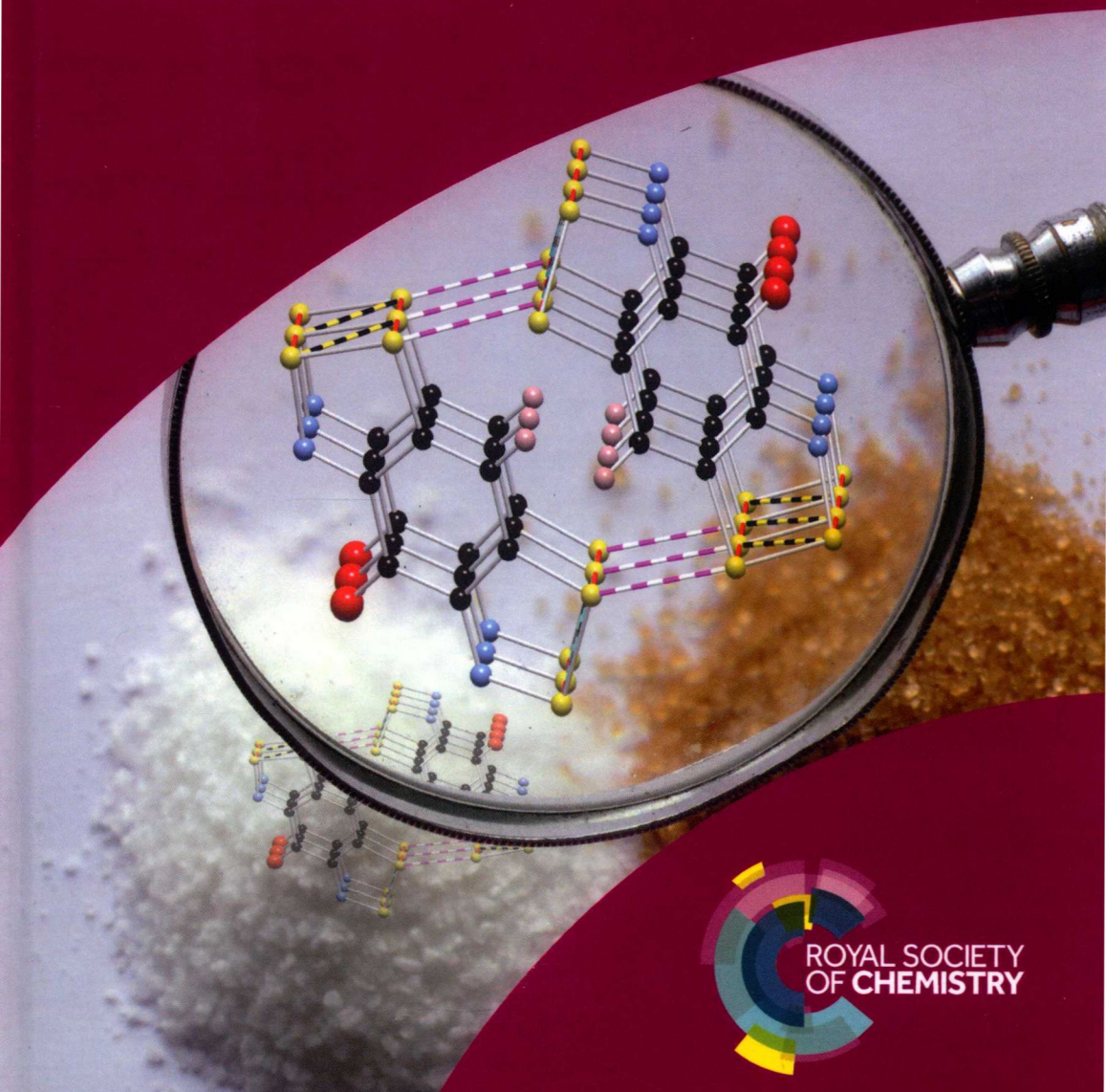
Intermolecular Interactions in Crystals

Fundamentals of Crystal Engineering

Edited by Juan J. Novoa



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The field of crystal engineering concerns the design and synthesis of molecular crystals with desired properties. This requires an in-depth understanding of the intermolecular interactions within crystal structures. This new book brings together the latest information and theories about intermolecular bonding, providing an introductory text for graduates.

The book is divided into three parts. The first part covers the nature, physical meaning and methods for identification and analysis of intermolecular bonds. The second part part describes representative examples of the most relevant types of intermolecular bonds currently known to occur in molecular crystals. The third part describes how cooperativity affects the properties of intermolecular bonds, how they can be identified in crystals and how the information on intermolecular interactions and bonds can be used to design new molecular crystals. Each chapter is written by specialists in the topic being covered.

This comprehensive textbook will provide a valuable resource for all students and researchers in the field of crystallography, materials science and supramolecular chemistry.

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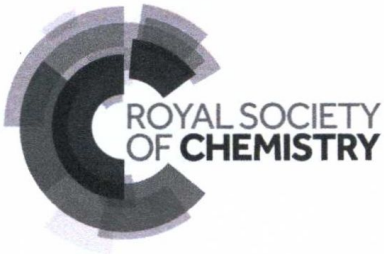
Juan J. Novoa

University of Barcelona, Spain
Email: juan.novoa@ub.edu



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Preface

The aim of this book is to present the current knowledge on the intermolecular interactions found in crystals, including the latest discoveries. But in doing so, we have tried to present the information in a pedagogical form, in order to make its contents understandable for non-specialists. We have tried to make it a textbook for Masters and PhD students who require an in-depth knowledge of intermolecular interactions, such as those working in Crystal Engineering or in the broader area of Supramolecular Chemistry. We have also tried to make it a reference book for researchers in these two fields who want a reference book containing the state-of-the-art knowledge on intermolecular interactions.

