Symmetry-constrained Monte Carlo to predict the experimental crystal structure of small organic molecules

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Crystal structure prediction (CSP) of molecular materials [1] is probably the "Holy Grail" of computational crystallography [2,3] due to its paramount impact, among others, in polymorph control and tailored synthesis of solids with desired properties.

Brute force CSP algorithm share more or less the same strategy. First, a number of putative structures are generated based on a specific criterion, e.g. the packing efficiency, then the structure landscape is analyzed and the independent structures are optimized by maximizing their cohesive energies. The result is a handful of plausible structures which are ranked according to their relative energy. Unfortunately, the task is not so easy [3-4] and several CSP methods have been developed in the last two decades, with alternate success [5-6].

Most of the available algorithms work on static structures and do not explicitly take into account the thermodynamic boundaries conditions, like temperature and pressure. To go a step further, we propose a new CSP method based on a symmetry-constrained Monte Carlo (SC-MC) algorithm. The program relies on the free MiCMoS platform [7] and shares its built in force fields, which proved to successfully reproduce the packing features of several molecular crystals [7]. The idea is to set up a bunch of classical MC trajectories, where only user-defined symmetry-independent molecules are free to change, while the symmetry-dependent ones are generated by the appropriate symmetry operators (Figure 1). Relying on the degrees of freedom of the sole asymmetric unit, the algorithm is potentially very fast and can quickly explore the energy landscape of several space groups, allowing to locate the most thermodynamically favorable structures in a few hours on a standard laptop computer.

The project is ongoing, but preliminary results are encouraging and suggest that the algorithm may be easily implemented also for other applications, like the structure solution from accurate X-ray powder diffractograms.
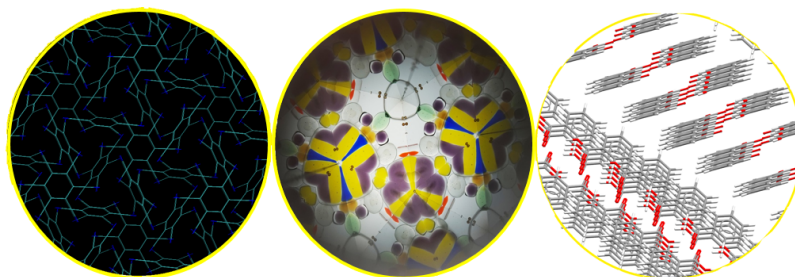
Figure 1. SC-MC evolves the lattice by reproducing a small asymmetric unit with user-defined symmetry elements, as in a kaleidoscope (center). Left: hexacyanobenzene; right: benzoic acid.

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