PHYSICAL CHEMISTRY

A Series of Monographs

Molecular Crystals and Molecules

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Preface

This book deals with some of the problems of molecular crystallography, and certain aspects of molecular structure. At first sight the selection of material may appear somewhat unsystematic. True, the treatment of molecular crystals is restricted to the problems of lattice structure, dynamics, and thermodynamics, and molecular structure itself is discussed only from the viewpoint of molecular conformation.

However, the material in the book has by no means been selected at random; if anything, it is somewhat one-sided. This book is neither a textbook nor a manual. It contains mainly results obtained by the author and this makes unavoidable some degree of imbalance in the treatment of the subject.

The general idea that brings together the entire range of problems discussed in the book is the atom–atom potential model. An analysis of the electronic structure of molecules is not fundamental to the purposes of this book. On the contrary, a much more rational approach is to consider the atoms composing a molecule as the basic building blocks of our model. The energy of the relationships involved are thus confined to atomic interactions only.

Thus, we deal with a certain type of model which is undoubtedly approximate but which, nevertheless, rather successfully deals with the problems of the structures and thermodynamic properties of molecular crystals, and also those concerning the conformations of small and large molecules. The model in question is that of noncovalent interactions, and it is precisely these interactions that underlie the problems treated in the book.

The author hopes that the two parts of the book which deal, respectively, with crystals and molecules are sufficiently self-consistent. Both parts deal with organic substances; inorganic molecular crystals occur but rarely, and, conversely, organic crystals, with the exception of organic salts, always belong to the class of molecular crystals. The physics of molecular crystals is essentially organic crystal physics.

Preface

Until now textbooks on solid-state physics have devoted but a few pages to molecular crystals and, as a rule, have not gone beyond the properties of nitrogen, oxygen, carbon oxide, and other similar crystals. This approach distorts the real situation. Crystals composed of small molecules are by no means representative of the class. The "common salt" of molecular crystal physics is the naphthalene crystal.

For a long time solid organic substances have been ignored as materials. Therefore, several major problems of molecular crystal physics are still awaiting their investigator. The thermal and mechanical properties of crystals, their molecular composition, and other problems treated from the point of view that organic matter is a solid have, until recently, attracted the attention of very few physicists.

As to chemists, they usually ask merely for information on the structure of a molecule, since this information is relevant to chemical reactions. This kind of pressure on the part of chemists has resulted in an unbalanced development of our subject: organic crystal structures have been studied mostly because the only way to establish the structures of complex molecules is to examine them in the crystalline state.

The lack of active interest in the structures and properties of organic crystals as such, and the very few publications which seek to correlate the arrangement of molecules in a crystal with the crystal's properties, may be excused as long as organic substances are regarded as dissolved chemical reagents. In recent years, however, researchers have begun to take a closer look at problems associated with solid organic substances. Synthetic polymeric compounds have come to the fore, peculiar features of solid-state reactions have been observed and, finally, and this is perhaps the most important development, it is becoming obvious that numerous biological processes are most intimately linked with the mutual arrangement of organic molecules and their parts in protein and nucleic acid crystals. Molecular crystal physics will undoubtedly become the basis for research along these lines.

The author began studying the regularities in the mutual orientations of molecules in crystals 25 years ago. At the first stage of these studies, a simple geometrical model was proposed for the interpretation of crystal structures. It was found that if a molecule is bounded by van der Waals' radii and is thus "shaped," a crystal can be represented as a close packing of solid molecules. This geometrical model—a first approximation model—and its potential use for predicting the structures of crystals are dealt with in the author's book "Organic Chemical Crystallography" (Akademizdat, 1955; Consultants Bureau, New York, 1961).

The principle of close packing of molecules in crystals naturally suggests the idea of describing the energy of molecular interactions as the sum of the interactions of the component atoms. This idea gave rise to a new improved model which can be used to predict a crystal's structure to a greater degree of accuracy, and also to estimate quantitatively the thermodynamic properties of a crystalline compound.

