxanes and pseudorotaxanes, as well as catenanes, are described, but only a few structures and applications are presented. Nevertheless, these two chapters provide a well-written overview of the field.

Reactions catalyzed by cyclodextrins (covalent and noncovalent catalysis, acid–base catalysis) are explained well in Chapter 4, and examples are provided to illustrate each case. This is a short but useful section, clearly written.

One of the most important applications of cyclodextrins is their use in chromatographic separation, and particularly that of enantiomers. Chapters 5 and 6 briefly summarize chiral recognition by cyclodextrins, and its applications to enantiomer separation. This part starts by discussing characterization of the complexes by GC and LC, and leads into enantiomer separation by GC, LC, supercritical fluid chromatography, and capillary electrophoresis. The first three of these are treated briefly, whereas the latter one is well documented with the help of some examples. The chiral selectivity of α-, β-, and γ-cyclodextrins towards a mixture of enantiomers is explained as being due to differences in complexation. Unfortunately, the lack of a chapter devoted specifically to relevant advances in the chromatography of cyclodextrins and

