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9.7. The space-group distribution of molecular organic structures

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9.7.1. *A priori* classifications of space groups

The space group $P2_1/c$ accounts for about 1/3 of all known molecular organic structures, whereas the space group $P2/m$ has no certain example. Why? Ultimately, the space group of a crystal of a particular substance is determined by the minimum (or a local minimum) of the thermodynamic potential (Gibbs free energy) of the van der Waals and other forces, but a very simple model goes a long way towards 'explaining' the relative frequency of the various space groups within a crystal class or larger grouping. Nowacki (1943) discussed the basic idea that space-group frequency is determined by packing considerations, and had earlier (1942) given statistics for the structures known at the time. Nowacki's statistics were used by Kitajgorodskij* (1945), and recent writers tend to cite Kitajgorodskij as having originated the idea. Kitajgorodskij pointed out that the most frequent space groups are those that permit the close packing of triaxial ellipsoids. Later, Kitajgorodskij (1955) showed that the same space groups allowed close packing of objects of any reasonable shape, 'close packing' meaning packing with 12-point contact. Wilson (1988, 1990, 1993*d*) used the complementary idea that space groups are rare when they contain symmetry elements – notably mirror planes and rotation axes – that prevent the molecules from freely choosing their positions within the unit cell. A twofold axis excludes molecular centres from a column of diameter equal to some molecular diameter (say M), a mirror plane from a layer of thickness M, and a centre of symmetry from a sphere of diameter M. The volumes excluded by screw axes and glide planes are small in comparison.

9.7.1.1. *Kitajgorodskij's categories*

In his book† *Organicheskaya Kristallokhimiya*, Kitajgorodskij (1955) treated the triclinic, monoclinic and orthorhombic space groups in considerable detail, analysing the possibility of (*a*) forming close-packed layers (six-point contact), and (*b*) close stacking of the layers. On this basis, he divided the layers and the space groups into four categories each. For the layers they are:

(1) *Coordination close-packed layers*. A coordination close-packed layer is one in which molecules of arbitrary shape and symmetry can be packed with six-point coordination.
(2) *Closest-packed layers*. A closest-packed layer is one in which one can select the orientation of molecules of given shape and symmetry so as to produce a cell of minimal dimensions.
(3) *Limitingly close-packed layers*. A limitingly close-packed layer for a given symmetry is a closest-packed layer in which a molecule retains inherent symmetry; in other words, in which it occupies a special position.
(4) *Permissible layers*. A permissible layer is coordination close packed but *neither* closest packed *nor* limitingly close packed.

The categories of space groups are:

(1) Closest-packed space groups are those that permit the closest stacking of closest-packed layers – the packing can be made no denser by varying the cell parameters and the orientation of the molecules. Closest stackings can be made by a monoclinic displacement (a translation making an arbitrary angle with the layer plane), a centre of symmetry, a glide plane, or a screw axis.
(2) Limitingly close-packed space groups are those that contain limitingly close-packed layers stacked as closely as possible.
(3) Permissible space groups fall into three subcategories: (*a*) Those containing closest-packed layers that can be closely stacked if the layer relief is suitable; this group contains layers stacked by centring (C, I, F) or by diad axes. (*b*) Those containing limitingly close-packed layers that can be most closely stacked if the layer relief is suitable. (*c*) Those containing permissible layers stacked in the densest fashion.
(4) Impossible space groups fall into two subcategories: (*a*) Those containing any layers (even closest-packed layers) that are related by mirror planes and translations normal to the layer plane. (*b*) Those containing permissible coordination close-packed layers not stacked in the densest possible way.

Kitajgorodskij expected the frequency of space groups to decrease in the order (1) > (2) > (3) > (4). In particular, 'permissible space groups should be found but rarely, as exceptions'. The categorization is summarized in Table 9.7.1.1, based on Table 8 of Kitajgorodskij (1955).