The use of the atom–atom potential scheme does not, however, fully define the model of a crystal. Lattice dynamics can be described in different ways. We have chosen a quasi-harmonic model. Simple models are more approximate, but then they are more general. For the purpose of our research, it is probably more important to be able to predict the structure and properties (even allowing the predictions to be not quite accurate), than to seek ideal agreement between theory and experiment by treating the subject in terms of special-purpose models. In my opinion it is more advantageous to have a rough theory applicable to most molecular crystals than a fine theory useful only for crystals of benzene or urotropin.

Our studies in the field of intermolecular interactions, i.e., in the sphere of the structures and properties of organic crystals, have been developing concurrently with our research on molecular conformations since we treated them as different applications of the same model.

Historically, studies of conformations have received considerably greater attention than have studies of the structures and properties of organic crystals. Therefore, the part of the book devoted to conformations of molecules is essentially a review of the results published in the literature. It is easy to understand the reasons for the spectacular progress of conformational research which has used the atom–atom potential method as a reliable starting point. While experimental structural investigations of small molecules are relatively easy to perform, the situation is just the opposite with macromolecules. It is often impossible to determine the conformation of a molecule experimentally; in other cases, such as, for example, protein molecules, the experiment becomes extremely complicated. Therefore, attempts to determine a priori the molecular conformations should be encouraged. It is particularly important to apply conformational calculations to biological substances since the results that may be expected justify the effort. Science takes an interest in all biopolymers since each such molecules has a part in the life cycle.

This book has been written with the assistance of my younger colleagues. I am especially grateful to R. M. Myasnikova for her valuable cooperation in writing the first chapter. The part of the book dealing with molecular conformations has been written by V. G. Dashevsky. In other chapters I have used material from the publications, reviews, and theses of K. V. Mirskaya, A. P. Ryzhenkov, B. V. Koreshkov, V. F. Teslenko, Yu. T. Struchkov, R. L. Avoyan, E. Mukhtarov, Yu. V. Mnyukh, E. I. Fedin, and G. K. Semin. I. E. Kozlova has been a great help with the calculations and in preparing the manuscript for publication.

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Chapter I

Structure of Crystals

A. Close-Packing Principle†

1. GEOMETRICAL MODEL OF A MOLECULAR CRYSTAL

The distinguishing geometrical peculiarity of a molecular crystal is self-evident. If it is possible to single out groups of atoms in a crystal in which the distance from each atom of the group to at least one other atom of the same group is significantly smaller than the distances to the adjacent atoms of other groups, the crystal is said to be molecular. Thus, for example, in hydrocarbon crystals spacings between H atoms in different molecules are not less than 2.2–2.4 Å, whereas distances from these atoms to chemically bonded C or N atoms are about 1 Å. Intramolecular spacings between bonded C atoms are 1.2–1.5 Å, while the atoms of different molecules are at least 3.3 Å apart. The order of difference between intramolecular and intermolecular distances in crystals composed of diatomic O and N molecules is about the same.

Organic molecules containing hydroxyl (OH) and amine (NH_2) groups

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† For a detailed description of the principle of close packing of molecules and illustration of this principle on a large body of material, see Ref. [1].

display a tendency to form so-called hydrogen bonds. In a hydrogen-bonded structure, two O atoms, or one O atom and one N atom, or two N atoms of adjacent molecules are often so arranged that the proton is situated approximately on a straight line drawn between these two atoms. In this case, the difference between the intramolecular and intermolecular distances is somewhat smaller: The proton positioned between two O atoms lies 1 Å from the O atom of the same molecule, and 1.6–1.8 Å from that of a different molecule. But in this case, too, the molecule may be quite unambiguously defined as a group of closely bonded atoms.

When speaking about molecular crystals, we shall mean mainly crystals of organic substances. Only relatively few inorganic compounds, such as nitrogen or oxygen crystals, or molecules built from nitrogen and phosphorous atoms, or carbonyls or complex compounds of certain metals, form molecular crystals. There are inorganic substances which may be classified as molecular crystals only formally, since their intramolecular and intermolecular distances do not differ by more than 5–10%. As to organic substances, they are all molecular crystals, with the obvious exception of organic salts. The class of organic compounds is infinite, and, therefore, the physics of molecular crystals is primarily the physics of organic crystals.

