Pervasive approximate symmetry in organic P1 structures

Carolyn Brock[1]

[1]University of Kentucky

cpbrock@uky.edu

Investigation of the packing in the nearly 1500 organic, well-refined (R≤0.050), P1, 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. The nearly 250 P1, Z=1 structures that meet the same criteria and that are composed of molecules or ions that could lie on special positions were also analyzed; ca. 70% were found to have approximate symmetry.

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 P1 crystals of achiral or racemic materials, which account for 11% of all the Z>1 structures considered. For the Z=1 structures that could have imposed symmetry the percentage is 10% overall and 17% for the crystals of achiral or racemic material.

In the abstract of his (1999) paper titled "P1 or P1-bar? Or something else?" [2] R. E. Marsh wrote:

"In approximately one-third of the structures in which chiral molecules crystallize in P1 with Z=2, the two molecules are related by an approximate center of inversion."

The present study found that 32% of the P1, Z=2 structures of enantiomerically pure material are P1-bar mimics. Molecular features that promote P1-bar mimicry have been identified.

The approximate symmetry is often subperiodic. The ratio of structures having 2-D to those having 3-D approximate periodic symmetry is about 2:3 but that ratio is imprecise because of the difficulty of deciding on the dimensionality. The approximate subperiodic symmetry was described with the labels for layer and rod groups found in Vol. E of International Tables [3].

Strategies for identifying approximate symmetry will be discussed.

[1] Groom, C. R. Bruno, I. J. Lightfoot, M. P. & Ward, S. C. (2016), Acta Cryst. B72, 171-179.

[2] Marsh, R. E. (1999). Acta Cryst. B55, 931-936.

[3] Kopský, V. & Litvin, D. B. (2002). Editors. International Tables for Crystallography, Vol. E, Subperiodic groups, Kluwer Academic Publishers, Dordrecht/Boston/London, 2002.

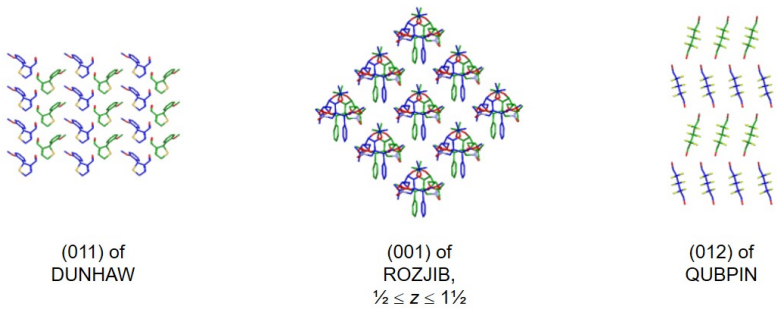

Figure 1