Kitajgorodskij's categorization proved very successful in broad outline, but Wilson's (1993*b*,*c*) detailed statistics revealed about a dozen anomalous space-group types. The anomalies were of two kinds. The first was the frequent occurrence of molecules in general positions in space groups in which Kitajgorodskij expected molecules to use inherent symmetry in special positions. Wilson (1993*a*) pointed out that in such cases structural dimers* can be formed, with two molecules in general positions related by the required symmetry elements – both enantiomers would be required if the element were $\bar{1}$ or m. Such space groups could therefore be added to Kitajgorodskij's table, in the column for 'molecular symmetry 1'. The second kind of anomaly was the fairly frequent occurrence of structures with the 'impossible' space groups Pc and $P2/c$. These could be transferred from 'impossible' to 'permissible', subgroup (*a*), by the same packing argument that Kitajgorodskij had used for $P1$. These and a few other reclassifications are indicated in Table 9.7.1.1, the new entries being enclosed in square brackets for distinction. Where the change is a transfer to a higher category, the original position of the space group is indicated in round brackets.

9.7.1.2. *Symmorphism and antimorphism*

Wilson (1993*d*) classified the space groups by degree of symmorphism. A fully symmorphic space group contains only the 'syntropic' symmetry elements

$$2,\ 3,\ 4,\ 6;\ \bar{2} = m,\ \bar{3} = 3 + \bar{1},\ \bar{4}, \bar{6} = 3/m$$

and a fully antimorphic space group contains only the 'antitropic' elements

* Names in Cyrillic characters are transliterated in many ways in non-Russian languages. In this chapter, 'Kitajgorodskij' is used thoughout the text, but the source transliteration is retained in the list of references. Similar complications arise with other names in Cyrillic characters.

† The US translation (Kitajgorodskij, 1961) differs from the original in several respects. Only relevant differences are noted in this chapter.

* Empirically, only dimers involving a centre of symmetry or a diad axis are important in the systems under consideration. In principle, n-mers involving any point-group symmetry could be formed.

Table 9.7.1.1. *Kitajgorodskij's categorization of the triclinic, monoclinic and orthorhombic space groups, as modified by Wilson (1993a)*

Wilson's additions are enclosed in square brackets [· · ·] and the original positions of space groups transferred by him by round brackets (· · ·). Space groups not listed belong to the 'impossible' category.

Molecular symmetry	1	$\bar{1}$	2	*m*	2/*m*	222	*mm*	*mmm*
Closest	$P\bar{1}$	$P\bar{1}$						
packed	$P2_1$							
	$P2_1/c$	$P2_1/c$						
	[$C2/c$]	$C2/c$	[$C2/c$]					
	$P2_12_12_1$							
	$Pca2_1$							
	$Pna2_1$							
	[$Pbca$]	$Pbca$						
Limitingly			($C2/c$)		$C2/m$			
close packed	[$P2_12_12$]		$P2_12_12$			$C222$		
						$F222$		
						$I222$		
				$Pmc2_1$			$Fmm2$	
				$Cmc2_1$				
	[$Pbcn$]		$Pbcn$	$Pnma$			$Pmma$, $Pmmn$	
					$Cmca$	$Ccca$		$Cmmm$
						*		$Fmmm$
								$Immm$
Permissible	$P1$							
	$C2$		$C2$					
	[Pc]							
	Cc			Cm	$Pbam$			
	[$P2/c$]		[$P2/c$]	$P2_1/m$				
	($P2_12_12$)							
	[$C222_1$]		[$C222_1$]					
				$Pmn2_1$				
			$Aba2$	$Ama2$				
			[$Fdd2$]	$Ima2$				
	($Pbca$)			$Pbcm$†				
	[$Pccn$]	$Pccn$						

* Kitajgorodskij (1961) includes *Pnnm* at this position, but this is inconsistent with the text of either the Russian or the English version.
† Kitajgorodskij (1961) correctly includes *Pbcm* at this position.

