Molecular interactions and packing of molecules

Molecular Interactions in HCN Crystals

This dipolar molecule ($\mu = 1{\cdot}174$) has two crystalline modifications, both consisting of parallel linear H-bonded chains ---H—C≡N---H—C≡N---H—C≡N--- with a transition between the two forms at 170 K resulting in slightly different chain packing (Figure 6-28). The crystal internal energy

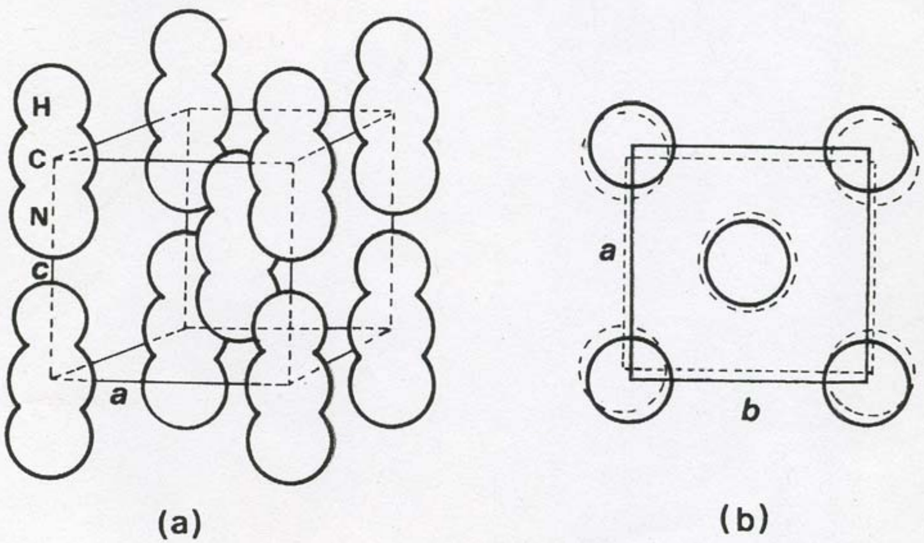
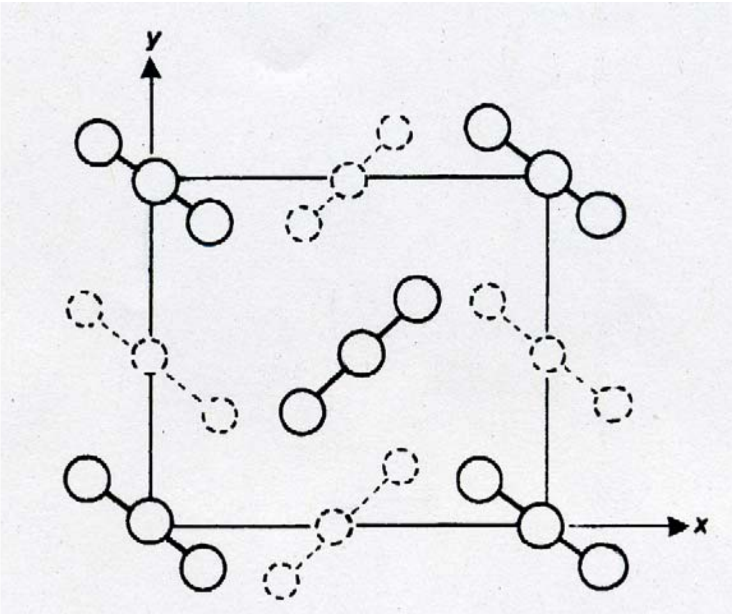


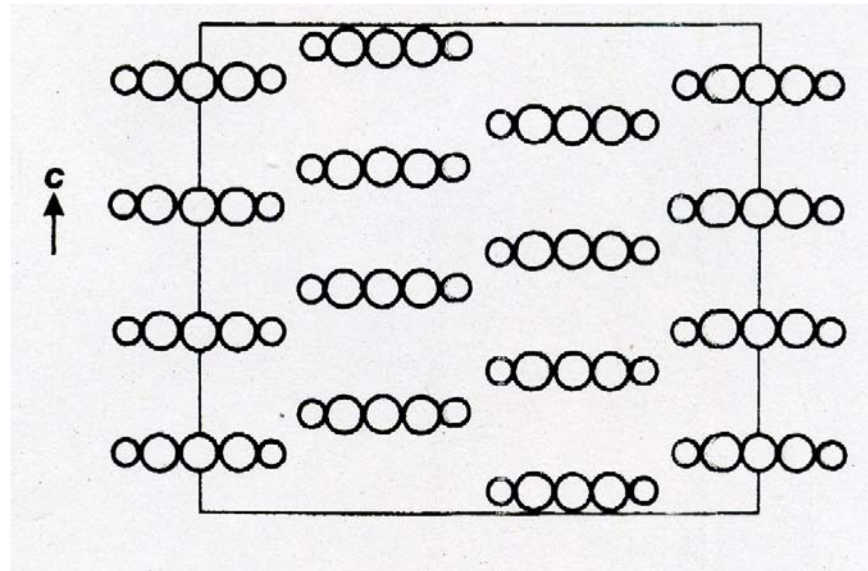
Figure 6-28 The structures of crystalline HCN. (a) The chains of H-bonded molecules. (b) The slightly different modes of packing in the high (—) and low (---) temperature phases. (Rae (1969))

