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.

references