$$2_1,\ 3_{1,2},\ 4_{1,3},\ 6_{1,5};\ \text{any glide plane.}$$

The remaining symmetry elements

$$1,\ \bar{1};\ 4_2;\ \bar{4};\ 6_{2,4} = 2 + 3_{1,2};\ 6_3 = 2_1 + 3$$

are 'atropic'. The two triclinic space groups, $P1$ and $P\bar{1}$, contain only 'atropic' elements, and are thus not classified by these criteria. The rest are divided into five groups, in accordance with the balance of symmetry elements within the unit cell. For the 71 non-triclinic space groups symmorphic in the strict sense (Wilson, 1993*d*; Subsection 1.4.2.1), the classification gives:

(1) Fully symmorphic (only syntropic elements): 14.
(2) Tending to symmorphism (mainly syntropic elements): 28.
(3) Equally balanced (equal numbers of syntropic and antitropic elements): 20.
(4) Tending to antimorphism (mainly antitropic elements): 9.
(5) Fully antimorphic (only antitropic elements): 0.

The distribution of the 230 space groups (11 enantiomorphic couples merged) by arithmetic crystal class and degree of symmorphism is given in Table 9.7.1.2.

A few points about the symmorphic groups are worth noting. The 14 'fully symmorphic' space groups are those that (i) have primitive cells and (ii) have no secondary or tertiary axes (three each monoclinic, orthorhombic, tetragonal, hexagonal; two trigonal; no cubic). Secondary axes, even though syntropic in the conventional space-group notation, generate additional antitropic axes in accordance with the principles set out by Bertaut (1995, Chap. 4.1). These additional axes are not indicated in the 'full' Hermann–Mauguin space-group symbol, but should appear in the 'extended' symbol (Bertaut, 1995, Table 4.3.1‡). As a result of the additional axes, 21 symmorphic space groups with primitive cells are shifted to the 'tending to symmorphism' column (five tetragonal, six trigonal, five hexagonal, five cubic). Lattice centring has a similar or greater effect; the 36 centred symmorphic space groups are spread over the three columns 'tending to symmorphism' (seven), 'equally balanced' (20) and 'tending to antimorphism' (nine).

‡ Table 4.3.1 is not strictly consistent in its treatment of the 'extended' symbols. Tetragonal space groups are extended in full detail, but the extension of orthorhombic space groups is minimal.

Table 9.7.1.2. *Space groups arranged by arithmetic crystal class and degree of symmorphism (Wilson, 1993d), as frequented by homomolecular structures with one molecule in the general position (in superscript numerals; according to Belsky, Zorkaya & Zorky, 1995)*

