Approximate Symmetry in \(\text{P}2\) and c2 Organic Structures

Professor Carolyn P Brock\(^1\)

\(^1\)University of Kentucky
cpbrock@uky.edu

The crystal packing in well-determined, organic, \(Z^* \geq 1\) structures in groups #3 (P2) and #5 (C2/A2/I2) has been analyzed. The study completes the survey of packing in organic structures archived in the CSD that have \(R \leq 0.050\) and that were reported in low-symmetry (SG\# \(\leq 8\)), low-frequency (< 5000 entries) space groups. Surveys of the structures described in P1\(^1\) and in group #7 (Pc/Pn/Pa)\(^2\) have already been published.

There are only 6 such structures in group #6 (Pm) and only 12 in #8 (Cm), with a number of those being either suspicious or very inorganic. In only 2% of the ca. 550 \(\text{P}2\) and C2, \(Z^* \geq 1\) structures investigated does crystallographic symmetry seem to have been overlooked; for the structures in P1 and Pc that value was 8%. Approximate periodic symmetry, however, is again found in more than 80% of the structures in which it is possible (\(Z^* > 1\) or molecular symmetry). The most common categories are approximate translations, mimics of SG #15 (C2/c, etc.), and structures having additional symmetry that is periodic only within layers.

In most cases the distortions that make a translation approximate seem too large to have been the result of cooling through a phase transition. That observation suggests that it may be common for a crystal nucleus to have a smaller (or perhaps more symmetric) unit cell than does the macroscopic crystal.

In another important group of C2 structures there are two independent layers related by an approximate rotation perpendicular to the monoclinic axis (e.g., a rotation around \(a\)) that is paired with a translation that is not close to either 0 or (e.g.) \(a/2\). That observation suggests slippage of layers during the very early stages of crystal growth.

\(\dagger\) \(Z^*\) is the number of independent formula units. If \(Z^* = 1\) but both units lie on twofold axes then \(Z^* = 2\).

References