# Pervasive approximate symmetry in organic *P*1 structures

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A careful investigation of the packing in the nearly 1500 organic, well-refined ($R \leq 0.050$), *P*1, *Z*>1 structures archived in the 2019 version of the *Cambridge Structural Database* [1] has revealed that the molecules (or ions) in *ca*. 85% of those structures are related by obvious approximate symmetry that is periodic in at least two dimensions. An example is shown in Fig. 1. The nearly 250 *P*1, *Z*=1 structures of molecules that could lie on special positions were also analyzed; *ca*. 70% were found to have approximate symmetry.
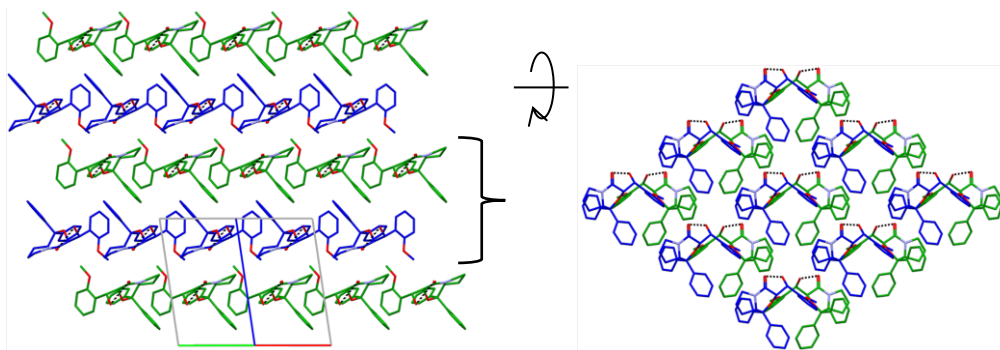
Figure 1. Views of LUSMAN, *P*1, *Z*=2 [2]; the second view, of a bilayer, is rotated by 90° around the horizontal from the first. The approximate *c*211 symmetry of a layer (001) with $0.5 < z < 1.5$ (axes [110], [11,$\bar{}$0]; angle 89.9°) is obvious. The angles of those axes with **c** are 77.8° and 81.8°.

In only 8% of the *Z*>1 structures does it seem likely that refinement in a higher symmetry space group or smaller unit cell would have been preferable. That percentage is, however, much higher (39%) for *P*1 crystals of achiral or racemic material, which account for 11% of all *Z*>1 structures considered. For *P*1, *Z*>1 crystals that are enantiomerically pure the frequency of overlooked symmetry is only 2%. For the *Z*=1 crystals the percentage is 10% overall and 17% for the crystals of achiral or racemic material.

In the abstract of R. E. Marsh's (1999) paper titled "*P*1 or *P*1,$\bar{}$? Or something else?" [3] he wrote
> In approximately one-third of the structures in which chiral molecules crystallize in *P*1 with *Z*=2, the two molecules are related by an approximate center of inversion.

The present study found that 32% of the *P*1, *Z*=2 structures of enantiomerically pure material are *P*1,$\bar{}$ mimics. Molecular features that promote *P*1,$\bar{}$ mimicry have been identified; they may have implications for the probability of formation of solid solutions.

The approximate symmetry is often subperiodic, as it is in the example shown in Fig. 1. The ratio of structures having 2-D to those having 3-D approximate periodic symmetry is about 2:3 but the ratio is imprecise because of the difficulty of deciding on the dimensionality. In some structures the approximate symmetry is clearly 3-D and in others it is clearly 2-D, but in many others the dimensionality is at the 3-D/2-D borderline. In only 22 structures, however, was the approximate symmetry identified as 1-D. The approximate subperiodic symmetry was described with the labels for layer and rod groups found in Vol. E of *International Tables* [4].

The surprisingly exact approximate symmetry found in many *P*1 crystals could result from a distortion during growth or cooling of a more symmetric nucleus, but in more than 3% of the *Z*>1 structures quite different layers alternate so that the *P*1 symmetry must have been established at the time of crystal nucleation.

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