(*a*) Triclinic, monoclinic and orthorhombic systems. The triclinic space groups are a special case, with 'degree of symmorphism' undefined, and they are not assigned to any particular column. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$1P$			$*P1\dagger^{(90)}$		
$\bar{1}P$			$*P\bar{1}\dagger^{(1796)}$		
$2P$	$*P2^{(0)}$	...	...	...	$P2_1\dagger^{(1327)}$
$2C$	...	...	$*C2\dagger^{(109)}$	...	...
mP	$*Pm^{(0)}$	...	...	...	$Pc\dagger^{(58)}$
mC	...	...	$*Cm^{(0)}$	...	$Cc\dagger^{(144)}$
$2/mP$	$*P2/m^{(0)}$	...	$P2_1/m^{(0)}$ $P2/c^{(11)}$	...	$P2_1/c\dagger^{(5951)}$
$2/mC$	...	...	$*C2/m^{(0)}$	$C2/c\dagger^{(587)}$	...
$222P$	$*P222^{(0)}$	$P222_1^{(0)}$	...	$P2_12_12^{(30)}$	$P2_12_12_1\dagger^{(2795)}$
$222C$	...	$*C222^{(0)}$	...	$C222_1\dagger^{(11)}$	...
$222F$	...	...	$*F222^{(0)}$	...	...
$222I$	...	...	$*I222^{(0)}$ $I2_12_12_1\dagger^{(0)}$	...	...
$mm2P$	$*Pmm2^{(0)}$	$Pma2^{(0)}$	...	$Pmc2_1^{(0)}$ $Pcc2^{(1)}$ $Pnc2^{(1)}$ $Pmn2_1^{(0)}$ $Pba2^{(1)}$ $Pnn2^{(1)}$	$Pca2_1^{(153)}$ $Pna2_1\dagger^{(367)}$
$mm2C$	...	$*Cmm2^{(0)}$	...	$Cmc2_1\dagger^{(0)}$ $Ccc2^{(0)}$	...
$2mmC$	...	$*Amm2^{(0)}$	...	$Abm2^{(0)}$ $Ama2^{(0)}$ $Aba2\dagger^{(11)}$	...
$mm2F$			$*Fmm2^{(0)}$	$Fdd2\dagger^{(35)}$	
$mm2I$	...	...	$*Imm2^{(0)}$	$Iba2\dagger^{(14)}$ $Ima2^{(0)}$	
$mmmP$	$*Pmmm^{(0)}$	$Pccm^{(0)}$ $Pmma^{(0)}$	$Pnnn^{(0)}$ $Pban^{(0)}$ $Pmna^{(0)}$ $Pmmn^{(0)}$	$Pnna^{(1)}$ $Pcca^{(3)}$ $Pbam^{(0)}$ $Pccn^{(37)}$ $Pbcm^{(0)}$ $Pnnm^{(0)}$ $Pbcn^{(60)}$ $Pnma^{(0)}$	$Pbca\dagger^{(827)}$
$mmmC$	...	$*Cmmm^{(0)}$	$Cmma^{(0)}$	$Cmcm^{(0)}$ $Cmca^{(0)}$ $Cccm^{(0)}$ $Ccca\dagger^{(0)}$	...
$mmmF$	...	...	$*Fmmm^{(0)}$	$Fddd\dagger^{(2)}$	...
$mmmI$	...	...	$*Immm^{(0)}$	$Ibam^{(0)}$ $Ibca^{(0)}$ $Imma^{(0)}$	

From the nature of the definitions, no symmorphic space group can be 'fully antimorphic'. The 14 groups under the latter heading consist of (i) 12 space groups with no special positions (Subsection 9.7.4.1), and (ii) two space groups whose only special positions have symmetry $\bar{1}$ (Subsection 9.7.4.2). On these criteria, the two triclinic groups excluded from discussion would fall naturally into the column 'fully antimorphic'. The remaining space groups have no obvious outstanding characteristics. Most of them fall under the heading 'tending to antimorphism', though there are some in each of the columns 'tending to symmorphism' and 'equally balanced'.

9.7.1.3. *Comparison of Kitajgorodskij's and Wilson's classifications*

Since both Kitajgorodskij's and Wilson's classifications were made with a view to 'explaining' the empirically observed frequencies of space groups – though neither makes any use of

Table 9.7.1.2. *Space groups arranged by arithmetic crystal class and degree of symmorphism (cont.)*

