Program to Find and Characterize Commensurate Modulations in Molecular Crystals

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Half of the organic structures archived in the CSD [1] that have more than four independent molecules ($Z'>4$) have been found to be modulated [2], which is to say that small molecular translations, rotations, and/or conformational changes would decrease Z' by reducing the size of the unit cell and/or increasing its symmetry. Because the pseudosymmetry is not always easy to find by eye, a program has been written to find pseudotranslations and to quantify their conformational, orientational, transverse, and longitudinal components.

During program development results were checked against the organic, $Z'>4$ structures archived in the CSD, most of which had been already been considered carefully [2]. When the program is finalized it will be run for structures having smaller Z' values.

An important complication is that a pseudotranslation vector $[m_1\, m_2\, m_3]/n$, n and m_i integers, can be combined with any lattice vector $[l_1\, l_2\, l_3]$. Furthermore, if n has an integer factor p (*i.e.*, 2 and 3 for n =6) then there are also modulations $p[m_1\, m_2\, m_3]/n + [l_1\, l_2\, l_3]$. The shortest pseudotranslation relating the greatest number of molecules is unique. If n has factors p then that unique pseudotranslation may or may not be a consequence of combining two (or possibly more) lower order pseudotranslations. In the absence of reliable energy calculations it is impossible to say.

For a few compounds both $Z'<4$ and $Z'>4$ structures are known, with the latter usually determined at lower temperature. A relationship between such phase pairs can often be worked out, but not always easily. In many of the other $Z'>4$ structures a basic (*i.e.*, unmodulated) cell can be identified that might exist at higher temperature or during the early stages of crystal nucleation and growth.

It is easy to spot structures that were almost certainly refined in unit cells that are too large because the pseudotranslations found for such structures are too perfect.

In some pseudotranslations one component (conformational, orientational, transverse or longitudinal) dominates, but in most pseudotranslations there is a balance of the first three of those. Longitudinal components are both less common and smaller.

This work would have been impossible without the CCDC's visualization program *Mercury* [3]. The new option to specify the view direction by a vector $[m_1\, m_2\, m_3]$ was especially valuable.

[1] Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst*. **B72**, 171-179. (Note that the CSD entries do not include atomic coordinates for structures that are modulated incommensurately.)

[2] Brock, C. P. (2016) *Acta Cryst*. **B72**, 807-821.

[3] 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.