

Pervasive approximate symmetry in organic $P1$, $Z>1$ structures

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There are ca. 2500 well determined ($R \leq 0.050$) organic crystal structures in space group $P1$ archived in the Cambridge Structural Database [1]; ca. 56% of them have $Z>1$. For this study just over half of those $P1$, $Z>1$ structures have been investigated in detail. The structures examined were not chosen randomly; ca. 60% of them have a cell angle in the range $88.5 - 91.5^\circ$. Ca. 10% are kryptoracemates, quasiracemates, and compounds of diastereomers; those structures were located as described previously [2]. Another ca. 10% are modulated structures that were found using a program written to identify and characterize pseudotranslations [3]. All the structures were scrutinized individually using the CCDC display program *Mercury* [4] and were checked with *PLATON* [5].

There is good reason to believe that about 10% of the $P1$, $Z>1$ structures examined should have been refined in a higher-symmetry space group or a smaller unit cell. The remaining 90% seem to have been described appropriately. The frequency of questionable structures is especially high for those having a cell angle in the range $89.5 - 90.5^\circ$ (18% rather than 10%) and for kryptoracemates (32%).

Obvious approximate symmetry has been found in ca. 80% of the $Z>1$ structures for which $P1$ seems to be the appropriate space group. Approximate screw axes, pseudoinversion centers, and pseudotranslations all occur frequently; approximate glides are less common. Pseudoscrew axes are more than 1.5 times more frequent than pseudoinversion centers and pseudotranslations.

In the case of approximate symmetry it is usually possible to identify a smaller or higher-symmetry approximate unit cell (*i.e.*, a *basic* cell). In the reported structure that basic cell is distorted such that symmetry other than translation is lost and/or there is an n -fold lengthening of some cell vector $[uvw]$. The structures that are not modulated often have approximate inversion centers that relate two homochiral molecules, which often have different conformations.

About a quarter of the $P1$, $Z>1$ structures examined have obvious layers with approximate 2-D symmetry higher than the approximate 3-D symmetry of the crystal. Offsets between adjacent layers account for the symmetry lowering. If interlayer forces are weaker than intralayer forces then deformations during the early stages of crystal growth are more likely between layers than within them.

References

- [1] Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171-179.
- [2] Fábíán, L. & Brock, C. P. (2010). *Acta Cryst.* **B66**, 94-103; Kelley, S. P., Fábíán, L. & Brock, C. P. (2011). *Acta Cryst.* **B67**, 79-93.
- [3] R. Taylor & C. P. Brock (2019). In preparation.
- [4] Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., Streek, J. v. d. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466-470.
- [5] Spek, A. L. (2009). *Acta Cryst.* **D65**, 148-155.