The mutual orientation of molecules in a crystal is conditioned by the shortest distances between the atoms of adjacent molecules. In most instances the packing of the molecules is determined by the interactions between H atoms, or the interaction of H atoms with atoms of other elements.

In early X-ray analyses, the coordinates of the H atoms were not determined, and the summary tables which presented the results listed only the distances between the C atoms of adjacent molecules, which is completely insufficient for determining the type of packing.

Recent papers report the coordinates of H atoms obtained by computing the smallest R-factor by the least-squares method (see Chapter IV). These data should be treated with caution. As a rule, the values of the valence bond lengths of a H atom derived by X-ray diffraction analysis are considerably underestimated. Apart from such systematic errors, X-ray analysis is also often plagued with large random errors. In determining proton coordinates, particular attention should be given to neutron diffraction studies. The nuclear magnetic resonance (NMR) technique also offers many potentialities so far largely unexplored. However, one need not necessarily resort to experimental analysis, because the a priori localization of H atoms does not involve any particular difficulties.

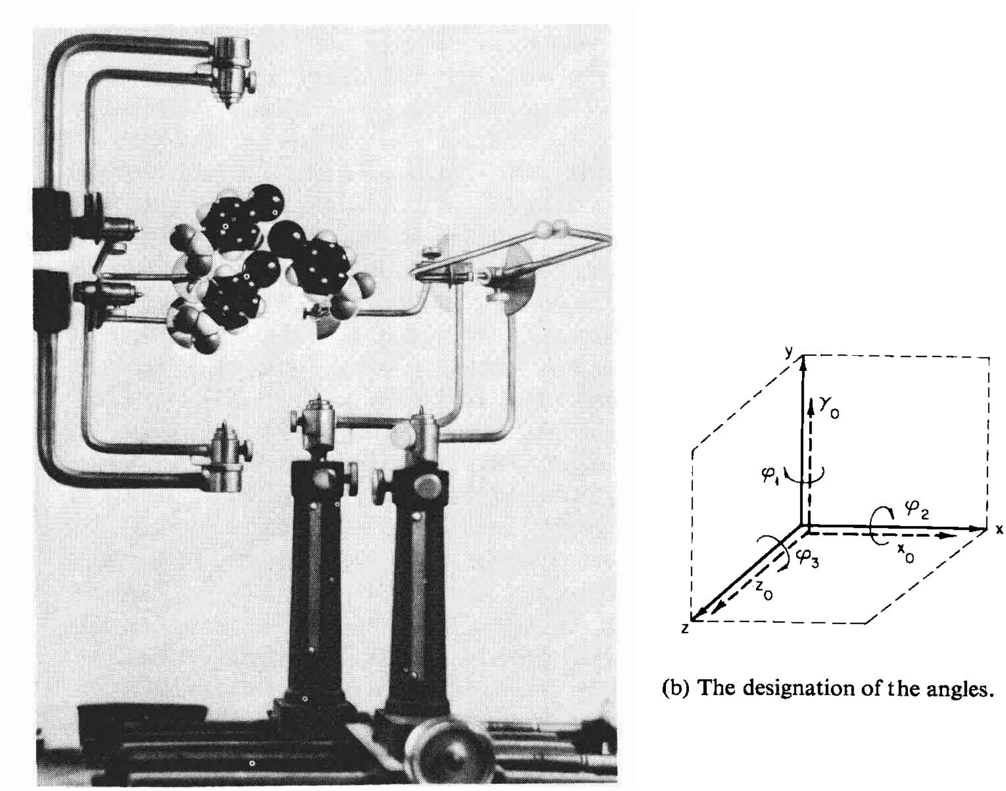
Studies of gas molecules have furnished a great body of information on the lengths of C–H, O–H, etc. bonds; this enables the correct prediction of the bond lengths in a majority of the compounds that have not yet been studied. Data obtained from gas molecule experiments can, with a high degree of certainty, be applied to the crystalline state in molecular crystal studies. The crystalline field has no effect whatsoever on bond lengths and influences but slightly the valence angles. The only material effect of the crystalline field is that it changes the conformation of the molecule whenever the possibility of rotation about single bonds presents itself. The effect of the crystalline field will be discussed in Section II.11, therefore, I will restrict myself to pointing out that this effect does not handicap the a priori determination of the coordinates of H atoms.