Packing/arrangement of H-bonded polar molecules of HCN

Molecular interactions and packing of molecules



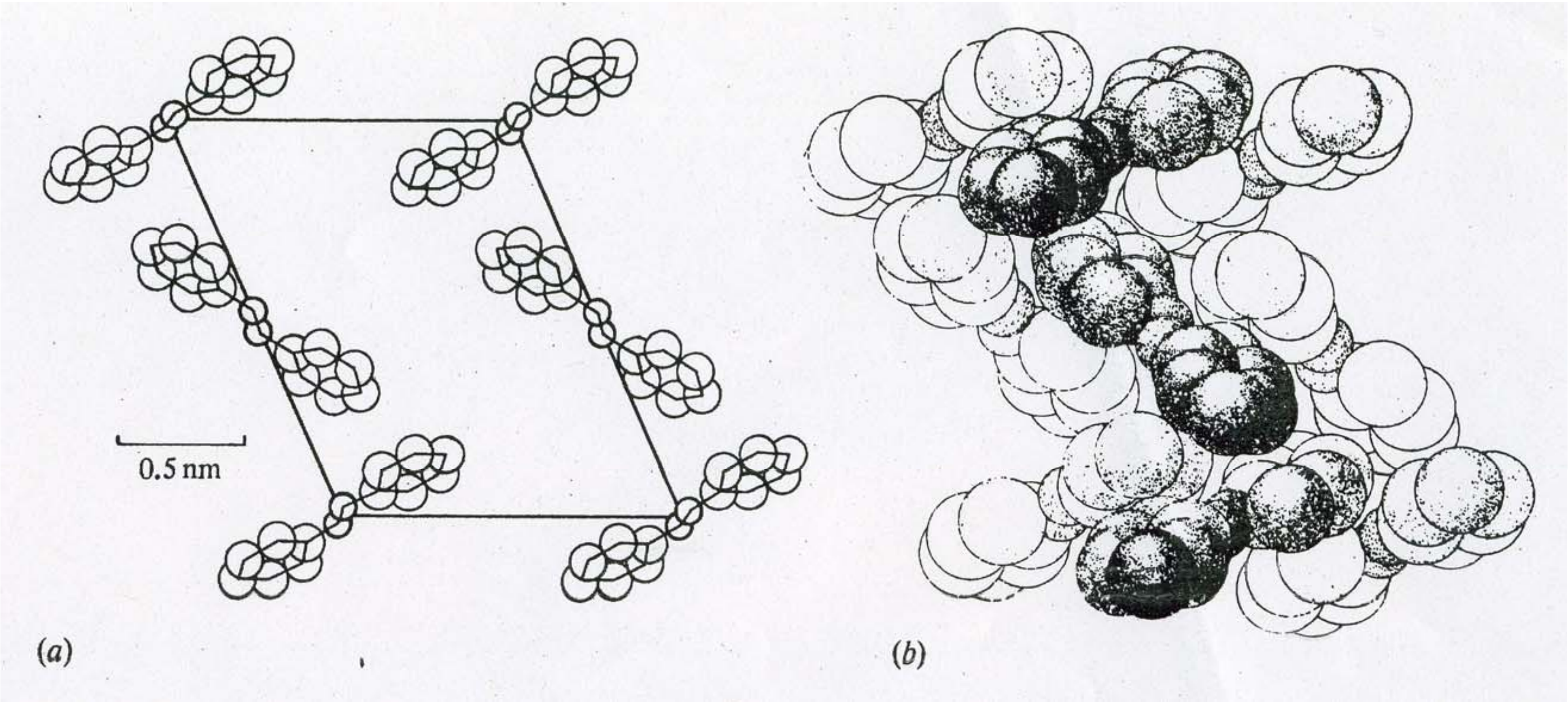
The crystal structure of benzene (H···π-bonds?)



The columnar crystal structure of sym-triazine (H···N bonds?)

Packing/arrangement of non-polar molecules

Molecular interactions and packing of molecules



Packing/arrangement of non-polar molecules
(a) at height 0 and (b) at height 0 and 1/2

