Crystal Engineering

(in four lectures)

http://www.amazon.de/Crystal-Engineering-Textbook-Gautam-Desiraju/dp/9814366862/ref=sr_1_fkmr0_1?ie=UTF8&qid=1338473179&sr=8-1-fkmr0

From molecules to crystals
Why molecules?

The molecule is paramount in chemistry

Assemblies of molecules. How do molecules associate with each other. In specific ways?

Crystal engineering teaches us how to bring molecules together exactly as we want.

A crystal is a very precise and specific type of molecular assembly
# Concept of Molecularity

## Zero, One, Two and Three-dimensional Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dimensionality</th>
<th>Molecularity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0D</td>
<td>3D</td>
</tr>
<tr>
<td>Fullerene</td>
<td>0D</td>
<td>3D</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>1D</td>
<td>2D</td>
</tr>
<tr>
<td>Graphite</td>
<td>2D</td>
<td>1D</td>
</tr>
<tr>
<td>Diamond</td>
<td>3D</td>
<td>0D</td>
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Crystal
A solid form of a substance with a definite and periodic internal structure.
- an external shape made up of symmetrically arranged plane surfaces.
- gives a discrete X-ray diffraction pattern.
- atoms, ions or molecules are in some degree of order.
- a manifestation of mutual recognition.
- enthalpic factors gain over entropy.

Crystal structure
The arrangement of atoms, molecules, or ions that constitutes the internal structure of a crystal.

Crystal Engineering
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.
Topics to be covered today

X-ray Crystallography
Organic Solid State Chemistry
The Crystal as a Supramolecular Entity
Modern Crystal Engineering

Horizontal and Vertical Divisions of Chemistry
Organic Crystal Engineering
Properties of Crystals

Summary and time line
X-ray crystallography

Visualization of a crystal as a periodic array

**Hexachlorobenzene** and **Urotropin** were the earliest organic crystal structures to be determined.

One of the fundamental questions of crystal engineering is

**Given the molecular structure of a compound, what is its crystal structure?**
Organic solid state chemistry

Gerhard M. J. Schmidt (1919–1971)
The crystal as a supramolecular entity

Supramolecular chemistry
The chemistry of molecular assemblies, intermolecular bonds, non-covalent interactions and hydrogen bonds.

signifies that which is beyond the molecule
concerned with strategies for the controlled organization of multiple components into complex matter

In the context of crystal engineering, crystals are ordered supramolecular systems, and crystallization is an impressive display of periodic molecular assembly.
How crystal engineering is set up

It is a horizontal discipline

What do we do?
Make crystals by using interactions (lecture 2)

How do we do it?
Synthetic strategies (lecture 3)

Why do we do it?
Properties (lecture 4)
Crystal Engineering Time Line

1921: W. H. Bragg relates the crystal structures of naphthalene and anthracene.

1935: J. D. Bernal advocates the study of groups of crystal structures.

1948: H. M. Powell describes the β-hydroquinone structure as a network.

1955: R. Pepinsky uses the term crystal engineering, the first time anyone does so.


1971: G. M. J. Schmidt formally introduces the term crystal engineering in his paper in Pure and Applied Chemistry.
Crystal Engineering Time Line


1990: **M. C. Etter** identifies the hydrogen bond as an important design element in crystal construction.

1991: **J. D. Dunitz** terms the crystal as a *supramolecule par excellence* in his paper.

1995: The relationship between crystal engineering and organic synthesis is highlighted in a review by G. R. Desiraju.


2011: The first textbook devoted exclusively to crystal engineering is published (is co-authored by **G. R. Desiraju**, **J. J. Vittal** and **A. Ramanan**).
Next lecture - Intermolecular interactions

How crystals are stabilized

The crystal structure of a molecule
A free energy minimum that results from a balance of attractive and repulsive forces.

Intermolecular interactions in molecules are of two types

- Isotropic interactions – short range
- Anisotropic interactions – long range

Electrostatic interactions
- Ionic interactions (salts)
- Strong and weak hydrogen bonds
  - (O–H⋯O, C–H⋯O)
- Interactions between heteroatoms
  - (halogen⋯halogen)