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About Whole-Molecule Disorder. Håkon Hope, Dept. of Chemistry, Univ. of California, Davis, 1 Shields Ave., Davis, CA 95616.

Crystals grow by adding particles (molecules, atoms or ions) to an existing crystal. The approaching particle will only be added if its orientation is energetically favorable. If one particular orientation has an energetic advantage over all other orientations, the particle will settle in that orientation. If two or more orientations are close in energy, the particle may settle in one of these several orientations. Ideally, the orientations will follow a Boltzmann distribution. For example, if two orientations have the same energy, they will be represented by equal probabilities; the result will be a 50-50 disorder.

The crystal structure of azulene provides a well-studied example where the crystal is unable to discriminate between the two rings.

A false appearance of disorder can be the result of incorrect determination of unit cell size. Impurity molecules can compete for a place in the crystal. Alpha-D-galactose provides a tricky example. Ingenious studies of effects of impurity inclusion by Lahav, Leiserovitz and coworkers (e. g. in Faraday Discuss. 1993, 95, 307) have shown that reduction of local symmetry in regions of an intact crystal can occur, although the average symmetry of the whole crystal may be the same as for the pure material. The result could be the appearance of disorder.