Molecular interactions and packing of molecules

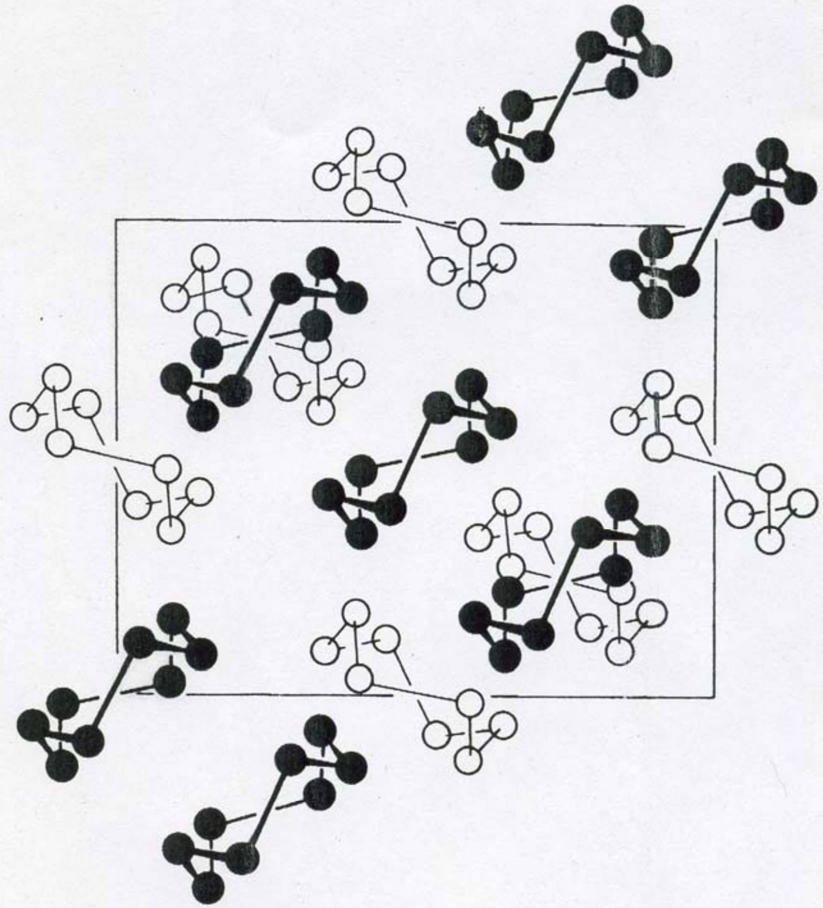
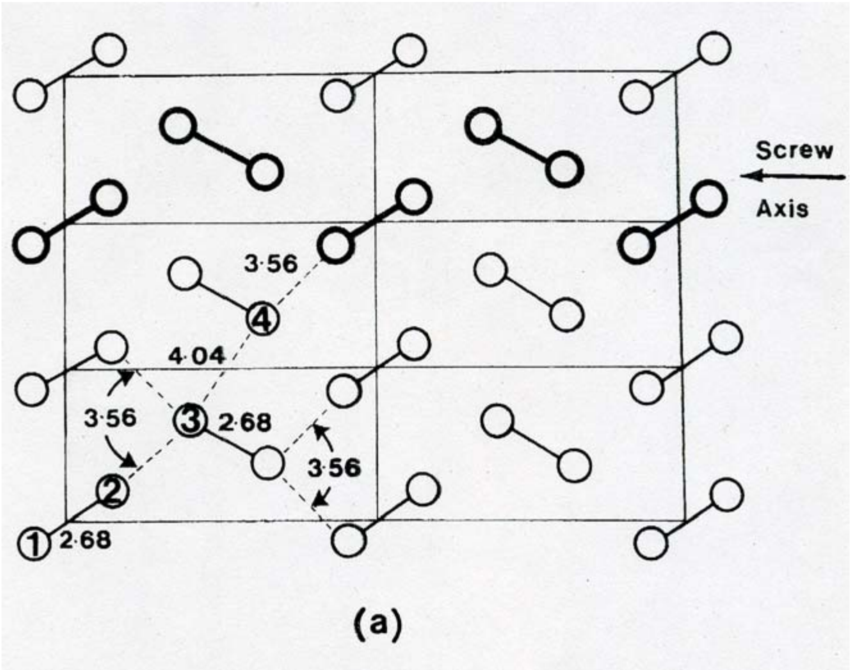


Figure 6-11 The packing of S_8 rings in crystalline orthorhombic sulphur. (Modified from *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission)

Packing/arrangement of non-polar molecules (d⋯d repulsion?)

Molecular interactions and packing of molecules



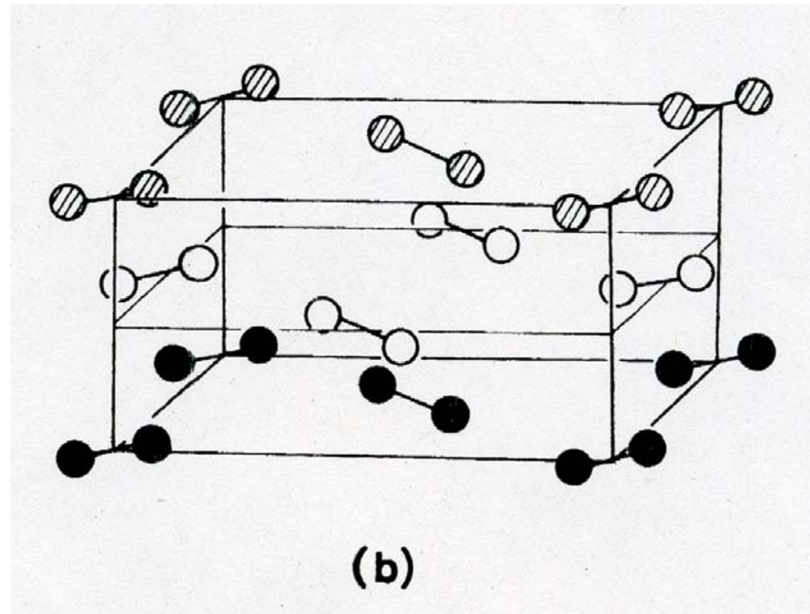


Figure 6-10 (a) Detail of one layer of the iodine crystal. (b) The layer stacking found in crystalline chlorine, bromine and iodine. Note the formal analogy with c.c.p. (From *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission)

