Oral presentation

Analyzing Approximate Periodic Symmetry in Molecular Structures

Carolyn Pratt Brock

Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA cpbrock@uky.edu

Pervasive approximate periodic symmetry has been found in well determined ($R \leq 0.05$) $Z'>1$ organic structures in space groups #1 ($P1$),[1] #7 (*e.g.*, Pc),[2] and #5 (*e.g.*, $C2$),[3], and in all space groups when $Z'>4$.[4] Approximate symmetry has also been found for $Z'=1$ structures in $P1$ when the molecules can adopt or mimic inversion symmetry,[1] and for $C2$ structures in which there are two independent molecules, each located on a twofold axis.[3] Structures in SG#9 (*e.g.*, Cc) are currently being investigated.

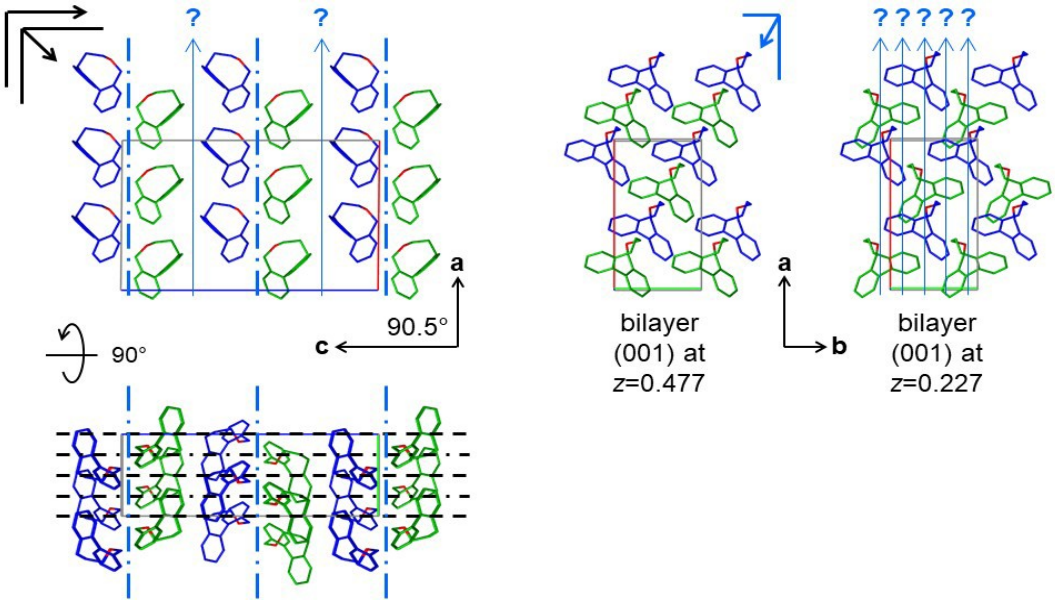

Figure 1. Projections of the Cc, $Z'=2$ structure BALNIO[5] showing that the bilayers (001) at z=-0.023 and 0.477 have excellent approximate symmetry $p11a$ (axes [110]/2, **-b**). (Approximate symmetry elements are in blue.) There must then be axes 2_n along **a**, but n is neither 0 nor 1, and the molecules are not spaced evenly. There is no space group having a setting $C2cn$ or $C2_1cn$. The structure must then be understood as composed of $p11a$ layers that are related by the c and n glides of the group Cc.

Spotting and documenting approximate periodic symmetry requires a greater understanding of the structure of space groups (*e.g.*, the interaction of symmetry elements) than is now being taught to new crystallographers. It is necessary to recognize when the approximate symmetry corresponds to a non-standard setting (*e.g.*, $Pbc2_1$ and $P2_1ca$ are non-standard settings of #29, $Pca2_1$) and when it cannot (what may look like approximate symmetry $C2_1cn$ does not correspond to any space group). Because approximate symmetry is quite often periodic in only two dimensions, and sometimes in only one, familiarity with the subperiodic layer and rod groups (Vol. E of *International Tables for Crystallography*)[6] is also necessary. It can be challenging to distinguish between approximate symmetry that is periodic in 3-D and in only 2-D. The tables in Vol. E of sectional layer groups are then very useful.

Also important is facility with specifying lines [*uvw*] and planes (*hkl*), and with calculating the angles between them and the projections of one on another.

Examples of procedures for identifying and documenting approximate periodic symmetry will be presented.

[1] Brock, C. P. (2022). *Acta Cryst.* **B78**, 576-588.
[2] Brock, C. P. (2023). *Helv. Chim. Acta*, e202200170.
[3] Brock, C. P. (2024). *Cryst. Growth Des.*, in press.
[4] Brock, C. P. (2016). *Acta Cryst.* **B72**, 807-821.
[5] Corrie, T. J. A., Ball, L. T., Russell, C. A., Lloyd-Jones, G. C. (2017). *J. Am. Chem. Soc.* **139**, 245-254.
[6] Kopský, V. & Litvin, D. B. (2010). Editors. Subperiodic Groups, 2nd ed. Chichester: Wiley.