

9. BASIC STRUCTURAL FEATURES

Zorky (1995) show that about half the possibilities are realized in symmorphic space groups with centred cells. The situation is set out in Table 9.7.4.1.

Although about half the point groups are not represented in symmorphic space groups with one molecule in the appropriate special position, it is interesting to look for molecules of these symmetries in space groups of higher symmetry. A few are in fact to be found in non-symmorphic space groups, but seven point groups have no established examples.

9.7.5. Structural classes

As developed so far (Belsky, Zorkaya & Zorky, 1995), structural classes relate primarily to homomolecular structures – structures in which all molecules are the same. Nevertheless, they are important in a study of the space-group distribution of molecular organic structures, as structures belonging to the same space-group type but to different structural classes are found to have very different frequencies. The germ of the idea is implicit in Kitajgorodskij's subdivision of his four categories by molecular symmetry.

In its general form, the symbol of a structural class has the form

$$SG, Z = n[(x)^a, (y)^b, \dots],$$

where SG is the standard space-group symbol, n is the number of molecules in the unit cell, x, y, \dots are the symbols of the point-group symmetries of the Wyckoff positions occupied, and a, b, \dots are the numbers of occupied Wyckoff positions of those symmetries. An example will make this clearer. There is a structural class

$$P\bar{4}m2, Z = 32[(mm)^4, m^4, 1].$$

This indicates that the space group is $P\bar{4}m2$ and that there are 32 molecules in the unit cell occupying four positions of symmetry mm , four of symmetry m , and one general position. On consulting the multiplicity of the special positions for this space group in Volume A of *International tables for crystallography* (Hahn, 1995), one finds that the 32 molecule total is accounted for as $(4 \times 2) + (4 \times 4) + (1 \times 8)$. If (as is usually the case) the square brackets are unnecessary, they are omitted, as in

$$P\bar{4}n2, Z = 2(222) \text{ and } P4/nnc, Z = 4(4).$$

Occasionally, two distinguishable structural classes will lead to the same symbol. As yet, Belsky, Zorkaya & Zorky prefer to deal with this problem on an *ad hoc* basis, rather than by attempting to devise any general rules.

Belsky, Zorkaya & Zorky divide the structural classes into six groups, in accordance with the number of examples found. The groups are 'anomalous' (up to five examples, 199 structural classes); 'rare' (up to 19 examples, 55 classes); 'small' (up to 49 examples, 24 classes); 'big' (13 classes); 'giant' (eight classes); and 'supergiant' (six classes). The last three are not explicitly defined, but examination of the tables shows that the dividing line between 'big' and 'giant' is about 250, and between 'giant' and 'supergiant' is about 750. All these statistics, of course, are subject to modification as the number of known structures increases.

9.7.6. A statistical model

Wilson (1988, 1990, 1991) has discussed the factors that, on statistical analysis, appear to govern the relative frequency of occurrence of the space groups of molecular organic crystals. In

its developed form (Wilson, 1990), the statistical model postulated that, within an arithmetic crystal class (see Chapter 1.4), the number of examples, N_{sg} , of a space-group type would depend exponentially on the numbers of symmetry elements within the unit cell, thus:

$$N_{sg} = A \exp \left\{ - \sum_j B_j [e_j]_{sg} \right\}. \quad (9.7.6.1)$$

In this equation, A is a normalizing constant depending on the arithmetic crystal class, $[e_j]_{sg}$ is the number of symmetry elements of type e_j within the unit cell in the space group, and B_j is a parameter depending on the arithmetic crystal class and the symmetry element e_j ; A and B_j are independent of the space group. Empirically, B_j has a positive sign for the syntropic symmetry elements (k and \bar{k} , where $n = 2, 3, 4, 6$) and a negative sign for 1 and the antitropic symmetry elements (glide planes and screw axes). Often, however, laws of 'conservation of symmetry elements', of the type

$$[2] + [2_1] = c, \quad (9.7.6.2)$$

or in general

$$\sum_j [e_j] = c, \quad (9.7.6.3)$$

where c is a constant for the crystal class, eliminate a separate dependence on one or more of the e_j 's (Wilson, 1990). Often a cohort larger than an arithmetic crystal class can be used, with arithmetic crystal class included as an additional factor.* With this adjustment, the model can be used for such cohorts as geometric crystal class or even crystal system, giving fits within the usual crystallographic range ($R_2 \lesssim 0.05$), but, for some classes (in particular mmm), statistical tests based on the scaled deviance indicated residual systematic error (Wilson, 1980). This was traced (Wilson, 1991) to the failure of an explicit postulate: 'The second possibility is that the distribution is seriously affected by molecular symmetry. Some molecules possess inherent symmetry . . . , and this symmetry could coincide with the corresponding crystallographic symmetry element, again increasing the variance and/or bias of the number of examples per space group. . . . The comparative rarity of utilization of molecular symmetry suggests that it can be ignored in an exploratory statistical survey . . .' (abbreviated from Wilson, 1988). This procedure was perhaps reasonable in a first 'exploratory' survey, and in fact agreement in the usual crystallographic range ($R_2 \lesssim 0.05$) was achieved (Wilson, 1988, 1990). However, the scaled deviance indicated that systematic errors still remained (Wilson, 1980), and the discrepancy was traced to the use of molecular symmetry in many structures (Wilson, 1990, 1992). If such structures are eliminated, R_2 falls to trivial values, and the agreement between observed and calculated frequencies becomes too good to be interesting.

9.7.7. Molecular packing

9.7.7.1. Relation to sphere packing

The effect of molecular symmetry cannot be ignored in overall statistical surveys as well as in structure prediction. However, in most structures, the molecular symmetry is low or it is not used

* Statistical modelling programs distinguish between variates and factors. The values of variates are ordinary numbers; $[2]$, $[m]$, . . . are variates. Factors are qualitative. In the immediate context, 'arithmetic crystal class' is a factor, but other categories, such as metal-organic compound, polypeptide, structural class (Belsky & Zorky, 1977), . . . , could be included if desired. The programs allow appropriately for both variates and factors; see Baker & Nelder (1978, Sections 1.2.1, 8.5.2, 22.1 and 22.2.1).