Packing/arrangement of non-polar molecules (→ 2_1 symmetry)

Molecular interactions and packing of molecules

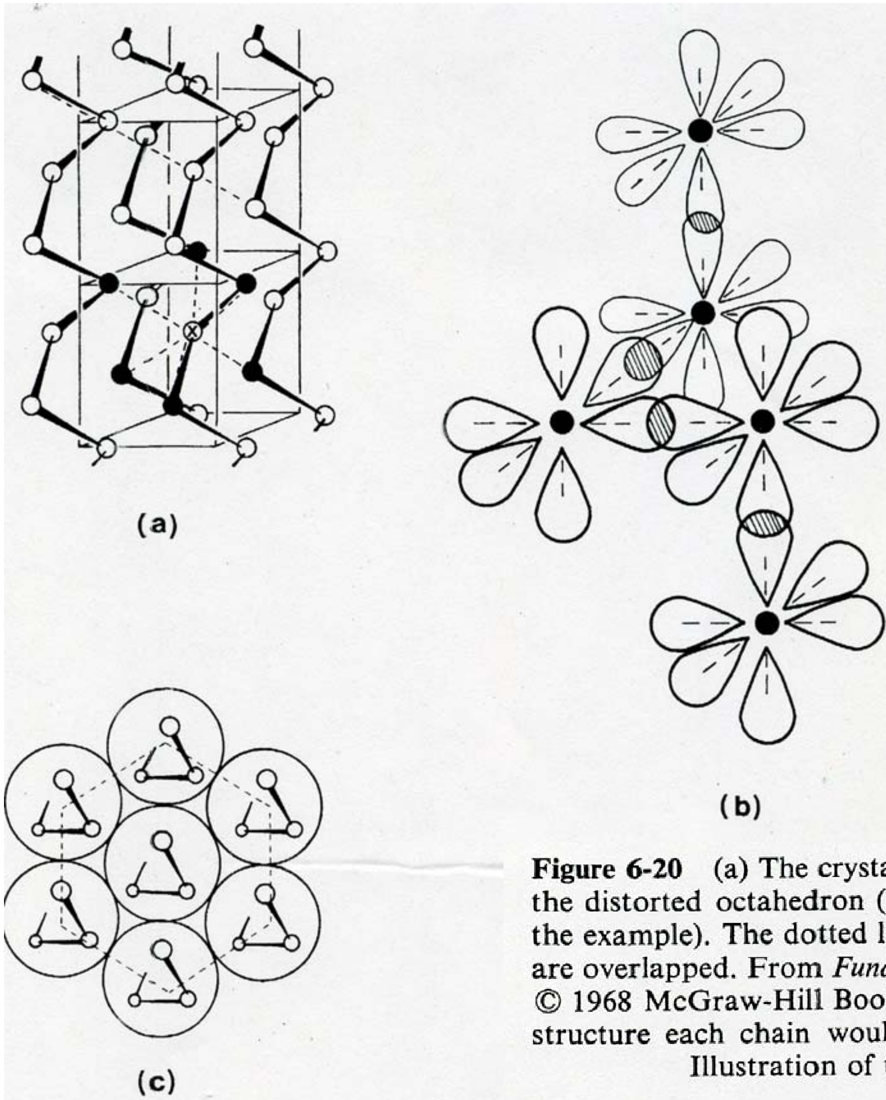


Figure 6-20 (a) The crystal structure of hexagonal selenium and tellurium. Note the distorted octahedron (black atoms) formed about each atom (x is taken as the example). The dotted lines indicate the directions in which the sp^3d^2 hybrids are overlapped. From *Fundamentals of Inorganic Crystal Chemistry* by H. Krebs. © 1968 McGraw-Hill Book Company (UK) Ltd. Used with permission). (b) The structure each chain would have if only *p*-orbitals were used in bonding. (c) Illustration of the packing of the chains (cf. Figure 3-1b)

Influence of space filling, free electron pairs and configurat. requirements on molecular arrangement (Se and Te like octahedral surroundings)

Packing/arrangement of non-polar molecules

Molecular interactions and packing of molecules

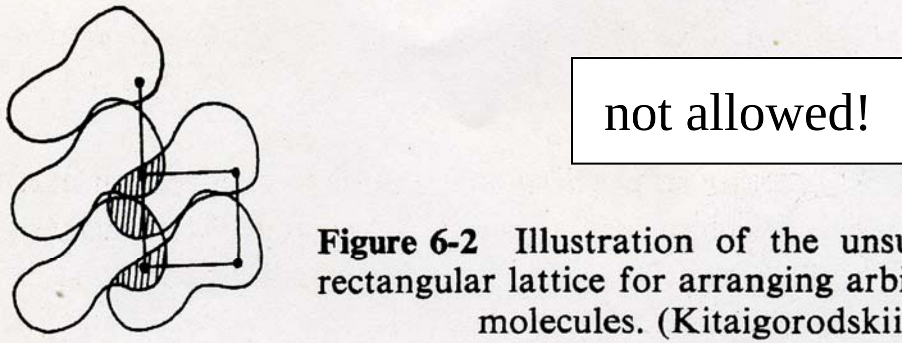


Figure 6-2 Illustration of the unsuitability of a rectangular lattice for arranging arbitrarily shaped molecules. (Kitaigorodskii (1961))