The book contains 20 chapters written by active researchers in the field, in some cases, the originators of important ideas in the field. These chapters cover from fundamental studies on intermolecular interactions, up to special properties and techniques required by their interconnected existence in crystals. A third area is devoted to a review of the state-of-the-art knowledge of the most common types of intermolecular interactions encountered in crystalline molecular solids. Chapters have been grouped into one of these three areas, according to their contents. Within each area, theoretical and experimental chapters have been mixed, ordered in a most-fundamental-first sequence. Although not as complete as originally planned, due to reasons external to this editor, the book covers the major topics on intermolecular interactions, the most common methods and techniques employed in their study, and a description of their most relevant properties, for intermolecular interactions found in molecular crystals with properties of technological interest (such as magnetic, or

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conducting, or superconducting properties, to name only the most common).

Intermolecular interactions are the interactions produced between stable molecules oriented in regions of space where spontaneously they do not form new chemical bonds. This definition classifies as intermolecular those produced between two stable radicals at all distances and relative orientations, as in the interaction between two oxygen molecules. It also identifies as intermolecular the interaction between two $TCNE^{\bullet -}$ radical-anions (TCNE = tetracyanoethylene) around 3 Å where $TCNE^{\bullet -}$ neither dissociates nor forms a C–C bond between the radical anions. This is the metastable region of $TCNE^{\bullet -}$ radicals, where the potential energy curve as a function of the shortest separation between the radical anions presents a metastable minimum, a large barrier for the formation of a covalently bonded σ-$[TCNE]_2^{2-}$ molecule, and a smaller barrier towards dissociation (both barriers are overcome in some cases, but not in others). Notice that this definition does not include as intermolecular the interaction between two $CH_3^{\bullet}$ radicals, even if at long distance these radicals exist, because their potential energy curve shows a minimum for the spontaneous formation of ethane; that is, is the curve for the formation of a C–C intramolecular bond.

From a more practical point of view, intermolecular interactions, and particularly intermolecular bonds (loosely considered by this editor as the dominant energetically stabilizing interactions found in supramolecular aggregates), play an essential role in rationalizing in simple terms the structure and relative stability of supramolecular aggregates, not to mention the speed of their transformation into other species. It was said more than 25 years ago that "supramolecular aggregates are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond". In another words, despite their different electronic structures, intermolecular bonds play in supramolecular aggregates the same role as chemical bonds play in molecules. The main difference is in the electronic structure of intra- and intermolecular bonds, which explains the different orders of magnitude of the optimum distance (about 2–3 Å) and interaction energy (in most cases less than 10 kcal mol^{-1}). Improving our control of the outcome of crystallization will only be possible after improving our control of the mechanism by which intermolecular interactions compete.

Intermolecular interactions are also key in determining the structure of the outcome of crystallization and the relative stability against other polymorphic forms. They also determine the speed of the thermodynamically allowed polymorphic transformations. And the structure of the crystal determines other physical properties of the

crystal. For instance, it determines the bulk ferromagnetic properties shown by the β-phase crystal of the *p*-nitrophenyl nitronyl nitroxide radical, a property absent in other polymorphs. It can be shown that the observed experimental structure of a crystal corresponds to the geometry of one of the minima on the free energy surface of the crystal (not always the most stable one), and that its relative stability is the energy difference between this minimum and others, while the speed of the polymorphic transformation depends on the height of the transition state connecting the two minima involved. Overall, energy, the free energy of the system, is the language chosen by nature to write the information concerning the main properties of a crystal. For this reason, the use of the term "intermolecular force" as equivalent to "intermolecular interactions" is misleading, as forces are different to energy. For similar reasons, we advocate the use of the term "bonds" (in its energetic interpretation, see above) or others with energetic meaning, rather than alternative concepts where the energetic meaning is lost (as in the term "bridges", based on geometrical concepts). After all, if one has to talk about the energetic stability of a system as the sum of the stability of all its parts (as implied in the use of the Scientific Method), it is going to be more convenient to add components that have an energetic meaning.

Intermolecular interactions are sometimes called non-covalent interactions, as an equivalent name. This is equivalent to saying that covalent bonds are the only type of intramolecular bonds, and the IUPAC Gold Book contemplates a few other intramolecular bonds, among them ionic bonds (one can consider dative bonds, and dipolar bonds, considered to be coordination bonds, therefore to be one type of covalent bond), and also electron-deficient bonds (a two-electron three-center bond). Therefore, we believe that the terms intermolecular bond and intermolecular interaction are better defined. Finally, the term "intermolecular" was that used by the scientist who started the research on the interaction between molecules at the dawn of the 20th Century.

The fast progress in the knowledge on intermolecular interactions that has taken place during the last two decades makes a book collecting this progress very valuable; particularly when each chapter has been written by a specialist caring about delivering all essential information, in a pedagogical form, to the non-specialist. Here are the results. I hope that you like them.

Juan J. Novoa
Professor of Physical Chemistry
University of Barcelona

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