(*b*) Tetragonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$4P$	$*P4^{(0)}$	$P4_2^{(1)}$	...	...	$P4_{1,3}\dagger^{(40)}$
$4I$	...	...	$I4_1\dagger^{(3)}$	$*I4^{(3)}$	...
$\bar{4}P$	$*P\bar{4}\dagger^{(0)}$	...	...	...	...
$\bar{4}I$	...	...	$*I\bar{4}\dagger^{(7)}$	...	...
$4/mP$	$*P4/m^{(0)}$	$P4_2/m^{(0)}$ $P4/n^{(1)}$	$P4_2/n\dagger^{(20)}$	...	...
$4/mI$	...	...	...	$*I4/m^{(0)}$ $I4_1/a\dagger^{(29)}$	...
$422P$	...	$*P422^{(0)}$ $P4_222^{(0)}$	$P42_12^{(0)}$ $P4_{1,3}22^{(1)}$	$P4_{1,3}2_12\dagger^{(49)}$ $P4_22_12^{(1)}$	...
$422I$	...	...	$I4_122\dagger^{(0)}$	$*I422^{(0)}$	...
$4mmP$	...	$*P4mm^{(0)}$	$P4bm^{(0)}$	$P4_2cm^{(0)}$ $P4_2nm^{(0)}$ $P4cc^{(0)}$ $P4nc^{(0)}$ $P4_2mc^{(0)}$ $P4_2bc\dagger^{(1)}$	...
$4mmI$	...	...	...	$*I4mm^{(0)}$ $I4cm^{(0)}$ $I4_1md^{(0)}$ $I4_1cd\dagger^{(5)}$	...
$\bar{4}2mP$	...	$*P\bar{4}2m^{(0)}$	$P\bar{4}2c^{(0)}$ $P\bar{4}2_1m^{(0)}$	$P\bar{4}2_1c\dagger^{(12)}$	...
$\bar{4}m2P$	...	$*P\bar{4}m2^{(0)}$	$P\bar{4}c2^{(0)}$ $P\bar{4}b2^{(0)}$ $P\bar{4}n2^{(0)}$	...	...
$\bar{4}m2I$	...	...	$*I\bar{4}m2^{(0)}$	$I\bar{4}c2\dagger^{(0)}$	...
$\bar{4}2mI$	...	...	$*I\bar{4}2m^{(0)}$	$I\bar{4}2d\dagger^{(0)}$	...
$4/mmmP$	...	$*P4/mmm^{(0)}$ $P4_2/mmc^{(0)}$ $P4_2/mcm^{(0)}$	$P4/mcc^{(0)}$ $P4/nmm^{(0)}$	$P4/nbm^{(0)}$ $P4/nnc^{(0)}$ $P4/mbm^{(0)}$ $P4/mnc^{(0)}$ $P4/ncc^{(0)}$ $P4_2/nbc^{(0)}$ $P4_2/nnm^{(0)}$ $P4_2/mbc^{(0)}$ $P4_2/mnm^{(0)}$ $P4_2/nmc^{(0)}$ $P4_2/ncm^{(0)}$	...
$4/mmmI$	...	$*I4/mmm^{(0)}$	...	$I4/mcm^{(0)}$ $I4_1/amd^{(0)}$ $I4_1/acd\dagger^{(0)}$	

empirical frequencies – it would be expected that there should be considerable correlation between them. All 'closest-packed' space groups are also 'fully antimorphic', and most of the 'limitingly close packed' and 'permissible' are 'tending to antimorphism'; a few requiring high molecular symmetry (222, *mm*2, *mmm*) and a couple of others are 'equally balanced'. Two 'fully antimorphic' groups, *Pc* and *Cc*, are merely 'permissible'. All 'fully symmorphic' space groups are 'impossible'.

9.7.1.4. *Relation to structural classes*

Structural classes (Belsky & Zorky, 1977, and papers cited there and below) are not an *a priori* classification of space groups but are a classification of structures within a space-group type in accordance with the number and kind of Wyckoff positions occupied by the molecules. As a considerable knowledge of the structures is required before their structural classes can be assigned, they form an *a posteriori* classification, and will be described (Section 9.7.5 below) after the empirical frequencies of space groups have been discussed.

9.7.2. Special positions of given symmetry

As noted by Kitajgorodskij, in many crystal structures molecules with inherent symmetry may occupy Wyckoff special positions, so that molecular and crystallographic symmetry elements coincide, and this may affect the relative frequencies of occurrence of structures with particular space groups. Tables of the frequency of occurrence of space groups have been published by many authors, from Nowacki (1942) onwards. Some typical recent papers are Brock & Dunitz (1994), Donohue (1985), Mighell, Himes & Rodgers (1983), Padmaya, Ramakumar & Viswamitra (1990), Wilson (1988, 1990,

references