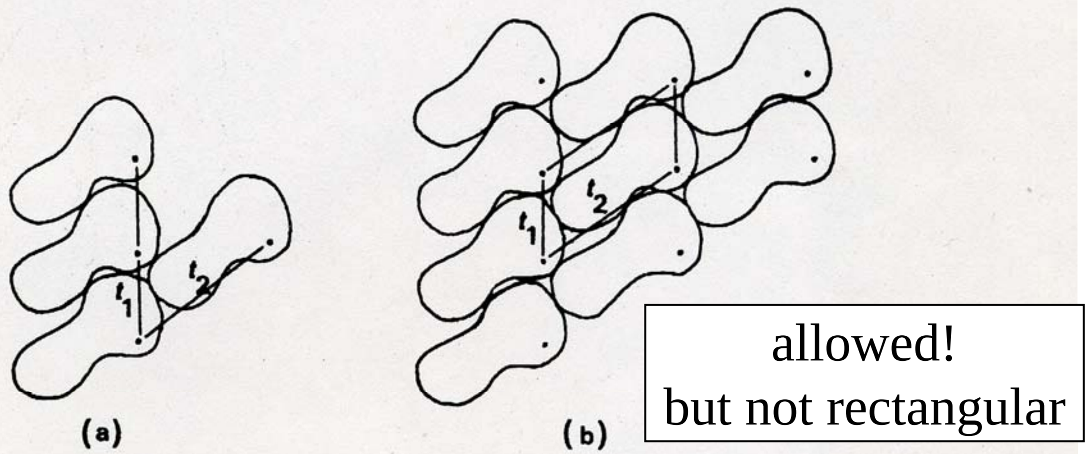
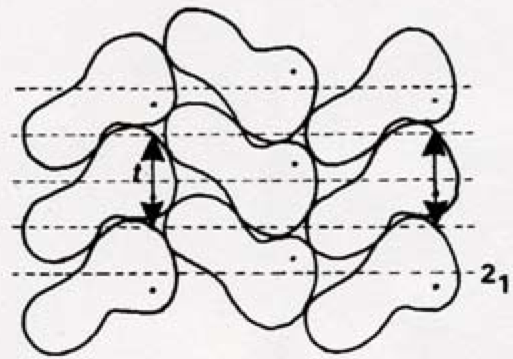


Figure 6-3 A close-packed planar layer of non-directionally bonded molecules of arbitrary shape. (a) A chain of type 1 (see text) to which one additional molecule has been added, determining the second translational repeat, t_2. (b) More of the layer. (Kitaigorodskii (1961))

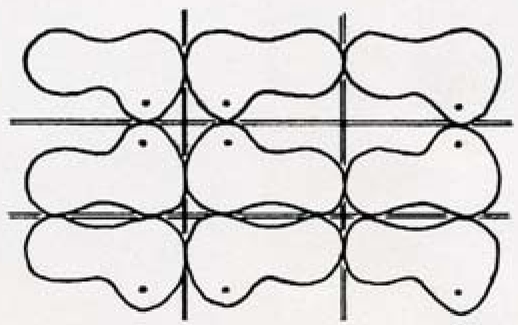
Packing/arrangement of arbitrarily shaped non-polar molecules (after Kitaigorodskii)

Molecular interactions and packing of molecules



allowed!
forming of 2_1

Figure 6-4 Another close-packed layer of molecules formed from chains of type 1. (Kitaigorodskii (1961))



not allowed!

Figure 6-5 An undesirable form of molecular packing derived from chains of type 5. (Kitaigorodskii (1961))