After the positions of all the atoms in a molecule have been determined by appropriate methods, we can pass on to the analysis of the molecular packing. The fundamental result of such an analysis is that the shortest distances between the atoms of the same chemical elements vary quite insignificantly; this fact graphically demonstrates that a crystal can be, to a fair approximation, described by a model, which may be called a geometrical model or a first-approximation model. The geometrical model is constructed as follows: We start by analyzing spacings between the atoms of neighboring molecules to find the shortest interatomic distances for all molecular pairs (e.g., for molecules related by translations along the *a* axis, the *c* axis, and by the symmetry operations of the twofold screw axis for the group $P2_1/a$). These are "determining contacts." Then, we select the values of the intermolecular atomic radii whose sums show the closest agreement with experimental data. These intermolecular radii are the mean radii for a given structure. With the aid of these radii, a volumetric model of the molecule can be constructed. It is obvious that since the sums of the mean intermolecular radii differ somewhat from the actual distances, the model will constitute a packing in which some atom pairs overlap slightly, while other pairs do not touch each other. It will always be possible to produce ideal packing (i.e., a packing in which no molecules are suspended in empty space and none overlap) by minor translational and rotational shifts of the molecules.

The difference between the ideal and actual packings is usually very small. For example, for a naphthalene crystal, the ideal packing with coordination number 12 in an experimentally observed cell at room temperature is obtained if we take a radius of 1.76 Å for carbon, and a radius of 1.18 Å for hydrogen. The orientations of the molecules in the ideal and the experimentally observed structures do not differ by more than 2–3°. A fact essential for the technique of X-ray diffraction analysis is that the ideal packing derived from strictly geometrical considerations furnishes a structural model that can be employed for the initial calculation of structure amplitudes.

The mean values of the intermolecular radii vary, though within narrow limits, from structure to structure.

Consider several typical examples illustrating the validity of the geometrical model, in other words, the possibility of representing an organic crystal structure by close packing of molecules connected by intermolecular radii.



(a) The structure seeker apparatus.

(b) The designation of the angles.

Fig. 1.

(The projections of one molecule are inserted into the hollows of others.) To make such a representation more descriptive, it is desirable to have both volumetric models of molecules and a structure seeker, which is an instrument enabling the determination of the various types of molecular stacking in a unit cell of a given size. Figure 1 illustrates this operational technique. In certain cases the nature of the molecular packing can be clearly seen from appropriate figures. For example, Fig. 2 shows the *xyO* projection of the structure of 1,5-dinitronaphthalene [2]. The structure is characterized by a rather planar unit cell: $a = 7.76$, $b = 16.32$, $c = 3.70$ Å, $\beta = 101° 48'$, space group $P2_1/a$, $Z = 2$. The plane of the naphthalene nucleus of the molecule practically coincides with the *ab* plane of the unit cell. The N atoms lie in the same plane, while the O atoms project from the plane alternately upward and downward by about 0.79 Å. The planes of the nitro groups make an angle of 49° with the plane of the aromatic ring, and the molecule retains its centrosymmetry. If we position the hydrogen atoms in each molecule and connect

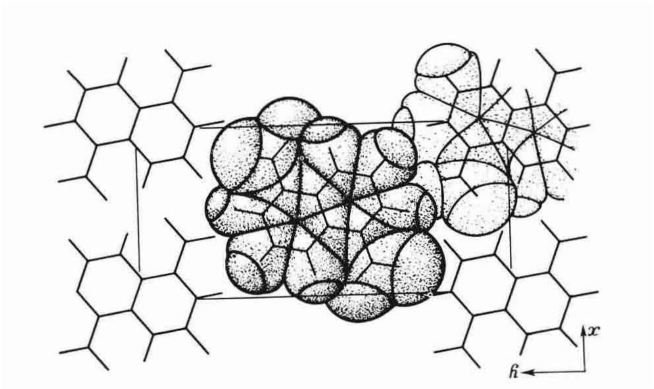


Fig. 2. Projection xyO of the 1,5-dinitronaphthalene structure.