Packing/arrangement of non-polar molecules after Kitaigorodskii

Molecular interactions and packing of molecules

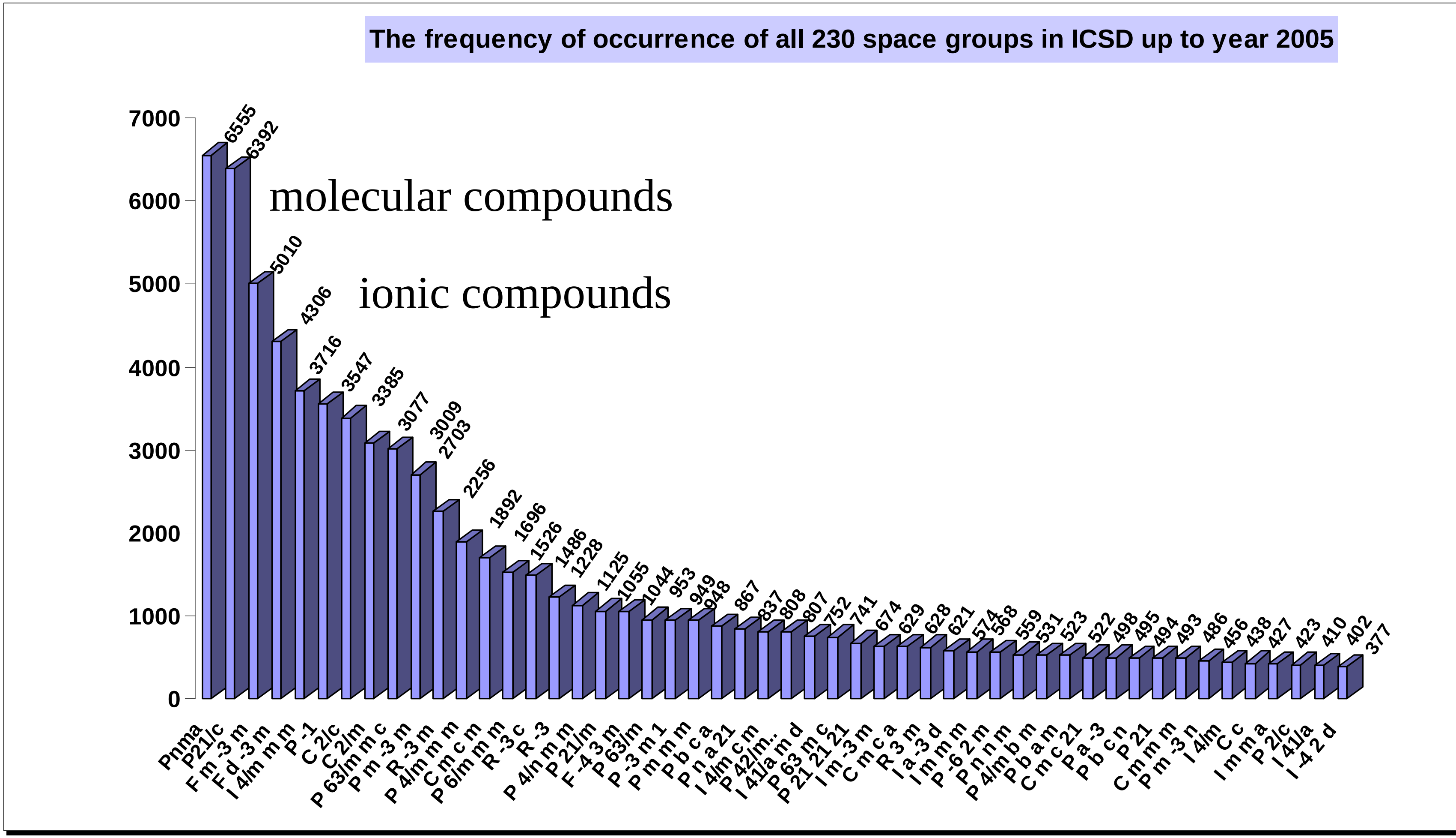
Table 1. Most-probable space groups for molecular crystals (A. I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau, New York, 1961)

Inherent molecular symmetry	1, 2, *m*		$\bar{1}$, 2, *m* *mmm*		*mmm*				222	
Molecular symmetry in crystal	1		$\bar{1}$		2		*m*		2	
	Space group	*Z*	Space group	*Z*	Space group	*Z*	Space group	*Z*	Space group	*Z*
Space group and multiplicity (*Z*) of position occupied by the molecule	$P\bar{1}$	2,4	$P\bar{1}$	1,2	$C2/c$	4	*Pmc*	4	$C2/c$	4
	$P2_1$	2,4	$P2_1/c$	2,4	$P2_12_12$	2,4	*Cmc*	4	$P2_12_12$	2,4
	$P2_1/c$	4	$C2/c$	4	*Pbcn*	4	*Pnma*	4	*Pbcn*	4
	Pca	4	*Pbca*	4						
	Pna	4								
	$P2_12_12_1$	4								

P represents a primitive unit cell, i.e., atoms at corners only. A *C*-centred cell has twice as many atoms as its equivalent cell but the axes are more conveniently arranged.

Packing/arrangement of arbitrarily shaped non-polar molecules according to Kitaigorodskii mostly results in space groups with 2_1 and/or *c* symmetry like $P2_1/c$, P*nma* or $P2_12_12_1$