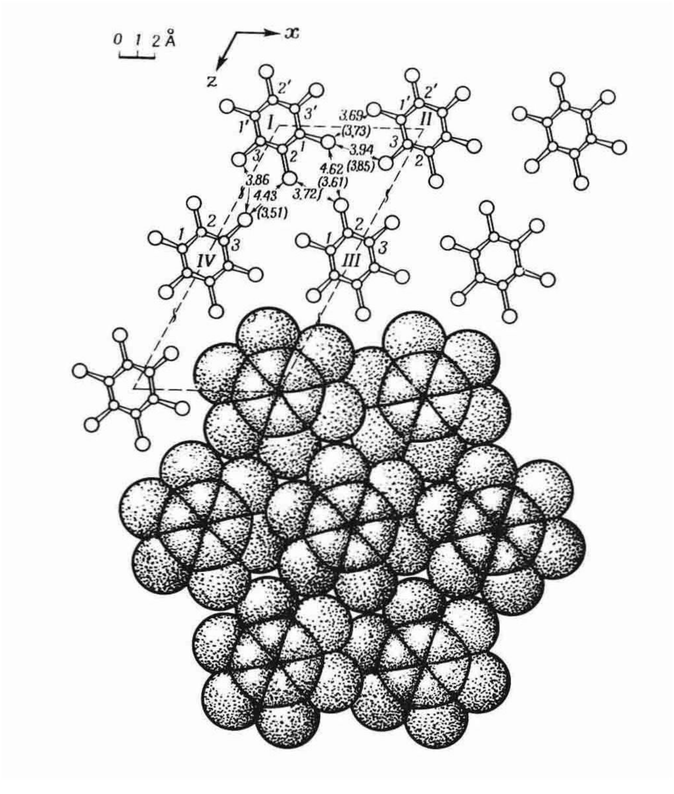


Fig. 3. Projection xOz of hexachlorobenzene structure.

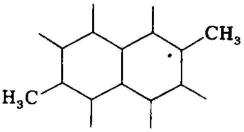
all the molecules by appropriate intermolecular radii, a peculiar feature of the molecular packing becomes obvious: The "projections" of one molecule get into the "hollows" of adjacent molecules, so that the molecules are closely packed with the minimum voids between them possible for the given cell.

Another simple example demonstrating the projection-to-hollow principle is the structure of hexachlorobenzene [3] (unit cell: $a = 8.08$, $b = 3.87$, $c = 16.65$ Å, $\beta = 117.0°$, space group $P2_1/c$, $Z = 2$). The plane of the hexachlorobenzene molecule is inclined to the plane xOz at a small angle (approximately 22°), therefore, molecular packing can be seen well in the projection on the *ac* face (Fig. 3).

It should be emphasized once again that, as is evidenced by the analysis of a large number of molecular structures, molecular packing on the dovetail principle is a general rule of organic chemical crystallography. Because of such packing, organic structures usually have a high coordination number, i.e., a large number of contacting molecules. Due to the irregular shape of the molecules, this circumstance is not evident and must be proved (see Section I.9). One can also refer to the experiment which shows that the coordination number 12 is the most common for organic structures (the same as for the closest spherical packing). Structures with 10 or 14 contacting molecules are less frequent.

This "model" approach to the principles of structure of organic crystals permitted the author to develop 25 years ago the geometrical-analysis technique that made possible (at any rate for a cell of known dimensions) the a priori determination of the structure of a molecular crystal, i.e., before making direct X-ray diffraction study.

The essence of the geometrical analysis will be made clear from the description of the structure of 2,6-dimethylnaphthalene, which was obtained using this method [4]. 2,6-Dimethylnaphthalene crystals are orthorhombic; the parameters of the units cell are: $a = 7.54$, $b = 6.07$, $c = 20.20$ Å, space group $V_h^{15} = Pbca$, $Z = 4$. Thus, the 2,6-dimethylnaphthalene molecule (I) takes a centrosymmetric position in a crystal. Four models of these molecules constructed by means of approximate intermolecular radii $R_C = 1.72$ Å and $R_H = 1.2$ Å were arranged on the structure-seeker apparatus so that the distances between their centers corresponded to the unit-cell dimensions. It



(I)