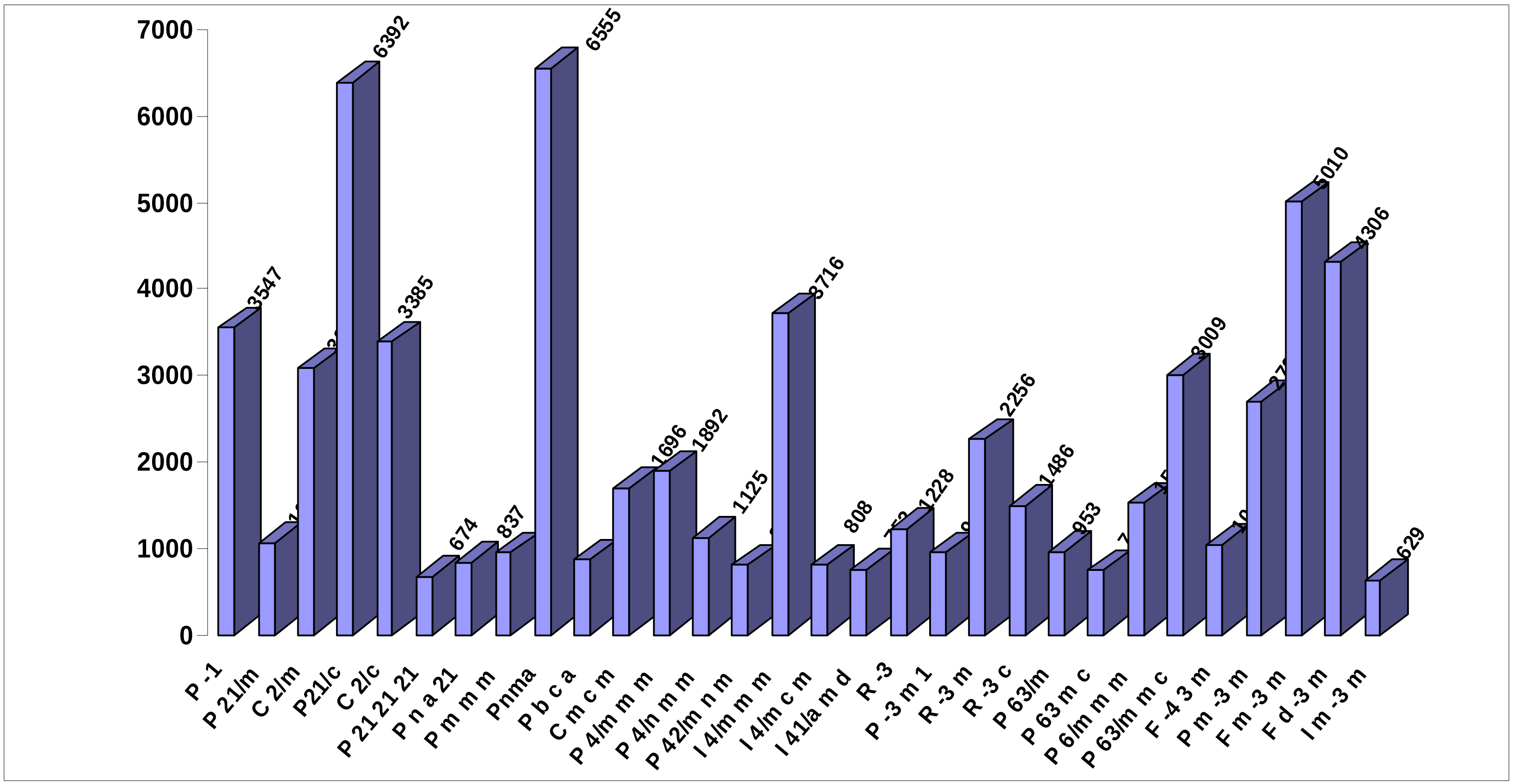
Molecular interactions and packing of molecules



Space group population statistics of inorganic compounds

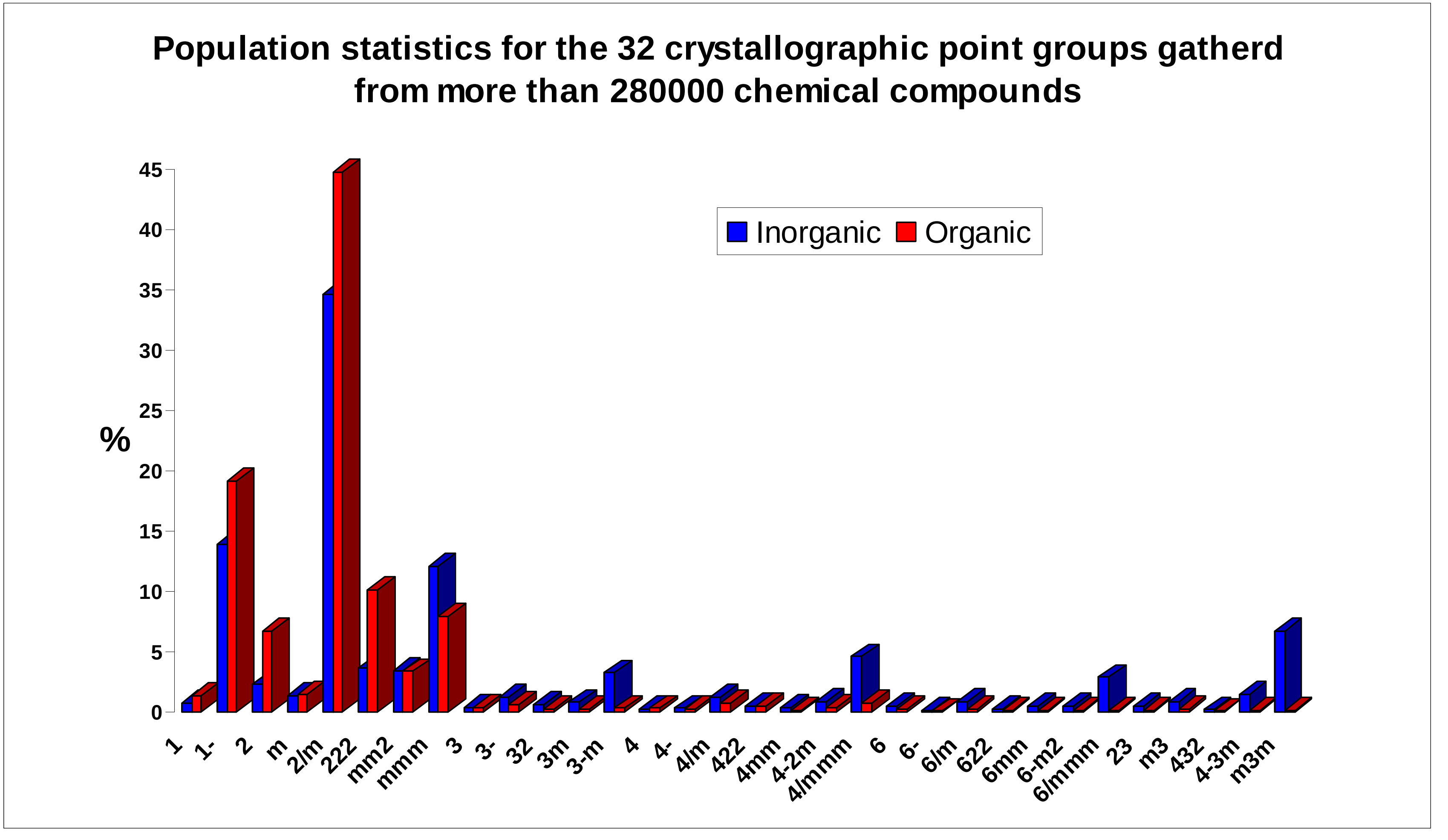
Molecular interactions and packing of molecules

Space group frequency of the 30 most frequent space groups in the ICSD of the year 2005



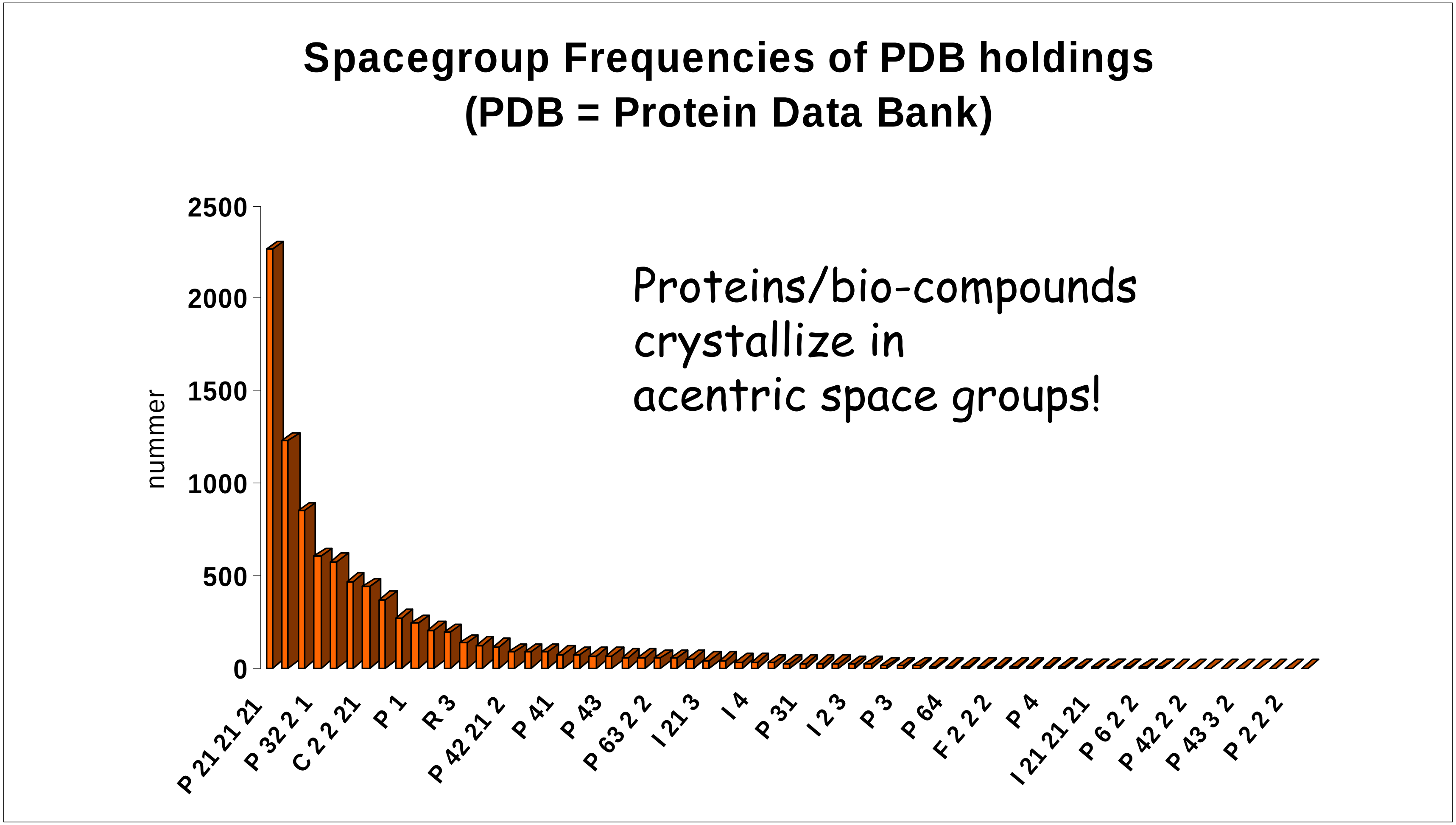
Space group population statistics of inorganic compounds

Molecular interactions and packing of molecules



Point group population statistics of organic and inorganic compounds

Molecular interactions and packing of molecules



Point group population statistics of proteins/bio-compounds